Radiation Technology in Emerging Industrial Applications

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## CONTENTS

Summary ..................................................................................................................................................1

Radiation crosslinking of polymer blend system: radiation degradative polymer
blended with radiation crosslinking polymer .........................................................................................2
  Sun Jia Zhen

Polyethylene blends for heat shrinkable product fabrication .................................................................8
  I. Legocka, Z. Zimek, K. Mirkowski, M. Zielonka

Thermal and radiation degradation of PVC materials .............................................................................18
  B. Bartoníček, V. Hnát, B. Otáhal, V. Plaček

The factors affecting EB curing of epoxy resin in the presence of cationic initiator .........................23
  Huiliang Wang, Wenxiu Chen, Jianwen Bao

Electron processing of advanced composites for aerospace applications .............................................30
  V. Lopata, A. Puzianowski, C.B. Saunders, J.W. Barnard, T.M. Stepanik

Development of SiC/SiC composites from precursor polymer by radiation
application ..............................................................................................................................................35

Preparation of gypsum/polymer composites using gamma radiation ....................................................41
  Z. Ajji, H. Al-Kassiri

Radiation processing of natural polymers for industrial and environmental applications .....................46
  A.B. Majali, S. Sabharwal, Y.K. Bhardwaj, S.P. Ramnami

Properties of radiation modified sago starch and its potential as biodegradable foams .......................51
  Z. Ghazali, K.Z. Dahlan, B. Wongsuda, S. Idris, S. Kharidah

Effect of acid additives on grafting efficiency and water absorption of hydrolyzed
cassava starch grafted polymers ...................................................................................................59
  S. Kiatkamjornwong, K. Mongkolsawas, M. Sonsuk

Recent progress in RVNRL ......................................................................................................................65

Improvement of RVNR Latex film properties by using fumed silica and hydroxy
appatite as rubber particle binder ........................................................................................................71
  C. Siri-Upathum, N. Na Ranong, M. Sonsuk, A. Thiengthanya

Natural anti-oxidants for radiation vulcanized natural rubber latex ....................................................78
  L.V. Abad, L.S. Relleeve, C.T. Aranilla, A.K. Aliganga, C.M. San Diego,
  A.M. dela Rosa

Electron processing for the viscose process: An economic analysis .....................................................85
  T.M. Stepanik, J.W. Barnard

Radiation processing of polysaccharides for agriculture ......................................................................90
  T. Kume

Radiation processing technology for production of plant growth promoter from
brown seaweed and plant protector from shrimp shell ........................................................................95
  N.Q. Hien, L.Q. Luan, P.T.L. Ha, T.T. Hanh, T.T. Thuy, L. Hai, F. Yoshii,
  K. Makuuchi, T. Kume

Biological activities of radiation degraded carrageenan ........................................................................98
  L.S. Relleeve, L.V. Abad, C.T. Aranilla, A.K. Aliganga, A.M. dela Rosa,
  F. Yoshii, T. Kume, N. Nagasawa

Pre-irradiation grafting polymerization of DMAEMA onto cellulose fabrics .....................................109
  Lu Jun, Yi Min, Li Jiuliqiang, Ha Hongfei
Radiolysis of chloramphenicol and its eye ointment during gamma sterilisation
L. Hong, H. Altorfer

Gamma radiation induced effect in sodium alginate as a component for capsule formation
M. Rapado Paneque, I. Ceausoglu, D. Hunkeler

Fungicidal effect of irradiated chitosan
T.L. Ha, T.T. Thuy, N.Q. Hien, T. Kume

Electron beam technology for production of new anti-tuberculosis drug
V.A. Shkurupiy, Y.N. Kurunov, N.N. Kurunova, A.V. Troitskiy, O.V. Grishin,
E.P. Gulyaeva, L.A. Bogdanova, V.L. Auslender, M.V. Korobeinikov

Permeability control of metal ions through temperature and pH-sensitive copolymer gel membranes
M. Yoshida, Y. Maekawa, J. Hendri, R. Kataka

Thermally stable and highly sensitive polymer membranes for ion and electron beam radiation
Y. Maekawa, Y. Suzuki, N. Yonezawa, M. Asano, H. Koshikawa,
T. Kume, M. Yoshida

Stimuli-responsive hydrogels for drug delivery obtained by radiation copolymerization
E.S.A. Hegazy, H.A. Abdel-Rehim, K.A. Kandeel, A. El-Hag Ali

Experience of electron beam treatment for production of polyethylene oxide gels for medical applications
A.M. Gonchar, V.L. Auslender, M.V. Korobeinikov

Controlled release from polyDMAEMA gels prepared by gamma irradiation
Ning Liu, Min Yi

Preparation of poly (acylamide-co-methacylic acid) hydrogels by gamma radiation.
Influence of the absorbed dose on the swelling process, 5-fluoroacil release
M. Rapado, S. Prado, S. Altanes, D. Zaldivar, S. Padron

Radiation synthesis and application of n-vinyl 2-pyrrolidone based hydrogels containing mono-, di-, tri-protic acid moieties
Ö. Kaantoğlu, M. Şen, T. Çaykara, O. Güven

Radiation preparation and characteristics of sodium carboxymethyl cellulose hydrogels
Pengfei Liu, Maolin Zhai, Jilan Wu

Radiation processing of stimuli-responsive hydrogels and membranes based on vinyl ethers
G.A. Mun, Z.S. Nurkeeva, I.K. Nam, V.V. Khutoryanskiy, P.I. Urkimgaeva,
S.M. Koblanov, V.A. Kan, E.M. Shaikhutdinov

Industrial plant for electron beam flue gas treatment
A.G. Chmielewski, E. Iller, B. Tymiński, Z. Zimek, A. Ostapczuk, J. Licki

Electron beam purification of flue gas with high concentration of sulfur dioxide
M. Tanase, H. Namba, S. Hashimoto

Electron beam treatment of textile dyeing wastewater
B. Han, J.I. Ko, J.K. Kim, Y. Kim, W. Chung, J.S. Choi, H.J. Kang,

Radiation processing of seawater for COD reduction
P. Gehringer, H. Eschweiler

The importance of radiation microbiology on environmental and health care applications
L.G. Gazsó
Studies for radiation treatment of polluted water in Shanghai .............................................................210
  Jin-liang Zhu, Jian-zhong Gu, Min-hong Wu, Bo-rong Bao, Jie Chen,
  Quan Zhang, Zeng-liang Li, Li-hua Wu

Consistency in evaluation of a few MeV electron dose and Co-60 gamma ray dose
  in radiation processing ...............................................................................................................216
  T. Kojima, H. Sunaga, R. Tanaka

Irradiation of frozen biological material — dose mapping, process control,
  traceability and uncertainty in measurement..............................................................................220
  G.J. Gant

The study on dose check in IDAS at SSDL Shanghai.................................................................224
  Zhang Limin, Gu Jiqing, Tang Fangdong

Ion beam technology for biological applications in Tiara.........................................................227
  M. Saidoh, T. Kamiya, Y. Kobayashi, A. Tanaka, K. Arakawa, T. Kojima,
  H. Watanabe

High power electron accelerator for environmental applications...............................................232
  Yu.I. Golubenko, M.E. Weis, N.K. Kuksanov, S.A. Kuznetsov, B.M. Korabelnikov,
  P.I. Nemytov, V.V. Prudnikov, R.A. Salimov, S.N. Fadeev

Alliance™ — The new multi-modal flexible irradiation system...................................................235
  Liu Ge, R.M. Brinston

New progress on radiation processing in China ...........................................................................240
  Wang Chuanzhen, Hou Fu Zhen, Zhang He Hu

Implementation of EB radiation sterilization process in Poland ..............................................248
  Z. Zimek, I. Kaluska

State and prospects of radiation processing technologies in Tunisia ..........................................253
  A. Mahjoub, K. Farah, M.M’ Saad, G. Lassoued, H. Ben Kraiem

Promotion strategy at multipurpose irradiation facility – IRASM, Romania............................259
  C.C. Ponta, I.V. Moise

List of Posters ....................................................................................................................................... 265

List of Participants ............................................................................................................................... 269
invited paper

Radiation Crosslinking of Polymer Blend System: Radiation Degradative Polymer Blended with Radiation Crosslinking Polymer

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Abstract

Radiation degradative polymer such as PMMA Polyisobutylene (PIB) cannot be crosslinked by radiation without any addition of polyfunctional monomer. Until now no literature has reported on this topic. We try to radiation crosslink PMMA by blending with other radiation crosslinking polymers [1].

1. Radiation Crosslinking of PMMA Blend System

Polyblend system may be considered for compatibility. We selected a series of polyblend system and did irradiation with different dose. The results are listed in Table I. From Table I we can see that only PMMA-PEO blend system can get radiation crosslinking products.

Table I. Radiation Crosslinking of Polyblend System

<table>
<thead>
<tr>
<th>Polyblend System</th>
<th>Compatibility</th>
<th>gel(PMMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-PDMVS(siliame rubber)</td>
<td>Bad</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-NBR(Butadiene-nitrile rubber)</td>
<td>Bad</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-1,2 PB(polybutadiene)</td>
<td>Bad(in Toluene)</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-GR-S(Butadiene-Styrene rubber)</td>
<td>Bad(in Toluene)</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-PVC</td>
<td>Good(THF)</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-P(St-co-AN)</td>
<td>Good(THF)</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-PVAC</td>
<td>Good(CHCl₃)</td>
<td>Trace</td>
</tr>
<tr>
<td>PMMA-PVDF</td>
<td>Good(DMF)</td>
<td>Degrad</td>
</tr>
<tr>
<td>PMMA-PEO</td>
<td>Good(C₂H₄Cl₂)</td>
<td>Crosslink</td>
</tr>
</tbody>
</table>

The relationship between gel content and radiation dose is shown in Table II.

Table II. Gel Content of PMMA in Irradiated PMMA/PEO Polyblend System

<table>
<thead>
<tr>
<th>PMMA, % gel, %</th>
<th>30</th>
<th>60</th>
<th>70</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>R, Kgy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>31.9</td>
<td>43.7</td>
<td>7.2</td>
</tr>
<tr>
<td>70</td>
<td>53.5</td>
<td>54.3</td>
<td>77.1</td>
<td>19.5</td>
</tr>
<tr>
<td>100</td>
<td>58.5</td>
<td>56.0</td>
<td>78.1</td>
<td>35.1</td>
</tr>
<tr>
<td>150</td>
<td>62.1</td>
<td>61.6</td>
<td>76.5</td>
<td>48.0</td>
</tr>
<tr>
<td>200</td>
<td>54.0</td>
<td>59.5</td>
<td>67.2</td>
<td>53.2</td>
</tr>
<tr>
<td>300</td>
<td>53.3</td>
<td>53.4</td>
<td>54.3</td>
<td>45.8</td>
</tr>
</tbody>
</table>

If we cancel the pure radiation crosslinked gel content of PEO, we can see that there is a large amount of PMMA that entered the gel. It means that PMMA is crosslinked in this polyblend system and entered the gel. Table III lists the net gel content of PMMA in the whole polyblend system.
TABLE III. NET PMMA GEL CONTENT IN POLYBLEND SYSTEM

<table>
<thead>
<tr>
<th>PMMA, %</th>
<th>Dose, Kgy</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>15.7</td>
<td>19.8</td>
<td>34.6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>28.8</td>
<td>34.2</td>
<td>62.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>31.9</td>
<td>34.7</td>
<td>62.1</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>34.7</td>
<td>39.6</td>
<td>60.1</td>
<td>34.3</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>26.0</td>
<td>37.1</td>
<td>50.4</td>
<td>36.9</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>24.8</td>
<td>39.2</td>
<td>36.9</td>
<td>31.3</td>
<td></td>
</tr>
</tbody>
</table>

From Table III we can see that the maximum gel content is found when PMMA composition is at 70% and the best dosage is around 70-150KGy.

We have studied the phase change by electron microscope and found that 70% PMMA is the phase inversion region of the polyblend system; we considered this point to be very important.

Figure 1 shows the TMA curve of three crosslinked polyblend system.

Figure 1 shows that curves (a) (b) both have a rubber plateau region; it means that net work structure or gel exists.

The abnormal phenomenon of radiation crosslinking of polyblend in the phase inversion region has already been discovered in our laboratory, but we could not explain why and how to use it at that time.
FIG. 1. TMA scans on PMMA-PEO blends. PMMA/PEO ratio: (a) 67/33; (b) 75/25; (c) 80/20.
2. RADIATION CROSSLINKING OF POLYDIMETHYL VINYL SILOXANE – POLYETHYLENE VINYLACETATE (PDMVS-EVA) POLYBLEND SYSTEM

We found that:

(1) \( G(x) \) and \( q_0 \) appeared minimum
(2) dose of gelation \( R_g \) changed rapidly at phase inversion region, as shown in Fig. 2
(3) parameter \( \beta \) of sol-gel and dose relationship existed.

\[ R (s + \sqrt{s}) = \frac{1}{q_0 \ U^1} + \frac{\alpha \ 0^1}{q_0} R^\beta \]

for PDMVS content 20,25,33,55%(phase inversion region)

\[ \beta \text{ value} \rightarrow 0.5 \]

but for PDMVS content 10,12,16,66,78%

\[ \beta \text{ value} \rightarrow 1.0 \]
At phase inversion region of the polyblend system, both two phases had a continuous phase; at that time the system have a maximum interfacial area, minimum domain. The large contact interfacial area results in the active species to have more chance to react to each other so the chain fracture species may be grafted on the radiation crosslinked polymers.

3. RADIATION CROSSLINKING OF POLYBLEND SYSTEM OF PIB

We successfully studied PMMA/PEO polyblend at their phase inversion region. But can this rule be used for radiation crosslinking of other radiation degradative polymers? So we [2] studied the radiation crosslinking of PIB polyblend system. After trying many polyblend systems, finally we found PIB/EPDM to be the best couple.

The blend technique is also a very important factor influencing the crosslinking results. Table IV shows the results of different blend methods. It seems that hot melt mixed method is better than solution mixed.

<table>
<thead>
<tr>
<th>PIB, %</th>
<th>solution mixed</th>
<th>hot melt mixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose, KGy</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>50</td>
<td>9.0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>8.6</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>16.3</td>
<td>1.8</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Electron microscope results show that the PIB content 50%-60% is the phase inversion region of this polyblend system. At that time both PIB and EPDM had a continuous phase.

Results listed in Table V show that net gel content of PIB in the total gel content of blend system has a maximum at PIB 50%, that is the phase inversion region of blend system.

<table>
<thead>
<tr>
<th>PIB, %</th>
<th>gel, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>gel, %</td>
<td>20</td>
</tr>
</tbody>
</table>

PIB entering the gel means that the radiation degradative polymer is crosslinked by radiation. The degree of crosslinking of PIB in the system is shown in Fig. 3.

![FIG. 3. The relationship of degree of crosslinking and radiation dose (a) PIB%=50 ; (b)PIB% =70.](image-url)
It shows that at phase inversion region the degree of radiation crosslinking reaches a maximum.

4. CONCLUSION

By irradiating radiation degradative type polymer blended with radiation crosslinking polymer at the phase inversion region of the polyblend system, radiation crosslinking reaction occurs. The network structure or gel is formed; in the gel both radiation degradative and crosslinked polymers are contained.

REFERENCES


POLYETHYLENE BLENDS FOR HEAT SHRINKABLE PRODUCT FABRICATION

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Abstract

Heat shrinkable tubes and tapes made of irradiated polyethylene have been produced for years. The memory effect of such products is widely used in many industrial applications. New types of polyethylene based materials offered on the market, economic and customer demands are creating a broad field for research and development in polymer radiation processing technology. Lower dose required in radiation induced crosslinking process and better performances of the final products are typical scopes of the research that leads to better economic parameters and better response on customers demands regarding product quality. The study was started at INCT on development of new PE composites better suited with heat shrinkable products application properties, also on the effect of electron beam irradiation on blends of the LDPE with ionomer resin based on ethylene/methacrylic acid (Surlyn). The effectiveness of the gel forming process under influence of radiation in wide dose range was investigated for prepared mixtures. The mechanical properties were investigated and rheorogical properties were evaluated for examination of visco-elasticity performance. Generally, the obtained characteristics of PE blends significantly differ to those relating to pure LDPE. Particularly, the dose required for the effective crosslinking process was significantly reduced.

1. INTRODUCTION

Heat shrinkable tubes and tapes made of irradiated polyethylene have been produced for years. The memory effect of such products is widely used in many industrial applications. Thermomeltable glue is added for certain products and specific application. Heat shrinkable products found various applications as in insulation of electric wires, protection in heavy environmental conditions (chemical, biological and atmospheric corrosion), marking and many others.

Irradiated polymers are non-melting, exhibiting perfect elasticity above their crystalline melting point. Supplied in oriented form, the application of heat will shrink this material to its original dimension, the phenomenon referred to as elastic memory. Three dimensional network of bonds is formed between polymer chains during crosslinking process initiated by ionizing radiation. It creates shape memory effect. Crosslinking of polyethylene products may improve their properties like flexibility, impact and chemical resistance and modified their tensile and thermal properties. It is necessary to add that polyethylene chains can be also degraded what is being observed for higher dose level. On the other hand, irradiation creates the hydrocarbon radicals, which, with suitable additive presence, react more quickly to what leads to higher efficiency of crosslinking process and lowering of the irradiation dose.

New types of polyethylene based materials are offered on the market. The mixtures based on semicrystalline polyethylene give composite materials with different supermolecular structures and visco-elastic properties. The selection should be performed to determine material with best physical properties. The radiation dose and degree of crosslinking should be optimized as well. Economic and customer demands are creating a broad field for research and development in polymer radiation processing technology. Lower dose required in radiation induced crosslinking process and better performances of the final products are typical scopes of the research – what leads to better economic parameters and better response on customers demands regarding product quality.

Multiphase polymers are of great importance in the development of new synthetic materials. However, the development of new useful blends is severely limited by the strong immiscibility of many polymer pair of interest. The miscibility of homopolymer/copolymer blends has been successfully achieved by the presence of specific intermolecular interactions [1] (also: D.R. Paul, S. Newman, 1978; P. Dubin, et al., 1994). These interactions include hydrogen bonding in bulk or...
solution and charge transfer complexes (M. Rutkowska, A. Eisenberg, 1984). Numerous studies have been based on anion-cation and ion-dipole interactions as miscibility enhancers (M. Plante, et al., 1997; A. Hansen, et al., 2000). Addition of selected compounds which may promote better miscibility, increases the crosslinking homogeneity of irradiated polymer blends as it was described in literature [2-4]. The effect of electron beam irradiation on blends of the LDPE with some ionomeric polymer was studied. Applied polymer modifier promotes the formation of miscible blends. The following component was applied: ionomeric resin based on ethylene/methacrylic acid (Surlyn).

INCT is a producer of regular, flexible and non-flammable heat shrinkable tubes and tapes. The heat shrinkable tubes technology was initiated at INCT in the 1970’s. Several industrial type instruments for tube irradiation and expansion were designed and built together by Energokabel R&D Office. The production on industrial scale of heat shrinkable tubes according to INCT license was obtained in the Technological Equipment Factory in Człuchów where accelerator and other equipment were installed in 1984. The equipment for tubes expanding were exported to several countries. The heat shrinkable tapes technology was initiated at INCT in the 1980’s. The regular, flexible and flame resistant tapes and tapes with hot-melt adhesive and butyl caoutchouc material of various thickness are being developed since then, and are being produced on a pilot plant scale. Necessary technological lines for tape irradiation and expansion have been designed and built at INCT. Due to above activity the study was started at INCT on development of new PE composites better suited to heat shrinkable products.

2. METHODS OF SAMPLE CHARACTERIZATION

The physical properties of the samples were measured to established the effectiveness of irradiation process and sample composition influence on final product parameters. The following analytical methods have been applied:

(1) The gel fraction measurements were done by extracting soluble component in boiling xylene for totally 8 h at temperature of 125°C using Soxhlet apparatus and after drying the residue at 135°C for 15 min.

(2) The effect of radiation on the mechanical properties of sample was measured on Instron tensile testing machine. The results of the tests included: elongation at break and tensile strength of the samples.

(3) The melting behavior of the samples was studied on Perkin-Elmer DSC-7 differential scanning calorimeter. Sample, approximately 7 mg in weight was heated at 10°C/min in nitrogen. Two main characterization values were derived from the recorded DSC curves: the peak temperature and heat of fusion.

(4) Rheological characteristics of the samples were investigated by Dynamic Spectrometer RDS-II machine, at 150°C temperature. The following parameters were measured: viscosity $\eta^*$, complex dynamic shear modulus $G^*$ ($G'$- shear storage modulus; real part of $G^*$ and $G''$ – shear loss modulus; imaginary part of $G^*$) vs. vibration frequency ($10^{-1}$-$10^3$ rad/s) to evaluate the tendency of structural changes and formulate conclusions leading to optimization of the dose and LDPE blend composition.
3. EXPERIMENTAL

3.1. Materials

LDPE Bralen type from one producer was included to perform investigation. Commercially available additive ionomeric resin was applied as well. Raw material and added components were in a form of pellets suitable for conventional extrusion equipment. Inomeric resin Surlyn type is a metal salt of an ethylene/organic acid copolymer.

LDPE–Bralen RB-0323 (MFI: 0.35 g/10 min; density: 918 kg/m$^3$)
Ionomeric resin Surlyn

3.2. Preparation of the LDPE blends

Samples were obtained by mixing and extruding raw materials at 130°C using Brabender type machine. Samples were prepared in proportions:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100% Bralen</td>
</tr>
<tr>
<td>1</td>
<td>95% Bralen + 5% Surlyn</td>
</tr>
<tr>
<td>2</td>
<td>90% Bralen + 10% Surlyn</td>
</tr>
<tr>
<td>3</td>
<td>85% Bralen + 15% Surlyn</td>
</tr>
</tbody>
</table>

3.3. Irradiation of the samples

The samples were irradiated at room temperature (20±3°C). Electron beam with energy 10 MeV was applied during sample irradiation in LAE 13/9 accelerator. The total dose 70; 90; 120; 150 kGy was collected in multi pass system. The one pass absorbed dose level was not higher than 25 kGy. The dose rate during irradiation process was controlled by calorimetric method.

3.4. Results

The relation between gel fraction content and absorbed dose in the samples is given in Table I. It can be stated that for samples prepared on the basis of Bralen and low dose level, the gel fraction is significantly higher than for investigated raw material. Significant improvement was obtained for polymer blends in respect of based polymer matrix. The best results were found for the mixture (85% PE + 15% Surlyn).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>LDPE sample Composition</th>
<th>Dose [kGy]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Bralen</td>
<td>70 90 120 150</td>
</tr>
<tr>
<td>1</td>
<td>Bralen + 5% Surlyn</td>
<td>59,1 63,1 67,0 70,6</td>
</tr>
<tr>
<td>2</td>
<td>Bralen + 10% Surlyn</td>
<td>59,8 62,9 65,3 69,0</td>
</tr>
<tr>
<td>3</td>
<td>Bralen + 15% Surlyn</td>
<td>60,2 66,2 68,0 68,8</td>
</tr>
</tbody>
</table>

The results of measurements related to tensile strength and elongation at break of irradiated samples are shown in Table II. These results were obtained for the dose up to 150 kGy. Higher gel fraction level corresponds with higher tensile strength in mechanical tests performed. The samples irradiated with dose 120, and especially 150 kGy, are characterized by lower tensile strength value that indicates the influence of degradation process on mechanical properties of those samples [5]. The analysis of elongation at break results of measurements led to similar conclusions.
TABLE II. MECHANICAL PROPERTIES

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Performances</th>
<th>Dose [kGy]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>Tensile strength [MPa]</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>Elongation at break [%]</td>
<td>519</td>
</tr>
<tr>
<td>1</td>
<td>Tensile strength [MPa]</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>Elongation at break [%]</td>
<td>502</td>
</tr>
<tr>
<td>2</td>
<td>Tensile strength [MPa]</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>Elongation at break [%]</td>
<td>450</td>
</tr>
<tr>
<td>3</td>
<td>Tensile strength [MPa]</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>Elongation at break [%]</td>
<td>480</td>
</tr>
</tbody>
</table>

The results of performed measurements of the melting behavior of the samples with different composition and irradiated with dose 90 kGy are shown in Table III. Some changes in curves shape were observed. The endotherms related to selected samples based on Bralen are shown on Fig. 1. In Fig. 1.a, curve A represents non-irradiated sample made of raw material, curve B is related to the irradiated one. Fig. 1.b shows the curves that are related to two irradiated component mixtures based on Bralen (samples 1-3). Comparison of these curves indicates the significant change of heat of fusion after irradiation, especially for samples 2 and 3 (10 and 15% of Surlyn content). The wider and splitted melting peak is observed that is related to structural reconfirmation processes in those samples [6].

TABLE III. MELTING BEHAVIOR OF RAW MATERIALS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Peak temperature [°C]</th>
<th>Heat of fusion [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dose [kGy]</td>
<td>Dose [kGy]</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>0</td>
<td>116,78</td>
<td>115,85</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>115,70</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>115,94</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>115,75</td>
</tr>
</tbody>
</table>

The influence of the sample composition on viscosity Eta* and modulus G' and G” in non-irradiated samples can be observed on Fig. 2. The shape of the curves indicates high homogeneity of LDPE blends with ionomeric resin Surlyn type. The uniform interaction with ionizing radiation can be expected due to that. The influence of the dose on modulus G* (G’ and G”) was investigated using sample No. 2 (90% Bralen + 10% Surlyn). The applied dose range 0-150 kGy. Fig. 3 shows modulus components G’ and G” behave vs. vibration frequency. Fig. 4 is related to viscosity coefficient Eta*. It can be noticed that the value of G’, G” and G”/G’ of non-irradiated samples are the lowest (excluding value obtained for dose 120 kGy where saturation effect is observed). The shape of curves for irradiated samples is slightly different, comparing with non-irradiated ones. It indicates homogeneity of the polymer blends to compare with initial polymer and lack of significant distortion of the material structure. It should be noticed that the shape of the curves G’(ω) and G”(ω) for the samples irradiated with the dose 72 kGy and non-irradiated ones are similar but the value of G’ and G” coefficients are higher after irradiation. It is correlated with crosslinking process proved by gel fraction content. The sample becomes stiffer but the effect of degradation has not been observed yet (increasing value of G” coefficient). The gel fraction and mechanical properties are not satisfactory for the dose 72 kGy. When the dose 90 kGy is applied, the values of G’ and G” coefficients are lower but the G”/G’ is higher than for the dose 72 kGy. The gel fraction content and mechanical properties are better. In spite of more intense degradation process the final properties were significantly improved. Degradation process is manifested by lower viscosity what also leads to lower homogeneity of the material what can be observed for sample irradiated with dose 120 kGy (lower value of G’ and G” coefficients and higher G”/G’). It should be noticed that gel fraction has practically the same level, and mechanical properties are deteriorated. Higher value of G’, G” and G”/G’ for the dose 150 kGy and similar gel fraction coefficients are observed. The mechanical properties are becoming worse, as well as elongation at break that is related to material degradation. The same time recombination process of macroradicals
may create more branched polymer forms what makes more difficult material deformation. Taking into account the above consideration, the dose 90 kGy was selected as an optimum due to certain level of gel fraction and mechanical properties of the material.

The influence of added modifier and irradiation process on LDPE properties is illustrated on Figs 5-7. As it can be noticed from Fig. 5 the value of $G'$ and $G''$ coefficients for samples 1 and 3 are lower than for sample 2 (dose 72 kGy). It can indicate that for such low dose the added material has not been used sufficiently well (sample 3). At the same time it makes the sample softer. On the other hand, when the modifier content is to low (sample 1) its influence on material properties is limited as well. When the dose is higher (Fig. 5; 90 kGy) the value of $G'$ and $G''$ coefficients for the samples 1 and 2 are similar but $G''/G'$ value for sample 2 is significantly higher for higher vibration frequencies what may suggest higher viscosity caused by differentiated structure. When added modifier content is higher (sample 3) the value of $G'$ and $G''$ coefficients grows effectively what suggests more stiff structure caused by crosslinking process. The value of $G''$ for higher vibration frequency level may indicate polymer degradation, but without adequate influence on mechanical properties in ambient temperature. When the dose is 120 kGy (Fig. 7) the samples with different modifier content are showing similar results. The observed higher value of $G'$ coefficient may indicate non-homogenous structure caused by crosslinking and degradation processes. It is also reflected in measurements of mechanical properties performed in ambient temperature.

4. REMARKS AND CONCLUSIONS

The application of ionomeric resin as an LDPE modifier allows to obtain homogenous blends. With gel fraction all samples increases with the increase of the dose level. The gel fraction of irradiated LDPE blends are higher than for pure LDPE. The dose 90 kGy was found sufficient to obtain suitable gel fraction content. It has been supported by mechanical and rheological properties measurements. The obtained results prove the assumption that different polymer compositions require different dose to obtain suitable crosslinking efficiency. The results of the tensile tests of irradiated samples show changes of tensile strength and elongation induced by crosslinking density of the sample. The effect of oxidative degradation leading to main chain scission can be observed as well. The results of melting behavior shows that peaks of melting endotherms of unirradiated samples are slightly higher than irradiated ones. The peaks of irradiated samples moved to the low temperature side and became shorter and broader; the heat of fusion also decreased. The experimental data coming from rheorogical property measurements performed in higher temperature are well correlated with mechanical properties measured in ambient temperature and provide more complex information regarding structural changes incorporated by crosslinking process initiated by ionizing radiation. Generally, the obtained characteristics of PE blends significantly differ from those relating to pure LDPE. Particularly, the dose that is required for the effective crosslinking process was significantly reduced. The final conclusion regarding the optimum content of added modifier (10-15% of ionomeric resin content) may require more precise optimization.

REFERENCES

FIG. 1.a. The endotherms of Bralen samples:
A – non irradiated; B – irradiated with dose 90 kGy.

FIG. 1.b. The endotherms of irradiated (90 kGy) two component mixtures based on Bralen, modified Bralen (samples No 1-3).
FIG. 2.a. The viscosity $\eta^*$ vs vibration frequency rate: non irradiated samples (0; 1; 2).

FIG. 2.b. The modulus $G'$ and $G''$ vs vibration frequency rate: non irradiated samples (0; 1; 2)
FIG. 3. The modulus $G'$ and $G''$ vs vibration frequency rate: irradiated sample No 2 for different dose level.

FIG. 4. The viscosity $\eta^*$ vs vibration frequency rate: irradiated sample No 2 for different dose level.
FIG. 5. The modulus $G'$ and $G''$ vs vibration frequency rate: irradiated samples 1-3 (dose 72 kGy).

FIG. 6. The modulus $G'$ and $G''$ vs vibration frequency rate: irradiated samples 1-3 (dose 90 kGy).
FIG. 7. The modulus $G'$ and $G''$ vs vibration frequency rate: irradiated samples 1-3 (dose 120 kGy).
THERMAL AND RADIATION DEGRADATION OF PVC MATERIALS*

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Abstract

The most significant environmental stressors for polyvinyl chloride (PVC) cable materials in nuclear power plants (NPP) are temperature, radiation dose rate and the presence of oxygen. The significant effect of the sequence of the thermal and radiation ageing has been found and large dose rate effect observed. In this paper, the methodology based on differential scanning calorimetry (DSC) is presented. This technique enables to assess cable life under NPP conditions. DSC methodology was successfully applied to several cable types, and – as an example – its application on the KPOBOV cable type is described. As promising condition monitoring technique, the density measurements of the PVC cable materials is proposed.

1. INTRODUCTION

NPPs contain thousands of kilometres of electrical cables and wires of several hundreds different types and sizes throughout the plant. Insulation and jacket materials used in electrical cables are often based on PVC, particularly in older plants. Operational experiences indicate that NPP cables gradually embrittle owing to enhanced temperature and ionizing radiation in the presence of air. Understanding of cable ageing is the key to its effective management, which is needed at all NPPs.

Elongation at break is the conventional test method for measuring embrittlement. Its absolute value of 50% is recommended to use as the cable life endpoint criterion. The disadvantage of this destructive method consists in the requirement of a large sample size for analysis. This fact was solved by applying the DSC method that enabled evaluation of the cable condition from the microsamples taken in situ from cables installed in the Dukovany NPP (Czech Republic). The cable life has been determined for 15 cable types by means of two calibration curves: DSC response versus elongation at break, and elongation at break versus simulated time of NPP operation [1]. This method for the cable type KPOBOV is described here. The pioneering application of this method for cable condition monitoring in Dukovany NPP has provided successful results in the life assessment of commercial cables.

2. EXPERIMENTAL

2.1. Samples and ageing conditions

The commercial cable type KPOBOV (manufactured in the former Soviet Union) was insulated with PVC, and inner sheath and jacket material were based on PVC, too. Cable samples were irradiated with $^{60}$Co gamma source at the dose rate of 36 Gy/h to the total doses of 10, 20 and 30 kGy (simulating 10, 20 and 30 years of radiation service ageing). The irradiated samples were thermally aged in forced-air circulation ovens at the temperature of 120°C for 9, 18 and 27 days (simulating 10, 20 and 30 years of thermal service ageing).

* This work was carried out with the support of the International Atomic Energy Agency, Vienna, Austria, as part of IAEA Research Contract No. CZR-9340.
2. 2. Tests

2. 2. 1. Elongation at break measurements

The tensile tests were carried out by the INSTRON 4301 machine equipped with extensometer at the test rate of 200 mm/min. For each sample in a given environment, at least four identically aged tensile specimens were tested (tubes for cable insulations and dumbbells for sheath and jacket).

2. 2. 2. DSC measurements

DSC measurements were carried out by the instrument DSC 7 Perkin Elmer. The microsamples (1.5–2 mg) were taken from the cable jacket at NPP Dukovany by the use of special tool that only sliced the cable surface (the thickest sample slice remained under 50 µm).

2. 2. 3. Density measurements

The density measurements were made by using the density gradient column with the aqueous solution of calcium nitrate. The density in the range of 1.32–1.43 g/cm³ was determined from the calibration curve [2].

3. RESULTS

Before simulation of the NPP, operational ageing was undertaken, and the effect of the sequence of the thermal and radiation ageing carried out for the jacket material of the KPOBOV cable. The effect of the sequence of individual ageing steps for the elongation at break values is evident (Table I).

TABLE I. EFFECT OF THE SEQUENCE OF THERMAL AND RADIATION AGEING FOR THE ELONGATION AT BREAK OF THE JACKET MATERIAL OF THE KPOBOV CABLE

<table>
<thead>
<tr>
<th></th>
<th>e/e₀ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged sample</td>
<td>1.00 ± 0.08</td>
</tr>
<tr>
<td>Radiation aged sample b</td>
<td>0.66 ± 0.13</td>
</tr>
<tr>
<td>Thermally aged sample c</td>
<td>0.53 ± 0.09</td>
</tr>
<tr>
<td>Thermally followed radiation aged sample</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>Radiation followed thermally aged sample</td>
<td>0.010 ± 0.005</td>
</tr>
</tbody>
</table>

a Elongation at break for aged sample, e, divided by elongation at break for the unaged one, e₀ (e₀ = 333 %).

b ⁶⁰Co gamma radiation; dose rate: 430 Gy/h, total dose: 145 kGy, irradiation temperature: 27 °C.

c Thermal ageing at 150 °C / 14 days.

These results confirm the strong synergism observed in our earlier experiments with EVA, EPR and XLPE cable materials [3] when substantially greater degradation occurred in the case of radiation ageing followed by a thermal one. Therefore, the NPP operational ageing of KPOBOV cable was simulated in the same sequence. The ageing effects were explained in terms of a chain branching degradation mechanism involving thermally induced breakdown of peroxides which are formed in reactions initiated by the radiation [4].

The existence of a strong dose rate dependent degradation effect was found for many plastics, e.g. for polyethylene (PE) and PVC materials [4]. In our experiments with KPOBOV jacket material the dose at which the elongation at break reaches the half of its initial value was determined. For the dose rate of 430 Gy/h this dose is equal to 210 kGy, while for the dose rate of 30 Gy/h only, to 15 kGy. These results show significant dose rate effect in the PVC materials, which must be taken into account in case of the cable life assessment.
For the assessment of the lifetime of the KPOBOV cable under condition Dukovany NPP, two calibration curves have been determined. Several samples of the KPOBOV cable have been subjected to the accelerated ageing (as described above) and their elongation at break values have been determined. The first calibration curve is given in Fig. 1.

**FIG. 1. Dependence of the elongation at break on the simulated time of NPP operation for the KPOBOV cable jacket. NPP operating temperature: 55°C, NPP dose rate: 1 kGy/year.**

The second calibration curve shows the dependence of the DSC response on the elongation at break for the KPOBOV cable jacket (Fig. 2). This curve has been determined from microsamples that were taken from the undeformed locations of test specimens after tensile measurements.

For the samples taken *in situ* at NPP, the DSC responses were measured under the same experimental conditions under which the calibration curves were determined. On the basis of the calibration curve in Fig. 2, elongation at break values was determined, and then, using the first calibration curve in Fig. 1, the residual cable life was assessed. Accuracy of the residual cable lifetime assessment depends on a good knowledge of the NPP environmental conditions, especially operating temperature and dose rate of gamma radiation, on exact values of activation energy of material degradation, and on a reliable ageing simulation when the synergistic and the dose rate effects are taken into account.
In addition to the elongation at break and the DSC response measurements, the density measurements were verified as a condition monitoring technique for cable materials. Above mentioned samples of the KPOBOV cable jacket were measured by using a liquid column containing a gradient in density. Details of the technique are described [2]. The dependences of the elongation at break values and of the density on the simulated KPOBOV cable jacket lifetime are shown in Fig. 3.

FIG 2. DSC response versus elongation at break for the KPOBOV cable jacket after the simulation of 0, 10, 20 and 30 years of NPP operation.

FIG 3. Density and relative elongation-at-break values versus simulated operation life of the NPP.
Above results showed that density of the KPOBOV cable jacket material increases linearly as the cable degradation increases. This method requires a small sample (about 1 mg), hence is considered essentially non-destructive. Density measurement seems to be an effective condition monitoring technique for PVC cable materials.

4. CONCLUSIONS

The KPOBOV cable based on PVC insulation and jacket material was studied under simulated environmental conditions in Dukovany NPP. The experimental results showed that significant sequential ordering effect and large radiation dose rate effect occur. The DSC method makes possible the cable lifetime assessment using in situ sampling at the NPP. The main requirements for an exact residual cable lifetime assessment were defined. The density measurement of PVC cable materials belongs to the most promising condition monitoring technique and further experimental work is necessary.

REFERENCES

THE FACTORS AFFECTING EB CURING OF EPOXY RESIN IN THE PRESENCE OF CATIONIC INITIATOR

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Abstract

The factors affecting the radiation curing of epoxy resin in the presence of cationic initiator are briefly studied in this paper. In all the epoxy resin used, the epoxy resin 616 very easy to cure; whereas, the epoxy resin 771 is very difficult to cure. In all the additives, diphenylketone and iodine are helpful to the curing reaction, however, phenol and hydroquinone restrain the curing reaction. The effect of solvent on the EB curing of epoxy resin is also studied. It is found that when benzene is added in the curing system of epoxy resin 616 added cationic initiator 1012, the curing reaction is almost not affected, when alcohol is added, the system can not cure. The radiation curing is not affected by temperature greatly. The effect of the atmosphere on radiation curing is also studied. After effect is found in all the curing systems used.

1. INTRODUCTION

Radiation curing is a rising processing technique developed in recent years. Because of its low energy consumption, high production efficiency, low curing temperature, easy application and pollution free, radiation curing become the branch of radiation processing developing most quickly [1].

The use of electron beam (E.B.) radiation to induce the rapid polymerization of multifunctional acrylate or methacrylate monomers or oligomers, is a well-established technique, in particular for coatings applications. These compounds undergo a free radical polymerization which is initiated by solvated electrons and free radicals produced by bond scission [2]. By contrast, only a limited number of studies, which have all been published fairly recently, have dealt with the cationic polymerization of epoxy monomers induced by high energy ionizing radiation in the presence of onium salts [3-6].

In recent times, electron beam curing of resin compositions has become an important technique for the application and curing of coatings, inks, adhesives, and compositions. High energy EB curing is also desirable for use in reinforced composite applications because of great penetration of electron beam radiation which allows it to pass through considerable thickness of many different materials. Epoxy resins are widely employed by the aerospace and high-performance sporting goods industries for use in composite fabrication. EB curing of epoxy resin for reinforced composite fabrication has been studied in recent years [7-10]. In this article, we will briefly study the factors affecting the EB curing of epoxy resin in the presence of onium salts, as a fundamental work of EB curing of epoxy resin for reinforced composite fabrication.

2. EXPERIMENTAL

2.1. Materials

Cationic initiator SarCat CD1012 (Diaryliodonium hexafluoroantimonate, shortened as 1012) and SarCat CD1010 (Triarylsulfonium hexafluoroantimonate, 50% in propylene carbonate, shortened as 1010) are supplied by Sartomer. Irgacure 261 (shortened as 261) produced by Ciba-Geigy is a cumene hexafluoroantimonate Iron II cyclopentadienyl.
Epoxy resins used are, as follow:

Bisphenol-A 616  
TDE-85  
711

In this article, a curing system of an epoxy resin added a cationic initiator is expressed as (epoxy resin + cationic initiator), for example, 616+1012.

Diphenylketone, iodine phenol and hydroquinone are analytic reagents.

2.2. Methods

A weighed epoxy resin, cationic initiator and additive are mixed homogeneously in beaker in 50–60°C water bath. The prepared samples are irradiated under Electron Beam (EB), dose rate is 6kGy/m. After irradiation, and the samples are extracted by acetone in Soxhlet, then dried in vacuum. Curing Percentage is measured by weighing the samples before and after extraction and calculated as follow:

\[
\text{Curing \_Percentage(\%) = \frac{W}{W_0} \times 100}
\]

where

\(W\) is the weight of sample after extraction,
\(W_0\) is the weight of sample before extraction

Curing degree is measured by FTIR method.

\[
\text{Curing \_Degree(\%) = \left[1 - \frac{A_1}{A_{1,0}} \right] \times 100}
\]

where

\(A_1\) is the absorbance of epoxy group peak at 915cm\(^{-1}\),
\(A_2\) is the absorbance of reference group (for benzene ring at 1510cm\(^{-1}\), carbonyl at 1732 cm\(^{-1}\)),
\(A_{1,0}\) is the absorbance of epoxy group peak at 915cm\(^{-1}\) unirradiated,
\(A_{2,0}\) is the absorbance of reference group peak unirradiated.

3. RESULTS AND DISCUSSION

3.1. The selection of curing system

The EB curing of several epoxy resins in the presence of cationic initiator 1012 is shown in Fig. 1. In all the epoxy resin used, the Bisphenol-A epoxy resin 616 is very easy to cure; whereas, the epoxy resin 771 is very difficult to cure. These results show that the chemical structure of epoxy resin is a key factor affecting its radiation curing. The benzene ring structure in Bisphenol-A epoxy resin makes it more stable under high energy irradiation than other epoxy resins used.
FIG. 1. The change of curing percentage of epoxy resins added cationic initiator 1012 with radiation dose.

As shown in Fig. 2, in all the initiators, diaryliodonium salt 1012 shows the best effect to initiate curing, triarylsulfonium salt 1010 can initiate the EB curing of epoxy resin also, however, iron arene complex 261 can only partially initiate the EB curing of epoxy resin 616. These results show that cationic initiator is another key factor affecting the radiation curing of epoxy resins.

FIG. 2. The change of curing percentage of epoxy resin 616 added different cationic initiator separately with radiation dose.

3.2. The effect of additives

As shown in Figs 3 and 4, in the curing systems 616+1012 and 616+261, diphenylketone and iodine are helpful to the curing reaction. Diphenylketone and iodine act as sensitizer in the systems, energy is transferred from the excited state of the sensitizer to the onium salts, producing an excited state onium salt, which undergoes further reaction.

FIG. 3. The change of curing degree of 616+1012 added diphenylketone or iodine separately with radiation dose.
FIG. 4. The change of curing percentage of 616+261 added diphenylketone or iodine separately with radiation dose.

It can be seen from Fig. 5 that the curing percentage of curing systems 616+1012 added phenol or hydroquinone is lower than that of 616+1012 when radiation dose is relatively higher. The curing percentage of curing system added phenol is the lowest. These results show that phenols restrain the radiation curing of epoxy resins.

FIG. 5. The change of curing percentage of 616+1012 added phenol or hydroquinone separately with radiation dose.

3.3. The effect of solvents

The effect of solvent on the EB curing of epoxy resin is also studied. Fig. 6 shows that when benzene is added in the curing system of 616+1012, the curing reaction is almost not affected, but when alcohol is added, the system can not cure.

FIG. 6. The change of curing percentage of 616+1012 added benzene, alcohol or CCl₄ separately with radiation dose.
The effect of solvents on diaryliodonium salts has been studied [11] (also: Ma, X.H. et al., 1989). In the presence of onium salts, solvated electron reacts with onium salts, as follows:

\[
e_{\text{solv}} + \text{Ph}_2\text{IPF}_6^- \rightarrow \text{PhI} + \text{Ph}^+ + \text{PF}_6^-
\]

Because its conjugated \(\beta\) bond can diffuse radiation energy, benzene is very stable under high-energy irradiation. It has very low G value of solvated electron; therefore the cationic initiator decomposed by solvated electron is less. Whereas, alcohol is very easy to form solvated electron under irradiation, so onium salts is very easy to be decomposed in alcohol.

3.4. The effect of temperature

The effect of reaction temperature on the radiation curing of 616+1012 is studied in the temperature range of -185 \(^\circ\)C to 92 \(^\circ\)C, as shown in Fig. 7. The radiation curing is not affected by temperature greatly. The curing degree of 616+1012 is very similar when irradiated at different temperature. The curing degree of 616+1012 increases with temperature slowly.

![Fig. 7. The change of curing degree of 616+1012 with radiation temperature.](image)

Normally, cation mechanism reaction requires very low (even negative value) activation energy, so it is not (or very little) affected by reaction temperature. Fig.5 shows that the effect of temperature on curing reaction is very little, curing degree's difference is only about 20% in the temperature range of about 300\(^\circ\)C. This indicates that the curing reaction is processed via cation mechanism. The difference in curing degree is induced by monomer diffusion speed, monomer diffusion speed is low at low temperature, therefore the speed of curing reaction become lower.

3.5. The effect of atmosphere

Fig. 8 shows the effect of atmosphere on radiation curing of epoxy resin 616 in the presence of cationic initiator 1012. It is found that the curing percentage of curing system 616+1012 irradiated in Nitrogen is lower than that in air at the same radiation dose when the dose is lower than 24kGy. When the radiation dose is higher than 24kGy, the radiation curing is not affected by radiation atmosphere.
The reason for the results is not clear. That's may be the O₂ in air is excited to O₂*, it transfer its energy to the onium salts, producing an excited state onium salt, which undergo further reaction to initiate curing reaction.

3.6. After effect

After effect is found in all the curing systems used above. Fig.9 shows the after effect of the curing system of TDE-85+1012. The curing percentage of curing system placed one week after irradiation is higher than that of the system treated immediately after irradiation.

There are after effects exist in polymerization reactions through free radical mechanism or ion mechanism. For cation mechanism reaction, it has a longer after effect. That's because cation still has reactivity after a relatively long time after irradiation. The existence of after effect is favorable for processing, it reduces radiation time and costs.

REFERENCES


The use of advanced composites made with carbon-, glass-, aramid-, or polyethylene fibres and epoxy- or acrylated resins is becoming increasingly prevalent within the aerospace sector. The advantages these materials offer compared to metal are making them suitable alternatives not only for secondary components but also for primary structural components on aircraft. Composites are presently cured in autoclaves using heat and pressure. Electron processing offers several advantages over thermal curing and has been investigated by Acsion personnel for over a decade. This paper discusses the latest developments at Acsion on using electron curing to manufacture components for the next generation of aerospace vehicles and to repair damaged structures on aircraft.

1. INTRODUCTION

The use of advanced composites is increasing within many sectors such as the transportation, infrastructure, sporting goods and the military industries [1]. Composites have been used for manufacturing secondary structural components on aircraft for several years. These components are presently thermally cured. However, with current trends in aircraft design leaning towards larger and thicker composite structures, autoclave curing may not be suitable or may be cost prohibitive [2].

Electron (EBeam) curing has several advantages over thermal curing [3]. EBeam curing can be performed at ambient temperatures, which allows inexpensive tooling materials (plastic, wood, foam and composites) to be used and limits internal stresses within the product. Other advantages include faster curing rates, reduced waste, and the elimination of toxic agents. The overall result is a process that is more economical, promotes a safer working environment, and is capable of curing larger and thicker parts.

Acsion staff has been at the forefront in developing EBeam curing for advanced composites containing epoxy resins [1, 3-9]. Acsion has been involved in one Co-operative Research and Development (CRADA) program sponsored by the US Department of Energy to conduct research and product/process development on EBeam-curable composites [10], and is currently participating in a second CRADA project entitled “Interfacial properties of electron beam-cured composites” to investigate the effects of fibre sizing and fibre surface preparation on the properties of EBeam-cured composites. Acsion has worked with both US and European aerospace agencies on manufacturing composites [4], and has pioneered the use of EBeam curing for repairing composite structures on civilian aircraft [5].

This paper describes developments in E-Beam curing programs involving Acsion, such as the IATA project, the manufacture of a one-tenth scale liquid hydrogen tank for the Reusable Launch Vehicle (RLV) project, the repair of components on Air Canada aircraft, and the Joint Strike Fighter Project.

2. MANUFACTURING

2.1. IATA project

The IATA (Integrated Airframe Technology for Affordability) program was a US Defence Advanced Research Projects Agency program run by Lockheed Martin Aeronautics-Palmdale (formerly Lockheed Martin Skunkworks) to investigate the feasibility of producing an advanced short take-off and
vertical landing aircraft in which 95% of the aircraft frame and wingskin were to be made from composite materials. The objective was to investigate composite technology for producing larger components thereby reducing the number of parts required from over 2500 down to approximately 500. As part of this program, Lockheed was interested in investigating EBeam curing for producing these parts. One major advantage of using EBeam curing would be the capability to cure parts in which different sections of the same part required different service temperatures. An example could be a part in which one section is near the engine and is exposed to significantly higher temperatures than other sections that are further away. Production of such parts is feasible by EBeam curing but not by thermal curing.

The EBeam portion of the project involved the construction of a 150 x 150 x 150 cm structure, which consisted of five individual components; a keelson which had a single fabric impregnated in different sections with different resins because these sections would be exposed to different temperatures, two ribs, and an upper and lower skin. This structure was one of the most complex, highly loaded sections of the airframe and incorporated metal components for accommodating landing gear. The objective of this project was to: 1) manufacture the keelson and upper and lower skins using low cost tooling materials and EBeam curing; 2) manufacture the ribs using conventional high-cost tooling materials and thermal curing; and 3) assess how well the components assemble together to form the overall structure, since very low tolerances in the dimensions of each section were required for the five components to fit together properly. When the three EBeam-cured sections and two thermally cured sections were manufactured and assembled, it was found that all five sections were within specifications and that the parts did fit together “hand in glove”. This project demonstrated that EBeam-curing of even the most difficult of aircraft components was feasible and that the use of relatively inexpensive tooling materials can produce structures within specifications.

2.2. Reusable launch vehicle project

The fabrication of cryogenic fuel tanks in co-operation with Lockheed Martin Aeronautics is another example of an EBeam curing program geared to manufacturing. Lockheed Martin and NASA are developing the X-33 RLV to demonstrate that cheap, low-risk and routine access to space is possible. The X-33 is intended to be a half-scale forerunner of the Venture Star, the next generation space shuttle. The fuel tanks for the X-33 will hold liquid hydrogen (LH2) and oxygen and will be inside the RLV. Lockheed Martin Aeronautics is interested in using composite LH2 tanks. As part of their development program, Lockheed Martin Aeronautics is working with Acsion to fabricate a one-tenth scale composite LH2 tank using EBeam curing. Lockheed Martin’s interest stems from work performed with Acsion, which shows that EBeam-cured composites have superior barrier qualities with respect to hydrogen permeability, excellent resistance to microcracking and exceptional thermal cycling properties within the range of temperatures these materials will be exposed to during flight.

The fabrication of the one-tenth scale model of the Venture Star LH2 tank is presently underway at Acsion. In August and September 2000, sections of the tank were laid up using foam and wood tooling materials and partially cured using Acsion’s 1 kW, 10 MeV I-10/1 accelerator. The components were then assembled for final curing. The dimensions of the tank were approximately 90 x 180 x 180 cm. This size was too large to fit on the conveyor under the scan horn of the I-10/1. To accommodate this tank, a cradle was built around the horizontal accelerating structure of the I-10/1. This cradle is connected to the ceiling of the shielding vault and allows the accelerating components, bending magnet and scan horn to be lifted vertically as much as 15 cm above its floor-based support cabinets. In addition, the cradled structure can be moved horizontally up to 1 metre away from its support cabinets providing more room between the scan horn and the floor-based support cabinets for accommodating wider parts. With another conveyor slaved to the accelerator conveyor, this will allow the LH2 tank and even wider components to be easily cured (this accelerator mobility is also very important for repairing large composite structures; see below). The final curing stage for the LH2 tank is in progress.
3. REPAIR

3.1. Air Canada

Acsion is also developing EBeam curing as a method for repairing composite parts on aircraft. Repair trials are being conducted in collaboration with Air Canada on their fleet of A319, A320, and A340 Airbus aircraft [5]. Composite materials are used in several sections of these aircraft and they make up between 20-25% of the structural weight of the aircraft.

In the first type trial, a wing to body fairing on a commercial A319 aircraft was EBeam repaired using patching made from fibreglass and a proprietary epoxy resin developed at Acsion. The panel was monitored frequently over a period during which the aircraft logged more than 1800 hours of flying time and 900 take-offs and landings (cycles). The results were very encouraging and led to a second type trial in which two patches were used (one on the inside of the fairing and one on the outside) and the honeycomb core was replaced. This fairing was frequently monitored over a period of more than 4000 hours of flying and more than 2000 cycles. The results were encouraging enough to have the EBeam-cured patches declared a permanent repair. Air Canada and Acsion have now embarked upon a third type trial. In this trial, another fairing was repaired with a fibre glass - epoxy patch and an engine fan cowl was repaired with a graphite-epoxy patch in an area on the cowl which is subjected to high stress and temperatures greater than 150 °C while the aircraft is in operation. The patches on the repaired fairing have performed according to expectations for over 1000 hours of flight time and 500 cycles. The patch on the repaired fan cowl has also performed well through a period of 700 flight hours and 360 cycles.

The information gained in these type trials has shown that, in addition to producing repaired components with better mechanical properties, EBeam curing also offers several other advantages over conventional thermal curing with respect to man-hours for repair, materials, utilities and down-time costs. A comparison of the man-hours required for repairing a damaged fairing, fan cowl, or landing gear door incorporating conventional thermal curing or EBeam curing is given in Table I.

<table>
<thead>
<tr>
<th>TABLE I. EBEAM VS. CONVENTIONAL REPAIR; COMPARISON OF MAN-HOURS a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step</strong></td>
</tr>
<tr>
<td>1. Clean and dry</td>
</tr>
<tr>
<td>2. Removal of damage</td>
</tr>
<tr>
<td>3. Inspection</td>
</tr>
<tr>
<td>4. Remove and replace core</td>
</tr>
<tr>
<td>5. Preparation sanding</td>
</tr>
<tr>
<td>6. Inspection</td>
</tr>
<tr>
<td>7. Clean</td>
</tr>
<tr>
<td>8. Kitting (pre-preg thaw)</td>
</tr>
<tr>
<td>9. Lay-up</td>
</tr>
<tr>
<td>10. Bond and cure</td>
</tr>
<tr>
<td>11. Inspection</td>
</tr>
<tr>
<td>12. Paint</td>
</tr>
<tr>
<td>13. Assemble</td>
</tr>
<tr>
<td>14. Paperwork</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

a Estimates for a typical repair on a fairing, fan cowl or landing gear door.
Significant differences in man-hours are found in three steps: step 1, clean and dry; step 8, kitting; and step 10, bond and cure. In step 1, drying is a critical issue for autoclave curing. The interior of damaged parts often become contaminated with water or de-icing fluid which, if not completely removed, can lead to explosive debonding of the outer composite skins from the inner aluminium or nomex core. Thus, 24 hours is often required when thermal curing is used to remove any volatile contaminants. While drying is also important for EBeam curing, drying to the extent needed for thermal curing is not required since EBeam curing is an ambient temperature process. In step 8, conventional prepreg material must be kept frozen before use because the hardeners present will cause autocuring. Up to eight hours is required for thawing the prepreg material before use. EBeam-curable materials do not autocure; consequently, freezing is not required. In step 10, thermal curing requires 6-8 hours while EBeam curing typically requires less than 1 hour. The overall result is that EBeam curing can reduce the number of manhours required for a repair by a minimum of 11% and a maximum of 47%. Similar calculations for a two-sided repair indicate that a more dramatic 40% minimum reduction is possible, while the maximum reduction can be 51%.

In addition to the cost savings associated with reduced man-hours for the repair, EBeam curing offers several other advantages. If a spare part is not available, EBeam curing can reduce the time an aircraft is out of operation by up to 1 day. This by itself can translate into savings in down-time costs of more than $100,000 CDN per day. Large freezers are no longer required for the prepreg, eliminating freezer costs. The prepreg material is only available in finite sizes, which often results in a significant excess of thawed prepreg material not used for the patch that must be discarded. As well, frozen prepreg material has a finite shelf life, and must be discarded after its expiration date. These material waste costs can run into the hundreds of thousands of dollars per year. With EBeam curing, excess material left after cutting the patch can be kept to a minimum and there are no problems with material expiration. Repatching costs due to patch deterioration with age and exposure to the elements while on the aircraft are expected to be reduced by as much as 50%. Tooling costs can be reduced by as much as 90% and electricity costs can be reduced by a comparable amount. These economic evaluations, together with the encouraging type trial results, and the potential for developing EBeam-curable resins with superior properties indicate that EBeam curing will likely play a significant role in future composite repair processes for commercial aircraft.

3.2. Joint strike fighter

Based on the success experienced in these and previous projects, Acsion is proposing to extend EBeam manufacturing and repair to include both existing and future generation military aircraft. The Joint Strike Fighter (JSF) program is a multi billion dollar multinational program lead by the US to affordably build the next generation of fighter aircraft [11]. The program will result in a “family” of aircraft designed to serve the needs of the Navy, the Air Force, the Marines and US allies. Each aircraft in the family will have common, high-cost subsystems that can be built on the same production line. Component commonality will also bring benefits from common depot maintenance, a commonly supported logistics tail, and increased service interoperability resulting in an estimated 40% saving in costs.

In the first phase of the program, the Concept Demonstration phase, Boeing and Lockheed Martin are building concept demonstrator aircraft. Based on the performance of these aircraft, one of these companies will be awarded a contract to proceed with the program’s second phase, a $25 B US Engineering and Manufacturing Development (EMD) phase, followed by a production phase anticipated to last 30 years, during which an estimated 6000 aircraft will be constructed. The value of the production phase is projected to be in excess of $315 B US.

The US Department of Defence is encouraging its allies to participate in the JSF program. Four levels of involvement have been established for participants. These are: level I, a full partner; level II, an associate/limited partner; level III, an informed partner; and level IV, a major participant. Canada was an informed partner in the first phase of the program and is presently assessing its status for the EMD phase that is scheduled to begin in 2001.
Acsion is working as part of the Aerospace Industries Association of Canada (AIAC) to persuade the Canadian government to opt for level III participation in the EMD phase. If Canada decides on level III participation, the return to AIAC members is projected to be $70 M worth of work in the EMD phase, rising to $6.2 B in anticipated business in succeeding phases of the program [12]. Acsion’s role in Canada’s portion of the program will be to assist in developing EBeam curing for manufacturing and repairing composite structures on these aircraft.

4. SUMMARY AND CONCLUSIONS

EBeam curing has many advantages over thermal curing for several aerospace applications. These include faster, more economical curing, and the production of composite materials with improved properties. Acsion, in collaboration with Air Canada and Lockheed Martin Aeronautics, is demonstrating that additional advantages are found in practice, both for the manufacture and repair of composite materials. These results indicate that EBeam curing has the potential to play a significant role in aerospace applications in the future.

REFERENCES

DEVELOPMENT OF SiC/SiC COMPOSITES FROM PRECURSOR POLYMER BY RADIATION APPLICATION

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Abstract

The fabrication of silicon carbide (SiC)/SiC composite by using the radiation-cured preceramic polymer process was studied. The SiC/SiC composite was obtained by only single impregnation of the preceramic slurry containing fine SiC powder into SiC fiber preform. We succeeded to improve the fracture properties of composites using slurry of polymer blend such as polycarbosilane (PCS) and polyvinylsilane (PVS).

1. INTRODUCTION

The ceramic matrix composites (CMC) with high strength and high heat-resistance are strongly required for the advanced technologies such as nuclear fusion reactors and space planes (T.M. Besmann, et al., 1993; K.M. Prewo, et al., 1986; P.J. Lamicq, et al., 1986; S. Yajima, 1985). Silicon carbide (SiC) fiber has high potentiality for the application to the fiber reinforcement. We have already succeeded to improve the heat resistance of the fiber by decreasing the oxygen content and using electron beam (EB) irradiation in the curing process Sugimoto, et al., 1995).

The fabrication process of silicon carbide (SiC) fiber reinforced SiC (SiC/SiC) composite has been studied and several manufacturing processes were developed, and polymer impregnation and pyrolysis process (PIP) has been well studied [1,2] (also: K.M. Prewo, et al., 1986). This process consists of two stages; the precursor polymer for SiC is impregnated in the SiC fiber preform and the polymer is converted to the ceramics by pyrolysis reaction. The precursor must be sufficiently fluid to penetrate the pores of the preform. It must wet the surface of the fibers. It should have the appropriate chemistry for cross-linking, a high pyrolysis conversion yield. The main problem of PIP is related to the shrinkage of the polymer during the pyrolysis. As a result, a large number of impregnation / pyrolysis cycles (typically, 6-10 cycles) are necessary to reach a final density of 90-95% of theoretical [1]. Also, the fiber must be coated with carbon or boron nitride (BN) to avoid catastrophic fracture. It is because, if the interface between the fiber and the matrix is locked tightly, the growth of crack in the matrix could not be stopped at the interface, then the fiber broken together with the matrix fracture. In this case, the composite shows a brittle mechanical property.

In our process, EB irradiation was applied for the curing of impregnated polymer as the matrix. Also, new polymer such as polyvinylsilane (PVS) [3] (also: M. Itoh, et al., 1998) was incorporated into the precursor polymer (PCS). In this process, PCS is crosslinked by irradiation without oxygen so that the obtained SiC/SiC composite might have higher thermal resistance (Sugimoto, et al., 1995). And, there is no need of high pressure to cast the pre-composite in the firing process. On the other hand, there are difficulties in elimination of entrapped voids in the preceramic composite, and also in the control of crack formation by shrinkage of the polymer in the firing process in corporate with the PVS polymer.
2. EXPERIMENTAL

The fabrication process of SiC/SiC composites by radiation-cured preceramic polymer is shown in Fig.1. The polymer blend made from Polycarbosilane (PCS) and Polyvinylsilane (PVS) are dissolved in benzene with fine SiC powder (Betarundum). The characteristics and the manufactures of these materials are shown in Table I. The mixed solution was converted to the slurry by the treatment of stirring and ultrasonic wave mixing. The two-dimensionally woven SiC fabric (Hi-Nicalon) was immersed in the slurry under ultrasonic vibration for 1 hr to impregnate the slurry around the fiber and into the inter-fiber space. The SiC fabrics containing the slurry were dried in evacuated chamber and kept at 373 K for 24 hrs to remove solvent completely. Dried composites were placed into a press machine and was heated up to 523–573 K which is higher than the melting point of polymer blend in argon atmosphere, compressed up to 15 MPa by the press machine, and cooled down to ambient temperature under the pressure.

![Diagram of SiC/SiC composite fabrication process]

**FIG. 1. Fabrication of SiC/SiC composites by radiation cured preceramic polymer.**

**TABLE I. PROPERTIES OF SiC/SiC COMPOSITE COMPONENTS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacture</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC fabric</td>
<td>2D woven Hi-Nicalon NCK</td>
<td>Tensile strength: 2.8 GPa Density: 2.7 g/cm³</td>
</tr>
<tr>
<td>Preceramic polymer</td>
<td>Polycarbosilane (PCS) NCK</td>
<td>Melting point: 511 K Mn: 2000</td>
</tr>
<tr>
<td></td>
<td>Polyvinylsilane (PVS) Mitsui Chemicals</td>
<td>Liquid at R.T. Mn : 1000</td>
</tr>
<tr>
<td>SiC powder</td>
<td>BETARUNDUM (Ultrafine grade) Ibiden</td>
<td>Particle diameter: 0.27 µm</td>
</tr>
</tbody>
</table>
The obtained pre-ceramic composite was irradiated by 2 MeV-electron beam (EB) generated by the electron accelerator (Cockcroft Walton type, JAERI, Takasaki) at ambient temperature in order to crosslink PCS contained in the composite. The preceramic composites placed into the irradiation chamber is shown in Fig. 2, and were irradiated up to 15 MGy at a dose rate of 1 kGy/s under helium gas flow. After the EB irradiation, the composite in the chamber was heated up to 773 K for 1 hr in argon gas flow to quench the residual radicals of polymer blend in the matrix of the composite. If the residual radicals were not be quenched, the radicals would react rapidly with oxygen in air even at ambient temperature to result in oxidation of the matrix (T. Seguchi, et al., 1992; K. Okamura, et al., 1992).

The cured preceramic composites were fired at 1573K for 30 min in an electric furnace with a heating ramp rate of 200 K/hr to get the final SiC/SiC composites, and were cooled down to room temperature.

The weight and the volume of the final SiC/SiC composites were measured and their open porosity was also measured from the amount of absorbed liquid into the final composites. According to the JIS method (K-7203), three point bending tests were carried out at a cross-head speed of 0.5 mm/min and a span length of 40 mm by using a load tensile testing machine (Instron, model 4302) at ambient temperature.

**FIG. 2. Irradiation chamber for EB curing of the preceramic composite.**

### 3. RESULT AND DISCUSSION

Fig. 3 shows the photograph of the final SiC/SiC composite fired at 1573K in argon gas. By applying EB curing technique, the CMC was obtained by only single impregnation / pyrolysis cycle, and the shape and the size of the composite do not change between before and after firing without pressure or casting in a furnace. The fiber volume fraction of the SiC/SiC composite could be increased up to over 50%, which is very high in the case of 2D-reinforced CMC. This polymer blend with low viscosity was difficult to be fired without shape change during firing process, but EB curing technique is very useful for this new polymer blend.

Fig. 4 shows the relationship between absorbed dose of the cured preceramic composites containing 40 vol% 2D plane woven SiC fiber and their ceramic conversion yield in firing process at
1573K in argon gas. The sample A was impregnated by PCS containing slurry, and the sample B was impregnated by polymer blend (PCS + PVS) slurry.

In the case of the sample A, the yield of the cured composite is 88 % at 5 MGy irradiation, and above 8 MGy irradiation, the yield is constant at about 93 %. This 7 % weight loss corresponds to 20 wt% weight loss of PCS in the matrix during pyrolysis reaction, which is nearly equivalent to the value of weight loss in the case of SiC fiber fabrication by the radiation curing. Therefore, below 8 MGy irradiation, PCS, which has not crosslinked, is volatilized in firing process, and it is concluded that the absorbed doses above 8 MGy are needed to cure PCS sufficiently in the composite. Though more doses (above 12 MGy) are needed for SiC fiber fabrication to hold a condition of a fine fiber during firing process (Sugimoto, et al., 1995) less doses (above 8 MGy) are required for the cured composite. On the other hand, the sample B shows lower yield compared with the sample A. It needs more than 15 MGy to get the yield over 90%. Since the PVS has lower molecular weight and low viscosity, it is easy to decompose during pyrolysis reaction. Therefore, high irradiation dose is needed to get the same yield as that of the sample A.

FIG. 3. Photograph of SiC/SiC composite (Irradiation: EB 2MeV, 15Mgy; Firing: 1573 K in argon).

FIG. 4. Yield of cured preceramic composite containing 40 vol% SiC fiber in firing at 1573 K in argon gas. (A) matrix : PCS, B) matrix: Polymer blend (25 mass% PVS).
4. CONCLUSION

We succeeded to improve the fracture properties of the SiC/SiC composites using the radiation-cured preceramic polymer process. The EB irradiation technique is very useful to fabricate the composite without impurities and to get the high ceramic conversion yield through the polymer impregnation and pyrolysis method. It could use the new polymer blend such as polycarbosilane (PCS) and polyvinylsilane (PVS). The composite showed a ductile properties without fiber coating and we could make the composites with over 50 vol% fiber volume fraction.
REFERENCES


PREPARATION OF GYPSUM/POLYMER COMPOSITES USING GAMMA RADIATION

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Abstract

Polymer gypsum composites were prepared using gamma radiation. Natural and chemical pure, dried and partially wet, gypsum powders were mixed with butyl methacrylate and methyl methacrylate and irradiated by different doses. The prepared composites were investigated using thermogravimetry (TG) to follow the kinetics of the polymerization reaction. The obtained data show that a polymerization ratio of about 100% can be achieved using a dose of 15 kGy. Furthermore, the glass transition temperatures (Tg) of the prepared composites were determined using differential scanning calorimetry (DSC) and thermomechanical analysis (TMA).

1. INTRODUCTION

Composites with desired properties can be made by incorporating particulate fillers into a polymer matrix to suit various applications [1-5]. The rubber industry has long utilized the addition of finely divided particulate fillers, such as carbon black and silicate, to polymeric materials. Wood polymer composites were also prepared in order to improve the specific properties of wood [6-10].

The aim of this study was the preparation of new composites consisting of poly (butyl methacrylate) or poly (methyl methacrylate)/gypsum, which would account for different thermal and mechanical properties.

2. EXPERIMENTAL

Natural gypsum or chemically pure calcium sulfate dihydrate powders (Merck, purity >99%) were used for preparing the mixtures. The natural gypsum powders were obtained from natural rocks from a mine near the City Latakia in Syria. After sieving the powders, the diameter of particles was less than 0.3mm. The obtained powders were used directly or after drying at 200 °C for 2 h. The gypsum powder was added to the pure monomer step by step during stirring at room temperature until a weight ratio of 1:1 was achieved in all experiments of this study. Two monomers (butyl methacrylate, methyl methacrylate, obtained from Merck) were used in this work so that we obtained eight different mixtures:

a) Dried natural gypsum + butyl methacrylate (N. G. BuMA. D.)
b) Wet natural gypsum + butyl methacrylate (N. G. BuMA. W.)
c) Dried pure gypsum + butyl methacrylate (Ch. G. BuMA. D.)
d) Wet pure gypsum + butyl methacrylate (Ch. G. BuMA. W.)
e) Dried natural gypsum + methyl methacrylate (N. G. MMA. D.)
f) Wet natural gypsum + methyl methacrylate (N. G. MMA. W.)
g) Dried pure gypsum + methyl methacrylate (Ch. G. MMA. D.)
h) Wet pure gypsum + methyl methacrylate (Ch. G. MMA. W.)

The monomer/powder/mixtures were filled up in polyethylene tubes (inner diameter ca. 2.3 cm, length ca. 10 cm) and then subjected to a 60Co γ irradiator (Russian type: Issledovatel – 251.6 TBq). Irradiation was carried out at room temperature and a dose rate of 3.3 kGy/h to different doses.
2.1 Composite characterization

2.1.1. Thermogravimetry (TG)

The dynamic weight loss tests were conducted by using a Mettler instrument. All tests were conducted in a nitrogen purge (30 ml/min) using sample weights of 10-15 mg at a heating rate of 10°C/min. The resolution of the balance is given as 1 microgram for weights less than 100 milligram, and the temperature precision of the instrument is ±2°C. The total experimental errors in the determination of the decomposition temperatures were estimated to be not more than ±3°C.

2.1.2. Differential scanning calorimetry (DSC)

The glass transition temperatures of the composites were determined by the use of a Mettler DSC20 instrument. All samples were tested in aluminum pans at a heating rate of 10°C/min over a temperature range from room temperature to 200°C. The precision of the used instrument is ±0.2°C, and the experimental errors in the measurements were estimated to be about ±0.5°C.

2.1.3. Thermomechanical analysis (TMA)

Probes of the same samples were also investigated using a Mettler TMA40 instrument in order to locate the glass transition temperature of the prepared composites for comparison with the DSC data. The used instrument has a precision of ±2°C, and the total experimental errors in the measurements were estimated to be about ±3°C.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetry

Thermogravimetry (TG) was used to follow the kinetics of polymerization. Typical TG thermograms are shown in Figs 1 and 2. The conversion ratios of polymerization were determined from the TG thermograms for the eight composite systems. The conversion ratios of these prepared samples are listed in Table I and show that the conversion ratio of polymerization reactions depends, as expected, on the used dose. Furthermore, a conversion ratio of near 100% of polymerization can be achieved using a dose of about 15 kGy. The dependence of polymerization ratio on the used dose differs slightly from one composite system to another.

Fig. 1 shows typical TG thermograms for poly (methyl methacrylate)/gypsum composites, which were prepared by gamma irradiation of the monomer/gypsum mixture to doses of 5 kGy, 10 kGy and 15 kGy. The thermograms show two steps; the thermogram of the sample prepared at 15 kGy shows that there is only a very small amount of the monomer. The first step in the thermograms corresponds to the evaporation of the rest monomer and the second step, to the decomposition of the polymer.

**TABLE I. CONVERSION RATIOS OF THE POLYMERIZATION FOR THE EIGHT COMPOSITE SYSTEMS**

<table>
<thead>
<tr>
<th>Composite system</th>
<th>Dose [kGy]</th>
<th>2.5</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
<th>12.5</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ch. G. BuMA. D.</td>
<td>3.54</td>
<td>8.06</td>
<td>19.92</td>
<td>29.56</td>
<td>60.63</td>
<td>99.79</td>
<td></td>
</tr>
<tr>
<td>Ch. G. BuMA. W.</td>
<td>0.56</td>
<td>6.05</td>
<td>10.21</td>
<td>23.48</td>
<td>42.71</td>
<td>99.65</td>
<td></td>
</tr>
<tr>
<td>N. G. BuMA. D.</td>
<td>2.79</td>
<td>7.95</td>
<td>14.26</td>
<td>28.68</td>
<td>50.69</td>
<td>99.86</td>
<td></td>
</tr>
<tr>
<td>N. G. BuMA. W.</td>
<td>1.01</td>
<td>9.56</td>
<td>24.01</td>
<td>44.62</td>
<td>69.13</td>
<td>98.88</td>
<td></td>
</tr>
<tr>
<td>Ch. G. MMA. W.</td>
<td>5.41</td>
<td>15.84</td>
<td>25.08</td>
<td>39.89</td>
<td>57.54</td>
<td>99.45</td>
<td></td>
</tr>
<tr>
<td>Ch. G. MMA. D.</td>
<td>2.79</td>
<td>7.95</td>
<td>14.26</td>
<td>28.68</td>
<td>50.69</td>
<td>99.86</td>
<td></td>
</tr>
<tr>
<td>N. G. MMA. D.</td>
<td>3.54</td>
<td>8.06</td>
<td>19.92</td>
<td>29.56</td>
<td>60.63</td>
<td>99.79</td>
<td></td>
</tr>
<tr>
<td>N. G. MMA. W.</td>
<td>5.407</td>
<td>15.84</td>
<td>25.08</td>
<td>39.89</td>
<td>57.54</td>
<td>99.45</td>
<td></td>
</tr>
</tbody>
</table>
The decomposition temperatures were determined for all composite systems and pure poly (methyl methacrylate) which were prepared using a dose of 20 kGy. It was found that the decomposition of the polymer in the composite takes place at 303°C at least, and of the pure polymer at 288°C. Thus the decomposition temperature of the polymer was increasing by 15°C at least.

![FIG. 1. TG thermograms of poly (methyl methacrylate)/gypsum/composites prepared at doses 5 kGy, 10 kGy, and 15 kGy.](image1)

Fig. 2 shows the TG thermograms of poly (butyl methacrylate)/gypsum/composites prepared at doses 5 kGy, 10 kGy, and 12.5 kGy. There are in all cases two steps corresponding to the evaporation of the rest monomer and to the decomposition of the polymer.

The decomposition temperatures of all poly (butyl methacrylate)/gypsum/composites and the pure poly (methyl methacrylate) as a reference were determined, which were prepared using a dose of 20 kGy. The decomposition of the composites took place at 276°C at least, and of the pure polymer at 271°C. Thus the decomposition temperature of the polymer was increasing by 5°C at a minimum.

![FIG. 2. TG thermograms of poly (butyl methacrylate)/gypsum/composites prepared at doses 5 kGy, 10 kGy, and 12.5 kGy.](image2)
3.2. DSC and TMA

Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) have been used to locate the glass transition temperature (T_g) of the prepared samples; Polymer/gypsum/composites and pure polymers of both monomers (MMA, BuMA) were prepared using a dose of 20 kGy. Typical DSC thermograms are shown in Fig. 3 of poly (butyl methacrylate)/gypsum/composite 3a, and of pure poly (butyl methacrylate) 3b.

For better determination and comparison, all composites were also investigated using TMA.

Fig. 4 shows TMA thermogram of poly (butyl methacrylate)/gypsum/composite 4a, and a TMA thermogram of pure poly (butyl methacrylate) 4b. The glass transition temperatures of all samples were determined using the onset method.

The glass transition temperatures of poly (methyl methacrylate)/gypsum/composites were determined using both techniques to be about 123°C irrespective of the type of the filler involved in this work. This value does not show a significant difference to the glass transition temperature of pure poly (methyl methacrylate), although an increasing of the T_g was expected. The increasing of the T_g of composites compared with the pure polymer have been documented in a number of other composite systems and have been explained on the basis of reduced mobility of molecular segments in the vicinity of the filler [2].

The glass transition temperatures of the prepared poly (butyl methacrylate)/gypsum/composites were also determined using both techniques and found to be about 33°C irrespective of the type of the filler. This value is significantly different from the T_g of pure poly (butyl methacrylate) which is 28°C. This harmonizes with the literature and could be explained with on the basis of interaction between the filler (calcium sulfate) and the polymeric chain [2]. The butyl rest on the chain side of poly (butyl methacrylate) reduces the mobility of the polymeric chain stronger compared with the methyl group in poly (methyl methacrylate).

![Graph showing glass transition temperatures for PMMA-G and PMMA](image)

**FIG. 3. DSC thermograms of poly (methyl methacrylate) / gypsum/ composite and pure poly (methyl methacrylate), which were prepared using radiation dose of 20 kGy.**
FIG. 4. TMA thermograms of poly (butyl methacrylate)/gypsum/ composite and pure poly (butyl methacrylate), which were prepared using radiation dose of 20 kGy.

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Invited Paper

RADIATION PROCESSING OF NATURAL POLYMERS FOR INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS

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Abstract

Radiation modification of chitin and modified cellulose was carried out. Films of polyethylene blended with starch, cellulose and agrowaste were prepared. Radiation Processing reduced the processing time for chitin, modified cellulose grafted with acrylic acid exhibited high water uptake while PE films blended with irradiated agrowaste were found to be biodegradable.

1. INTRODUCTION

Industrial development and the need to protect the environment, are placing escalating demands on the natural resources and improved technologies. Our society is becoming richer and at the same time it is realising that earth’s resources are not everlasting and the effect of rapid growth on the environment will adversely affect the future developments. Radiation technology has been used to produce high performance polymeric materials with unique physical and chemical properties. However most of the applications of radiation technology in polymer industry so far have centred around the synthetic polymers such as polyethylene, polypropylene etc. It is now being realised that this technology can successfully be utilised to upgrade natural polymers as well, yielding value added products for diverse applications.

Cellulose is the most abundant natural polymer on this planet, its high abundance and the presence of reactive hydroxyl groups in the chain promise an array of potential applications. The modified celluloses like carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) etc. are more useful in producing specialised polymers due to their solubility in water. CMC is the most promising derivative of cellulose that can be used for the production of hydrogels, since it has an ionisable carboxyl group. These hydrogels find applications in health care products like baby diapers, sanitary napkins etc., in agriculture for maintaining the moisture level of soil and in chemical and textile industry for removing hazardous metal ions and dyes from the effluent.

Chitin is the second most abundant polymer, and is found in the exoskeleton of marine life such as shrimps, crabs, shell fish etc. However utilisation of chitin is far less than that of cellulose. This polymer will gain its prominent position in the very near future. The most promising feature of this polymer is that it is recovered from the waste of fisheries industry that often causes environmental pollution. Chitosan, a derivative of chitin has many applications due to its solubility in aqueous acidic medium unlike chitin which is insoluble in water in the entire pH range. Radiation technology offers a cleaner system for crosslinking chitin/chitosan in aqueous medium for producing bioactive hydrogels. These hydrogels have many applications such as wound dressing, haemostatic agents and in drug delivery systems. Starch is the third most important natural polymer that finds use in traditional applications such as, thickening agent, adhesive etc. However bulk of starch is consumed as food and in related supplements.

All these polymers are presently being exploited for industrial use. However by judicious use of radiation these polymers can yield high value products with interesting applications. Possibility of blending man made polymers with natural polymers also opens up a new avenue for novel
applications. Although a number of possibilities exist the economics of radiation processing is yet to be worked out.

At BARC work has been carried out in the following specific areas of radiation modification of natural polymers, (i) chitin, (ii) modified celluloses and (iii) PE-Cellulose copolymer. The paper briefly describes the details of this work. Some work has also been carried out on radiation grafting on man made polymers with a view to blend them with natural polymer like chitin in the future.

2. RADIATION PROCESSING OF CHITIN/CHITOSAN

Shrimp waste contains about 23% chitin, India generates 80,000 tons of this waste annually. Chitin which is present in this waste as a composite with proteins, minerals etc. can be extracted by successive acid (demineralization) and alkali (deproteinization) treatments as shown in the scheme 1. As can be seen from scheme 1, high concentrations of acid /alkali are required and also the process is carried out at high temperature for long duration. In recent study, it has been reported that irradiation of shrimp shells with gamma irradiation dose of 25 kGy reduces the time of reaction of deproteinization from 8 hr to 1 hr resulting in tremendous amount of energy and cost saving in the process [1]. Radiation method of extraction of chitin from waste is shown in scheme 2.

2.1 Scheme 1: Conventional method

Shrimp shells $\rightarrow$ Demineralization with 2 N HCl for 48 hr $\rightarrow$ Deproteinization with 1 N NaOH at 100°C for 8 hours $\rightarrow$ Chitin

2.2 Scheme 2: Radiation method

Shrimp shells $\rightarrow$ Irradiated to 25 kGy with gamma radiation $\rightarrow$ Demineralization with 2 N HCl for 48 hr $\rightarrow$ Deproteinization with 1 N NaOH at 100°C for 1 hour $\rightarrow$ Chitin

It is understood that upon exposure to radiation, chitin undergo chain scission in a manner similar to cellulose, as the backbone structure of chitin is very similar to that of cellulose.

Insolubility of chitin in aqueous media restrict its applications, however, chitin can be easily converted into chitosan by deacytylation using ~50% w/w NaOH, whereby acetyl group of chitin is converted into a free amino group. Thus chitosan is readily soluble in acidic media. Chemical structures of both chitin and chitosan are shown in Fig. 1.

![Chemical structures of Chitin and Chitosan](image)

**FIG. 1. Structure of (A) Chitin and (B) Chitosan.**

There is a great potential for increasing the use of chitin/chitosan in numerous applications in the health care industry, food and beverage, agriculture, waste and water treatment, provided the solubility of chitin/chitosan can be enhanced. Conventionally, the degradation of chitin/chitosan is carried out by enzymatic reaction. This process requires control of temperature as well as purification of the finished products. In comparison, radiation processing of chitin/chitosan provides a simple and fast
method for its degradation. The materials could be treated either in dry or solution form, at ambient temperature without any additive. There is no contamination from the additives and thermally decomposed materials; in addition, the radiation degradation results in the formation of chitosan having a narrower molecular weight distribution as compared to the conventionally degraded chitosan [2].

The antibacterial activities of chitosan with different forms such as powder, cream and in solution has been well documented [3]. Bioactive hydrogel can be produced by radiation crosslinking of chitin/chitosan in aqueous solution by copolymerizing it with suitable polymers such as poly vinyl alcohol (PVA). The results of some of our recent studies of hydrogel formation are presented in Table I.

| TABLE I. GEL FORMATION CHARACTERISTICS OF PVA (10%) IN PRESENCE OF CHITOSAN (1%) IN AQUEOUS SOLUTIONS (ELECTRON BEAM IRRADIATION) |
|---|---|---|
| S. No. | Dose (kGy) | Gel fraction | Swelling ratio |
| 1. | 30 | 0.1 | Nd |
| 2. | 40 | 0.32 | 38 |
| 3. | 50 | 0.48 | 27 |
| 4. | 60 | 0.60 | 21 |
| 5. | 70 | 0.70 | 14 |
| 6. | 90 | 0.74 | 12 |

These hydrogels may have many medical applications such as wound dressings, haemostatic agents and drug delivery systems of immense benefit to health care industry. It has been reported that the radiation processed PVA-chitosan hydrogels could be very effective in treatment of burn wounds of first, second and third degree [4].

3. RADIATION MODIFICATION OF CARBOXY METHYL CELLULOSE TO PRODUCE SUPER ABSORBING HYDROGELS

Carboxy methyl cellulose (CMC) is an important water-soluble derivative of cellulose. On exposure to high-energy radiation in aqueous solutions, it undergoes degradation. However, its irradiation in presence of monomers like acrylic acid, leads to the formation of three dimensionally crosslinked net work structure that can absorb large quantities of water and can act as a super absorbing hydrogel. Radiation Technology Development Section of BARC has developed a superabsorbent gel using Co-60 gamma radiation. The method for the synthesis of this gel involves the irradiation of aqueous solution of carboxymethyl cellulose, acrylic acid partially (70%) neutralized with NaOH and various other additives to a dose of 5 kGy dose. The resultant gel is dried under vacuum and ground to get a fine superabsorbing powder. It absorbs water 460 times of its dry weight. However a product with atleast double this (~ 1000 times) will make this process economically viable. Influence of various additives on the water absorption characteristics of this gel is shown in Table II.

| TABLE II. EFFECT OF VARIOUS ADDITIVES ON WATER ABSORBENCY OF SUPERABSORBENT GEL |
|---|---|---|
| S. No | Additive | Concentration (wt %) | Absorbency |
| 1 | Ca [2+] | 0.2 | 740 |
| 2 | Mg[2+] | 0.13 | 630 |
| 3 | Al [3+] | 0.5 | 360 |
| 4 | Triton X-100 | 0.5 | 800 |
| 5 | Urea | 0.1 | 680 |
| 6 | HEMA | 5.0 | 270 |
| 7 | HEMA | 10.0 | 140 |
| 8 | HEMA | 20.0 | 60 |
The presence of ionic groups within the gel due to grafted acrylic acid are chiefly responsible for high affinity towards water. Such super absorbing hydrogels have found many applications in a number of areas such as personnel health care and as soil conditioner in rain shadow regions. Seeds have been successfully germinated in the swollen gel and studies on soils amended with gel did not show any significant change in soil microflora, indicating that such gels can be gainfully utilized in agriculture as soil conditioner. Studies to assess its use in actual agricultural application are planned.

4. BIODEGRADABLE PE- AGROWASTE BLENDS

LDPE with MFI 1.7 g min-1 was blended with pure cellulose and starch in three proportions. 1, 5 and 7.5 % w/w (0.2 mm thick). Thus six different blends were obtained, the films (0.2 mm thick) were prepared on a two roll mill. The films were irradiated up mto 50 kGy and then buried in soil. In another experiment the filler was irradiated up to 50 kGy and then the films were prepared and the films were further irradiated to 50 kGy. No weight loss was observed after 90 days. Similar studies were carried out with bagasse, paddy husk and saw dust. Pre-irradiated paddy husk blended films gave the best results and showed total degradation of composite after one year.

5. RADIATION GRAFTED MEMBRANES FOR RECOVERY OF HEAVY METALS FROM INDUSTRIAL EFFULENTS

Extensive investigations on developing polymeric adsorbents capable of recovering heavy metals from seawater have been reported in literature. Among the various adsorbents, chelating resins containing amidoxime groups have been found to be most selective in recovering heavy metals at a fast rate. Radiation grafting technique has been suggested for synthesis of such adsorbents as it offers a very simple and effective way for incorporating required functional groups onto the polymer backbones. Keeping in view the functional requirements of the material, such as long time contact with the sea water and high permeation rate of metal ions in the trunk polymer, porous polypropylene (PP) non-woven fibre was chosen as a material of choice for backbone polymer. The grafting of acrylonitrile onto trunk polymer has been carried out using a 2-MeV electron beam accelerator by post-irradiation grafting method, followed by chemical conversion of the cyano (CN-) group to an amidoxime (C(NH2)-NOH) group. The influence of radiation dose, dose rate, grafting time, solvent effect, grafting temperature, oxidation time of irradiated polymer, irradiation geometry, ambient atmosphere during irradiation and horizontal stacking while grafting on the grafting yield have been investigated. The process parameters have been optimized to achieve a high degree of grafting (about 110% -120% ) using technical grade acrylonitrile onto 6” x 6” samples. FTIR technique has been used to confirm the grafting reaction and its subsequent conversion into amidoxime chelating group.

6. CONCLUSION

Irradiation of chitin before deacetylation has decreased the time of reaction, it is also possible to carry out the deacetylation at room temperature. This will certainly go a long way in establishing this technology.

With the encouraging results obtained with modified cellulose (CMC) - a super absorbent irradiated, grafted CMC scaling up of the process is being proposed since its use in agriculture seems encouraging.

PE-Paddy husk blended PE films will be produced in-house at BARC for market assessment. The 500 keV EB accelerator will be used for this work. The film conveyor has already been installed.

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PROPERTIES OF RADIATION MODIFIED SAGO STARCH AND ITS POTENTIAL AS BIODEGRADABLE FOAMS

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Abstract

The potential of producing biodegradable foam from blend of sago starch and water-soluble polymers was investigated. Blends with various formulations of sago starch and polyvinyl alcohol (PVA), and polyvinyl pyrrolidone (PVP) polymers were prepared and subjected to radiation modification using electron beam irradiation. The effect of irradiation on the blends properties such as colour, viscosity, clarity, and morphology were evaluated and reported. Foams from these blends were produced using microwave oven and its properties such as water absorption, expansion ratio, and biodegradability were characterized and reported in this paper.

1. INTRODUCTION

Research and development on biodegradable and recyclable polymer is gaining momentum to offer alternative eco-friendly products. Natural polysaccharides are among the most promising materials for the production of biodegradable foams. Starch, essentially a polysaccharide is totally biodegradable in a wide variety of environments and could assist in developing totally degradable materials to meet niche market demands for biodegradable plastics. One kind is sago starch, which is abundant in Malaysia. Malaysia is the principle sago exporter to the world market (Anon, 1996). The total area cultivated with sago crop is estimated to be more than 20,000 hectares with around 90,000 tonnes annual production. In 1994, a total amount of almost 40,000 tonnes of sago starch was exported, worth over RM 24 millions and has since increased to RM 42.2 millions in 1998. It is produced from pith of sago palm and has served as a useful indigenous resource for commercial raw materials and foodstuff products (Takeda, et al., 1989). Its abundance and availability have made it an attractive candidate for use in development of biodegradable starch foam and other composites.

Information of the electron beam (EB) irradiation of sago starch is very limited. The inception of the IAEA/CRP Programme on Radiation Modification of Indigenous Natural Polymer has been a stimulus in our current work on the EB modification of sago starch. This paper reports on the effects of EB irradiation on some characteristics of sago starch as a raw material for starch based foam production. Characteristics of irradiated tapioca starch were also studied for comparative purposes.

2. EXPERIMENTAL

Powder sago used of industrial grade was given by Nitsei Sago Industries Sdn. Bhd., Mukah, Sarawak. Water soluble polymer such as PVP (Polyvinyl pyrrolidone), HEMA (Hydroxyethyl methacrylate) HEA (Hydroxyethyl Acrylate), PVA 117 (Polyvinyl alcohol) were obtained from Kuraray and Aldrich.

2.1. Determination of colour

The colour of sago and tapioca starch was measured using a Hunter Lab colorimeter (Model D25-2) standardised with a white chromatic reflectance standard (L=98.94; a=-0.17; b=0.04). Samples were put in the transparency plastic bag. The L, a and b values denotes lightness, redness and yellowness, respectively (Hunter and Harold, 1987).
2.2. Clarity

The clarity (%T_{650}) of 1% starch paste, which had been heated in a boiling water bath for 30 min and cooled to 25°C for 1 hour, was evaluated using percent transmittance at 650 nm against a water blank in a spectrophotometer.

2.3. Blends and foam morphology

Blends and foams morphology was investigated using a Joel JSM-35 (Joel Ltd., Tokyo) scanning electron microscope (SEM) with an acceleration voltage of 10-15 kV. Samples were mounted onto circular aluminium stubs with double side sticky tapes. The stubs were then gold coated and photographed in a Hitachi (S570) scanning electron microscope at an accelerating speed of 25 kV.

2.4. Preparation of sago water soluble polymer blends

PVA solution (100 ml) of known concentration was heated continuously in a water bath at 90°C. Sago powder of known weight was added slowly and stirred for 2 minutes or until a gelatinized solution was about to achieved. The sago gel was then poured into a petri dish (9 x 9 mm) and cooled to a room temperature to form solid sample of about 4 mm. These samples were then subjected to irradiation and foaming processes.

PVP-sago, HEMA-sago and HEA-sago blends were prepared in the same manner as PVA-Sago gel.

2.5. Irradiation crosslinking

Petri dishes containing sago-gel were irradiated at 10, 15, 20, and 30 kGy. The irradiation parameters used were 3 MeV acceleration voltage and 10 mA current.

2.6. Gel content measurement

Triplicate irradiated sago-gel samples were cut into small pieces of known weight (about 0.2 g) and placed in stainless steel pouches. The pouches were placed in glass bottle containing 0.5 M NaOH overnight. Samples were rinsed thoroughly to neutral state and dried in a vacuum oven at 60 ºC overnight. The final weight of the sample was measured and the gel content was calculated from the ratio of final weight over the original weight (taking into account the initial water content in gel samples).

2.7. Foaming

Irradiated samples of 30 x 45 mm sizes were foamed in a microwave oven for 3 minutes at 150 ºC (high heating mode). The foams were evaluated of its foamability, resilience, water absorption, expansion ratio and biodegradability.

2.8. Expansion ratio

Expansion capability of sago to foam was calculated from the difference of weight over initial weight after expansion as expansion percent.

2.9. Degradability

Biodegradability of sago foams was evaluated using soil burial method. The soil burial test was performed by burying the samples in the clay 20 cm depth with a pH from 6.5 to 7.5. The soil was not supplemented with any additional nutrients or microorganisms. Sample foams (4cm X 5em) of known weight were cut from prepared foams prior to exposure in the soil testing systems. Sago foams were
labeled and placed in a quadrant of 1 feet deep dug-up soil. The area was then carefully filled with soil. The foams appearance and weight was monitored at selected days.

3. RESULTS AND DISCUSSION

3.1. Radiation effect on starch

3.1.1. Colour

The effect of irradiation dose on the colour of sago and tapioca starch is shown in Figs 1, 2 and 3. The lightness (b value) did not increased while the yellowness (a value) and redness (b value) were significantly increased. The increment of the yellowness and redness of sago starch was observed to be higher than that of tapioca starch. This might be due to the formation of the pigment by the releasing of the enzyme Polyphenol Peroxidase after the starch granule was damaged (Ozawa and Arai, 1986). According to Rosenthal (1992), the enzymes are not very much effected by doses of ionizing radiation, which would be inoffensive to the wholesomeness of a food product. Therefore, even in radappertised products, the deactivation of endogeneous enzymes is more easily achieved by a preliminary thermal treatment. However, he also reported that enzymes usually survive exposures of up to 10 kGy.

\[ \text{FIG.1. Effect of irradiation dose on the L-value of sago and tapioca starch.} \]

\[ \text{FIG. 2. Effect of irradiation dose on the a-value of sago and tapioca starch.} \]
3.1.2. Clarity

Fig. 4 shows the clarity of sago and tapioca starch after irradiation. The clarity increases when the irradiation dose is increased. Clarity is an important aesthetic quality of a starch paste with respect to transparency or opacity. In some instances, as with starches used to thicken salad dressings, opacity is desirable to enhance a light bright colour (Pomeranz, 1991). In this experiment, opacity should be preferred as it would be acceptable for the foam production and less irradiation dose was required. The clarity of sago starch was higher than tapioca starch. This might be due the damage of amylose in the starch granule.

3.2. Crosslinking of sago and sago blends

Sago on its own does not readily crosslink by electron beam irradiation. Fig. 5 shows that highest gel content of around 9% was observed at 25 kGy irradiation. PVA and PVP are both crosslinkable type polymers. Comparatively, the PVP is more crosslinkable than the PVA. This property is shown in Fig. 5. At 20 kGy dose, as much as 60% gel content can be obtained for PVP. However, only about 25% gel content can be observed in the case of PVA. The value does not increase further even at a higher irradiation dose of 50 kGy.
It is interesting to note that blending sago with water soluble polymers such as PVA and PVP shows a significant increase in gel content value indicating greater crosslinking ability. This is observed in Fig. 6. As much as 35% gel was observed in blends of 20:20 ratio (Sago:PVA) at 30 kGy dose. The PVA content added in the blend does affect to certain extends the crosslinking ability of sago blends especially at higher irradiation dose of more than 20 kGy.

The Sago-PVP blends however, showed a contrast crosslinking properties compared to Sago-PVA. The presence of sago reduced the crosslinking ability of PVP as seen in Fig. 5. In general, the gel content values of these blends are 23% for the one containing 10% PVA and about 30% for blends containing 20% PVP.

Fig. 7 shows the crosslinking properties of sago with HEMA and HEA monomers, respectively. The gel content values obtained are much higher compared to Sago-PVP and Sago-PVA blends. This is especially so in the case of sago-HEA formulations having more than 40% gel content. An increased in irradiation doses however did not increase further the gel value. There is a possibility that these monomers acted as a crosslinking accelerator and thus promotes crosslinking efficiency.
Fig. 7 also shows the relationship of gel content and amount of N,N'-methylene-bis-acrylamide) (BMA) added at various irradiation doses. Similar crosslinking properties were observed in sago blends containing BMA, as crosslinking accelerator. As Fig. 7 shows, the BMA helped increase the crosslinking of sago in which case the highest gel content values were obtained at high concentration of BMA. To certain extent, however, increasing irradiation dose reduced their crosslinking ability. The gel content value for sago added with 10% BMA is about 60% at 15 kGy dose.

3.3. Sago foams

Sago on its own was observed to be non-expansible. It is hoped that blending sago with water soluble polymers such that PVA would assist foaming. Electron beam irradiation was used to induce crosslinking. At present foam expansion was achieved using microwave oven.

Even though, the BMA, HEMA and HEA were observed to help increased crosslinking efficiency in sago blends, these blends were not readily foamable. In most cases, it produced poor quality and rigid foams. Formulations with higher BMA concentration did not foam at all and the sample turned brittle and hard upon heating in the oven.

Fig. 8 shows the morphology of sago foams. The sago-PVP formulations foamed very well but produced hard foams. Formulations having more than 20% sago and irradiated at 15 kGy produced better foams than others. It was observed also that irradiation dose of more than 25 kGy tends to give rigid foams.
In general, sago-PVA formulations gave softer and more resilient foams than the others. For sago-PVA blends, the optimum irradiation dose was between 15-20 kGy. It was observed that best foams could be obtained with more than 15% PVA content. As much as 80% sago can be added. Evaluation on water absorption properties, expansion and biodegradability were evaluated using these Sago-PVA blends.

Blends should have sufficient mechanical properties to sustain foam cell from collapsing. In the production of polyolefin foam such as polyethylene foams, crosslinking was introduced to achieve required mechanical properties to avoid this phenomenon. Having too much crosslinking also restricts formation of foam cells during expansion process. This dynamic properties requirement is clearly shown in Fig. 9. The highest expansion for sago-PVA blends (S40PVA20) was achieved at 15 kGy irradiation dose, i.e. indicating balanced properties of expansion and mechanical strength. At irradiation dose exceeding higher than 15 kGy, the blend ability to foam decreases tremendously.

3.4. Biodegradability of sago foams

Exposures in natural environments provide the best true measure of the environmental fate of a polymer because these tests include a diversify organisms and achieve a desirable natural closeness of fit between the substrate, microbial agent and the environment (Ching, C. et. al., 1993). Measuring the degradability of materials after exposure testing can be relatively straightforward. In this work, the soil burial test was performed by burying the samples in the clay 20 cm depth with a pH from 6.5 to 7.5. Sample foams (4 x 5 cm) of known weight were cut from prepared foams prior to exposure in the soil testing systems. The soil was not supplemented with any additional nutrients or microorganisms.
Initial soil burial test indicated that the sago-PVP and sago-PVA foams are biodegradable. It was observed that after one week, all samples tested disappeared. The photographs taken for samples after two and five days clearly indicate the biodegradability of sago foams. It was presumed that termites digested the foams.

In another experiment, samples were dipped in 10% (w/v) soil water and incubated in shaker at 27°C and 90 rpm. After each interval, the samples were removed from the soil and cleaned with running water and dried in an oven to constant weight at 60°C. Fig. 10 shows that the weight loss of foamed sample increases with burial time. Living organisms are capable of producing enzymes that can attack these foams more easily due to the presence of a large number of cells. The lower percentage in weight loss is also due to very short burial time, and there was insufficient number of active microorganisms to attack these foams. There are several factors such as temperature, pH, oxygen concentration, humidity and availability of mineral nutrients that may affect this result.

REFERENCES

EFFECT OF ACID ADDITIVES ON GRAFTING EFFICIENCY AND WATER ABSORPTION OF HYDROLYZED CASSAVA STARCH GRAFTED POLYMERS

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Abstract

Gelatinized cassava starch was radiation graft copolymerized with acrylamide, acrylic acid or their mixture in the presence of sulphuric acid or maleic acid. Various acid concentrations were used from 0.001 to 0.1 M of sulphuric acid while the maleic acid concentrations were varied from 1 to 3% (by weight). The optimum total dose and dose rate were investigated. The saponification temperature and time had the marked effects on grafting characteristics and water absorption capacity. We found that the effect of maleic acid addition gave a profound effect on water absorption. The CHNS/O analyses indicated significant changes in the nitrogen content in the hydrolyzed starch grafted polyacrylamide with 2% maleic acid. The article explains the possible causes for the enhancement influence of mineral acid and maleic acid on grafting behavior and water absorption of the saponified cassava starch grafted polyacrylamide superabsorbent polymer.

1. INTRODUCTION

Acid additive was historically one of the first additives in radiation processing. Several synergistic effects of acid addition were reported earlier [1-4]. Generally, high acid concentration can hydrolyze both starch and cellulose backbone, which gives rise to glucose units. However, careful addition of the acids provides two significant effects [5]. For the maleic acid addition on radiation polymerization of acrylamide, Gueven et al. [6] found a positive effect on water absorption. Hence, it is the objective of the present research to investigate their effects on radiation copolymerization of gelatinized cassava starch with acrylamide, acrylic acid or their mixture on water absorption capacity in the presence of acid additives.

2. EXPERIMENTAL

Cassava starch was gelatinized in water at 85±3°C for one h to form paste-like slurry. The gelatinized cassava starch was graft copolymerized with acrylamide (AM) or acrylic acid (AA) or a mixture of 1:1 AM/AA in the presence of mineral acids or maleic acid (MA). The mixture was irradiated by γ rays at a dose rate of 1.71 kGy h⁻¹ to a total dose of 6 kGy. The reaction mixture was precipitated with acetone and dried in a vacuum oven at 56°C for 24 h. The ground mixture was centrifuged to separate the graft copolymer. The graft copolymer was washed with distilled water and centrifuged. The supernatant was precipitated to give polyacrylamide (PAM). The graft copolymer was treated in situ with acetone to remove the absorbed water, dried in a vacuum oven at 50°C for 24 h and weighed to determine the amounts of the homopolymer and free copolymer. The grafted (co)polymer was also separated from the starch by heating with 1.5 M HCl for 2 h under reflux. The grafted polymer was filtered and washed with acetone until pH 7 was reached. It was then dried to determine the amount of grafted polymer chain as add-on. The residual starch remained in the grafted polymer after the acid hydrolysis was checked with iodine solution.
2.1. Effect of mineral acid additives on graft copolymerization of AM, AA or AM/AA mixture

Ten gram of the gelatinized starch and 20 g of AM or AA were mixed with 10 cm³ of various concentrations of nitric acid (0.01 \( M \)) or sulphuric acid (0.001 to 0.01 \( M \)) for graft copolymerization. The dose rate of 1.71 kGy h⁻¹ to a total dose of 6.0 kGy was given to the above mixture.

2.2. Effect of maleic acid (MA) additive on graft copolymerization of AM

Ten gram of the gelatinized starch and 20 g of AM were mixed with 1 to 3% (by weight) of MA. Graft copolymerization was carried out with the dose rate of 1.71 kGy h⁻¹ to a total dose of 6.0 kGy.

2.3. Effect of saponification temperature and time on water absorption

Ten gram of the gelatinized starch was mixed with 20 g AM in the presence of 2% (by weight) of MA. The mixture was irradiated by \( \gamma \)-rays with the dose rate of 1.71 kGy h⁻¹ to a total dose of 6.0 kGy. Three saponification levels were carried out in a 5% sodium hydroxide for the following conditions:

- Saponification temperature at 30°C for 30, 60 or 90 min.
- Saponification temperature at 50°C for 30, 60 or 90 min.
- Saponification temperature at 75°C for 30, 60 or 90 min.

2.4. Analysis of CHNS/O of the saponified starch grafted polyacrylamide superabsorbent

Ten samples of the saponified starch grafted polyacrylamide superabsorbent polymer including a control sample were subject to CHN/O analysis (Perkin Elmer PE 2400 Series II). The samples were pyrolyzed in high-purity oxygen via static-state oxidation. The sample was then gas chromatographically separated by frontal analysis, which was quantitatively detected by thermal conductivity detector.

2.5. Effect of total dose on graft copolymerization of AM with 2% MA

The same recipe of the starch and AM in 2% MA was prepared. They were irradiated by \( \gamma \)-rays with the dose rate of 1.71 kGy h⁻¹ to a total dose of 2 to 12 kGy with an increment of 2 kGy. They were then saponified at room temperature for 90 min.

3. RESULTS AND DISCUSSION

3.1. Effect of mineral acid additives on graft copolymerization of AM, AA or AM/AA mixture

The sulphuric acid concentration used in the range of 1 x 10⁻³ to 1 x 10⁻¹ \( M \) affected the grafting reaction and water absorption of superabsorbent polymers in several ways. Table I shows the effects of the mineral acid additive on graft copolymerization of gelatinized starch and the vinyl monomer as follows.

Normally, the acid addition contributes to an increase in hydrogen atoms to yield a higher G(H) from the secondary electron capture by \( H^+ \). Acid can also increase partitioning monomer in the grafting region of the grafting backbone. In Table I, the water absorption in the starch-polyacrylate superabsorbent polymer increased when 0.01 M HNO₃ was added in the gelatinized starch with AA. Kiatkamjornwong et al. [7] explained the cause of the increased water absorption in terms of nitrate and/or nitrite compounds, which are relatively hydrophilic as shown in equation 1. Irradiation of nitric acid solution gives radiolysis products of H₂O₂ and NO₂⁻ with G(H₂O₂) and G(NO₂⁻) of 0.74 and 0.3, respectively.
TABLE I. EFFECT OF THE ACID ADDITIVE ON GRAFT COPOLYMERIZATION OF AM, AA OR AM/AA ONTO THE GELATINIZED CASSAVA STARCH

<table>
<thead>
<tr>
<th>Sample</th>
<th>% conversion</th>
<th>% free polymer</th>
<th>% add-on</th>
<th>% GE</th>
<th>WA (g g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive a</td>
<td>99.4</td>
<td>7.3</td>
<td>58.7</td>
<td>88.2</td>
<td>593 ± 33</td>
</tr>
<tr>
<td>0.01 M H₂SO₄ a</td>
<td>96.2</td>
<td>2.5</td>
<td>50.0</td>
<td>95.1</td>
<td>343 ± 42</td>
</tr>
<tr>
<td>No additive b</td>
<td>89.3</td>
<td>2.2</td>
<td>53.3</td>
<td>95.9</td>
<td>237 ± 18</td>
</tr>
<tr>
<td>0.01 M H₂SO₄ b</td>
<td>97.5</td>
<td>2.4</td>
<td>54.7</td>
<td>95.8</td>
<td>210 ± 44</td>
</tr>
<tr>
<td>0.01 M HNO₃ b</td>
<td>95.6</td>
<td>2.4</td>
<td>51.8</td>
<td>95.4</td>
<td>283 ± 49</td>
</tr>
<tr>
<td>No additive c</td>
<td>98.0</td>
<td>9.8</td>
<td>58.9</td>
<td>84.4</td>
<td>1,230 ± 27</td>
</tr>
<tr>
<td>0.001 M H₂SO₄ c</td>
<td>92.8</td>
<td>6.5</td>
<td>51.6</td>
<td>88.2</td>
<td>414 ± 33</td>
</tr>
<tr>
<td>0.01 M H₂SO₄ c</td>
<td>97.9</td>
<td>7.9</td>
<td>56.9</td>
<td>86.9</td>
<td>332 ± 50</td>
</tr>
<tr>
<td>0.01 M HNO₃ c</td>
<td>95.6</td>
<td>2.4</td>
<td>51.8</td>
<td>95.4</td>
<td>110 ± 15</td>
</tr>
<tr>
<td>0.1 M H₂SO₄ c</td>
<td>91.6</td>
<td>15.6</td>
<td>59.7</td>
<td>76.3</td>
<td>277 ± 79</td>
</tr>
</tbody>
</table>

a graft copolymerization of acrylamide onto cassava starch; b graft copolymerization of acrylic acid onto cassava starch; c graft copolymerization of acrylamide and acrylic acid (1:1) onto cassava starch.

![Chemical structure of starch](image)

\[ \text{CH}_2\text{OH} \quad + \quad 3 \text{HONO}_2 \quad \rightarrow \quad \text{CH}_2\text{ONO}_2 \quad \text{O} \quad + \quad 3\text{H}_2\text{O} \quad (1) \]

n = degree of polymerization (DP) = 500-2,500

However, when sulphuric acid was added regardless of its concentration, the water absorption decreased markedly. The higher the acid concentration added the lower the water absorption. Almost all cases, the percentages of homopolymer, and free polymer were decreased. Only in the case of AA/AM, the increase in acid concentration produces a marked increase in homopolymer with a substantial decrease in grafting efficiency. We anticipated that the amount of acid might be too high and the starch backbones might be hydrolyzed before it was grafted with AM or AA. Too high an acid concentration caused random cleavage of the $\alpha-1\rightarrow4$ and $1\rightarrow6$ linkages in the starch molecules to become the shorter chains of oligosaccharide. These short chains produced low values of grafting efficiency. Hydrolysis of amylose in a highly concentrated acid decreased the amylose content and increased its crystallinity, which resulted in a rigid molecular structure and thus reduced water absorption. In the presence of high acid concentration and a long reaction time (3 h), imidization of the amide pendants in the copolymer could occur. Imidization gives a stronger gel structure of the superabsorbent polymers because of the crosslinking reaction.

3.2. Effect of maleic acid (MA) additive on graft copolymerization of AM

Maleic acid is a diprotic acid with one unsaturation. When MA was used as an additive, interesting results were obtained as shown in Table II. The percentage conversion was decreased slightly while percentage free polymer and percentage grafting efficiency increased. Water absorption of the graft copolymer increased slightly with increasing MA concentration. When 2% MA was added, the highest percentage add-on and water absorption of the superabsorbent polymer saponified for 90 min at room temperature were achieved at 62.8% and 1,216 time its dried weight, respectively. Therefore, we chose this MA concentration for the investigation of influences of saponification conditions of the superabsorbent polymer.
TABLE II. EFFECT OF THE MALEIC ACID CONCENTRATION ON GRAFTING CHARACTERISTICS AND WATER ABSORPTION OF THE SAPONIFIED STARCH GRAFT POLYACRYLAMIDE AT 1.71 KGY H\(^{-1}\) AND 6.0 KGY

<table>
<thead>
<tr>
<th>Sample</th>
<th>% conversion</th>
<th>% free polymer</th>
<th>% add-on</th>
<th>% GE</th>
<th>WA (g g(^{-1}))(a)</th>
<th>WA (g g(^{-1}))(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive(c)</td>
<td>99.4</td>
<td>7.3</td>
<td>58.7</td>
<td>88.2</td>
<td>593 ± 33</td>
<td>939 ± 11</td>
</tr>
<tr>
<td>AM-1%MA</td>
<td>90.6</td>
<td>19.5</td>
<td>60.2</td>
<td>71.3</td>
<td>438 ± 69</td>
<td>901 ± 14</td>
</tr>
<tr>
<td>AM-2%MA</td>
<td>99.1</td>
<td>22.5</td>
<td>62.8</td>
<td>68.4</td>
<td>482 ± 21</td>
<td>1,216 ± 14</td>
</tr>
<tr>
<td>AM-3%MA</td>
<td>96.1</td>
<td>26.9</td>
<td>52.6</td>
<td>58.8</td>
<td>540 ± 58</td>
<td>936 ± 13</td>
</tr>
</tbody>
</table>

Saponification of the starch graft polyacrylamide was carried out in 5% alkaline solution at 30°C for (a) 30 min and (b) 90 min.

In the absence of MA, the high amount of PAM was found at 7.3%. In the presence of MA, part of the MA molecules was anticipated to form free copolymer of AM-MA and some of the PAM homopolymer. After the monomers of AM and MA have been irradiated by γ-rays, free radicals are generated. Random reactions of these radicals with the monomers lead to the formation of copolymers of AM and MA [6], because \(r_1\) and \(r_2\) values for AM and MA are 2.2 and 0, respectively [8]. The high amount of homopolymer mixed with the free copolymer might possibly be the PAM due to its relatively high \(r_1\) value. The free copolymer of AM/MA or the grafted copolymer of AM/MA on the cassava starch backbone could be converted into the carboxylate moieties upon alkaline saponification. The result shows that both monomers might prefer copolymerization as an ungrafted, free copolymer of AM/MA, to grafting onto the starch backbone as grafted copolymers. The water absorption in (a) decreased due to the ungrafted free copolymer at the sacrifice of the grafting monomer of AM. Since MA is a diprotic acid, when the saponification time is longer, the carboxylic acid moieties can be converted more completely as the carboxylate group, which enhances the extent of water absorption. Therefore, the saponification effect should be further studied. In addition, Garnett et al. (9) were the first group who used change transfer (CT) monomer complexes as additives in grafting of methyl methacrylate (MMA) to cellulose and polypropylene (PP) with UV and ionizing radiation. The CT complexes such as ether containing an electron rich vinyl group as a donor (D) with maleic anhydride containing an electron poor vinyl group as an acceptor (A) for the photografting of MMA in tetrahydrofuran to cellulose were investigated. Their data show that the CT complex can enhance the grafting yield at least five fold in comparison with the control. They also proposed a typical mechanism for the formation of the excited-stated DA complex.

For the present work of AM and MA in a grafting reaction of AM onto the gelatinized cassava starch, we also proposed a CT complex between AM and MA, because AM as a D is an electron rich vinyl monomer due to the carboxamide group while MA as an A is an electron poor vinyl monomer due to the anhydride group. The CT complex could be an intermediate in the grafting reaction, although the concentration of MA is only 2% since it can be recycled repeatedly. In view of the data in Table II, an unexpected result was found. The amount of homopolymer unfortunately increased while the grafting efficiency and water absorption decreased when compared with the control. One possible reason could be the concentration effect of MA (electron acceptor), which might not be able to stabilize the CT complex.

3.3. Effect of saponification on the acrylamide moiety

The degree of saponification depends on the reaction time, temperature, and concentration of the alkaline solution (10). The degree of saponification of starch-g-polyacrylamide prepared at the total dose of 6.0 kGy with the dose rate of 1.71 kGy h\(^{-1}\) in a 5% potassium hydroxide solution at room temperature for various periods of time is presented in terms of the amount of nitrogen in Table III.
TABLE III. EFFECT OF THE SAPONIFICATION TEMPERATURE AND TIME ON NITROGEN CONTENT AND WATER ABSORPTION

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Nitrogen content (%)</th>
<th>Water absorption (g g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>30</td>
<td>10.8</td>
<td>592 ± 30</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>9.6</td>
<td>1,057 ± 21</td>
</tr>
<tr>
<td>30</td>
<td>90</td>
<td>9.3</td>
<td>1,216 ± 14</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>6.2</td>
<td>934 ± 54</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>5.9</td>
<td>946 ± 12</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>5.9</td>
<td>972 ± 28</td>
</tr>
<tr>
<td>75</td>
<td>30</td>
<td>4.9</td>
<td>960 ± 10</td>
</tr>
<tr>
<td>75</td>
<td>60</td>
<td>4.7</td>
<td>1,296 ± 41</td>
</tr>
<tr>
<td>75</td>
<td>90</td>
<td>4.6</td>
<td>1,159 ± 19</td>
</tr>
</tbody>
</table>

The control sample before saponification (unsaponified sample) contained 11.9% nitrogen.

Table III shows a continuous increase in the degree of saponification as the saponification time increases. The longer the saponification time and temperature, the more the amide groups on the polyacrylamide chains were changed to the carboxylate groups; and the higher the saponification temperature, the greater number of the carboxylate group, as indicated in equation 2. It is of great interest that an increase in saponification temperature hydrolyzes more carboxamide moieties into the carboxylate group than those obtained by the influence of long saponification time. Thermal energy along with the strong alkaline solution can better hydrolyze the acrylamide moiety into the acrylate groups. The ionizable carboxylate ion is responsible for the differential osmotic pressure between the superabsorbent polymer and its surrounding. In equation 2, the x is the amount of the carboxylate group converted by the alkaline hydrolysis of the acrylamide moiety. The optimum ratio between the carboxamide and the carboxylate groups, which controls the water absorption capacity, should be investigated further.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{C}=\text{O} \quad \text{KOH} \quad \text{CH}_2\text{CH}_2\text{C}=\text{O} \quad \text{O}^{-}\text{K}^+ \\
\text{NH}_2 \quad n \quad n-x \quad \text{NH}_2 \\
\end{align*}
\]

\[ (2) \]

3.4. Effect of the total dose on grafting characteristics and water absorption of the hydrolyzed PAM - starch superabsorbent polymer

The effect of total dose under the dose rate of 1.71 kGy h\(^{-1}\) on grafting characteristics and water absorption is shown in Table IV.

TABLE IV. EFFECT OF THE TOTAL DOSE ON GRAFTING CHARACTERISTICS AND WATER ABSORPTION OF THE GRAFTED STARCH/PAM \(^a\) THE DOSE RATE OF 1.71 KGY H\(^{-1}\)

<table>
<thead>
<tr>
<th>Total Dose, kGy</th>
<th>% conversion</th>
<th>% free polymer</th>
<th>% add-on</th>
<th>% grafting efficiency</th>
<th>WA, 30°C, 90 min (g g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>96.6</td>
<td>48.4</td>
<td>54.6</td>
<td>36.8</td>
<td>1,877±16</td>
</tr>
<tr>
<td>4</td>
<td>97.7</td>
<td>30.8</td>
<td>60.5</td>
<td>57.6</td>
<td>2,026±18</td>
</tr>
<tr>
<td>6</td>
<td>98.7</td>
<td>22.9</td>
<td>60.8</td>
<td>67.2</td>
<td>1,216±14</td>
</tr>
<tr>
<td>8</td>
<td>99.9</td>
<td>17.8</td>
<td>61.9</td>
<td>74.1</td>
<td>651± 8</td>
</tr>
<tr>
<td>10</td>
<td>98.4</td>
<td>16.0</td>
<td>63.2</td>
<td>76.8</td>
<td>649± 7</td>
</tr>
<tr>
<td>12</td>
<td>98.5</td>
<td>14.9</td>
<td>67.9</td>
<td>79.8</td>
<td>594± 4</td>
</tr>
</tbody>
</table>

\(^a\)All samples are prepared in the presence of 2% MA as an acid additive.
Increasing the total dose increased the percentage conversion. However, the increase was not significant. Generally, an increase in the total dose enhances the formation of radicals in the reaction mixture of monomer, starch, and water. All molecules are activated to induce a higher conversion for both homopolymer formation and the grafting reaction. As shown in most of the tables, the conversion of the monomers is very high regardless the different amounts of total dose for the cases in Table IV, because the gelatinized starch is still of very high molecular weight. Branching and self-crosslinking reactions take place and induce difficulties in extraction of ungrafted polymers either in the form of homopolymer or the free copolymer. One can anticipate that a semi-interpenetration network could be formed either chemically or physically. Increases in the total dose reduced the amount of free polymer or polyacrylamide. At the high total dose, starch might be partially degraded to result in a relatively low molecular weight product, which can be extracted much easier. The higher the total doses the greater the percentage add-on and grafting efficiency with the reduced water absorption. Too high a grafting frequency or too large a grafting efficiency of the polymer chain reduced the elastic-retraction force of the superabsorbent polymer.

4. CONCLUSION

Cassava starch grafted polyacrylamide superabsorbent polymers were successfully synthesized by a simultaneous irradiation of γ-rays. Influences of mineral acid and maleic acid inclusion as acid additives were studied. The effects of the acid concentration, saponification condition and total dose on grafting characteristics and water absorption were also investigated. We found that the effect of maleic acid addition gave a profound effect on water absorption. The extent of saponification of the grafted PAM strongly depended on the saponification time and temperature. The article explains the possible causes for the enhancement influence of mineral acid and maleic acid on grafting behavior and water absorption of the saponified cassava starch grafted polyacrylamide superabsorbent polymer.

REFERENCES

RECENT PROGRESS IN RVNRL

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Japan

Abstract

A di-functional monomer, 1,9-nonanediol diacrylate (ND-A) was used as an accelerator for radiation vulcanization of natural rubber latex (RVNRL) by $\gamma$-rays and electron beam (EB). Different aspects of irradiation conditions were studied with this new radiation vulcanization accelerator (RVA). The maximum tensile strength of ~30 MPa is achieved from the RVNRL film prepared by gamma rays irradiated latex using 5 phr ND-A and 20 kGy radiation dose. The latex was also irradiated under EB for various lengths of time using fixed volume of latex, RVA and defoamer concentrations and stirring speed of latex. Maximum of ~26 MPa tensile strength was obtained from the film prepared by irradiating latex for 30 minutes with 5 phr ND-A with a latex stirring speed of 210 rpm. The effect of degree of hydrolysis of polyvinyl alcohol (PVA) on the removal of extractable proteins (EP) from RVNRL films was studied. About 60% EP is removed from the RVNRL film having 2 phr PVA and leached for 10 minutes with 1% ammonia but the degree of hydrolysis of PVA has no significant effect on the removal of EP from the RVNRL film.

1. INTRODUCTION

Radiation vulcanization of natural rubber latex (RVNRL) is the process of radiation induced cross-linking of natural rubber ($\text{cis}$-1,4-polyisoprene) in an aqueous dispersed phase. It requires no curatives like sulfur, zinc oxide and chemical accelerators. So there is less or absence of toxicity problem, acid forming gases and ashes. Moreover, the products from RVNRL are free from radioactivity and thus safe to hand. However, a small amount of radiation vulcanization accelerator (RVA) is used with latex to reduce the radiation dose. Until now the monomers (most common is the $n$-butyl acrylate, $n$-BA) are used as the RVA but the bad smell of the monomer deteriorates the working environment and so needed to be improved.

Recently latex protein allergy problem is of concern worldwide. It is reported that by the combined effect of dilution, addition of water-soluble polymer (WSP) and centrifugation, the amount of extractable protein (EP) in RVNRL is reduced to a level less than 5 µg/g [1]. It is also reported that low energy electron accelerators could be used for RVNRL [2]. Combining these results a new RVNRL process has been designed as shown in Fig. 1 [3].

Recently a pilot plant with 250 kV electron beam (EB) is installed at Takasaki Radiation Chemistry Research Establishment (TRCRE), Takasaki, Japan for RVNRL. In this paper progress in RVNRL is reported in the following three topics.

1.1. New RVA, 1,9-nonanediol diacrylate (ND-A)
1.2. Operation of EB pilot plant with 250 kV for RVNRL
1.3. Reduction of EP in RVNRL
2. EXPERIMENTAL

1.4. Irradiation of natural rubber latex (NRL) with ND-A by $\gamma$-rays

A high ammonia latex concentrate (Microtex, Malaysia) was used after diluting with 1% aqueous ammonia to 50% total solids. ND-A obtained from Kyoeisha, Japan, was mixed with latex without further purification by stirring for 30 minutes. Irradiation was done by $\gamma$-rays from Co-60 source at a dose rate of 10 kGy/h for various doses at room temperature. The irradiated latex was cast on glass plates for making films and they were dried, leached in 1% aqueous ammonia and heated at 80°C for an hour. The tensile and related properties were measured with a tensile machine, Strograph-R1, Toyoseiki, Japan. The swelling ratio (wt.) was determined by immersing latex film in toluene for 24 hours.

1.5. Irradiation of latex with EB pilot plant for RVNRL

A defoamer, BYK022, from BYK-Chemie GmbH Co. Ltd., Germany was mixed with latex to suppress the foam formation. The latex was irradiated under EB after mixing with ND-A with constant stirring at a fixed rpm. The length of irradiation time, volume of latex and cover of the reactor vessel were varied to have a proper setting of the plant for latex irradiation.

1.6. Determination of extractable proteins content in RVNRL

To determine the effect of degree of hydrolysis of polyvinyl alcohol (PVA) on the removal of EP from RVNRL film PVAs with varying degree of hydrolysis from Kuraray Co. Ltd., Japan were added to the latex after irradiation as 10% solution at 2 phr concentration each. The degree of polymerization of PVA used in this work is 500. The EP contents in the rubber films were determined following micro BCA protein assay and ASTM D5712 was used for the removal of interferences. The protein concentrations were measured at 562 nm using an UV-visible spectrophotometer, Shimadzu-800, Japan.

3. RESULTS AND DISCUSSION

3.1. New RVA

The accelerating efficiency of a di-functional monomer, ND-A for RVNRL has been investigated to replace $n$-BA. ND-A has no smell. It possesses low primary irritation index (PII = 2). The ND-A mixed latex remains in a very good physical state (in terms of color and viscosity) up to several days.
3.1.1. Optimization of irradiation dose and RVA concentration

NRL with 50% total solids was mixed with ND-A by stirring for 30 minutes and irradiated at various doses of gamma rays. Fig. 2 shows the tensile strength of RVNRL films against the radiation doses for various concentrations of RVA. It is found that for each concentration of RVA tensile strength increases with the increase of radiation dose but the maximum value of tensile strength corresponds to various doses for various concentrations of RVA. The maximum values of tensile strength are 31.28, 30.44 and 23.89 MPa with 2.5, 5 and 10 phr of RVA respectively and the corresponding doses are 30, 20 and 5 kGy. The swelling ratios of these films are shown in Fig. 3. The swelling ratio values become minimum at around 20 kGy radiation dose. If the level of the values of tensile strength and doses are compared (Fig. 4), 20 kGy with 5 phr RVA may be considered as optimum in this condition of latex irradiation. This dose is similar to that required with \(n\)-BA.

---

**FIG. 2. Tensile strength versus doses of RVNRL films with various concentrations of RVA.**

**FIG. 3. Swelling ratios versus doses of RVNRL films with various concentrations of RVA.**

**Fig. 4. Maximum tensile strengths and optimum doses versus various concentrations of RVA**
3.2. Operation of EB pilot plant for RVNRL

The photograph* below shows the front view of recently installed EB pilot plant. It has a reaction vessel with the capacity of 18 liters latex to irradiate at a time. The accelerating voltage and beam current of the plant are 250 kV and 10 mA respectively. The length and width of the beam window are 20 and 6 cm respectively. The latex irradiation vessel under EB is a cylindrical stainless steel vessel (29 cm Φ and 30.5 cm height) containing four baffle plates onto the inner wall at 90’ intervals and fitted with a propeller type stirrer and outer jackets. The vessel is covered with a cooling plate having titan film (thickness = 0.0015 cm) window (20 cm X 8 cm). It is expected that RVNRL with this type of low energy accelerator would reduce the initial investment and irradiation cost. The pilot plant is being optimized in order to obtain a suitable setting of experimental for RVNRL under EB.

3.2.1. Optimization of defoamer concentration

If the latex is stirred bubbles are formed and create problem during irradiation. So the defoamer is used to suppress the bubble formation. To optimize the defoamer concentration varying quantities of defoamer were added to the 5 phr ND-A impregnated latex separately and stirred with low to high speed for 20 minutes. 0.2 phr concentration of defoamer was sufficient to suppress the bubble formation when latex was stirred at 360 rpm. The maximum rotational speed of the stirrer in the EB reactor vessel is 360 rpm. So 0.2 phr of the defoamer concentration could be used at any stirring speed of the stirrer. The foam formation was examined by taking 16 liters of latex at various stirring speed. No bubbles were formed.

3.2.2. Optimization of irradiation time

For this purpose NRL was irradiated under EB for various lengths of time using fixed volume, RVA concentration, defoamer concentration and stirring speed at the beam current of 10mA and accelerating voltage of 250 kV. Fig. 5 shows the tensile strength and elongation at break plotted against the irradiation time. It is found that the maximum value of tensile strength obtained from the RVNRL film prepared with the latex irradiated for 30 minutes is ~26 MPa. Elongation at break however, decreases gradually with increased irradiation time. This irradiation time seems to be long and the maximum value of tensile strength is also not up to the level of maximum tensile strength obtained from γ-rays irradiated latex film. Further investigation is continuing by varying the individual...
parameter at constant sets of the other variables to determine the ideal setting for maximum efficiency of the machine.

![Graph](image)

FIG. 5. Tensile properties of EB irradiated latex film versus length of irradiation time.

3.3. Reduction of EP in RVNRL

3.3.1. Effect of degree of hydrolysis of PVA on the removal of EP

EP content in the NRL products should be as low as possible to prevent latex allergy. It is reported that low molecular weight water-soluble polymers (WSP) is more favorable to leach out EP than higher molecular weight WSP [1]. The effect of degree of hydrolysis of PVA on the removal of EP from NRL has been determined using PVA with varying degree of hydrolysis. PVAs were added to RVNRL before casting. Leaching of the RVNRL films was done with ammonia for 10 minutes. After leaching the remained EP in the RVNRL films were determined. The EP contents in RVNRL films containing PVAs with various degrees of hydrolysis and their tensile strengths are furnished in Table I.

<table>
<thead>
<tr>
<th>PVA added</th>
<th>Degree of hydrolysis (%)</th>
<th>Protein content (µg/g)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>-</td>
<td>95.0</td>
<td>30.44</td>
</tr>
<tr>
<td>PVA-105</td>
<td>98.0-99.0</td>
<td>37.5</td>
<td>30.43</td>
</tr>
<tr>
<td>PVA-205</td>
<td>86.5-89.5</td>
<td>38.0</td>
<td>29.69</td>
</tr>
<tr>
<td>PVA-405</td>
<td>80.0-83.0</td>
<td>39.8</td>
<td>27.65</td>
</tr>
<tr>
<td>PVA-505</td>
<td>72.5-74.5</td>
<td>42.0</td>
<td>25.28</td>
</tr>
</tbody>
</table>

According to the report, addition of water-soluble polymer, dilution and centrifugation reduce the content of the EP to the level less than 5 µg/g [1]. For this purpose 20-30 minutes of leaching time was needed. In this investigation RVNRL were used without further centrifugation and dilution before adding the water soluble PVAs. The films were leached with shorter time (10 minutes) than it is needed to remove almost all the EP (<5µg/g). This condition was selected to understand the difference between the effects of the PVAs with varying degree of hydrolysis on the removal of EP. It was found that the films containing PVA contain less EP than that of the film without added PVA. About 60%
EP is removed from RVNRL film having 2 phr PVA and leached for 10 minutes with 1% ammonia but the degree of hydrolysis of PVA has no significant effect on the removal of EP. The proteins are likely to be leached out together with soluble PVA [1]. The tensile strength is reduced to a very small extent with the decreased degree of hydrolysis. So higher degree of hydrolysis of PVA is favorable.

REFERENCES


IMPROVEMENT OF RVNR LATEX FILM PROPERTIES BY USING FUMED SILICA AND HYDROXY APPATITE AS RUBBER PARTICLE BINDER

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2Rubber Research Institute of Thailand,
3Chemistry Division, Office of Atomic Energy for Peace,
4Faculty of Science, Prince Songkhla University,
Thailand

Abstract

A study has been carried out to investigate the effect of addition of fumed silica and hydroxy apatite into RV NR latex for the purpose of improvement of tear property of the films. Determination of water soluble protein in rubber films was also done using modified Lowry method to quantify the protein immobilization by the additives. Binding of the protein to the additives was found to enhance by addition of ZnO. Stability of the RV NR latex with fumed silica and hydroxy apatite was also evaluated.

1. INTRODUCTION

Physical properties of RV NR latex film are known to be inferior to that of SV NR latex film from vulcanizable latex, especially in tear and tensile strength. Many attempts have been made to improve the physical properties of RV NR latex film. Blending of PMMA in emulsion form prepared by redox reaction [1] can increase tensile strength (Tb) of RV NR latex film by about 12 %. RV NRL grafted PMMA also increases Tb of the films from its product to some extent [2]. However, there is no report on the improvement of tear strength. Co-vulcanization of redox vulcanization followed by radiation vulcanization can improve tear strength to about 100 % but aging property of the film is very poor [3]. Recently it has been reported that fumed silica prepared in dispersion form, when added into sulfur pre-vulcanized latex, can give the rubber films of slightly improved Tb with greatly improved tear strength [4]. Fumed silica added in the pre-vulcanized latex may serve as rubber particle reinforcement. Enhancement of the physical properties of the rubber films is postulated to base on binding of the binder (hydrophylic) to the rubber protein (amphoteric) and to the surface of rubber particle (hydrophobic). In this experiment fumed silica and another binder, namely hydroxy apatite, which is well known to be a biomaterial, shall be used as rubber particle binders for such purpose. Investigation of the consequent effect: rubber protein immobilization shall also be made to add as an advantage for solving the problem related to protein allergy in natural rubber dipped products.

2. EXPERIMENTAL

2.1. Material

Concentrated high ammonia (HA) latex was from Chanatex Co. Ltd. (Thailand). Technical grade n-butyl acrylate (n-BA), ammonia, KOH, ZnO were supplied by established companies in the country and were used without further purification. Fumed silica aggregate with average diameter of 120 nm was from Cabot Corporation, USA. Hydroxy apatite, particle size 15-25 µm was from Taihei Chemical Industrial Co. Ltd., Japan. The latter binder was further ball milled to about 0.2 µm before preparation to dispersion.
2.2. Preparation of binder dispersion

Except for fumed silica dispersion that is obtained directly from the supplier, other binders including ZnO were prepared to dispersions by ball milling with a dispersing agent (Vultamol). The dispersions were prepared to have a total solid content (TSC) of 15%, and pH was adjusted to 9.5-10 by KOH solution.

2.3. Irradiation of HA latex

Concentrated HA latex was diluted to 50% dry rubber content by 1% of ammonia solution and stabilized by 0.2 phr KOH. 5 phr of n-BA was added dropwise into the latex while stirring, and continuously stirred for another 30 minutes before irradiation. About 5 liters of the mixture was irradiated in BSV-06 Gamma Irradiator, dose rate 1.1 kGy/hr to vulcanization dose of 13.5 kGy. RV NR latex was used without adding antioxidant to avoid interference.

2.4. Blending of the binder dispersion to the irradiated latex

The binder dispersion was added into irradiated latex at concentrations of 1, 2, 3 and 4 phr with and without 0.17 phr for each binder while stirring for 1 hour. Maturation of the mixture for at least 3 days before casting into film was needed to enhance tear strength of the film [4].

2.5. Measurement of physical properties of the films

The films of about 0.6 mm thick were prepared by casting about 20 ml of latex on to a glass plate (14x14 cm). The films were dried in air at room temperature until they became transparent. Leaching of the rubber films was done in water at room temperature or by hot water in a constant temperature bath as specified. The films were aired dried and finally oven dried at 70°C for 1 hour. The films were kept in a dessicator before cutting to dumbells or to trouser tear test pieces. The tensile strength of the films was measured according to ASTM-D-412-92 and trouser tear strength was measured according to ASTM-D-624-91 using Lloyd Tension Meter.

2.6. Determination of water soluble protein in rubber films

Determination of water soluble protein in rubber films was done using modified Lowry method with minor change according to the procedure developed by Rubber Research Institute of Thailand (RRIT) [5]. Soluble rubber protein was extracted with warm water, 35°C for 180 minutes. The leachate was centrifuged and to a known volume was added 0.15 % solution of sodium salt of deoxycholic acid.35 % solution of trichloro acetic acid (TCA) followed by 40 % solution of phosphotungstic acid (PTA), stirred well and collected the precipitates by a high speed centrifuge machine. Dissolve the precipitate by 0.2 M NaOH solution and added a solution of Na2CO3, CuSO4 and sodium citrate. To the solution was added 72 % solution of Folin-Ciocalto Reagent. Stirred by a Vortex mixer and transferred to a cuvette for UV absorbancy measurement by a UV spectrophotometer at a wavelength of 750 nm. The measurement was done in parallel with ovalbumin protein standard which followed the same procedure.

3. RESULTS AND DISCUSSION

3.1. Experiments on adding fumed silica into RVNR

3.1.1. Mechanical properties of RV latex films with fumed silica

Tensile strength (Tb), elongation at break (Eb), modulus (Mod) of RV NR latex films with different amounts of fumed silica are shown in Table I. There were no significant changes of the Tb, Eb and modulus of the films. Enhancement of trouser tear strength of the films from about 5 N/mm to about 10 N/mm could only be observed with the optimum content of 2 phr fumed silica. Table II shows no significant change of physical properties of the film after co-adding 0.17 phr ZnO with fume silica.
TABLE I. MECHANICAL PROPERTIES OF RADIATION VULCANIZED RUBBER FILMS WITH FUMED SILICA

<table>
<thead>
<tr>
<th>Fumed silica (phr)</th>
<th>( T_b ) (MPa)</th>
<th>Trouser tear strength (N/mm)</th>
<th>Eb (%)</th>
<th>100%</th>
<th>300%</th>
<th>600%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.59</td>
<td>5.8</td>
<td>960</td>
<td>0.11</td>
<td>0.32</td>
<td>0.63</td>
</tr>
<tr>
<td>1</td>
<td>21.25</td>
<td>9.8</td>
<td>945</td>
<td>0.16</td>
<td>0.37</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>21.51</td>
<td>10.4</td>
<td>980</td>
<td>0.14</td>
<td>0.36</td>
<td>0.69</td>
</tr>
<tr>
<td>3</td>
<td>21.23</td>
<td>10.4</td>
<td>930</td>
<td>0.18</td>
<td>0.48</td>
<td>0.84</td>
</tr>
<tr>
<td>4</td>
<td>17.78</td>
<td>9.6</td>
<td>956</td>
<td>0.18</td>
<td>0.42</td>
<td>0.78</td>
</tr>
</tbody>
</table>

TABLE II. MECHANICAL PROPERTIES OF RADIATION VULCANIZED RUBBER FILMS WITH FUMED SILICA AND 0.17 PHR ACTIVE ZNO

<table>
<thead>
<tr>
<th>Fumed silica (phr)</th>
<th>( T_b ) (MPa)</th>
<th>Trouser tear strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.40</td>
<td>5.4</td>
</tr>
<tr>
<td>1</td>
<td>19.68</td>
<td>9.6</td>
</tr>
<tr>
<td>2</td>
<td>21.62</td>
<td>10.2</td>
</tr>
<tr>
<td>3</td>
<td>20.24</td>
<td>10.8</td>
</tr>
<tr>
<td>4</td>
<td>19.12</td>
<td>10.4</td>
</tr>
</tbody>
</table>

3.1.2. Effect of leaching temperature on watersoluble proteins content of rubber films

Fig. 1 shows water soluble protein contents in rubber films after water leaching at different temperature and leaching time. The optimum leaching temperature and leaching time were 75°C, 7 minutes or, at room temperature: 15 minutes. Leaching time may be much longer than this (24 hours) to maximize \( T_b \) of RV NR films [6]. If only rubber protein content in the film is to be considered, short leaching time of 7 minutes at 75°C may be more practical in factory dipping line.

3.1.3. Effect of fumed silica on water soluble proteins content in rubber films

Effect of fumed silica with 0.17 phr active ZnO and without ZnO on water soluble protein content in RV NR rubber films is shown in Fig. 2. From these results it could be concluded that 3 phr of fumed silica with 0.17 phr ZnO could reduce water soluble protein to less than 30 \( \mu \)g/g. Without ZnO fumed silica could decrease soluble protein only slightly. This was in good agreement with previous report when using sulfur pre-vulcanized rubber films, which indicated that there was a complex binding of protein, ZnO and silica [4]. Further decrease of soluble proteins could be achieved if leaching was done at 75º C compared to leaching at room temperature might due to the combined effect of protein immobilization by silica/ZnO and higher protein solubility in hot water.
FIG. 1. Water soluble protein contents in rubber films after leaching in water at different temperature and leaching time.

FIG. 2 Effect of ZnO co-added with fumed silica into RV NR latex on water soluble protein content in rubber film after leaching at room temperature (RT) for 15 min. and at 75 °C for 7 min.
3.2. Experiment on adding of hydroxy apatite into RVNRL

3.2.1. Mechanical properties of RV NR latex films with hydroxy apatite

Tensile strength (T_b), elongation at break (E_b), modulus (Mod) of RV NR latex films with different amounts of hydroxy apatite are shown in Table III. There were no changes of the T_b, E_b and modulus of the films after adding hydroxy apatite 1-4 phr. As in the case of adding fumed silica, only enhancement of trouser tear strength of the films could be observed, with the optimum content of 2 phr hydroxy apatite. The tear strength increased from about 5 N/mm to about 8 N/mm.

TABLE III. MECHANICAL PROPERTIES OF RADIATION VULCANIZED RUBBER FILMS WITH HYDROXY APATITE

<table>
<thead>
<tr>
<th>Hydroxy apatite (phr)</th>
<th>T_b (MPa)</th>
<th>Trouser tear strength (N/mm)</th>
<th>E_b (%)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.42</td>
<td>5.2</td>
<td>942</td>
<td>0.15</td>
</tr>
<tr>
<td>1</td>
<td>22.18</td>
<td>7.4</td>
<td>968</td>
<td>0.17</td>
</tr>
<tr>
<td>2</td>
<td>24.15</td>
<td>9.2</td>
<td>934</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>23.64</td>
<td>9.1</td>
<td>922</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>23.24</td>
<td>9.3</td>
<td>938</td>
<td>0.16</td>
</tr>
</tbody>
</table>

3.2.2. Effect of hydroxy apatite on water soluble proteins content in rubber films

Effect of fumed silica with 0.17 phr active ZnO and without ZnO on water soluble protein content in RV NR rubber films was shown in Fig. 3. As in the case of adding fumed silica, decreasing of soluble protein content in rubber films could be observed only after ZnO was co-added with hydroxy apatite into RV NR latex. Two phr of hydroxy apatite with 0.17 phr ZnO could reduce water soluble protein in the rubber films to about 120 µg/g, not as low as in the case of adding fume silica. With out ZnO fumed silica could decrease soluble protein only slightly. Immobilization mechanism of soluble protein in the case of adding hydroxy apatite may be different from that of adding fumed silica. In the case of adding fumed silica, silica is proposed to bind to (positively charged) zinc-protein complexes. Binding of proteins to relatively large and immobile silica particles prevent their migration from inner part of the films to the surface [7]. Hydroxy apatite consists of calcium phosphate, thus containing positive and negative charges. With in the pH range of rubber latex, 9-10, rubber proteins which are in switter ionic state, ionic interaction as well as adsorption effects seem to contribute to protein binding. Acidic proteins may bind to calcium ions whereas basic proteins may bind to phosphate groups. Hydroxy apatite, however may not have as high surface area as fumed silica, which is usually in the range of 50-400 m²/g [4], protein immobilization thus does not as high as fumed silica. Enhancement of protein immobilization after co-added of ZnO with hydroxy apatite to the latex indicated that there was also a complex binding of protein, ZnO and calcium phosphate like in the case of SiO₂.

3.3. Determination of latex stability after addition of fumed silica and hydroxy apatite

RV NR latex stability after addition of fumed silica and hydroxy apatite in term of mechanical stability time (MST) is shown in Table IV. The MST of RV NR latex with fumed silica or hydroxy apatite, showed rapid decrease to less than 650 seconds in two months. In fact, the amount of the latex to be tested had to reduce from normal value of 80 g to 60 g to avoid foaming during the tests. The drastic decrease of MST of the RV NR latex with time after addition of fumed silica or hydroxy apatite indicated that the latex was not stable after prolong shelf life of more than two months.
FIG. 3 Effect of ZnO co-added with hydroxy apatite into RV NR latex on water soluble protein content in rubber film after leaching at room temperature (RT) for 15 min. and at 75°C for 7 min.

TABLE IV. MST OF RVNR LATEX WITH AND WITHOUT FUMED OR HYDROXY APATITE AT DIFFERENT STORAGE TIMES

<table>
<thead>
<tr>
<th>Sample</th>
<th>MST (s)</th>
<th>Storage time (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>RVNR latex</td>
<td></td>
<td>1950</td>
</tr>
<tr>
<td>RVNR latex with 2 phr fumed silica</td>
<td></td>
<td>1872</td>
</tr>
<tr>
<td>RVNR latex with 2 phr hydroxy apatite</td>
<td></td>
<td>1784</td>
</tr>
</tbody>
</table>

Spindle No.1, speed 30

4. CONCLUSION

Both fumed silica and hydroxy apatite at concentration of 2 phr in RV NRL can improve tear property of the latex films. Trouser tear strength of the films increases from about 5 N/mm to approximately 10 N/mm. The latex with the additives however must be used within two months after mixing with latex. Consequent effect of soluble protein immobilization in the films by addition of the additives may add as an advantage for solving the problem related to the Type I allergy caused by soluble proteins in natural rubber products. The stringent limit of the proteins has been proposed by US.FDA recently to be not more than 1,200 µg per glove [8].
ACKNOWLEDGEMENT

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REFERENCES


NATURAL ANTI-OXIDANTS FOR RADIATION VULCANIZED NATURAL RUBBER LATEX

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Philippine Nuclear Research Institute, Commonwealth Avenue, Diliman, Quezon City, Philippines

Abstract

The antioxidant properties of some non-water soluble amino acids were tested on RVNRL. Among these were cystine, tyrosine, asparagine phenyl alanine and alanine. Results indicated that all these amino acids have antioxidant properties with cystine, alanine and asparagine exhibiting higher anti-aging properties on RVNRL. Combination of these amino acids improved the antioxidant property on RVNRL.

Keratin from chicken feathers was also tested for its antioxidant property on RVNRL. Different methods of extraction of keratin gave different aging effects on RVNRL. Reduction of keratin with Sodium Bisulfite initiated antioxidant property on RVNRL. Extraction of keratin with alkaline solution however indicated pro-oxidant properties on RVNRL.

1. INTRODUCTION

Natural rubber (NR) like any other polymer is susceptible to oxidative degradation, which results in loss of physical properties. Its oxidation arises from the formation of peroxy free radicals that can propagate scission reactions of the rubber molecule [1,2]. Antioxidants, either natural or synthetic, are essential additives to prevent this oxidative reaction. Antioxidants can be classified according to the way by which they interfere with the oxidation process of the polymer.

a) The chain breaking donors (CB-D) are those that are capable of competing with the substrate (RH) for the alkylperoxyl radicals [1]. The hindered phenols and aromatic amines such as substituted p-phenylene diamines are the most important of these antioxidants. Some biological antioxidants such as tocopherols (Vit. E) also act by CB-D mechanism.

\[
\text{ROO}^\cdot + \text{AH} \rightarrow \text{ROOH} + \text{A}^\cdot \quad \text{(antioxidant)} \quad \text{CB-A} \quad \text{(stable radical)}
\]

b) Chain breaking acceptors (CB-A) are antioxidants which can compete with oxygen for the alkyl radicals. Quinones, nitro compounds and stable oxyl radicals are considered as CB-A antioxidants [1].

\[
\text{R}^\cdot + \text{Q} \rightarrow \text{RQ}^\cdot \quad \text{CB-D}
\]

c) Preventive antioxidants decompose hydroperoxides by a process which does not give rise to free radicals in the system or that can stabilize the hydroperoxide. The phosphite esters and a whole family of sulfur-containing compounds are among this set of compounds [1].

Natural rubber latex is known to contain some powerful antioxidants such as amino acids, phenols, phospholipids, tocotrienol and betaines. Hevein, a sulfur-containing water soluble protein is reported to be an antioxidant of NR [3]. Most of these antioxidants, however, are removed during the leaching process. Some commercial antioxidants such as TNPP and DAHQ are found to be effective with RVNRL [4]. Previous studies using these industrial antioxidants indicate good anti-aging properties on RVNRL [5] (see Table in page 2). These, however, are synthetic chemicals. An
alternative is to look for antioxidants from natural sources that could substitute for these synthetic antioxidants, thus, promoting a “chemically free and environment friendly” RVNRL technology.

<table>
<thead>
<tr>
<th>Antioxidant classification</th>
<th>%Tb retention after aging</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>TNPP Preventive</td>
<td>24</td>
</tr>
<tr>
<td>Vulcanox CB-D</td>
<td>37</td>
</tr>
<tr>
<td>DAHQ CB-A</td>
<td>37</td>
</tr>
</tbody>
</table>

2. MATERIALS AND METHODS

2.1. Materials

Philippine high ammonia concentrated latex specially prepared for RVNRL was obtained from JCA Rubber Development Corporation (TSC = 60%, MST > 1000). The amino acids and tocopherol were obtained from Sigma Chemicals.

2.2. Determination of aging properties of RVNRL

High ammonia concentrated latex was diluted to 50% with 1% NH4OH to which was added 5 phr n-BA. The latex was irradiated using a Co-60 irradiator at a dose rate of 2.57 kGy/hr and an absorbed dose of 15 kGy.

The antioxidants [homogenized and emulsified with 20% SDS (1:1)] were added to RVNRL and were cast unto plates to make a film of 0.4–0.6 mm thickness. The film was then removed from the glass plate, air dried and leached in 1% NH4OH overnight. The leached film was air dried and cured at 80°C for two hours. Accelerated aging of the rubber films was done at 100°C for 24 hrs. Tensile strength was measured using the Instron Tester Machine Model 1011.

2.3. Extraction of keratin from chicken feathers

Samples of chicken feathers (white leghorn) were thoroughly washed, dried in an oven and ground. Different methods were used to extract the keratin from chicken feathers.

A. Extraction with 1M NaOH

Ground chicken feathers were added with 1M NaOH (10g chicken feathers / 300.0 ml of 1M NaOH) and heated at 60°C for one hour. The resulting solution was neutralized with 1M HCl until the proteins were precipitated. The precipitate were centrifuged and freeze dried (Keratin A).

Ground chicken feathers (16g) were added to 100.0 mls of 1M NaOH and digested in a microwave oven using the following parameters:

- Maximum power = 750 watts
- Step 1 = 19% power, 15 mins.
- Step 2 = 17% power, 10 mins.

The resulting solution was then tested for antioxidant property on RVNRL (Keratin B).
B. Reduction with NaHSO₃

Ground chicken feathers (16 g) were added with a solution of SDS and NaHSO₃ (11:1 in 100.0 ml water). The samples were digested in a microwave oven using the following parameters (Keratin C):

- Maximum power = 750 watts
- Step 1 = 19% power, 5 mins.
- Step 2 = 17% power, 10 mins.
- Cooled and digested
- Step 1 = 19% power, 10 mins.
- Step 2 = 17% power, 10 mins.
- Cooled and digested
- Step 1 = 19% power, 10 mins.
- Step 2 = 17% power, 10 mins.

C. Dispersion with sodium dodecyl sulfate

Ground chicken feathers (4 g) were added with a solution of 20% SDS and dispersed in a microwave oven using the following parameters (Keratin D)

- Maximum power = 750 watts
- Step 1 = 19% power, 5 mins.
- Step 2 = 17% power, 10 mins.

2.4. DSC analysis of RVNRL films

DSC analysis of RVNRL films was done using the Shimadzu DSC-50 equipment with the following temperature program:

<table>
<thead>
<tr>
<th>Rate (°C/min)</th>
<th>Hold Temp (°C)</th>
<th>Hold Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>160</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>0</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

A. Anti-aging properties of amino acids on RVNRL

RVNRL contains proteins and amino acids which could contribute to the anti-aging effect on rubber films. Most of these components are degraded during the process of irradiation such that these are easily removed during the leaching process of RVNRL films. Preliminary studies indicated that the hydrolyzates of RVNRL proteins have some anti-aging properties [3]. The effect of some non-water soluble amino acids on the aging properties of RVNRL are shown in Table I. All amino acids studied (tyrosine, cystine, alanine, phenylalanine and asparagine) indicated some antioxidant properties. Cystine, alanine and asparagine have good anti-aging properties on RVNRL with tensile strength retentions ranging from 70% to 80%. These values are comparable to the tensile strength retention of unleached RVNRL films containing all the natural antioxidants (75%). Tyrosine and phenyl alanine have lower tensile strength retentions ranging from 50% - 60%. A combination of tyrosine and cystine (1:1) however increased its antioxidant property to 74%. Combination of tyrosine, cystine and asparagine (1:1:1) increased further the tensile strength retention to 80%. Previous study on the amino acid analysis of the protein hydrolyzates of RVNRL indicated the presence of all these amino acids but with a very high percentage of asparagine consisting of around 52% of the total amino acid residue [3]. The result would indicate that these amino acids, especially asparagine, together with the protein hevein may act as powerful natural antioxidants for RVNRL.
B. Anti-aging properties of keratin from chicken feathers

Chicken feathers contain around 97% keratin of which 44% is made up of the amino acid cystine [6]. Cystine has an S-S linkage that could act as an antioxidant from the following reaction.

\[
\frac{1}{2} \text{CysS-SCys} \rightarrow \text{R.} \quad \text{R-SCys} + . \text{SCys} \rightarrow \text{SO}_2 \quad \text{(antioxidant)}
\]

Keratin can be solubilized by several methods. One possibility is by hydrolysis under alkaline condition.

\[
\text{SS} + \text{OH} \rightarrow \text{S} + \text{SOH}
\]

The sulphenic acids (-SOH) may be considered as powerful antioxidants via the following reaction:

\[
\text{RSOH} \rightarrow \text{RSO}_2 \quad \text{H}_2\text{SO}_2 \quad \text{H}_2\text{SO}_3
\]

The sulphenic acids may also react with hydroperoxides giving rise to free radical products which can initiate autoxidation.

\[
\text{ROOH} \rightarrow \text{RS} \quad \text{RO} + \text{H}_2\text{O}
\]

The effect of keratin on the aging properties of RVNRL using this extraction method (Table II) indicated that this protein acts as a pro-oxidant instead of an antioxidant. Tensile strength retention of Keratin A (16%) is in fact lower than the blank (35%). Neutralization by the addition of an acid may have produced H\text{2S} gas as evidenced by the foul smell emitted during the preparation process, thus destroying the RS which may also act as an antioxidant.

Keratin B, which was not subjected to neutralization process, also does not contain anti-oxidant properties (40 % Tb retention). At higher concentration the solution becomes a pro-oxidant with a decrease in Tb retention to only 14%. It would be interesting to study the thermal aging kinetics of Keratin B to determine if this protein may have a rate limiting step such that at a certain point in the aging process, this becomes a pro-oxidant. At higher concentration, more pro-oxidants maybe formed resulting in the decrease of the Tb retention. Fig. 1 confirms this hypothesis. The tensile strength retention of Keratin B at higher concentration continues to decrease drastically after 10 hrs of aging. At lower concentration there is a slowing down of the aging process.

Reduction of keratin with sodium bisulfite gives rise to the following reaction.

\[
\text{SS} + \text{HSO}_3^- \rightarrow \text{SH} + \text{SSO}_3^-
\]

Sulfhydryl (-SH) compounds can also be considered as antioxidants. Results indicate the presence of antioxidant property of Keratin C on RVNRL (58% Tb retention). At higher concentration, no significant increase in antioxidant property was observed (60%). Keratin D has also an anti-aging property (55% Tb retention). Its antioxidant property may be due to the intact protein that contains the cystine linkages.

DSC analysis of the RVNRL films added with keratin are shown in Figs 2A and 2B. Oxidation pattern of all samples indicate exothermic peaks ranging from 314°C to 321°C. RVNRL film with keratin C has a higher peak temperature (321°C) than all other films. Degradation is much slower as shown in Fig. 2B. This result supports further the antioxidant property of Keratin C, indicated in the previous experiment on the measurement of tensile strength retention. Keratin D has two degradation
peaks (314°C and 328°C) with the major one close to the control (314°C). Though the major part of the rubber film is oxidized at 314°C, a certain portion is retained and is oxidized at a higher temperature of 328°C. This may account for its higher antioxidant property on RVNRL film. Keratin D is observed to have similar antioxidant property to that of Keratin C (see Table II). Keratin A, which in the previous result is a pro-oxidant, has an oxidation peak (314°C) also close to the control. It is however degrading faster than all other RVNRL films as shown in its DSC pattern (Fig. 2B). Keratin B has a very similar DSC pattern as that of the control. Both films have similar antioxidant properties (see Table II).

4. CONCLUSIONS

Non-water soluble amino acids have antioxidant properties. Among these, cystine, asparagine and alanine have good anti-aging effect on RVNRL. A combination of these amino acids would improve their properties as antioxidants.

Keratin from chicken feathers has a good potential as natural antioxidant. The method of extracting keratin would influence its antiaging effect on RVNRL. Keratin in its reduced form is a better antioxidant for RVNRL.

REFERENCES


TABLE I. TENSILE STRENGTH RETENTION OF RVNRL FILMS WITH AMINO ACIDS (2PHR)

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Percent tensile strength retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35 ± 9</td>
</tr>
<tr>
<td>Unleached RVNRL Film</td>
<td>75 ± 8</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>52 ± 9</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>52 ± 5</td>
</tr>
<tr>
<td>Alanine</td>
<td>71 ± 9</td>
</tr>
<tr>
<td>Cystine</td>
<td>77 ± 7</td>
</tr>
<tr>
<td>Asparagine</td>
<td>71 ± 9</td>
</tr>
<tr>
<td>Cystine + Tyrosine (1:1)</td>
<td>74 ± 7</td>
</tr>
<tr>
<td>Cystine + Tyrosine + Asparagine (1:1:1)</td>
<td>80 ± 7</td>
</tr>
</tbody>
</table>

TABLE II. TENSILE STRENGTH RETENTION OF RVNRL FILMS WITH KERATIN

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Percent tensile strength retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35 ± 9</td>
</tr>
<tr>
<td>Keratin A (2 phr)</td>
<td>16 ± 7</td>
</tr>
<tr>
<td>Keratin B (8.0 ml)</td>
<td>40 ± 6</td>
</tr>
<tr>
<td>Keratin B (16.0 ml)</td>
<td>14 ± 4</td>
</tr>
<tr>
<td>Keratin C (8.0 ml)</td>
<td>59 ± 4</td>
</tr>
<tr>
<td>Keratin C (16.0 ml)</td>
<td>60 ± 4</td>
</tr>
<tr>
<td>Keratin D (2 phr)</td>
<td>55 ± 4</td>
</tr>
</tbody>
</table>

FIG. 1. Aging properties of RVNRL films added with different concentrations of keratin B.
FIG. 2A. DSC of RVNRL films added with keratin from chicken feathers.

FIG. 2B. DSC of RVNRL films added with keratin from chicken feathers.
ELECTRON PROCESSING FOR THE VISCOSE PROCESS: AN ECONOMIC ANALYSIS

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Pinawa, Manitoba,
Canada

Abstract

Investigations at the lab-, pilot-, and plant scale have shown that electron treatment of dissolving pulp used to produce viscose can reduce the demand for chemicals in the viscose process by as much as 40%. In this paper, the annual costs for operating four different electron accelerators for treating dissolving pulp were compared to the savings in chemical costs expected from using electron treated pulp. The major assumptions/parameters made in deriving the economic model were as follows: 1) the accelerators were operated for 6000 h/a; 2) the accelerators were located in North America at a viscose plant where pre-existing infrastructure for pulp storage and handling could be utilized; 3) only chemical savings for carbon disulphide and caustic were considered; 4) three different doses (5, 10, and 15 kGy) which span the range of possible doses that can be used for treating dissolving pulp for the viscose process were used in the analysis. Based on these assumptions, the results indicated that, at high production capacities, all four accelerators could operate at a profit, while at low production capacities, the annual operating costs for one or more of the accelerators exceeded the savings obtained from reduced chemical demand. In the case of low production capacities, the number of accelerators operating at a loss depended on whether savings in carbon disulphide alone, caustic alone, or carbon disulphide plus caustic were considered.

1. INTRODUCTION

The viscose industry is a multi-billion dollar enterprise in which cellulose wood pulp or cotton linters are converted to staple fibre, filament, cord, casing, or cellophane film. These materials are used to produce clothing, fabrics, drapes, mattress covers, gauze, personal hygiene products, sausage casings, automobile tires, packaging material, conveyor belts, automobile belts and hoses, clutch linings, and sanding belts.

In the viscose process, the cellulose is treated with high concentrations of caustic and carbon disulphide (CS₂) to produce a metastable liquid intermediate called viscose [1]. Liquid viscose contains cellulose xanthate (the product from the reaction of cellulose with CS₂) dissolved in a dilute caustic solution. This solution is taken through a spinning step in an acid bath which neutralizes the caustic, converting it to sodium sulphate, and decomposes the xanthate to regenerate CS₂ and cellulose. The regenerated cellulose, solidified in its extruded form (i.e., as staple fibre, filament, cord, casing, or cellophane film), is then taken through a series of finishing steps to obtain the final product.

In addition to CS₂, another volatile chemical, hydrogen sulphide, is generated as a by-product of the viscose process. In some plants, these two chemicals are collected, separated, and the CS₂ is then recycled. However, in many plants, these toxic chemicals are vented to the atmosphere where they cause environmental problems.

Over the past few years, electron processing technology has been investigated for its potential to reduce CS₂ emissions and chemical demand in the viscose process [2,3-8] (also: Chincholkar, et al./Stavtsov, et al., 1997). Under the proper conditions, electron treatment of the dissolving pulp used to produce viscose can reduce CS₂ usage by as much as 25-40% and emissions of CS₂ and hydrogen sulphide by a comparable amount. In addition, similar reductions in alkali, zinc, and sulphuric acid consumption have been demonstrated. The purpose of this paper is to provide a basis for comparing these savings in chemical costs to the costs for owning and operating an accelerator facility for treating the cellulose pulp.
2. COST MODEL

2.1. Accelerators

Pulp utilization capacities can vary significantly from one viscose mill to another. These capacities can be from a few thousand tonnes of pulp/a to over one hundred thousand tonnes/a. To span this range, four accelerators with different powers were arbitrarily chosen. The accelerators selected possessed the following characteristics: 1) 2.5 MeV, 6 kW, self-shielded, with two scan horns for simultaneous double-sided treatment; 2) 10 MeV, 35 kW; 3) 10 MeV, 80 kW; and 4) 10 MeV, 150 kW. The latter three were considered to possess one scan horn.

The treatment capacity of any accelerator depends upon the dose. The dose required for treating dissolving pulp depends upon the type of pulp used and on the ultimate viscose product (i.e. filament, cord, casing, packaging film, etc.). Our experiences in investigating different viscose production processes have shown that the dose required is usually within the range 2-22 kGy. For this economic model, three doses (5 kGy, 10 kGy, and 15 kGy) were chosen to span this dose range. The treatment capacities of the four accelerators at these three doses are given in Table I. It is evident that, at the appropriate dose, the pulp utilization capacities of the viscose mills can be matched by the accelerator treatment capacities.

### TABLE I. PULP TREATMENT CAPACITIES

<table>
<thead>
<tr>
<th>Accelerator</th>
<th>Treatment capacity a (thousand tonnes/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dose: 15 kGy</td>
</tr>
<tr>
<td>2.5 MeV, 6 kW</td>
<td>4.32</td>
</tr>
<tr>
<td>10 MeV, 35 kW</td>
<td>20.16</td>
</tr>
<tr>
<td>10 MeV, 80 kW</td>
<td>46.08</td>
</tr>
<tr>
<td>10 MeV, 150 kW</td>
<td>86.40</td>
</tr>
</tbody>
</table>

a Calculated using the equation: Throughput (kg/sec) = [(Power)(efficiency)/dose]. Accelerator utilization factor was assumed to be approximately 70% (6000 h/a). The efficiency for the 2.5 MeV accelerator was assumed to be 0.5 for simultaneous double-sided treatment. The efficiency of each 10 MeV accelerator was assumed to be 0.4 for single sided treatment.

The annual processing costs for owning and operating the four accelerators for treating dissolving pulp are given in Table II. The following assumptions were made for calculating these costs: 1) the accelerator is completely dedicated to treating wood pulp sheets in bale form; 2) the accelerator is located at the viscose mill where pre-existing facilities and equipment for pulp handling and storage can be utilized. Thus facility size is restricted to that required for accelerator hardware, shielding vault (for the 10 MeV accelerators only), conveyor, pulp weighing stations, and limited pulp storage space; 3) the accelerator is operated to maintain a two-week inventory of electron treated pulp. This allows sufficient time for any repairs to be made without compromising production at the viscose mill, and; 4) The accelerator is located in North America.
### TABLE II. PROCESSING COSTS (CANADIAN DOLLARS)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amortization cost a ($ thousand/a)</th>
<th>6 kW</th>
<th>35 kW</th>
<th>80 kW</th>
<th>150 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salaries:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operators/shift</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Operator’s wage rate ($/h)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Handlers/shift</td>
<td>15 kGy</td>
<td>3 b</td>
<td>4 c</td>
<td>5 c</td>
<td>8 c</td>
</tr>
<tr>
<td>Handler’s wage rate ($/h)</td>
<td>10 kGy</td>
<td>4 b</td>
<td>5 c</td>
<td>8 c</td>
<td>14 c</td>
</tr>
<tr>
<td>Management and dosimetry</td>
<td>5 kGy</td>
<td>5 b</td>
<td>8 c</td>
<td>16 c</td>
<td>26 c</td>
</tr>
<tr>
<td>Total salaries d (thousand $/a)</td>
<td>15 kGy</td>
<td>130</td>
<td>175</td>
<td>220</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>536</td>
<td>670</td>
<td>805</td>
<td>1099</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>619</td>
<td>753</td>
<td>1053</td>
<td>1596</td>
</tr>
<tr>
<td>Electricity price ($/kW•h)</td>
<td>702</td>
<td>1002</td>
<td>1716</td>
<td>2590</td>
<td></td>
</tr>
<tr>
<td>Facility power required (kW)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Electricity ($ thousand/a)</td>
<td>60</td>
<td>350</td>
<td>800</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Utilities ($ thousand/a)</td>
<td>18</td>
<td>105</td>
<td>240</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>Maintenance ($ thousand $/a)</td>
<td>50</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Total operating cost e ($ million/a)</td>
<td>15 kGy</td>
<td>1.11</td>
<td>1.97</td>
<td>2.75</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>1.19</td>
<td>2.05</td>
<td>3.00</td>
<td>4.06</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>1.27</td>
<td>2.30</td>
<td>3.66</td>
<td>5.05</td>
</tr>
</tbody>
</table>

---

**2.2. Savings in chemical costs**

Investigations at the lab-, pilot- and plant scale have shown that using electron treated pulp can result in reductions in chemical demand of up to 40% for CS$_2$, caustic, and for the spin bath chemicals zinc sulphate and sodium sulphate. In addition, similar reductions in CS$_2$ and H$_2$S emissions are possible. In this model, cost savings were calculated based on reductions in CS$_2$ and caustic alone; any savings from reductions in spin bath chemicals or from reduced CS$_2$ and H$_2$S emissions were not considered. The level of reduction was set at 25% for CS$_2$ (reduced from 32% to 24% w/w based on cellulose) and 18% for caustic (reduced from 5.5% to 4.5%, w/w, in the liquid viscose prior to neutralization in the acid spin bath). Reductions to these levels have been shown to produce good quality viscose in plant scale trials [3].
The annual cost savings resulting from CS$_2$ and caustic reduction for each accelerator and dose are given in Table III. The values are based on the treatment capacities given in Table I, and include the following assumptions: 1) the moisture content for the pulp was 5%; 2) cellulose recovery in the viscose process was 100%; 3) CS$_2$ was not recycled; 4) CS$_2$ and caustic were both purchased from an independent supplier at $705 \text{ CDN/tonne}$ for CS$_2$ and $600 \text{ CDN/tonne}$ for caustic; 5) for calculating caustic savings, the % cellulose in viscose prior to spinning was 9%; 6) any potential patent licensing fees for incorporating caustic reduction were not included, and; 7) any cost recovery from purifying and selling the sodium sulphate produced upon neutralization of the caustic in the spin bath was not considered.

**TABLE III. CHEMICAL SAVINGS (CANADIAN DOLLARS)**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Accelerator:</th>
<th>6 kW</th>
<th>35 kW</th>
<th>80 kW</th>
<th>150 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Disulphide</td>
<td>15 kGy</td>
<td>0.24</td>
<td>1.08</td>
<td>2.47</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>0.35</td>
<td>1.62</td>
<td>3.71</td>
<td>6.95</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>0.70</td>
<td>3.25</td>
<td>7.41</td>
<td>13.89</td>
</tr>
<tr>
<td>Caustic</td>
<td>15 kGy</td>
<td>0.28</td>
<td>1.28</td>
<td>2.92</td>
<td>5.48</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>0.42</td>
<td>1.92</td>
<td>4.38</td>
<td>8.21</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>0.83</td>
<td>3.84</td>
<td>8.76</td>
<td>16.42</td>
</tr>
</tbody>
</table>

$^a$ Rounded to next highest integer.

**TABLE IV. COST COMPARISON**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Accelerator:</th>
<th>6 kW</th>
<th>35 kW</th>
<th>80 kW</th>
<th>150 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Disulphide</td>
<td>15 kGy</td>
<td>-0.87</td>
<td>-0.89</td>
<td>-0.28</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>-0.84</td>
<td>-0.43</td>
<td>0.71</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>-0.57</td>
<td>0.95</td>
<td>3.75</td>
<td>8.84</td>
</tr>
<tr>
<td>Caustic</td>
<td>15 kGy</td>
<td>-0.83</td>
<td>-0.69</td>
<td>0.17</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>-0.77</td>
<td>-0.13</td>
<td>1.38</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>-0.44</td>
<td>1.54</td>
<td>5.10</td>
<td>11.37</td>
</tr>
<tr>
<td>Carbon Disulphide</td>
<td>15 kGy</td>
<td>-0.59</td>
<td>0.39</td>
<td>2.64</td>
<td>6.55</td>
</tr>
<tr>
<td>Plus Caustic</td>
<td>10 kGy</td>
<td>-0.42</td>
<td>1.49</td>
<td>5.09</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>5 kGy</td>
<td>0.26</td>
<td>4.79</td>
<td>12.51</td>
<td>25.26</td>
</tr>
</tbody>
</table>

$^a$ Annual chemical saving minus annual operating cost for the accelerator facility.

A comparison between the cost savings expected from chemical reduction and the costs for owning and operating the accelerator facilities is given in Table IV. The results indicate that the annual operating cost for the 6 kW accelerator facility exceeds the savings in chemical costs expected in all cases except one; when the accelerator is treating pulp at 5 kGy and savings from both CS$_2$ and caustic are considered. For the 35 kW accelerator facility, the operating cost exceeds savings from either CS$_2$ or caustic alone except at high treatment capacities (5 kGy dose). However, the savings for CS$_2$ and caustic combined exceed the facility operating cost at all three doses. For the 80 kW accelerator facility, chemical savings exceed operating cost in all cases except one; when the treatment dose is 15
kGy and savings in CS₂ alone are considered. For the 150 kW accelerator facility, cost savings due to chemical reduction exceed the operating cost for the facility in all cases considered.

3. SUMMARY AND CONCLUSIONS

A simple cost model has been presented for evaluating the economic feasibility of using electron treated pulp in the viscose process. Under the conditions specified, the results indicate that for viscose mills with medium to high throughput capacities, the savings in chemical costs exceed the costs for owning and operating an accelerator, and, in most cases, this excess is quite significant. For viscose mills with low throughput capacities, the results indicate that alternatives for electron treatment other than owning and operating an accelerator facility may need to be considered.

REFERENCES


Invited Paper

RADIATION PROCESSING OF POLYSACCHARIDES FOR AGRICULTURE

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Abstract

Radiation of polysaccharides generates various types of degraded fragments by random scission. Polysaccharides can be easily degraded both in powder foam and solution. The radiation degraded-polysaccharides induce various kinds of biological activities such as anti-microbial activity, promotion of plant growth, suppression of environmental stress, phytoalexins induction and can be applied not only in agriculture but also in medical fields. In this paper, the biological activities induced by radiation of chitosan, alginate, carrageenan, cellulose and pectin are reviewed for the agricultural use.

1. INTRODUCTION

Natural polysaccharide such as cellulose, pectin, alginate, carrageenan, chitin/chitosan are largely available in nature and have widespread applications in the food and drinks, pharmaceutical and bioengineering industries. It is reported that the oligosaccharides from higher plant cell wall involved in capable of signal transduction, defense responses against pathogens and synthesis of phytoalexins [1]. Low molecular weight carbohydrates and oligosaccharides are usually prepared by acid hydrolysis or enzymatic degradation of polysaccharides. Although these enzymes are useful and important in preparing the degraded fragment, each enzyme catalyses only a limited reaction; preparation of enzymes is sometimes very difficult. Radiation is one of the potent procedures for fragmentation of polysaccharides and the various types of degraded fragments are easily generated by random scission. In this report, radiation degradation of various carbohydrates and their effect on plants are reviewed to improve the quality of natural polymers by radiation for plant cultivation.

2. CHANGE IN MOLECULAR WIGHTS OF POLYSACCHARIDES BY RADIATION

Polysaccharides such as chitosan [2] and alginate [3] can be degraded by irradiation. Radiation causes the cleavage of glycosidic link of polysaccharides, producing lower fractions. Fig. 1 shows the irradiation effect on molecular weight of alginate in liquid state (4% solution) and in solid state [4]. The results of HPLC indicate that irradiation of alginate for degradation in liquid state (4% solution) is of about ten times higher in comparing with that in solid state. However, from viewpoint of practical utilization of radiation technique to produce degraded alginate, irradiation of alginate in solid state is adversely higher in effectiveness of using radiation energy compared with that in liquid state.
3. INDUCTION OF ANTI-MICROBIAL ACTIVITY

Antibacterial activity of irradiated chitosan was studied against *Escherichia coli* B/r. Irradiation of chitosan at 100 kGy in dry state was effective in increasing the activity, and inhibited the growth of *E. coli* completely with the concentration of 3 µg/ml [5]. Fig. 2 shows that the antibacterial activity of chitosan irradiated in 1% solution with O₂. The chitosan irradiated at 0.4–1.0 kGy inhibited the growth of *E. coli* effectively and the necessary dose in O₂ was lower than that in N₂. The giant cells of *E. coli* observed by the treatment of irradiated chitosan suggested that the irradiated chitosan attached on the cell surface and inhibited the cell division.

For anti-fungal activity, highly deacetylated chitosan 10B (99% deacetylation) at low dose irradiation (75 kGy) was effective. The sensitivities of *Exobasidium vexans*, *Septoria chrysanthemum* and *Gibberella fujikuroi* for the irradiated chitosan were different and the necessary concentrations of chitosan were 550, 350 and 250 µg/ml, respectively.
These results show that the degraded chitosan by radiation have the potential to induce the antimicrobial activity for bacteria and fungi and the products can be used not only for agriculture but also for medical fields. Using the anti-fungal activity of irradiated chitosan, the coating of fruits is one of the promising application fields for fruits preservation.

4. INDUCTION OF PHYTOALEXINS

Pectic fragments prepared by irradiation and oligogalacturonan obtained by enzyme digestion (endo-PG) of pectin induced glyceollins (a kind of phytoalexin). The pectic fragments obtained by irradiation with 1000 kGy were the most effective for induction of glyceollins and induced almost the same amount of glyceollins induced by endo-PG [6].

Pisatin, a phytoalexin induced in pea, was also effectively induced by irradiated pectin and chitosan (Fig. 3). Induction of pisatin by pectic fragments prepared by irradiation was lower than that of pectin-PGase. Chitosan irradiated at 1000 kGy in solid state induced much higher activity than the pectic fragments but decreased at 2000 kGy. These results show that 1000 kGy is the optimum dose to obtain the effective fragments for induction of phytoalexins and a dose of more than 2000 kGy is too high to keep effective fragments.

5. PLANT GROWTH PROMOTION

Using the degraded alginate, the effect of growth-promotion of plant was tested under hydroponic cultivation condition [4]. For rice, degraded alginate from 4% alginate solution irradiated at 100 kGy (MW ca. 7000) impacts remarkable effect on growth promotion (Fig. 4). Similar effect is also observed for alginate powder irradiated at 500 kGy. The suitable range of degraded alginate concentration was 20–50 µg/ml. In case of peanut, dry matter of shoot significantly increased at 100 µg/ml of degraded alginate treatment (Fig. 5). Field test experiment is in progress and it is expected that the increase of peanut yield will be obtained at harvesting time. Additionally, preliminary results on field test of foliar spraying of degraded alginate on tea, carrot and cabbage with concentration of 20 to 100 µg/ml, led the increase of productivity of ca. 15 to 40%. The results suggest that foliar spraying degraded alginate at certain concentration causes increasing in biochemical and physiological functions of plant that lead to increase in dry matter.

Other carbohydrates such as chitosan and lignocellulose also show the similar promotion effect on plant growth.
6. SUPPRESSION OF ENVIRONMENTAL STRESS ON PLANTS

Effect of chitosan irradiated at wide range of irradiation doses on plants was examined showing chlorosis in various degrees at lower doses less than 50 kGy. The chlorosis was reduced or disappeared at higher doses ($\geq 70$ kGy) and the stimulation of the plant growth occurred at 100 kGy. Heavy metals such as vanadium (V) show the strong stress on soybean, rice, wheat and barley seedlings, whose roots were clearly injured at 5 $\mu$g/ml V (in VCl$_3$) in solution cultures [7]. The seedlings of rice were critically damaged at $\sim 10$ $\mu$g/ml and died completely at $\sim 50$ $\mu$g/ml. These damages were relatively reduced by application of radiation degraded chitosan. The recovery of
growth and reduction of V levels in seedlings were obtained by the treatments with 100 and 200 µg/ml chitosan irradiated at 100 kGy in 1% solution.

Lignocellulosic materials were also degraded by radiation and the extracts from oil palm fibre, sugar cane bagasse and sawdust of *fagus* were increased at 500 to 1000 kGy [8]. These extracts in hot water and ethanol show that the strong activity to suppress the heavy metal and salt stress on plants. Fig. 6 shows the effect of extracts from oil palm fibre on suppression of salt stress on barley growth. Salt stress at 5 mg/ml strongly inhibited the growth of barley seedlings causing a lower biomass production (62.6%), smaller shoot height (69.8%) and root length (54.9%). The growth of plants suffering salt stress was improved clearly with lignocellulosic extracts, especially 90 kGy irradiated extracts.

Thus, the polysaccharides irradiated at suitable doses could be suggested as heavy metal and salt eliminators in crop production.
RADIATION PROCESSING TECHNOLOGY FOR PRODUCTION OF PLANT GROWTH PROMOTER FROM BROWN SEAWEED AND PLANT PROTECTOR FROM SHRIMP SHELL

Nuclear Research Institute, Dalat, VAEC, Viet Nam
1Takasaki Radiation Chemistry Research Establishment, JAERI, Japan

Abstract

Two products (in solution state) namely plant growth promoter from brown seaweed (alginate) and plant protector from shrimp shell (chitosan) have been produced by the application of radiation processing technology. By foliar spraying, the irradiated alginate impacts the remarkable increase of the productivity of plant such as carrot, cabbage, onion, and the irradiated chitosan exhibits not only protection effect with highly antifungal activity but also growth promotion effect for plants.

1. INTRODUCTION

Polysaccharides such as alginate, chitin/chitosan, carrageenan, undergo main chain scission upon interaction of radiation. Thus polysaccharides can be suitably modified by radiation degradation to regulate molecular weight principally as low as required. Recently, preparation of oligosaccharides by radiation degradation technique has been of our research interest. The irradiated alginate exhibits significant effect of growth promotion for plants and the irradiated chitosan shows higher antifungal activity [1-3].

Oligochitosans with degree of polymerization (DP) from 6 to 11 have been recognized as the strongest phytoalexin inducer to prevent infection of many fungi for plants [4-6]. Thus oligochitosans are very promising to utilize in agriculture and medicine for enhancement of immune system against infection of diseases [6-9].

In addition, modification of polysaccharides through radiation grafting with hydrophilic and/or hydrophobic vinyl monomers will be one of promising ways to produce a variety of modified-grafted polysaccharides [10]. Thus, radiation technique is considered as a useful tool for modification of polymer materials including natural polysaccharides [10]. This paper describes the production of plant growth promoter from brown seaweed and plant protector from shrimp shell with the use of radiation processing technology.

2. MATERIALS AND METHODS

2.1. Plant growth promoter from brown seaweed

Brown seaweed Sargassum (glaucescens, incanum, hemiphyllum, duplicatum, mcclure) was supplied by a local factory and used as starting materials for extracting alginate and followed by irradiation to degrade alginate in aqueous solution of 5% (w/v) with gamma Co-60 radiation at the minimum dose of 75kGy. The stainless steel drums (d=40cm, h=50cm) each drum contained about 50liters of sodium alginate solution were used as irradiation container on the industrial Co-60 irradiator nearby Ho Chi Minh City. The irradiated alginate solution was then filtered through cotton fabric and treated with desired additives to obtain so-called plant- growth promoter. The product is a dark brown solution with sweetish odor. The effect of growth promotion has been tested on the field for several kind of plant such as carrot, tea, cabbage, tomato, grape, onion, by foliar spraying and the increase of the productivity was reconized of from 15 to 60% [11]. Furthemore, the quality of agro-products treated with irradiated alginate was remarkably improved for instance through lower nitrate and higher total sugar content. The significant advantage of this kind of plant growth promoter is safe
and highly effective and thus it is suitable for the environmentally sustainable development of agriculture.

2.2. Plant protector from shrimp shell

The crude dried shrimp shell was purchased from seafood factories. The shell was deproteinized by boiling with 3% sodium hydroxide solution for one hour, washed with tap water. The deproteinized shell was treated with 3% hydrochloric acid at ambient temperature for 3 hours for demineralizing. The shell chitin was rinsed until free from acid and dried. The chitin was treated in 40% NaOH solution for 3 hours in stainless steel vessel in opened air to convert chitin to chitosan. The chitosan product (about 80% degree of deacetylation) was washed in water to neutrality and dried. The viscosity average molecular weight (Mv) of chitosan was then regulated to about $M_v \approx 60,000$ ($\eta = 1.81 \times 10^{-5}, M_v^{0.93}$ at 25°C [12]) by irradiation with gamma ray from a Co-60 source. The chitosan solution of 10% (w/v) was prepared by dissolving irradiated chitosan in 2.5% acetic acid. The chitosan solution was irradiated on the Co-60 irradiator with the minimum dose of 45kGy using stainless steel drums as for alginate mentioned above.

The oligochitosan obtained from irradiated chitosan solution has DP~8 [13]. The plant protector was prepared by mixing the same volume of irradiated and non-irradiated chitosan solution, treated with required additives and filtered through plastic net. The product is a brownish viscous solution (~200 centipoises at 25°C). The antifungal effect has been tested on different kind of plant by foliar spraying with the dilution of 1/1000 and the results indicated that this product exhibits not only the protection effect with highly antifungal activity but also the growth-promotion effect for plants [14].

3. CONCLUSIONS

By the application of radiation processing technology to degrade polysaccharides namely alginate and chitosan, the plant growth promoter from irradiated alginate and the plant protector from irradiated chitosan have been produced. Based on the biological effects, these products are favorable for the environmentally sustainable development of agriculture.

REFERENCES


BIOLOGICAL ACTIVITIES OF RADIATION DEGRADED CARRAGEEenan

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1Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki, Takasaki, Gunma, Japan

Abstract

Carrageenans were irradiated in solid state to doses 50-1000 kGy in air at ambient temperature. Changes in their molecular weight and functional properties with respect to their FT-IR and UV spectra were evaluated. Irradiation of carrageenans resulted in a rapid decrease of molecular weight indicating main chain scission in their polymeric structures. Formations of some compounds were evident by new absorption peaks in their UV and FT-IR spectra and quantitative analyses of the FT-IR spectra which, in addition, support that there is a breakdown in the carrageenan structure. Irradiated carrageenans were investigated for their plant growth-promoting activities. Carrageenans were added to the nutrient solutions for rice seedlings under non-circulating hydroponics cultivation. Irradiated carrageenan induced weight gain in treated rice seedlings. Maximum weight gain was obtained with KC irradiated at 100 kGy while treatment with IC at 500 kGy. IC exhibited less growth promoting properties than KC. The growth of fungi on the roots disappeared with treatment of IC and KC irradiated at 500 kGy. Growth promotion of some leafy vegetables was also observed with application of degraded KC. The carrageenan molecule has been broken down to smaller molecule(s) or compound(s) that can be absorbed effectively as nourishment factors and anti-microbial agents by plants.

1. INTRODUCTION

Carrageenans are sulfated anionic polymers that comprise the main structural polysaccharides of red seaweed (Rhodophyceae) [1]. They are composed of D-galactose units linked alternately with \( \alpha 1,3 \) and \( \beta 1,4 \) linkages. These sulfated galactans are classified according to the presence of the 3,6 anhydrogalactose on the 4-linked residue and the number and position of the sulfate group (Tombs, Harding, 1998). The repeating units of the principal gel formers, kappa-, iota- and lambda carrageenans are shown in Fig. 1. The Philippines is one of the major producers of carrageenan, primarily of the kappa and iota types. Carrageenans are used commercially as thickeners and gelling agents in the food industry and binders in some consumer products.

Natural polymers like polysaccharides have been receiving a great deal of attention by many researchers because of their biodegradability and availability at low cost. The native structures and properties of the carrageenans may be exploited for non-food applications, i.e., hydrogel for microencapsulation, controlled-released of chemicals and biological products, and wound dressings. It has been known that gamma irradiation can modify the structures and chemical and biological properties of materials via either degradation, crosslinking or grafting. Enzyme- or radiation-degraded polysaccharides have been found to induce various kinds of biological activities such as anti-microbial, promotion of plant growth, suppression of heavy metal stress, etc. (Kume, Nagasawa, et al., 1999). This study aims to modify carrageenan by radiation degradation and to investigate their biological activities.

This paper presents the results of the various studies undertaken to investigate the effect of gamma radiation on the molecular weights and structures of kappa-, iota and lambda-carrageenan and the effect of radiation-degraded carrageenan on the growth of plants. The relationship of the growth-promotion activity and molecular weight of irradiated carrageenans and the influence of the sulfate group in the radiolysis of the three types of carrageenan are discussed.
2. MATERIALS AND METHODS

2.1. Materials/irradiation

Refined kappa-carrageenan (KC) and iota-carrageenan (IC) were obtained from Copenhagen Pectin A/S, Denmark and Shemberg Corporation, Philippines. The samples were used without further purification and gamma irradiated to doses 50-1000 kGy in air at ambient temperature. Carrageenans used for GPC and UV experiments were purchased from Marine Resources and Development Corporation, Philippines.

2.2. Analytical measurements

Molecular weights of irradiated carrageenan were determined by gel permeation chromatography using Waters HPLC instrument equipped with Waters Ultrahydrogel column, and elution was monitored by an RI detector using 0.1 M NaNO₃ as the mobile phase at a flow rate of 1 ml/min. The carrageenan concentration used was 0.1%. A calibration curve was constructed using PEO/PEG standards. FT-IR spectra were recorded using diffuse reflectance spectroscopy (DRS) with a Shimadzu FT-IR spectrometer. Samples for FT-IR were prepared by pipetting 20 µl of 1% carrageenan solution on an aluminum pan and dried in a vacuum oven at 40°C. UV spectra were measured in water with a Perkin Elmer Lambda 20 UV-Vis spectrometer in the range 200-400 nm at 0.25% carrageenan concentration.

2.3. Cultivation of rice and vegetable

Rice seeds (Japonica) were washed in running water for 24 hrs and germinated by immersion in water at 70°C in the darkroom. Twenty-five germinated seeds were then sowed onto plastic net floating in plastic pots containing 80 ppm of carrageenan in diluted hyponex solution (1/2000).

Bok choi seeds were sowed directly in cup containing perlite. The cup was then immersed in nutrient solutions contained in polystyrene box with holes (see diagram below). This set-up was adapted from the Asian Vegetable Research and Development Centre, Taiwan. Nutrient solutions for this experiment were prepared, as follows:

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO₃)₂</td>
<td>635</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>53</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>16</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>28</td>
</tr>
<tr>
<td>KNO₃</td>
<td>217</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>504</td>
</tr>
<tr>
<td>Fe-EDTA</td>
<td>22.6</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>1.54</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>0.08</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>0.22</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>2.86</td>
</tr>
<tr>
<td>NaMoO₄</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*concentration in ppm
After one month of growth in a greenhouse, rice seedlings and Bok choi were collected, gently washed and dried at 105°C for 12 hours. Percentage weight gain of dried rice seedling and Bok choi was determined for evaluation of growth promotion activity of carrageenan and calculated as:

$$\% \text{Weight gain} = \frac{\text{dry wt. of plant treated with carrageenan} - \text{dry wt. of plant untreated}}{\text{dry wt. of plant untreated}}$$

**Artemia salina L. Lethality test**

The assay was performed as described by Solis, et al. (1993) with minor modifications. Brine shrimp (*Artemia salina* Leach) cysts were hatched in artificial seawater supplemented with 6 mg/l dried yeast and oxygenated with an aquarium pump in an improvised double-chamber brine tank. After 48 hours, nauplii (baby shrimp or larvae) were gathered and placed in a multichannel micropipette reservoir. Approximately 15-20 larvae (in a total volume of 100 µl) were pipetted in 96-well microtiter plates (Nunc.). 100 µl of irradiated iota, kappa, and lambda carrageenan (0, 50, 100, 500 and 1000 kGy) diluted in salt water (with phosphate buffer, pH 7.0) at concentrations of 25, 250, 1000 and 5000 µg/ml were added. After 24 hours, non-viable shrimps were counted with the aid of a binocular microscope (Nikon). The plates were then incubated to 50 °C for 10 minutes to kill the remaining live shrimps and their total number was recorded. Percent survival was plotted against concentration of the test substance to obtain a survival curve.

3. RESULTS AND DISCUSSION

3.1. Effect of radiation on the molecular weight and structure of carrageenan

The properties of polymeric materials are affected upon irradiation as a result of chemical changes in the polymer molecules [2]. These changes include molecular weight and structure. GPC elution profiles or kappa-carrageenan at different irradiation doses is shown in Fig. 2. As expected, peak shifts to longer retention as the dose is increased. Irradiation of carrageenan led to the reduction in molecular weight. Carrageenan degraded at higher doses showed bimodal molecular weight distribution. Molecular weight of carrageenan decreases remarkably with dose as demonstrated in Fig. 3. KC and IC exhibited different degradation behavior. Degradation of KC at 100 kGy corresponds to dose of about 200 kGy for IC. The susceptibility of the compound to degradation can be compared by calculating the G-values. Radiation-chemical yields of degradation, $G_d$ were determined from the Charlesby-Pinner equation:
\[
\left( \frac{1}{Mn} - \frac{1}{Mn_0} \right) = G_d \times 1.04 \times 10^{-7} \times D
\]

where

- \( Mn \) is the number-average molecular weight of carrageenan at absorption dose,
- \( Mn_0 \) is initial number-average molecular weight,
- \( D \) is absorbed dose (kGy) [3].

From Fig. 4., the yields of degradation \((G_d)\) of carrageenans are calculated as follows: kappa; 2.13 and iota:1.51. Comparing the \(G_d\) values, kappa was found to be more susceptible to radiolysis than iota. This observation has also been reported in the literature (Morris, W.). Thus, the sulfate groups may have played a role in the radiolysis of the carrageenans. Analysis of lambda carrageenan will verify the hypothesis.

The UV spectra (Fig. 5) of irradiated carrageenans show an absorbance peak at around 265 nm and the intensity of which increases with increasing dose. This peak is probably due to the formation of double bond. Double bond formation has been proven by bubbling solution of irradiated alginate with ozone [4]. Fig. 6 shows the plot of ratio of the absorbance at 265 nm of irradiated and unirradiated carrageenan with dose. This plot gives the rate of formation of the double bond. It can be seen that greater formation of double bond was obtained with KC. These results were in good agreement with the MW measurement and support the assumption that sulfate groups influence the radiolysis of carrageenans.

Infrared spectral absorption of carrageenans, notably the glycosidic, 3,6 anhydrogalactose and the covalent sulfate, are listed in Table I and sample spectra of iota-carrageenan are shown in Fig 7. IC and KC differ chemically in the presence of another 2-sulfate in the disaccharide unit of iota and this is shown in their FT-IR spectra. KC does not have an absorption peak at 805 cm\(^{-1}\) (Table I). As illustrated in Fig. 8, important functional groups are retained even after irradiation at 500 kGy while there is the appearance of a new peak at 1728 cm\(^{-1}\). This peak could be attributed to the formation of a carbonyl group in the structure. The same is observed for kappa carrageenan. Quantitative FT-IR analysis was undertaken. Table II shows that for both IC and KC, there is a considerable decrease in the peak heights corresponding to the glycosidic, 3,6 anhydrogalactose and methylene groups with increase in radiation dose. Peaks due to covalent sulfates and sulfates of 3,6 anhydrogalactose were likewise decreased with radiation.

**TABLE I. MAJOR PEAKS FROM THE FTIR SPECTRA OF CARRAGEEAN**

<table>
<thead>
<tr>
<th>Absorption (cm(^{-1}))</th>
<th>Functional group</th>
<th>Intensity</th>
<th>kappa</th>
<th>iota</th>
</tr>
</thead>
<tbody>
<tr>
<td>1640-1645</td>
<td>polymer bound water</td>
<td>s</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>1370-1375</td>
<td>methylene group</td>
<td>m</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>1210-1260</td>
<td>covalent sulfate</td>
<td>vs</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>1010-1080</td>
<td>glycosidic linkage</td>
<td>vs</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>928-933</td>
<td>3,6 anhydro-D-galactose</td>
<td>s</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>840-850</td>
<td>D-galactose-4-sulfate</td>
<td>m</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>800-806</td>
<td>3,6 anhydro-D-galactose-2 sulfate</td>
<td>a</td>
<td>m</td>
<td></td>
</tr>
</tbody>
</table>

vs-very strong, s-strong, m-medium, a-absent
TABLE II. EFFECT OF RADIATION DOSE ON THE MAJOR FUNCTIONAL GROUPS IN CARRAGEEAN

(A) iota-carrageenan

<table>
<thead>
<tr>
<th>Absorption (cm⁻¹)</th>
<th>Peak height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC-0</td>
</tr>
<tr>
<td>1640-1641</td>
<td>13.16</td>
</tr>
<tr>
<td>1371-1375</td>
<td>5.29</td>
</tr>
<tr>
<td>1230-1250</td>
<td>7.59</td>
</tr>
<tr>
<td>1068-1072</td>
<td>37.89</td>
</tr>
<tr>
<td>929-931</td>
<td>26.16</td>
</tr>
<tr>
<td>846-847</td>
<td>18.17</td>
</tr>
<tr>
<td>804-806</td>
<td>12.80</td>
</tr>
</tbody>
</table>

(B) kappa-carrageenan

<table>
<thead>
<tr>
<th>Absorption (cm⁻¹)</th>
<th>Peak height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC-0</td>
</tr>
<tr>
<td>1640-1641</td>
<td>1.4185</td>
</tr>
<tr>
<td>1371-1375</td>
<td>0.8425</td>
</tr>
<tr>
<td>1230-1250</td>
<td>6.2183</td>
</tr>
<tr>
<td>1068-1072</td>
<td>1.0690</td>
</tr>
<tr>
<td>929-931</td>
<td>5.2440</td>
</tr>
<tr>
<td>846-847</td>
<td>2.2053</td>
</tr>
</tbody>
</table>

3.2. Growth-promotion effect of irradiated carrageenan

Upon irradiation, carrageenan is depolymerized with the formation of shorter fragments the molecular size of which depends on the radiation dose used. When solutions of the irradiated KC and IC were mixed with the growth medium for rice seedlings under hydroponic conditions, stimulation of growth was observed. As shown in Fig. 8a, the maximum % weight gain of rice seedlings was obtained with KC irradiated at 100 kGy. It decreased to the level of the unirradiated at doses of 500 and 1000 kGy, indicating that no toxic compounds are formed at high radiation dose. This observation is supported by the brine shrimp toxicity assay. Unirradiated IC and KC has also stimulated growth of rice to some extent. This strongly suggests that a certain range of molecular weight is suitable for growth-promotion of plants. Depending on the molecular weight, carrageenans exhibited various level of growth-promotion effect on rice. Table III summarized the results of MW by GPC experiment. In this study, KC at 100 kGy showed the highest effect of growth promotion, thus MW of about 24,000 is suitable for growth promoters of plants. IC exhibited less growth promoting properties than KC. Maximum weight gain was attained with the application of IC irradiated at 500 kGy. Like KC no toxic compounds are formed at higher radiation doses. Optimum growth-promotion of IC was not achieved since to get MW of 24,000, IC has to be degraded at about 255 kGy. This value was calculated from the Charlesby-Pinner equation using the calculated $G_d$. From these results, it is clearly suggested that growth-promotion effect of radiation-degraded carrageenan depends mainly on its molecular weight.
TABLE III. EFFECT OF RADIATION ON THE MOLECULAR WEIGHT OF CARRAGEENAN

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Molecular Weight (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kappa</td>
</tr>
<tr>
<td>0</td>
<td>1,032,905</td>
</tr>
<tr>
<td>50</td>
<td>65,550</td>
</tr>
<tr>
<td>100</td>
<td>26,625</td>
</tr>
<tr>
<td>500</td>
<td>5,457</td>
</tr>
<tr>
<td>1000</td>
<td>4,738</td>
</tr>
</tbody>
</table>

Fig. 8b shows the photograph of rice seedling treated with irradiated carrageenan. It is evident that chlorosis or yellowing of leaves was inhibited with the application of both KC and IC as compared to the control. Furthermore, growth of fungi was inhibited with treatment of KC at 500 kGy (Fig 9). It can be noticed from the photograph that IC can also inhibit growth of fungi on roots even at 0 kGy and inhibition increases with increasing dose. This noticeable anti-microbial activity will be further studied against *Escherechia choli* and other microorganisms. It has been reported that ethanolic extract of species of red algae showed strong anti-microbial activities against *Escherechia choli*, *Staphylococcus areus*, *Candida albicans* etc. [5]. Fig. 10 illustrates the growth-promotion activity of kappa-carrageenan on vegetables like bok-choi and mustard. Carrageenan was applied through hydroponics for cultivation of bok-choi while foliar spraying for mustards. Growth-promotion effect was observed for both cultivation conditions.

3.3. Toxicity of irradiated carrageenan

The irradiated carrageenans were subjected to a microwell cytotoxicity assay based on a 24-hour lethality of *Artemia salina* larvae. Brine shrimp larvae have been used as a convenient and reliable bioassay system to screen for a wide spectrum of potentially toxic substances such as mycotoxins, co-carcinogens, anti-tumor compounds, dinoflagellate toxins, pesticide residues and other pollutants [7,8]. LC₅₀ values of less than 200 µg/ml are considered cytotoxic. At physiologically neutral pH, irradiated carrageenan is unlikely to exhibit cytotoxicity. LC₅₀ values of irradiated carrageenan are summarized in Table IV. We predict two possible bioactive compounds of potential pharmacologic value: one has an LC₅₀ of around 1300 µg/ml and another at 400 µg/ml. Future work will need a preparative HPLC coupled to a bioassay-driven purification scheme.

TABLE IV. LC₅₀ VALUES OF IRRADIATED CARRAGEENAN

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>LC₅₀ (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lambda</td>
</tr>
<tr>
<td>0</td>
<td>&gt;2500</td>
</tr>
<tr>
<td>50</td>
<td>1350</td>
</tr>
<tr>
<td>100</td>
<td>1350</td>
</tr>
<tr>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>1000</td>
<td>400</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Carrageenans were highly sensitive to gamma radiation with significant changes in their molecular weight and structure. Kappa-carrageenan was found to be more susceptible to radiolytic breakdown. Carrageenan with specific molecular weight range can be readily produced by radiation degradation. Radiation degraded carrageenans promoted growth of rice and leafy vegetables. Carrageenan with molecular weight of about 24,000 can be used as growth-promoter of plants.
REFERENCES


FIG. 1. Idealized structures of different types of carrageenan.

FIG. 2. GPC elution profiles of kappa-carrageenan at different doses.
Fig. 3. Effect of radiation on the molecular weight of carrageenan

Fig. 4. Degradation yields of carrageenans

Fig. 5. UV spectra of kappa-carrageenan at different doses

Fig. 6. Absorbance at 265 nm as a function of dose
Fig. 7. FT-IR spectra of iota-carrageenan

Fig. 8. Growth promotion of rice by irradiated carrageenan (a) as a function of dose (b) at 100 kGy
Fig. 9. Growth of fungi on roots in hydroponics solution with carrageenan

Fig. 10. Growth-promotion effect of carrageenan on bok-choi and mustard
PRE-IRRADIATION GRAFTING POLYMERIZATION OF DMAEMA ONTO CELLULOSE FABRICS

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China

Abstract

The grafting yield of N,N\textsuperscript{-}Dimethylaminoethyl methacrylate (DMAEMA) on cotton cellulose fabric increased with grafting time, absorbed dose and concentration of the monomer in the aqueous solution, but decreased with grafting temperature. The dose rate had just a little effect on the grafting yield. The optimal grafting yields of DMAEMA on cotton cellulose were rather low, approximately 50% compared with N-isopropylacrylamide (NIPAAm), though both monomers could be synthesized to be thermally reversible hydrogels. The relationship between the grafting yield and the grafting temperature indicated that the trapped radicals located in the interphases between crystalline and amorphous regions of irradiated samples were the main active species inducing the grafting reaction.

Key words: cotton cellulose, DMAEMA, pre-irradiation grafting polymerization.

1. INTRODUCTION

Some investigations on pre-irradiation grafting of NIPAAm in aqueous solutions or in mixed solutions of water and alcohols on cotton cellulose have been performed in the author's lab [1,2]. Because of the special structure of NIPAAm and the environmental stimuli responsibility of polyNIPAAm [3,4], in these systems some new phenomena, such as the abnormal temperature effect the decrease of crystallinity of grafted samples, appeared. In order to study deeply, DMAEMA which has the similar structure and functional property [5-13] with NIPAAm was used the same way.

In this work, the main conditions of pre-irradiation grafting of DMAEMA onto cotton cellulose fabric were investigated. The temperature effect on the grafting reaction indicated that the results were similar to that of acrylamide as monomer, instead of that of NIPAAm. It meant that in the grafting system of DMAEMA and cotton cellulose, the grafting reaction was induced only by trapped radicals, while the peroxides produced in irradiated samples did not take part.

2. EXPERIMENTAL

2.1. Materials

The ordinarily bought cotton cloth was extracted with ethanol in the Soxhlet apparatus for 5 hrs and boiled in the solution of 1% NaOH for 3 hrs. Then it was washed with distilled water to neutral. The cleared cotton was dried in the vacuum oven and then stored in the desiccator for further use. The solutions for the grafting reactions were prepared by dissolving the monomer in tri-distilled water. The monomer DMAEMA was purified by distilled under reduced pressure. Other reagents were used without purification.

*Author to whom correspondence should be addressed (e-mail address: yimin920@ibmstone.pku.edu.cn).
2.2. Methods

The treated cotton was cut into pieces of about 0.1g and weighed. The samples were irradiated in the air to certain dose by $^{60}$Co-$\gamma$ source. The irradiated samples were immediately immersed in the solution of the monomer DMAEMA that was already deoxygenated by N$_2$ for about half an hour. At certain temperature in the water bath, the reaction lasted for certain time with N$_2$ aerated in. After grafted the cotton pieces were extracted with ethanol in the Soxhlet extractor for about 12hrs to remove the homopolymer of the monomer. Then they were dried in the vacuum oven and weighed again. The grafting yield (G.Y.%) was finally calculated according to the following formula.

$$\frac{W-W_0}{W_0} \times 100\%$$

where

- $W_0$ is the original weight of the ungrafted cotton fabric,
- $W$ is the weight of the grafted sample.

3. RESULTS AND DISCUSSION

3.1. Main conditions of grafting

3.1.1. Effect of reaction time on the grafting yield

The measurement of kinetic of the grafting reaction showed that the grafting yield increased with the reaction time. As shown in Fig.1, when the time was less than 2hr, the grafting yield increased drastically and then it did mildly. Along with the procedure of grafting reaction, the concentrations of both the monomer and free radicals produced in the irradiated sample decreased gradually, so the reaction rate slowed gradually. The reaction time for the experiments to equilibrium was 4hr.

![Fig.1 Effect of reaction time on grafting yield](image)

Dose: 16.13kGy; monomer conc.: 20%；
grafting temperature: 21$^\circ$C
3.1.2. Effect of dose rate on the grafting yield

It can be seen in Fig. 2 that the change of dose rate (within 300Gy/min) had little influence on the grafting yield. The result complied with the accepted theory of pre-irradiation grafting. Under certain overall dose, the dose rate did not affect the amount of the radical sites where the consequent grafting copolymerization happened in the cotton cellulose fabric. The dose rate in most of this work was 268.9Gy/min.

![Fig. 2. Effect of grafting temperature on grafting yield. Dose: 16.13 kGy; reaction time: 4 h; monomer concentration: 20%.]

3.1.3. Effect of dose on the grafting yield

As in typical pre-irradiation grafting procedures, the grafting yield first increased fast with the overall dose (Fig.3). After the overall dose reached at about 15kGy, the curve leveled off and the grafting yield increased much less since. Higher overall dose produced more free radicals in the sample, which initiated more grafting copolymerization. On the other hand, more free radicals led more chances of their termination. When the two effects counteracted, the grafting reaction reached its platform. So in the following experiments the overall dose chosen was 16.13kGy.

![Fig.3 Effect of dose on grafting yield. Reaction time: 4hr; monomer conc.: 20%; grafting temperature: 21°C]
3.1.4. Effect of monomer concentration on the grafting yield

The grafting yield first increased obviously with the increasing concentration of DMAEMA. When the concentration was higher than 30% (v:v), the increase of the grafting yield tended to stop (Fig.4). It could be concluded that the grafting reaction in this heterogeneous system was controlled by the diffusive rate of the monomer. The main concentration in this work was 20%.

Compared with the grafting yield of NIPAAm [1,2], another monomer to produce sensitive polymer, on cotton cellulose, the grafting yield of DMAEMA was rather low. This might be attributed to the relative sizes of their molecules. The DMAEMA molecule was larger than NIPAAm, and the grafted chains of polyDMAEMA during the chain propagation were larger than those of polyNIPAAm. Larger chains caused more impediment for continuing chain propagation. So the overall grafting yield of the larger monomer was relatively lower.
3.1.5. Effect of grafting temperature on the grafting yield

As the grafting temperature grew up, the grafting yield fell down almost linearly (Fig.5). This was also of the normal situation in pre-irradiation grafting. When the grafting temperature increased the rates of monomer diffusion and chain propagation both increased. However, the chance of free radicals' termination simultaneously increased. The overall tendency of the grafting yield according to temperature increasing was the cooperative effect of the above aspects. Main reactions of this work were performed under 21°C.

From Fig. 6 we could see that, in aqueous solutions, the changing tendency of grafting of DMAEMA was similar to that of AAm but was opposite to that of NIPAAm [1]. It might be concluded that the grafting copolymerization of DMAEMA or AAm was initiated by the trapped radicals, while that of NIPAAm was partly by peroxide hydrogen.

3.2. Property measurement of grafted samples

3.2.1. Result of X ray diffraction measurement

The X-ray diffraction measurement analyzed the change of crystallinity of samples. The crystallinity of the grafted sample with the grafting yield of about 65% was 63%, while that of the ungrafted sample was 67%. Because the grafting yield was not high enough, the crystallinity was not distinctly changed. That was consistent with the result of the grafting copolymerization of NIPAAm onto cotton cellulose fabrics [2].

3.2.2. Result of scanning electron microscope

SEM measuring tried to explore the surface properties of samples. Because of the coarse nature of the cotton fabric surface, the result of SEM did not apparently display the grafting condition. But some grafted change could be seen from photos.

REFERENCES


RADIOLYSIS OF CHLORAMPHENICOL AND ITS EYE OINTMENT DURING GAMMA STERILISATION

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Swiss Federal Institute of Technology,
Zuerich,
Switzerland

Abstract

The effects of γ radiation sterilisation on chloramphenicol (CAP), both in pure powder state and in eye ointment, were investigated with high performance liquid chromatography (HPLC) and HPLC-MS. Five radiation degradation products were observed and identified, the radiolysis mechanisms were elucidated, and the application of γ radiation sterilisation on chloramphenicol was discussed.

It has been determined that at irradiation dose of 25 kGy, the content of chloramphenicol decreases by 1.0% in powder state and by 3.3% in eye ointment. By comparing the radiolytic products of CAP in different matrices, it is concluded hydrolysis, oxidation and radical reduction are the main radiolytical degradation reactions of chloramphenicol, and the micro-environment surrounding chloramphenicol molecular plays an important role in the radiolysis process. Protection techniques to resist radiolyses are thus proposed based on the experimental findings.

1. INTRODUCTION

Gamma (γ) radiation sterilisation has gained in popularity over the years in pharmaceutical industry due to its simplicity and reliability, especially by the recent concerns about the safety of ethylene oxides and the possibility of toxic residues in the treated materials [1]. Consequently, radiation sterilisation has been assigned as the first alternative for thermal unstable pharmaceuticals in non-aqueous or dry powder products by EMEA (The European Agency for the Evaluation of Medicinal Products) in 1999 [2].

Due to the poor thermal stability [3], D-(threo)-chloramphenicol (CAP) powder can not be sterilised by dry heating (the first choice of sterilisation methods), and has currently to be sterilised by the ethylene oxide method. Furthermore, although eye ointment base is generally heat stable, thermal sterilisation of ointment products in the packed terminal container is not practicable since the ointment base will be fluidised well below the sterilisation temperature. Traditionally, ointment products have to be manufactured under aseptic conditions. The whole process is not only complicated, but also introduces numerous possibilities of secondary contamination.

CAP and its eye ointment are widely used pharmaceuticals. It is of great scientific and industrial interests to explore the possibilities of radiation sterilisation and behaviour of CAP under γ-irradiation.

2. EXPERIMENTAL

Chloramphenicol eye ointments (CAPEO) and CAP powder were offered by CIBA Vision Ltd. (Switzerland). Methanol and acetonitrile were of HPLC grade solvent, and all other chemicals were of reagent-grade or better.

Samples of CAP powder in glass bottle and CAPEO in aluminum tubes were simultaneously irradiated by 60Co to 25 and 50 kGy, in a radiation sterilisation plant of Studer AG (Switzerland) [4]. The investigation is outlined in Fig. 1. The extraction and HPLC procedures can be found in reference [5].

* Author to whom correspondence is to be addressed (Tel. +411 6356064; Fax +411 6356885; E-mail: altorfer@pharma.ethz.ch).
3. DEGRADATION CHARACTERISATION OF CAP

3.1. Assay test

Table I shows that γ irradiation induced degradation of chloramphenicol both in eye ointment and in powder states, and the degree of degradation was proportional to the irradiation doses. At the irradiation dose of 25 kGy (the reference dose of γ sterilisation [6]), CAP content decreases by 1.0 % in powder state, and by 3.3 % in eye ointment. Obviously, both the irradiation dose and the eye ointment base have played roles in the radiolytical degradation process.

FIG. 1. Effect of γ-irradiation on chloramphenicol (CAP) content determined by HPLC assay test (n = 6 at each point). The non-irradiated samples were set as 100% and the CAP eye ointment and CAP powder samples were packed respectively in conical glass flasks for irradiation.
TABLE I. INFLUENCE OF IRRADIATION DOSE ON THE CONTENT OF CAP IN DIFFERENT MATRICES (N = 6)

<table>
<thead>
<tr>
<th>Radiation dose</th>
<th>CAP in powder state</th>
<th>CAP in CAPEO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Content %</td>
<td>RSD %</td>
</tr>
<tr>
<td>0 kGy</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>25 kGy</td>
<td>98.99</td>
<td>1.29</td>
</tr>
<tr>
<td>50 kGy</td>
<td>97.88</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Note: Relative standard deviation.

3.2. Impurity test

Typical HPLC chromatograms are shown in Fig. 2. By comparing the chromatograms of non-irradiated and irradiated chloramphenicol samples, five compounds were found to be the main radiolysis products. The relative concentration of those compounds, as showed by the chromatograms, differs significantly between CAP powder and CAP eye ointment samples, further suggesting that CAP in powder state and in eye ointment behave differently under γ-irradiation processing.

**FIG. 2. Typical HPLC chromatograms of radiolysis products of CAP powder and CAPEO.**

In order to explore possible ways to eliminate this irradiation degradation, such as protection techniques of scavenger, it is of primary importance to identify the degradation products and the degradation mechanisms. The identification of radiolytic products was carried out by HPLC-MS (Hong, Altorfer, 2000), and the results are given in Fig. 3.
3.3. Mechanism scheme

Compound 1 is a typical hydrolysis product of the acyl group of chloramphenicol [7], and formation of compounds 2 & 3 involves in substitution of hydrogen atoms (reduction). Compound 4 is the oxidation product of the hydroxyl group, and compound 5 is a product of combined oxidation and reduction.

It can be concluded that hydrolysis, oxidation and reduction are the main radiolytical degradation reactions of chloramphenicol products. The radiolytical mechanism scheme can therefore be elucidated in Fig. 3.

The hydrolysis reaction is further demonstrated by the behaviour of compound 1, which only appears in CAP powder and not in CAPEO samples. Chloramphenicol in CAPEO was actually surrounded by the oily eye ointment base, which effectively separated the CAP ingredient from the atmospheric environment.
The same applies to the oxidation products. Compounds 4 and 5 were much smaller in CAPEO than in CAP powder samples, which could be inferred by the presence of oxygen in the case of CAP powder. The variation of peak 4, the direct product of oxidation, was more pronounced than that of peak 5, an indirect product. Those radiolysis reactions are illustrated in Fig. 3.

In addition, γ-irradiation certainly involves \( \cdot \)esolv and will unavoidably promote the formation of radicals, \( \text{H}^\bullet \), \( \text{H}_2 \), and \( \text{HO}_2^\bullet \) when radiation energy is absorbed by the target substance. The radical reduction is therefore unavoidable. This is demonstrated by the formation of compounds 2 & 3, the radical reduction products, which exist both in CAP powder and in CAPEO samples with almost identical peak intensity, regardless of the different micro environments.

4. CONCLUSION

Gamma irradiation brings about degradation of Chloramphenicol both in powder state and in eye ointment, and the degree of CAP degradation in the powder state is significantly lower than that in oily eye ointment. Since CAP degrades more than 1% under the standard irradiation dose of 25 kGy [8], it is concluded that γ sterilisation may not be directly applicable for CAP powder and its eye ointment products without protection.

Oxidation, hydrolysis, and radical reduction are the main radiolytical degradation reactions of chloramphenicol. In order to apply γ sterilisation to chloramphenicol products, the irradiation environment (matrix) has to be controlled to restrict the radiolytical degradations. Indifferent gas purging can be an easy solution to clean the surrounding of CAP molecule in powder state. Introducing proper radical scavengers to capture the radicals will certainly improve the stability of chloramphenicol in eye ointment during γ sterilisation processing, as radical reduction is main radiolysis reaction in the case of chloramphenicol eye ointment.

REFERENCES

GAMMA RADIATION INDUCED EFFECT IN SODIUM ALGINATE AS A COMPONENT FOR CAPSULE FORMATION

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Abstract

The paper presents the results related to the mechanical and viscometric studies of the radiation induced effects on sodium alginate as a component of quaternary system of cellulose sulphate, poly(metilene-co-guandine) and calcium chloride used for encapsulation. The influence of absorbed dose on the mechanical resistance of capsules obtained for different sodium alginate systems demonstrate the enhanced stability of capsules from sodium alginate irradiated in the solid state under systems irradiated in aqueous solutions. The mechanical properties of the obtained capsules seem to be stable up to absorbed dose of 50 kGy. The distinct decrease of intrinsic viscosity indicates that the main change scission was the dominating process.

1. INTRODUCTION

Recently a large number of natural and semisynthetic polymers have been used as pharmaceutical excipients and devices designed for implantation. Some of these systems works as a self-controlling bioreactors. From an engineering point of view, the most important parameters are the selection of suitable materials and preparation procedures to obtain a desirable membrane [1]. Due to their nature and method of production, these materials normally contain microorganisms. One of approaches to depyrogenation is irradiation treatment. Since alginate powder is less affected as a dose dependent a significant impact must be take in to account on the development of cell microencapsulation technology.

The present investigation involved the influence of absorbed dose on the mechanical resistance of capsules obtained from three different sodium alginate systems: 1) sodium alginate irradiated solution in presence of the atmosphere oxygen, 2) sodium alginate irradiated solution in vacuum, 3) sodium alginate irradiated powder; as a component of quaternary system of cellulose sulphate, poly(metilene-co-guandine) and calcium chloride used for encapsulation. A comparison of the capsules obtained from irradiated sodium alginate in three systems demonstrates the enhanced stability of capsules from sodium alginate irradiated in the solid state.

2. MATERIALS AND METHODS

2.1. Materials

Alginate (Keltone HV, from Kelco/Nutra sweet, San Diego, CA, USA), cellulose sulfate (CS, Acros Organic, Geel, Belgium), poly(methylene- co-guandine) hydrochloride (PMGC: 35% aqueous solution), phosphate buffer solution using tablets continent NaCl, Na₂HPO₄ and KH₂PO₄ were obtained from Fluka. The samples were purified by filtration on 0.22 µm micron cellulose filter, from Schleicher & Schuell Germany.

2.2. Solution preparation and characterization

The polyanion solution contained 0.6 % of alginate mixed with 0.6 % of cellulose sulphate in phosphate buffer solution. Polycation solutions contained 1.2 % PMCG dissolved in aqueous solution containing 1.0 % Ca Cl₂ and 0.9 % NaCl. The solutions were purified by filtration with a 0.22 micron cellulose filter from Osmotic Inc.
The molecular weight was evaluated by viscometry using a capillary viscometer (Viscosity TI 1, SEMA Tech, France). The reduced viscosity, $\eta_{\text{red}}$, were obtained by the expression [2]

$$\eta_{\text{red}} = \frac{\eta_{\text{rel}} - 1}{c}$$

(1)

where

$c$ is the concentration of the solution in g/dL,

$\eta_{\text{rel}}$ is the relative viscosity.

Reduced viscosity data were plotted as a function of concentration and extrapolated to zero concentration to obtain the intrinsic viscosity [$\eta$]. The viscosity average-molecular weight of sodium alginate was calculated using the Mark-Houwink-Sakurada equation [3].

$$[\eta] = KM^\alpha$$

(2)

where $K$ and $\alpha$ are constants.

The reduced viscosity $\eta_{\text{red}}$ of sodium alginate was measured in 0.1 M NaCl at 25 °C. The Mark-Houwink-Sakurada used constants were $K = 2.0 \times 10^{-2}$ ml/g, $\alpha = 0.83$ [4].

2.3. Ionizing irradiation of the samples

Alginate samples were irradiated in sealed glass ampoules in vacuum or with the atmosphere oxygen in a $^{60}$Co gamma source, at the Center of Applied Studies for Nuclear Development (CEADEN), Havana, Cuba. The activity of the radiation chamber was 10 kCi and the dose rate was 3.28 kGy/h, according to Fricke and ceric sulphate dosimetry. The applied doses ranged from 1 to 500 kGy.

2.4. Infrared spectroscopy

Infrared spectra for the product samples of sodium alginate were not irradiated, and irradiated powder at 5 and 50 kGy were obtained. The spectra were registered using a ATI Mattson Genesis FTIR with a spectral range of 4000-500 1/cm; employing 10 $\mu$g samples.

2.5. Microscopic observation

Capsule size and membrane thickness were visually examined under a standard inverted light microscope Axiovert 100, Carl Zeiss Jena GmbH, Jena Germany. Images were acquired by normal light microscope using the “photocap” PC program.

2.6. Mechanical characterization

The mechanical resistance of capsules was determined on a Texture Analyser (Ta-2xi, Stable Micro Systems, Godalming, U.K). The mechanical deformation tests were performed at 0.1mm/s. The apparatus consists of a movable probe moving vertically at a constant velocity. The force exerted by the probe on the capsule was recorded as a function of the displacement (compression distance), thus leading to a force vs. strain curve. Twenty-four capsules per batch were analyzed in order to obtain statistically relevant data.

2.7. Capsule preparation procedure

Capsules of various diameters were formed by dropping an aqueous polyanion solution into a polycation receiving bath. The standard reaction time was 3 minutes and airflows were varied in order
to obtain capsules of a desired diameter and membrane thickness. Following the reaction, capsules were isolated from polycation solution on the stainless steel screen grid and washed two times with 0.9 % NaCl solution. For the core liquefaction and calcium removal was used 50 mM solution of sodium citrate during 14 minutes prior to final washing with the 0.9 % NaCl. The chosen parameters are listed in Table I.

3. RESULTS

3.1. Capsule characterization

The selected system for the capsules formation was one of the most promising over a thousand combinations of polyanions tested to search new polymers amongst candidates that would be suitable for encapsulation of living cells [5] (also, Prokop, et al., 1998). This system consists in the combination of sodium alginate, cellulose sulfate, poly (methylene-co-guanidine) hydrochloride and calcium chloride.

Examination of the capsules under the optical microscope revealed an approximately spherical shape with a diameter in the range 2.4-2.6 mm. In many cases, the membranes were transparent (see Fig. 1).

![Capsules from sodium alginate: a) unirradiated powder, b) irradiated solution at 5 kGy in presence of the oxygen of the atmosphere, c) irradiated solution at 5 kGy in vacuum, d) irradiated powder at 25 kGy.](image)

The irradiated sodium alginate powder provided the best results for capsule preparation in comparison with the irradiated sodium alginate solutions. In the case of irradiated powder the capsules were stable up to 150 kGy. By increasing the absorbed dose (more than 75 kGy), the outline of the membranes became wrinkled. After this (300 and 500 kGy) the capsules obtained a white colour when they were washed with 0.9 % NaCl solution with deformation and finally breakage. On the other hand for the irradiated solutions the picture was more marked. For instance between a dose of 5 kGy, the capsules obtained with the sodium alginate irradiated in vacuum seem to be stable and of acceptable morphology. On the contrary, capsules from the solutions irradiated in presence of the oxygen were not sufficiently stable to bear washes and handling. At absorbed doses exceeding 5 kGy the formation of spherical capsules was problematic and only were obtained capsules with a “drop” shape.

3.2. Mechanical measurements

The effect of the irradiated sodium alginate powder capsules and related to this molar mass on the relative mechanical strength, measured by their bursting force in dependence of the absorbed dose, is illustrated in the data of Fig. 2. These are represented by a box plot. The horizontal lines within the boxes represent the median values of the specific observation and the limits of the box are given by the upper and lower quartiles. The box, therefore, represents 50 % of the data. The bars are delimited by the maximum and minimum values whereas the circles represent extremes. The mechanical properties of the capsules seems to be stable up to absorbed dose 50kGy, then is observed a decrease in the bursting force and capsule stability, due to the increase in sodium alginate degradation.

The bursting force of the capsules irradiated solutions (in the presence of the oxygen of the atmosphere and in vacuum) was found to decrease drastically when the adsorbed dose increases above 5 kGy. The weakening of these capsules could be explained by a pronounced decrease in the molecular weight of sodium alginate in solution and the latter is a strong function of the mechanical properties of this system.
3.3. Viscometry studies

In order to follow the processes of sodium alginate transformations caused by irradiation in the studied systems, changes of viscosity were measured. Plots of intrinsic viscosity and viscosity average molecular weight as a function of adsorbed dose are shown in Fig. 3 (a, b). The results reveal that the intrinsic viscosity decrease dramatically above radiation doses of 5 kGy for the sodium alginate irradiated solution in vacuum either for the sodium alginate solution with oxygen of the atmosphere. The values of the irradiated sodium alginate in presence of oxygen of the atmosphere are lower than the data for the system irradiated in vacuum and so for the system irradiated in solid state. Degradation is more intense if samples are irradiated in presence of oxygen. Is reported that the occurrence of chain reactions of oxidation during irradiation accelerates degradation [6]. At the irradiated solutions systems two processes seem to take place together: first, the interaction with the transients species of water radiolysis the hydrated electron (e\textsubscript{aq}); the H\textsuperscript{•} and OH\textsuperscript{•} radicals [7]; and second, the oxygen promotion of degradation apparently by formation of peroxy species, which prevents the permanent recombination of the germinated radical ends [8]. The distinct decrease of these parameters indicates that main change scission is the dominating process.

3.4. Infrared spectrometry

Infrared spectrometry is sensitive to some functional groups of polyelectrolytes. In this study alginate spectra were measured. The stability of the irradiated sodium alginate powder up to adsorbed dose of 50 kGy is in agreement with the IR Spectrometry made to unirradiated and irradiated sample at 50 kGy. Spectra are sensitive to functional groups for instance carboxylic group of the sodium alginate that shows a characteristic bond at wave number 1404 cm\textsuperscript{-1} as a reference. If we are comparing both spectra (see Figs 4 and 5), the spectra of irradiated at 50 kGy do not show any significant difference in comparison with the spectra of unirradiated sodium alginate. That indicates that the chemical structure is not significantly altered by absorption of such a dose.

4. CONCLUSION

The obtained results have some practical implication in the field of radiation sterilization using irradiated sodium alginate in solid state for capsule formation. However, it appears very probable that main-chain scission takes place at high radiation dose. In our case the effect is notable from absorbed doses more than 75 kGy.

<table>
<thead>
<tr>
<th>TABLE I. PARAMETERS FIXED FOR CAPSULE PREPARATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction time with PMCG</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>3 min</td>
</tr>
</tbody>
</table>
FIG. 2. Box plot for the comparison of bursting forces of capsules prepared from sodium alginate irradiated in solid state with non-irradiated quaternary system.

FIG. 3. Intrinsic viscosity and viscosity average molecular weight of sodium alginate as a function of absorbed dose: (a) intrinsic viscosity, (b) viscosity average molecular weight.
FIG. 4. FTIR spectra of unirradiated sodium alginate powder sample.

FIG. 5. FTIR spectra of irradiated sodium alginate powder sample at 50 kGy.

REFERENCES


FUNGICIDAL EFFECT OF IRRADIATED CHITOSAN

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1Takasaki Radiation Chemistry Research Establishment, JAERI, Japan

Abstract

Fungicidal effects of chitosan and 75kGy-irradiated chitosan were investigated. In in vitro test on 8 strains of fungi, fungicidal effect of irradiated chitosan was higher than that of unirradiated one. In in vivo test, irradiated chitosan protected tea leaves against infection by Exobasidium vexans. The frequency of diseased leaves was 0.173 for tea bed sprayed with irradiated chitosan compared to 0.421 for the control.

1. INTRODUCTION

Chitosan finds wide application in food, pharmaceuticals, flocculation, fungicide, antiviral resistance, etc. [1-3]. However, chitosan with high molecular weight sometime restricts its application. Recently interest in the biological activity of polysaccharides fractions has been increasing [4-7]. Chitosan fractions involved were capable of promoting the growth of plant, control the growth of fungi, and defense responses against pathogens by biosynthesis of phytoalexin [8-11]. Although chitosan can be degraded by chemical and enzymatic methods radiation technique can be usefully utilized to degrade polysaccharides such as starch, alginate, cellulose, chitosan, etc. Thus, various fragments of chitosan can be obtained by random scission by radiation [13,14]. Radiation technology can be used to expand the field of polysaccharide applications. In this paper the fungicidal effect of irradiated chitosan in vitro and in vivo was reported.

2. MATERIALS AND METHODS

Chitosan was irradiated in dry state with gamma Co-60 radiation at the dose of 75 kGy [7], dissolved in CH₃COOH, adjusted to pH 6.0 by 1N NaOH. Chitosan solution was filtered with Millipore MILLEX-GS (pore size: 0.22µm, Millipore MA, USA) and diluted from 2800-50µg/ml in the medium (Czapeck-Dox). Spores or micellial fragments of fungi were dispersed in the medium then incubated at 25°C. The fungicidal effect of chitosan and irradiated chitosan was tested by recording the fungal growth when the fungus in the control dishes attained maximum growth. The antifungal activity of irradiated chitosan (the product received was so-called plant protector [15]) in vivo was tested, as follows: 9 month old tea plants were divided into 3 beds, 50 plants for each. Bed 1 was the reference control and beds 2 and 3 were artificially inoculated with Exobasidium vexans (foliar pathogen) by spraying 3 times on the leaf surface and pouring over the soil surface with suspension of spores or micellial fragments of fungi (10⁶/ml). Two days after infection with fungi, bed 2 was treated with 0.1% irradiated chitosan, bed 3 was treated with 0.05% acetic acid. The number of leaves, plant height and infected leaf frequency (number of infected leaves per total of leaves) were recorded within 50 days.

3. RESULTS AND DISCUSSION

3.1. Fungicidal effect of irradiated chitosan

We reported recently [7] that chitosan could inhibit the growth of three fungi strains. In this report 8 fungi strains, which were plant pathogens, were investigated. The results shown Table I indicated that both unirradiated and irradiated chitosan inhibited the growth of all fungi strains studied, but irradiated chitosan showed higher fungicidal activity than the unirradiated one. The change in surface charge of chitosan by irradiation in dry state was small [14], so it was presumed that when chitosan was degraded by irradiation, more effective fragments were produced. The results in Table I also revealed that the concentration of chitosan that suppressed the growth was different for different strains of fungi. Colletotrichum sp. was the most resistant.
TABLE I. EFFECTS OF CHITOSAN AND IRRADIATED CHITOSAN ON THE GROWTH OF FUNGI

<table>
<thead>
<tr>
<th>Fungi</th>
<th>Chitosan</th>
<th>Irradiated chitosan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytophthora cactorum</td>
<td>300</td>
<td>250</td>
</tr>
<tr>
<td>Fusarium oxysporum</td>
<td>1150</td>
<td>800</td>
</tr>
<tr>
<td>Aspergillus awamori</td>
<td>400</td>
<td>250</td>
</tr>
<tr>
<td>Exobasidium vexans</td>
<td>1000</td>
<td>550</td>
</tr>
<tr>
<td>Septoria chrysanthemum</td>
<td>700</td>
<td>350</td>
</tr>
<tr>
<td>Gibberella fujikuroi</td>
<td>400</td>
<td>250</td>
</tr>
<tr>
<td>Septobasidium theae</td>
<td>1450</td>
<td>1000</td>
</tr>
<tr>
<td>Colletotrichum sp.</td>
<td>1500</td>
<td>1050</td>
</tr>
</tbody>
</table>

3.2. Effect of irradiated chitosan against infection by *Exobasidium vexans*

The frequency of infected leaves in Table II was similar for beds 1, 2 and 3 at the beginning of the test. After one week, the frequency of beds 2 and 3 became higher than that of bed 1 (the control). It was because the tea leaves in beds 2 and 3 were infected not only by pathogenic fungi naturally but also by artificial inoculation. After one month the disease frequency of bed 2 (treated with irradiated chitosan) was lower as compared to that of beds 1 and 3. It proves that irradiated chitosan can protect tea against infection by *Exobasidium vexans*.

TABLE II. EFFECT OF IRRADIATED CHITOSAN ON INFECTION OF *EXOBASIDIUM VEXANS* TO TEA LEAVES

<table>
<thead>
<tr>
<th>Bed</th>
<th>Infected leave frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recording date</td>
</tr>
<tr>
<td></td>
<td>June, 30</td>
</tr>
<tr>
<td>1</td>
<td>0.078</td>
</tr>
<tr>
<td>2</td>
<td>0.078</td>
</tr>
<tr>
<td>3</td>
<td>0.077</td>
</tr>
</tbody>
</table>
Table III shows that foliar spraying with chitosan not only protected the tea leaves against *Exobasidium vexans* but also promoted the growth of the tea plant in terms of height and number of leaves.

4. CONCLUSIONS

Irradiation could improve the fungicidal activity of chitosan. Of eight strains of fungi tested, the concentration of irradiated chitosan to suppress the growth of fungi was smaller than that of unirradiated chitosan. In *in vivo* test, the frequency of diseased leaves was 0.173 for tea bed sprayed with irradiated chitosan compared to 0.421 for the control.

REFERENCES


ELECTRON BEAM TECHNOLOGY FOR PRODUCTION OF NEW ANTI-TUBERCULOSIS DRUG

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Abstract

Possibility of electron beam usage for immobilization of hydrasidum of an isonicotinic acid (HIA) on dextrane was studied to produce a drug for treatment of a tuberculosis. As a result of irradiation of dextrane the processes of oxidation and formation of polysaccharide occur due to carbonyl groups which are capable to link isoniasidum. The HIA immobilized on dextrane may be used as an effective and having prolonged action medical preparation for action on endo- and extracellular population of *Micobacterium tuberculosis*. Keywords: Tuberculosis, micobacterium tuberculosis, electron beam, immobilization, hydrasidum of an isonicotinic acid (HIA), dextrane, HIA immobilized on dialdehyde of dextrane (HIAD).

1. INTRODUCTION

In recent years it is more and more often reported about the usage of electron accelerators for production of new medical preparations. Electron beam immobilization is used for production of medical drugs based on biologically active substances. Enzyme complex produced by *Bacillus subtilis* is immobilized onpolyethylenoxide by radiation grafting (immobilization) [1]. The immobilization of enzymes by electron beam treatment permitted to create principally new preparation «Imosimasum». The «Imosimasum» has shown in experiments in vivo and in clinical practice its high efficiency in correction of ischemic damages of vitally important organs of the body. As it is known, this problem is very actual in medicine up to now and its applied pharmacological aspects are discussed in detail in [2-9].

The report describes the technology for production of new antituberculosis preparation «Isodex» based on well-known preparation «Tubazid» (or «Isoniazidum») - hydrazide of the isonicotinic acid HIA). The radiation technology for production of medical drugs has advantages over the methods of chemical synthesis because toxic reagents that will be then removed are not used. The usage of electron beam technology permits to dispense with the expensive time- and labor-consuming processes of purification of final product from intermediate chemical agents and products. The electron accelerators [10] are most suitable sources because they provide high dose power rate, easy control and reproducibility of process.

2. TREATMENT OF TUBERCULOSIS

In connection with intensive increase in incidence of tuberculosis in the world the creation of new medicinal preparations that can effectively suppress growth of *Micobacterium tuberculosis* in cells, blood and lymph is relevant. Until now this problem is far from its solution and for basic treatment of this disease the HIA is still used. HIA has the low molecular mass and in this connection the drug is quickly removed from the body. More than 80% of HIA is destroyed in liver and does not cause antimicobacterial effect but results on the great load on liver and kidneys and causes intoxication of the body and destroys the liver and kidneys. Therefore treatment of patient having tuberculosis by HIA lasts for long time (1 year and more) with large frequency of toxic reactions.
The essence of the problems in treatment of tuberculosis is the absence of the drugs equally effective for action on *Mycobacterium tuberculosis* circulating in blood and lymph and persisting in the cells of immune system (phagocytes). The persisting micobacteria possess the high resistivity towards the basic anti-tuberculosis preparations (isoniazidum, rifampicinum, pyrazinamidum, etc.) because these preparations do not have the ability to be selectively accumulated in phagocytes containing persisting micobacteria. So there is the necessity to elaborate the antimicobacterial preparations capable to be selectively «delivered» for action on endocellular tuberculosis bacterial population. One of the ways to achieve this is the immobilization of tuberculostatic preparation on lymphotropic polysaccharide.

For treatment of the heavy forms of a tuberculosis in experimental conditions the good effect has shown the HIA immobilized on dialdehyde of dextrane with molecular mass 30-40 kDa (HIAD). HIAD is occluded by macrophages selectively that allows effectively and prolonged action on an endocellular population of pathogenic organisms. The drug is less toxic then HIA, it has prolonged antimicobacterial effect.

Despite of efficiency of HIAD in treatment of a tuberculosis, till now remains an actual problem of its chemical synthesis as it is continuous, composite and is not adapted for pharmaceutical industrial technology. The main difficulty of chemical synthesis is purification of HIAD from HJO₄ and other toxic reagents by dialysis and methanol’s sedimentation. The purpose of the this research was creation of a radiation technology for production of antituberculosis drug based on HIA immobilized on dextrane.

3. MATERIALS AND METHODS

In the work we have used 10% solution of dextrane with molecular mass of 30-40 kDa produced from *Leuconostoc mesenteroides*. This polysaccharide is widely used as blood substitute. Radiation activation of dextrane solution was achieved using electron radiation or X-rays (Bremsstrahlung) produced by the electron accelerator ILU-6 [10,11] (produced in the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences). The electron energy was 2 MeV, dose power rate was 0.5 Mrad/s, the range of investigated doses was 5-35 kGy. Due to action of generated free radicals the dextrane was oxidized with formation of highly active carbonyl groups. Concentration of carbonyl groups in the irradiated solution of dextrane was assayed by reaction with 2,4-dinitrophenyl-hydrazine.

The HIA was added into the electron beam treated water solution of dextrane and the reaction mixture was exposed at temperature of 100°C during up to 30 minutes to carry out the immobilization process. After the process completion the solution was assayed by ion-exchange chromatography. The resulting immobilization rate was 40-60% in the range of its initial concentration 4-40 mg/ml.
FIG. 1. Exit of carbonyl groups from dextrane solution depending on absorbed dose.

The chromatographic researches of the process of conjugation HIA with radiation-activated dextrane are executed on a liquid chromatograph GPC-800 (Czechia). For an ion-exchange chromatography we have used a column having size of 0.9 x 30 cm filled with DEAE-cellulose (DE-Servacel, 100-200 µ, "Reanal", Hungary). The volume of investigated sample was 150 ml. Eluant - 0.01 M Tris-HCl with pH 8.5 at speed of elution of 10 ml/hour. For gradient elution we have used 1.5 M solution of lithium chloride. For gel-filtration we have used a column with size of 0.9 x 30 cm with "Molselect P-30", 10-50 µ, ("Reanal", Hungary). Eluant - 0.05 M phosphate buffer with pH 7.5 at speed of elution of 5 ml/hour. The contents of HIA in chromatographic fractions were assayed in the UV-detector at wavelength of 290 nm.

4. RESULTS AND DISCUSSION

The treatment of dextrane solution by electron beam or X-rays causes its activation and formation of polymer due to carbonyl groups. The exit of carbonyl groups has direct relation with a irradiation dose as it is seen in Figure 1. At irradiation doses of more than 35 kGy the formation of hydrophilic gel was observed, and we failed to determine the concentration of carbonyl groups in it. We supposed that the molecular mass of dextrane can change as a result of irradiation process. The increase in molecular mass of cross-linked dextrane more then 100 kDa may cause the undesirable biological effects connected with longer period of removing of polymer from the body. It is important because molecular mass of dextrane and its pharmacokinetics are interdependent. The dose range chosen by us provides soft operating on dextrane and does not cause noticeable influence on its molecular mass.

Insignificant increase of light absorption at wavelength of 254 nm by irradiated solutions of dextrane at increase of absorbed dose was observed - see Figure 2. This effect may be connected with increase of concentration of carbonyl groups in irradiated polymer. For further research we irradiated dextrane solutions with doses up to 35 kGy. This dose gives maximum exit of carbonyl compounds and sterilizes the solution. The dose range of 25 - 35 kGy is accepted as sterilization dose in all countries, and this allows to easily organize production of HIAD in industrial technology with simultaneous sterilization of final preparations.
FIG. 2. Gel-filtration of dextrane.
1 - not irradiated, 2 - irradiated, absorbed dose 25 kGy, 3 - irradiated, absorbed dose 35 kGy.

For immobilization of HIA on radiation-activated dextrane the HIA is diluted in irradiated solution of dextrane up to final concentrations from 4 up to 40 mg/ml. The prepared solutions were exposed at 100°C within 15 minutes for completion of immobilization. During heating the colourless gained yellow colouring solution as result of formation of HIAD. Then the ready solutions were subjected to a chromatographic analysis. The results of research are shown in Figure 3. About 50% of dissolved HIA were linked to radiation-activated dextrane. The remaining part of HIA is in a free state. No correlation between quantity of HIA immobilized on dextrane and the concentration of HIA in initial solution was not found. We suppose that it is due to spatial limitations for immobilization of HIA on radiation-activated dextrane.

Free HIA can be removed through ultrafiltration or by chromatography method. However we suppose that the presence of free HIA is perspective and allow the drug to act on endocellular and exocellular population of *Mycobacterium tuberculosis*.

In the chemical technology for production of HIAD the HJO₄, HJO₃, methanol, ethyleneglycol are used, and after activation of dextrane they must be carefully removed because they are toxiferous impurities. Such clearing essentially complicates the technology of production the HIAD. Using a radiation method of activation these toxic impurities in dextrane are not required and therefore HIAD can be produced without complicated methods of cleaning. HIAD can be produced in one stage by irradiation of solution of dextrane containing HIA. However it is necessary to study the chemical and biological properties of products of radiolysis of HIA that may be the object of our next study.
FIG. 3. Results of chromatography studies.
I - solution containing 10% of dextrane and 4% of HIA, no irradiation.
II - solution containing 10% of dextrane and 0.4% of HIA, absorbed dose 35 kGy.
III - solution containing 10% of dextrane and 4% of HIA, absorbed dose 35 kGy.
5. CONCLUSION

New antituberculosis preparation “Isodex” is the balanced mixture of free HIA (hydrazide of the isonicotinic acid - well-known preparation “Tubazid” or “Isoniazipidum”) and HIA immobilized on dextrane to act on of *M. tuberculosis* everywhere inside the body.

The medical testing of «Isodex» have shown its lower toxicity and prolonged action in comparison with “Tubazid” (preparation of HIA). The special feature of «Isodex» is its ability to be absorbed by macrofags, which are the main places of persistence and vegetation of *M. tuberculosis*. The duration of treatment is reduced and the efficiency of preparation usage is increased.

We suppose that electron beam technology for immobilization of HIA on dextrane can be also successfully used for creation of other medical preparations and drugs – for example, for treatment of leprosy.

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PERMEABILITY CONTROL OF METAL IONS THROUGH TEMPERATURE AND PH-SENSITIVE COPOLYMER GEL MEMBRANES

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Abstract

The temperature- and pH-switchable porous membranes were synthesized by radiation-induced copolymerization of acryloyl-L-proline methyl ester (A-ProOMe) with acrylic acid (AAc) in aqueous solutions, followed by a self-bridging reaction of their polymer chains without any crosslinker. The pH threshold of swelling-deswelling states for a copoly(A-ProOMe/AAc, 70/30 mol %) gel at 30°C lays in the region between pH 4.00 and 5.00. The membranes, which show porosities of 82.5% or below, completely blocked the permeation of both lithium (Li) and cesium (Cs) ions in buffer solutions at pH 4.60. The permselectivity (PLi/Cs) reached the highest value of 1.33, when the porosity in the membrane is 84.5% at pH 4.65 and 30°C. The results of SEM observation showed that the shape of pores in the membrane treated at pH 4.65 consisted of apparently isolated pores and, contrary to this, such a porous structure perfectly disappeared at pH 4.60.

1. INTRODUCTION

The temperature-switchable gels have received attention for their potential technical importance in a variety of applications such as drug delivery systems and selective separation of substances. We observed that the polymer chains of A-ProOMe displayed a lower critical solution temperature (LCST) of 14°C in an aqueous solution, in which this polymer was soluble below LCST but collapses from its solution above LCST [1]. On the other hand, a poly(AAc) with pKa of 4.7 is known as an attractive pH-switchable material, which is characterized by an ionizable hydrophilic property. The COOH groups in poly(AAc) are not ionized at < pH 4.7, as it is in an aggregated state in an aqueous solution. In contrast, at > pH 4.7, the charged COO⁻ groups repel each other, whereby the polymer achieves a dissolved state [2]. Recently, we also found that the A-ProOMe monomer took place the self-bridging reaction immediately after radiation-induced polymerization in aqueous solutions without the use of any crosslinker to give gels with a characteristic three-dimensional network structure [3]. The results of the pulse radiolysis experiment proved that products generated by the radiolysis of water, HO•, H•, and e⁻aq play an important role in the formation of self-bridged gels.

Many workers have been done to achieve gels sensitive to both temperature- and pH-values by interpenetrating polymer networks, partially neutralized polymer complexes, and grafting polymer networks [4-5]. In this study, we prepare temperature- and pH-switchable copolymer gel membranes based on A-ProOMe and AAc by using a simultaneously occurring radiation reaction in aqueous solutions. The reversible swelling-shrinking behaviors of the gels obtained were investigated with regard to porosity, porous structure, and pore shape sensitivity to a slight change of external signals such as temperature and pH. The capabilities of this new gel membrane were evaluated from a selective separation of metal ions such as lithium (Li) and cesium (Cs) under various temperature and pH conditions.

2. EXPERIMENTAL

Acryloyl L-proline methyl ester (A-ProOMe) was synthesized according to coupling process of L-proline methyl ester hydrochloride and acryloyl chloride as described in the previous paper [1]. Acrylic acid (AAc) was obtained from Kishida Chemical Co., Ltd. (Osaka, Japan). The metal salts used in the permeation experiments, lithium chloride anhydrous (LiCl) and cesium chloride (CsCl) were
purchased from Kanto Chemical Inc. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Tokyo, Japan), respectively.

An 800-µm thick gel membrane was prepared by the cast technique. Fig. 1 illustrates the schematic diagram for the fabrication of copolymer gel membranes. The homogeneous solution consisting of 10 mmol of a mixture of A-ProOMe and AAc at desired compositions and 0.5 mL of water, which was bubbled with nitrogen, was charged into a cast having two glass plates (50 x 50 x 2 mm) separated by an 800-µm spacer film based on poly(ethylene terephthalate) purchased from Hoechst Japan (Tokyo). In order to obtain the gel membrane, the irradiation required for both radiation-induced polymerization and self-bridging reaction of A-ProOMe with AAc in aqueous solutions without the use of any crosslinker was done under nitrogen at 0°C for 3 hours at a dose rate of 10 kGy/h using γ-rays from a $^{60}$Co source.

![Schematic diagram for illustrating the preparation of copolymer gel membranes.](image)

To determine the equilibrium swelling ratio ($S_w$) of gel membranes, the specimens which were pre-swollen with water at 0°C (ice water temperature), were submerged in glass vials filled with an excess buffered solution of pH 1.0 at 0°C, until the gels reached the equilibrium. These specimens were then put in buffered solutions at constant pH and temperature. The $S_w$ value can be determined from the following equation:

$$S_w = \frac{W - W_o}{W_o}$$

where

$W$ is the weight of the swollen specimen,

$W_o$ is the dry weight.

On the other hand, the role of water content in the diffusion of metals through temperature- and pH-switchable gel membranes has been described by the free volume theory [6]. This water content is a strong factor for the predominant transport mechanism of substances through the gel membrane governed by the water channels. The porosity of a membrane was defined by:
where \( \rho_p \) is the density of the polymer constructing the membrane.

When the membrane is immersed into the buffer with the density of \( \rho_b \), the buffer penetrates into the pore inside the membrane. The porosity obtained by the swelling method can be calculated by measuring the weight of the membrane after immersion \( W \). The apparent density \( (\rho_p) \) of copoly(A-ProOMe/AAc) with compositions of 100/0, 70/30, and 0/100 mol. % estimated from their monomers was obtained to be 1.37 g/cm\(^3\) in all systems at 30°C, in contrast to 1.19 g/cm\(^3\) \( (\rho_b) \) for buffer solutions with pHs of 1.0 to 8.0.

The permeability constant \( (P) \) of metals, Li (atomic weight 6.94; ionic radius 0.60 Å; hydration radius 3.82Å) and Cs (atomic weight 132.91; ionic radius 1.69Å; hydration radius 3.29Å) [7], through temperature- and pH-switchable gel membranes was measured by using a modified Franz cell apparatus [8]. The 800-μm thick membrane with a diameter of 1.9 cm was sandwiched between two cells consisting of donor chamber and receiver chamber. The effective membrane area was approximately 2.83 cm\(^2\). The Franz cell apparatus connected with an Iuchi M-3 multistirrer (Tokyo, Japan) was placed in water thermostated at constant temperature, at which both donor and receiver chambers were first filled with buffered solution without metals. Then, only donor side of a cell was replaced with metal-containing buffered solution kept at constant temperature immediately before permeation measurement. The permeability constant \( (P, \text{cm}^2/\text{min}) \) was estimated from the following equation:

\[
P = \frac{V}{C_0} \cdot L \cdot \frac{1}{A} \cdot d \frac{C_t}{dt}
\]

where

\( V \) is the volume of the receiver chamber (50 cm\(^3\)),
\( C_0 \) is initial volume of equimolecular buffer solution of Li and Cs ions trapped in the donor chamber (5 cm\(^3\) of 0.2 mol buffer solution of two metals),
\( A \) is effective surface area of a chamber (roughly 2.83 cm\(^3\)),
\( L \) is thickness of a membrane at constant pH and temperature,
\( dC_t/dt \) is concentration of metals in the receiver at time \( t \).

The eluted media were collected from a sampling port at various time intervals. The concentration of permeated metals was measured with a Dionex DX-100 ion chromatograph (suppressed conductivity CSRS-II recycle mode as a detector; 1 mL as an injection volume; 1.0 mL/min as a flow rate; 20 mmol/L methanesulfonic acid as an eluent; IonPac CS12A <4 x 250 mm> and CG12A <4 x 50 mm> as columns.

The physical structures of temperature- and pH-switchable gel membranes were observed with a Jeol JXA-733 scanning electron microscope (SEM). The specimens treated at constant temperature and pH were immersed in liquid nitrogen (-196°C), lyophilized, coated with gold, and observed microscopically.
3. RESULTS AND DISCUSSION

Two monomers used in this study: A-ProOMe and AAc, easily dissolved in ethanol. A copolymer gel based on A-ProOMe and AAc with a monomer composition of 70/30 mol %, which was defined as an ethanol-insoluble fraction, was prepared by the simultaneously occurring process of radiation-induced polymerization and self-bridging in aqueous solutions without the use of any crosslinker with 30 kGy at 0°C, as an example. The gel yield of a copoly(A-ProOMe/AAc, 70/30 mol %), obtained by extracting an ethanol-soluble fraction was obtained to be approximately 98%. It is well known that a homopoly(A-ProOMe) gel in aqueous solution exhibits the volume phase transition around 14°C corresponding to a lower critical solution temperature (LCST) of its linear polymer, which this gel swells and collapses below and above, respectively. Such a gel is termed a temperature-switchable polymer. It was confirmed that a homopoly(A-ProOMe) gel is maintained a constant Sw value (approximately 0.8) in the pH 1.00 to 8.00 region at 30°C because of a non-ionic polymer. On the other hand, AAc is known as a pH-switchable polymer, exhibiting a pKa value of 4.7. When the pH is above its pKa, the AAc gel should swell owing to the ionic repulsion effect between the two ionized COO– groups. The appearance of these two functions can be seen clearly in Fig. 2 which shows the relationship between the pH and physical properties such as Sw and porosity at 30°C for a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane. It was found that at 30°C the threshold pHs for Sw and porosity of the copolymers used are present in the pH 4.00 to 5.00 region. Namely, at pH 4.00 the Sw value and porosity are approximately 0.5 and 22% (a shrunken state), whereas, at pH 5.00 the Sw value and porosity are approximately 10 and 96% (a swollen state). The permeation behavior of metal ions, Li and Cs, as functions of pH and porosity at 30°C through a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane is shown in Fig. 3. This membrane, which showed porosities of 82.5% or below in buffer solution at ≤ pH 4.60, completely blocked the permeation of two metals. Both metals could permeate through the membrane in buffered solutions at > pH 4.70, at which the permeation rate of Cs ions is much faster than that of the corresponding Li ions; at pH 4.80 the P value of Cs ions is 10.3 x 10^-4 cm²/min, in contrast to 6.3 x 10^-4 cm²/min for Li ions. The reason why the permeation of Li ions with an atomic weight 6.94 is depressed compared with that of Cs ions with an atomic weight of 132.91 is probably the difference in hydration radius between the two metals (3.82Å for Li and 3.29Å for Cs) in close relation to changes in carboxylate ion density, hydrophobicity, pore shape, and porosity according to temperature- and pH-changes [7].

The permselectivity (P_{Li/Cs}) was defined as the ratio of P values of each metal in order to evaluate the selective separation characteristic of temperature- and pH-switchable gel membranes. The P_{Li/Cs} value is plotted as a function of porosity at 30°C for a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane and the results are shown in Fig. 4. The P_{Li/Cs} value reached the highest value of 1.33 when the porosity in the membrane is approximately 84.5% at pH 4.65 and 30°C, at which the shape of pores was observed microscopically. It was found from the results of SEM observation in Fig. 5 that the pore shape in the membrane obtained with a porosity of approximately 84.5% (at pH 4.65) consists mainly of apparently isolated pores having radii below 50 µm. Such a structure of pore perfectly disappeared in the case of gel membrane with a porosity of approximately 82.5% (pH 4.60), whereas it leads to a characteristic labyrinth-like porous structure at a porosity of approximately 99.5% (at pH 5.00). Therefore, it is reasonable to conclude here that the large differences in shape of pores induced by controlling both temperature and pH plays an important role in permselectivity of two metals through such porous membranes.
FIG. 2. Relationship between the pH and physical properties such as Sw and porosity at 30°C for a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane.

FIG. 3. Permeation behavior of (E) Li and (J) Cs ions as functions of pH and porosity at 30°C for a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane.
FIG. 4. Permselectivity of Li and Cs as a function of porosity at 30°C for a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane.

FIG. 5. Surface SEM views of a copoly(A-ProOMe/AAc, 70/30 mol %) gel membrane treated in buffer solutions with pHs of (a) 4.60, (b) 4.65, and (c) 5.00 at 30°C.
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THERMALLY STABLE AND HIGHLY SENSITIVE POLYMER MEMBRANES FOR ION AND ELECTRON BEAM RADIATION

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Abstract

Thermally stable and highly sensitive polymer membranes for ion and electron beam radiation are developed by means of the precursor polymer films of thermally stable polymers and a chemically amplification system, respectively. When the partially imidized polyamic acid films, which are the precursor of the thermally stable polyimides, are irradiated with Xe ion beams followed by alkaline etching, both negative (projection) and positive (hole) images of polyimide films are obtained due to the slight different polymer structures. On the other hand, the copolymer films of diethyleneglycol diacrylate (EGA) with t-butyl acrylate (t-BA) as an acid liable comonomer and 4-methoxyphenyl-diphenylsulfonium perfluoro-1-butanesulfonate (MDS) as an acid generator were prepared as a chemically amplified poly-EGA according to a conventional cast polymerization. The copolymer film consisted of EGA and tBA (70:30) with 3 wt% MDS shows 200 times higher sensitivity than that of the original poly-EGA.

1. INTRODUCTION

High energy radiation such as heavy ion beams and electron beams is very powerful tools to create novel organic thin films with precisely controlled nanoscopic structures. In contrast to photolithography, a single heavy ion particle induces nanoscopic damage along the ion-path through the materials, which is susceptible to development in an etchant, resulting in the formation of nanoscopic through-holes [1]. Attractive targets of these thin films are separation membranes for toxic metal ions and biomolecules, and electronic devices such as conductive films, field emitters, and magnetic field sensors through hybridization with inorganic materials [1]. Therefore, we have developed novel ion track membranes to improve physical properties and sensitivity to ion and electron beams.

Ion track membranes with a high aspect ratio are fabricated from polycarbonates and polyesters, and are applied to separation membranes. However, thermally and physically stable polymers such as polyimides and polybenzoxazoles cannot be applied to ion track membranes using a practical alkaline etchant. Since the polyimide films are converted from their precursor (polyamic acid) films, which show less thermal and physical stability [2], we expected that thermally and physically stable ion track membranes could be converted from ion track membranes of the corresponding precursor, whose sensitivity should be high enough to form ion tracks. Therefore, we synthesized several polyimide precursors with different imidization degrees, and examined ion track formation of these precursor films by various alkaline etching conditions as shown in Fig. 1.

For improving the sensitivity of the polymer membranes to ion and electron beams, we have employed the chemical amplification systems [3] for poly(diethyleneglycol diacrylate) (poly-EGA), which is one of the highest sensitive materials to high energy ion beams and applied to an ion beam detector (Ogura, et al., 1997). Chemical amplification systems, which have been widely used in photolithography, are the very powerful method to improve the sensitivity of polymer films to photo or electron radiation because the system contains an acid generator, which generates strong acids by radiation, and acid liable comonomers, which comprise an acid liable protecting group and was decompose under an acidic condition to enhance the alkaline solubility of the films. Therefore, we
prepared the modified PEGA containing acid generators and acid liable comonomers, and examined its sensitivity to electron beams.

FIG. 1. The precursor method to prepare thermally stable ion track membranes (ITM) using polyimides.

2. EXPERIMENTAL

2.1 Thermally stable polymer membranes

Polyamic acids containing an ether group (PI-1) and a sulfone group (PI-2, PI-3) were prepared by a condensation reaction between tetracarboxyl acid dianhydrides and diamines according to a conventional synthetic method [4]. The number average molecular weights of the polymers (Mn) were measured by gel permeation chromatography (GPC) and calculated on the basis of a standard polystyrene calibration. PI-1, Mn=24,000; PI-2, Mn=24,000; PI-3, Mn=27,000. The polyamic acids in N-methylpyroolidinone (NMP) were spun onto grass substrates and prebaked on a hot plate to prepare partially imidized polyimide precursor films with film thickness ranging from 5 to 20 µm. The precursor films were irradiated at the TIARA cyclotron of Japan Atomic Energy Research Institute (Takasaki, Japan). The irradiation was carried out under vacuum at a room temperature. The ions \(^{129}\text{Xe}^{23+}, 3.49 \text{ MeV/nucleon}\) with a fluence of \(10^3 \text{ ions/cm}^2\) were used for ion beam radiation of the precursor films. The irradiated films were etched in an aqueous tetramethyl ammonium hydroxide (TMAH) solution. The surface of the etched films was observed by a JEOL JXA-733 scanning electron microscopy (SEM).

2.2 High sensitive polymer membranes

The copolymer films of EGA with t-butyl acrylate (t-BA) as an acid liable comonomer and 4-methoxyphenyl-diphenylsulfonium perfluoro-1-butanesulfonate (MDS) as an acid generator were prepared according to a conventional cast polymerization as follows (Ogura, et al., 1997). Diethyleneglycol diacrylate and t-BA were mixed with 70:30 weight ratio. To the mixture was added 3 wt\% of di-2-propylperoxydi-carbonate (IPP) and 3 wt\% of MDS. The solution was introduced to two polycarbonate plates with a 100 µm gap and heated at 70°C for 24 hours. The obtained films are irradiated with electron beams (1MeV, 1.0 mA) in the range from 0.1 to 10 MGy through a stainless electron beam mask with 3 mm thickness. The irradiated films were etched in 6 N NaOH at 60 °C to measure the dissolution rates of the films before and after irradiation.
3. RESULTS AND DISCUSSION

3.1 Thermally stable polymer membranes

The chemical structures of the partially imidized PI-1, PI-2, and PI-3 are depicted in Fig. 2. By Xe ion beam radiation and alkaline etching, 60 % imidized PI-1, which is the precursor of Kapton™ film, exhibited negative mode images, as shown in Figure 3. The negative image was resulted from decrease of the dissolution rate of the area, along which the ion beam passed through the film. By optimizing etching conditions, the most clear projection pattern with 2 µm diameter and 1.5 µm height was appeared on the surface of the films by etching in 5 % TMAH at 40 °C. However, when PI-1 was converted to 40 and 90 % partially imidized films, no negative image pattern was observed using the TMAH in the range from 0.1 to 10 % concentrations.

In order to obtain the polyimides ion track membrane with positive hole patterns, we synthesized the polyimide precursors, PI-2 and PI-3, containing sulfone groups, which are susceptive to electron beams (Chen, et al., 1989). Contrary to PI-1, the 97 % imidized PI-2 film gave pores with a 2µm diameter by etching in 1 % TMAH at 40 °C (Fig. 4 (a)). However, the density of the hole formation of the films are about 1/100 of the ion beam fluence (1.1 x 10^7 holes / cm²). The 70 % imidazed PI-3, which possesses sulfone and methylene groups in the main chain, gave pores with a 1µm diameter by etching in 15 % TMAH at 40 °C. The obtained ion films contained almost the same hole density as the ion beam fluence (1.8 x 10^7 holes/ m²), as shown in Fig. 3. Therefore, sulfone and methylene groups in the polyimide precursors are necessary for efficient positive hole formation by ion beams. The hole formation in PI-2 and PI-3 films indicates that ion beam radiation increased the dissolution rate of the partially imidized films containing a sulfone group (positive image) probably due to the degradation of the sulfonyl groups that should be sensitive to ion beams. These results also revealed that the partially imidized precursor method enables the formation of both negative (projection) and positive (hole) images of polyimide films by using the slight different polymer structures.

Figure 2  Chemical Structures of Partially Imidized PI-1, PI-2, and PI-3

![Chemical Structures of PI-1, PI-2, and PI-3](image)

In order to obtain the polyimides ion track membrane with positive hole patterns, we synthesized the polyimide precursors, PI-2 and PI-3, containing sulfone groups, which are susceptive to electron beams (Chen, et al., 1989). Contrary to PI-1, the 97 % imidized PI-2 film gave pores with a 2µm diameter by etching in 1 % TMAH at 40 °C (Fig. 4 (a)). However, the density of the hole formation of the films are about 1/100 of the ion beam fluence (1.1 x 10^7 holes / cm²). The 70 % imidazed PI-3, which possesses sulfone and methylene groups in the main chain, gave pores with a 1µm diameter by etching in 15 % TMAH at 40 °C. The obtained ion films contained almost the same hole density as the ion beam fluence (1.8 x 10^7 holes/ m²), as shown in Fig. 3. Therefore, sulfone and methylene groups in the polyimide precursors are necessary for efficient positive hole formation by ion beams. The hole formation in PI-2 and PI-3 films indicates that ion beam radiation increased the dissolution rate of the partially imidized films containing a sulfone group (positive image) probably due to the degradation of the sulfonyl groups that should be sensitive to ion beams. These results also revealed that the partially imidized precursor method enables the formation of both negative (projection) and positive (hole) images of polyimide films by using the slight different polymer structures.

Figure 3  SEM images of PI-1, PI-2, and PI-3 after Xe ion irradiation and alkaline etching.

![SEM images of PI-1, PI-2, and PI-3](image)
3.2 High sensitive polymer membranes

Poly-EGA, which is one of the highest sensitive materials to high energy ion beams and applied to an ion beam detector. However, its sensitivity to electron beams is not high enough to make fine patterns like ion track membranes. Therefore, we introduced chemical amplification system to the Poly-EGA to improve the sensitivity of the polymer membranes to electron beams. Four commercial sulfonium salts are examined for the acid generator; as the results, only an amorphous onium salt, MDS was miscible to EGA and t-BA and was incorporated into a homogeneous film with 100 µm thickness according to a conventional cast polymerization.

Figure 4 shows the dissolution rates versus electron beam doses of the copolymer film consisted of EGA and tBA (70: 30) with 3 wt% MDS. The dissolution rate of the film increased 300 times as fast as the original films only by 10 kGy of electron beams. On the other hand, Poly-EGA film required 200 kGy to show the same dissolution rate as that of the copolymer film. Therefore, the copolymer film exhibits 200 times higher sensitivity than that of Poly-EGA films. As blank experiments, we prepared the Poly-EGA film with 3 wt% MDS and the copolymer film of EGA and tBA (70: 30) without MDS. As shown in Fig. 5, these films, which contain only t-BA or MDS, showed almost the same sensitivity as that of Poly-EGA. This fact strongly indicates that MDS generates strong acids by electron beam radiation, followed by the acid catalyzed deprotection reaction of t-BA to improve the dissolution of the film in the alkaline solution. Further studies are currently underway in applying this system to highly sensitive detectors for ion beams.

**FIG. 4.** Dissolution rates vs. EB doses of the copolymer film.
(Consists of PEGA, tBA and MDS; film thickness: 100 µm; EB: 1 MeV, 1mA; post base: 100ºC/5 min; etching: 6N NaOH, 60ºC; PEGA: tBA: MDS (wt ratio)=70:30:3 (○); 100:0:0 (●); 100:0:3 (■); 70:30:0 (∗).
REFERENCES


STIMULI-RESPONSIVE HYDROGELS FOR DRUG DELIVERY OBTAINED BY RADIATION COPOLYMERIZATION

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Abstract

Preparation and characterization of different smart hydrogels were prepared for drug delivery systems by using gamma irradiation. The factors affecting the preparation and homogeneity of prepared hydrogels were thoroughly investigated. pH-sensitive hydrogels were prepared by radiation copolymerization of methacrylic acid (MAAc)/ Butyl acrylate (BA) and ketoprofene was used as a drug model. BA/MAAc copolymer gels showed a good sensitivity to pH. The aqueous equilibrium swelling properties of these copolymers were investigated. It was found that the percent swelling for copolymers prepared in acetone is higher than that prepared in other solvents at different pH’s. However, the percent swelling of the copolymer prepared in ethanol or ethanol /water is very low at lower pH’s. Therefore, the suitable solvent to meet the required properties for drug delivery to colon is ethanol and its mixture with water. The effect of water/ethanol composition on the swelling behavior was also studied to find out that the maximum swelling is obtained at (40/60 wt%). The extent of the transition from the collapsed hydrophobic state to hydrophilic one is depending on comonomer compositions. The release of ketoprofene -loaded during radiation process- under different pH’s from gel was determined. it was found that at pH 7, the release of ketoprofene increases as its concentration in the gel increases, but it decreases with increasing irradiation dose. However, at pH 1 the release of drug has no significant value. The release of loaded ketoprofene that immersed in the copolymer after irradiation was found to be much higher than that released from gel loaded drug during irradiation process. Swelling of (MAAc/ BA) copolymer is a highly pH dependent, at low pH the swelling is less than 10%, but at high pH is higher than 300%. This property candidate such copolymer to be pH-sensitive hydrogel for the use in drug-delivery systems. Intelligent hydrogels capable of swelling or collapsing in water below or above their low critical solution temperature (LCST), respectively, by γ- rays copolymerization of poly(vinyl alcohol), PVA, and N-isopropyl acrylamide (NIPAAm) were also prepared. Terpolymer hydrogels composed of PVA, NIPAAm and different pH-sensitive comonomers such as acrylic acid (AAc), MAAc acid and N-N dimethyl aminoethyl methacrylate (DMAEMA) were prepared. The equilibrium swelling for the prepared different terpolymers was thoroughly investigated at various pHs. The hydrophilicity of NIPAAm and other pH-sensitive comonomer greatly influence the critical collapse pH- of the terpolymer. By altering the copolymer composition, LCST can be controlled. The content of NIPAAm in the copolymer control and enabled the transition temperature to be easily shifted up and down. Also, it was found that the maximum swelling is obtained at pH 1 for all terpolymers investigated and its extent is depending on the composition of the hydrogel. In general, the prepared hydrogels are of great interest for possible practical uses as stimuli-responsive hydrogels for drug delivery systems under controlled release in specific sites.

1. INTRODUCTION

“Responsive” polymer gels are materials whose properties change in response to specific chemical environmental stimuli including temperature, pH, electric field, solvent quality, light intensity and wave length, pressure, ionic strength, ion identity and specific environmental triggers like glucose. The properties that often change most dramatically is the swollen volume, the unique properties of responsive gels have resulted in substantial application research, especially over the past decade. In general, this application can be classified as mechanical devices, controlled solute delivery, devices, or chemical separation techniques [1-4].

The application of polymers to medicine has become one of the principal challenges facing the polymer scientist. The scale and level of studies on the employment of radiation chemical methods for the preparation of polymeric biomedical designed for application in medicine and biotechnology has expanded significantly in recent years [5-8]. Radiation grafting for various biomedical applications remains an extremely active field of development [4]. Demand is growing for biomaterial usage in
dialysis and immobilization of enzymes and as artificial cells, organs, and prostheses, tissue adhesives and cements, plasma expanders and controlled drug release [8-10].

2. EXPERIMENTAL

2.1. Preparation of hydrogels

Hydrogel copolymers were prepared by radiation copolymerization of MAAc and other hydrophobic monomers such as MMA, BA and MA in the proper solvent without the use of any crosslinker. A mixture of 50%( wt/wt) MAAc and acrylate monomer and solvent was charged in a glass ampoules and then subjected to gamma irradiation at a dose rate 9 Gy/h.. The gels were then washed by soaking in ethanol for two days.

2.2. Loading of ketoprofene

The gel was immersed in saturated solution of ketoprofene for 48h and then washed with water and dried in oven at 400°C. Also it was loaded by mixing with the copolymer solution before irradiation process.

2.3. Drug release measurement

The release rate of ketoprofen from gel was determined at different pH's and interval times using UV spectrophotometer at 260nm.

3. RESULTS AND DISCUSSION

3.1. I-PH-sensitive hydrogel

A trial has been made to prepare pH-sensitive hydrogel by the use of radiation copolymerization of binary monomers such as MAAc/(BA), MAAc/MMA and MAAc)/MA and ketoprofene is used as a drug model. The factors affect on the copolymerization process such as type of solvent and irradiation dose were studied. The aqueous equilibrium swelling properties of copolymers based on MAAc and acrylate esters of various chain lengths are investigated as a function of pH at 37ºC.

3.2. Effect of solvent on swelling behaviour

It is well known that the solvent plays an important role to enhance the copolymerization process. In the photochemical polymerization, it is possible to find inert solvents. However, in radiation polymerization this is no longer possible. In this connection, different solvents are used for the copolymerization process such as acetone, ethanol and ethanol/water mixture and their influence on the swelling behavior of the prepared hydrogel is investigated. It was found that ethanol/water mixture is the proper solvent in which the swelling of the hydrogel is pH-responsive, it swells at pH 7 but its swelling at pH 1 is very negligible. The swelling of the copolymer prepared in acetone is higher than that prepared in other solvents at different pHs. Therefore, the proper solvent to meet the required properties for pH-responsive hydrogel is ethanol and its mixture with water.

The effect of water/ethanol composition on the swelling behavior was studied to find that the optimum swelling is obtained at 40/60 wt% (water/ethanol) as shown in Fig.1. The extent of the transition from the collapsed hydrophobic state to hydrophilic state is depending on the comonomer composition used (Table I).
3.3. Effect of dose and ketoprofene concentration on its release

Fig. 2 shows the effect of ketoprofene concentration and irradiation dose on its release at pH 7. It was found that as the drug concentration increases in the hydrogel, its release increases. However, as the irradiation dose increases the release of drug decreases also. It can be seen that, at pH 1, the release of drug has no significant value.

The results obtained suggested that at high irradiation dose the content of crosslinked network structure increased and resulted in more entangled structure around the ketoprofene drug consequently, the rate of its release decreased.

Figs 3-5 show the drug release hydrogel- loaded by immersing the copolymer in concentrated ketoprofene solution for 24h and from one loaded during irradiation process. The release of ketoprofene from the former hydrogel is much higher than that released from the latter one. This may confirm the aforementioned results indicating that the entangled structure by radiation crosslinking decreased the rate of ketoprofene release.

3.4. II-thermosensitive hydrogels

Intelligent hydrogels capable of swelling or collapsing in water below or above their low critical solution temperature (LCST); respectively, are prepared by radiation copolymerization of PVA and NIPAAm and shown in Fig.6. By altering the copolymer composition, LCST can be controlled. The content of NIPAAm enabled the transition temperature to be easily shifted up and down. Also, it was found that the molecular weight of PVA and irradiation dose affect the LCST of PVA-NIPAAm copolymer.

Temperature and pH- sensitive terpolymer for modulated delivery of drugs was also prepared from composed of PVA, NIPAAm and different pH-sensitive monomers such as Aac, MAAc and N,N-DMAEMA using gamma irradiation. The equilibrium swelling for the prepared different terpolymers was thoroughly investigated at various pHs. The hydrophilicity of NIPAAm and other pH-sensitive comonomer greatly influence the critical collapse pH- of the terpolymer (Table II). The maximum swelling percent for such terpolymer depends on the types of pH sensitive monomer used. It was found that the minimum swelling is obtained at pH 1 for all terpolymers used. However, the maximum swelling differs from terpolymer to another.

### Table I. Effect of BA/MAAc Composition on the Swelling of Its Hydrogel Prepared in Ethanol/Water Mixture, 40/60 WT% at 30 kGy

<table>
<thead>
<tr>
<th>Swelling time (h)</th>
<th>20/80</th>
<th>30/70</th>
<th>40/60</th>
<th>50/50</th>
<th>60/40</th>
<th>70/30</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>123</td>
<td>180</td>
<td>285</td>
<td>106</td>
<td>65</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>203</td>
<td>280</td>
<td>428</td>
<td>161</td>
<td>121</td>
<td>51</td>
</tr>
</tbody>
</table>

### Table II. Effect of PH-Sensitive Monomer on the Swelling of ThermoSensitive Hydrogels at Different PHs

<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>pH-1</th>
<th>pH-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-co-NIPAm</td>
<td>4:2</td>
<td>1812</td>
</tr>
<tr>
<td>PVA-co-NIPAm–DMAEMA</td>
<td>4:1:1</td>
<td>791</td>
</tr>
<tr>
<td>PVA-co-NIPAm-Aac</td>
<td>4:1:1</td>
<td>602</td>
</tr>
<tr>
<td>PVA-co-NIPAm-MAAc</td>
<td>4:1:1</td>
<td>537</td>
</tr>
</tbody>
</table>
4. CONCLUSION

It can be concluded that the different hydrogels prepared by radiation copolymerization are stimuli-responsive either for pH or temperature, depending on the chemical structure and solvent used. The drug release is consequently dependent on the environment (pH and temperature), which make such hydrogel possible for its practical use as a drug delivery under controlled release.

REFERENCES

FIG 1. Effect of time on the swelling percent of Ba/MAAc (50/50 wt%) copolymer prepared at different EtOH/water mixture composition (wt%); (▼) 40/60, (●) 50/50, (▲) 60/40, (▲) 70/30. Irradiation dose, 30 kGy.

FIG 2. Effect of time on the release of ketoprofen from (BA/MAAc) copolymer hydrogel that was prepared in different solvents. Comonomer composition: (50/50 mol%); comonomer concentration: 50 mol%; irradiation dose: 30kGy.
FIG. 3. The release of ketoprofen loaded during copolymerization from BA/MAAc copolymer hydrogel prepared at different doses (●) 30 kGy and (■) 40 kGy. Comonomer composition: 50/50 mol%, comonomer concentration: 50%, solvent: ethanol/water mix (60/40 mol%).

FIG. 4. Drug release from BA/MAAc copolymer hydrogel that contains different Ketoprofen concentration loaded during copolymerization. Comonomer composition: 50/50 mol%, comonomer concentration: 50%, irradiation dose: 30 kGy, solvent: ethanol/water mix: (60/40 mol%).

FIG. 5. The release of ketoprofen loaded by swelling in saturated solution from (BA/MAAc) copolymer hydrogel prepared at different solvents. Comonomer composition: (50/50 mol%), comonomer concentration: 50%; irradiation dose: 30 kGy. (●) Ethanol (■) Ethanol/water (50/50 wt%).
FIG. 6. Effect of temperature on the UV transmittance of the aqueous solution of the PVA-g-NIPA Am. 

$T\%$ was measured at 500 nm.
EXPERIENCE OF ELECTRON BEAM TREATMENT FOR PRODUCTION OF POLYETHYLENE OXIDE GELS FOR MEDICAL APPLICATIONS

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Abstract

The gels of polyethylene oxide (PEO) produced by electron beam cross-linking (polymerization) are finding the growing application in biotechnology and medicine as the matrices (carriers) for enzymes and other biologically active substances, and these new preparations are used for treatment of purulent-necrotic processes having various ethymology and localization, even for cleaning of carious cavities. The PEO gels are used for production of gel pastes purposed for endoscopy examinations and usage as contact media for ultrasonic diagnostics, electrocardio- and encelography. The viscosity of the produced gel ought to be chosen according the requirements to the final product made of this gel. We have carried out the study of the thermorheological properties of PEO gels produced by electron beam crosslinking of PEO solutions by the electron beam with energy of 2.5-3 MeV generated by electron accelerator ILU-6. The required viscosity of gels ranges greatly, so we are using the solutions of PEO having the concentrations from 20% to 60%.

1. INTRODUCTION

Composite means for external application are widely used in medicine. Now many medical preparations are produced by immobilization of the biologically active substances on the liquid and gel-like hydrophilic relatively inert bases (carriers) having high gas permeability and thus preventing the development of anaerobic microorganisms. Traditional hydrophobic bases (such as vaseline, lanolin and vegetable oils) have low gas penetrability and are incompatible with the majority of biologically active substances. Gels based on agar-agar, chyitosan, carboxymethylcellulose, etc., have high hydrophilic properties and gas permeability and can be used as such carriers. We have chosen the gels of low molecular weight polyethylene oxide PEO (low molecular weight PEO is also named polyethylenglycol PEG) produced by electron beam crosslinking (polymerization) [1] because they possess high resistance towards to microorganisms' cleavage. The PEO gels are finding the growing application in biotechnology and medicine - they are used as the bases (carriers) for enzymes and other biologically active substances, for production of gel pastes purposed for endoscopy examinations and usage as contact media for ultrasonic diagnostics, electrocardio- and encelography. These new preparations of immobilized enzymes are used for treatment of purulent-necrotic processes having various ethymology and localization, even for treatment of carious cavities. The PEO gels have great prospective in production of atraumatic dressings with various biologically active additives (enzymes, anaesthetics, styptic, etc.) for wounds. The working temperature range for preparations of immobilized enzymes and the medical gels is from 20 centigrades (minimum surface temperature on skin and possible temperature of the working head of ultrasonic diagnostic systems) till 40 centigrades and little more (wound temperature on the various stages of inflammation process). The viscosity of the final products (preparations and contact media) also depends on the application.
The proper usage of PEO gels requires proper knowledge of their rheological properties. The main technological parameter is the viscosity of gel that depends on temperature and shift velocity. In manufacturing processes the gel structures are subjected to the intensive deformations. But till now the thermorheological properties of PEO gels are not studied well enough.

2. MATERIALS AND METHODS

The production cycles of all the products based on PEO gels begin from the preparation of initial water solution of PEO and its irradiation for production of gel. The industrial electron accelerator ILU-6 was used as a source of radiation. The consistency of the gel is determined by the initial PEO concentration (from 20% to 60% for our products) and irradiation dose. After the crosslinking the gels are modified - dissolved by water, the solutions of enzymes, various preparations and chemical combinations are added, and for some preparations the irradiation is done again for immobilization of the active agents on the PEO matrix [1, 2].

Our research has shown that under influence of electron beam treatment or braking radiation on water solutions of polyethylene oxide the carbonyl groups (CG) are formed due to radiation-chemical oxidation. Carbonyl groups content in the irradiated solutions of PEO were assayed by method of Lappin and Klark [2]. O-phtalaldehyde [3] was used for calibration. The yield of CG has dose dependence at intervals from 2 up to 10 kGy as it is shown in Fig. 1.

Primarily it was considered that only trailer hydroxyl groups took part in radiation oxidation of polyethylene oxide and the mechanism of CG formation was similar to the oxidizing destruction of aliphatic alcohols. However, in this oxidation mechanism the yield of CG at polyethylene oxides with identical concentration of solutions and stationary dose of an irradiation but with different molecular weights should be also different. Our investigation has not revealed significant differences in behaviour of polyethylene oxides with various molecular weights after radiation-chemical oxidation both at a stationary absorbed dose and various concentration of solutions, and at stationary concentration of solutions and various dose (see Fig. 1). The absence of polyethylene oxide molecular weight influence on a CG yield is likely to be connected with radiolytic splitting of ether bindings in polyethylene oxide.

![FIG. 1. Dependence of concentration of carbonyl compounds on absorbed dose.](image-url)
It is known that action of radiation on some polymer solutions resulted in a gel formation. But radiation induced gel-formation is typical only for those polymers, in which the processes of linking prevail processes of destruction under action of radiation. Under radiolysis destructive processes at the presence of oxygen were previously established to be typical for [4, 5], however radiolysis of oxygen-free water solutions of polyethylene oxides is followed by a gel formation. The mechanism of radiation-chemical oxidation was investigated in a number of works [4-6].

As it has been stated above, the development of the polyethylene oxide gel production technology represents the special interest connected with prospective of creation the ointment medical forms with immobilized proteases. So it was hypothesized that enhancement of the absorbed dose of radiation along with simultaneous increase of a dose rate could lead to a gel formation even in oxygen-contained solutions of polyethylene oxide due to reaching of critical concentration of free radicals and reactive groups.

With this purpose the influence of electron beam with energy 2 MeV and high dose rate on water solutions of polyethylene oxide (molecular weight of 1500 Da) was investigated. The dose of gel-formation depended on the polyethylene oxide concentration and ranged from 40 up to 420 kGy for solutions with concentration from 1 up to 50 % as it is shown in Figure 2. As have been shown the irradiation of polyethylene oxide solutions with molecular weight of 1500 Da at the dose rate of 5 kGy/s and higher results in formation of gel without removal of the dissolved oxygen. Gels produced by this technology are colourless glassy substances. After homogenization their transformation into plastic gels (with dynamic viscosity from 3 up to 6 Pa/s depending on concentration of an initial polyethylene oxide solution) was observed.

We have carried out the study of the thermorheological properties of PEO gels produced by electron beam crosslinking on the linear electron accelerator ILU-6 at energy of 2.5-3 MeV. The required viscosity of gels ranges greatly, so we are using the solutions of PEO having the concentrations from 20% to 60%.

The interesting mechanical property of the studied gels is the constant value of viscosity when the shift tension exceeds the certain value. It witnesses that at great shift tensions the studied gels acquire the constant overmolecular spatial structure. The repeated measurements of viscosity of the same gel samples during the week as well as direct and reverse turn of the measurements did not witness neither mechanical nor thermal destruction of the studied polyethylene oxide gels. This feature demonstrates the important property - the steadiness of overmolecular structure of the polymerized gel towards mechanical and thermal disturbances. The dependence of gel viscosity from temperature was studied by a method of rotational viscosimetry in the stationary regime of Quett (viscosimeter Rheotest-2). The different constant gradients of velocity of shift (D, s-1) were set and the twisting moments (t, dn/cm2) measured at different temperatures. The dependence of twisting moment in PEO gel on velocity of shift at different temperatures is given in Fig. 3.

3. CONCLUSION

The data obtained in our studies witnessed the sufficient non-linear rheological properties of gels. We have studied the rheological properties of gels because they were required for applications of the final product and the technological needs of production. Our results permitted us to elaborate and optimize the production cycles for various medical and biotechnological preparations based on the PEO gels.

We are producing the gels having consistency from liquid to hard gel, their dynamic viscosity is from 0.5 to 60 Pa. The applications of these gels are given in Table I.

PEO gels are non-toxic matters, they do not possess cumulative, locally-irritating, skin-resorption properties and do not cause allergic reactions. PEO gels do not form toxic compounds in air and in wastewaters. Gels pertains to the group of are not inflammable compounds, the temperature of self-inflammation is 495 centigrades (after water evaporation they do not able to burn in interaction with water and oxygen).
FIG. 2. Dependence of gel formation dose on polyethylene oxide concentration.

FIG. 3. The dependence of twisting moment in PEO gel on shift velocity at different temperatures.
## TABLE I. MAIN APPLICATION AREAS OF THE GELS AND GEL PREPARATIONS BASED ON PEO IMMOBILIZED BY ELECTRON BEAM TREATMENT

<table>
<thead>
<tr>
<th>Name of product</th>
<th>Description of product</th>
<th>Application area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stomatozim</td>
<td>Gel composition containing immobilized proteinases</td>
<td>Stomatology Treatment of caries and parodontosis</td>
</tr>
<tr>
<td>Endogel</td>
<td>Gel paste for endoscopy studies</td>
<td>Medicine</td>
</tr>
<tr>
<td>Echogel</td>
<td>Gel paste for ultrasonic diagnostics</td>
<td>Medicine</td>
</tr>
<tr>
<td>Electrode paste</td>
<td>Gel paste for electrodes used in cardio- and encephalography</td>
<td>Medicine</td>
</tr>
<tr>
<td>Enzymoplast</td>
<td>Gel paste with biologically active substances for production of atraumatic dressings for wounds</td>
<td>Medicine</td>
</tr>
<tr>
<td>Gels for tooth pastes</td>
<td>Gel tooth pastes with various additives</td>
<td>Sanitation and hygiene</td>
</tr>
<tr>
<td>Gels for skin care cosmetic preparations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gels for hair care cosmetic preparations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gels for veterinary sanitary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gels for massage procedures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gels for industrial applications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorption low-abrasive pastes</td>
<td>Gel pastes with additives containing ceolytes</td>
<td>Ecology (Sorption of toxic and radiation pollutants)</td>
</tr>
<tr>
<td>Polishing pastes</td>
<td>Polishing of metal surfaces Treatment of stones</td>
<td></td>
</tr>
<tr>
<td>Stabilizers of charcoal suspensions</td>
<td>Coal ducts - transportation of charcoal suspension</td>
<td>Coal industry</td>
</tr>
<tr>
<td>Additives for the boring mortars</td>
<td></td>
<td>Geology prospecting</td>
</tr>
</tbody>
</table>

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CONTROLLED RELEASE FROM POLYDMAEMA GELS PREPARED BY GAMMA IRRADIATION

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Abstract

Poly N, N-dimethylaminoethyl methacrylate (polyDMAEMA) hydrogels prepared by γ-irradiation showed obvious temperature-sensitivity at a temperature range of 38~40°C and pH-sensitivity at pH=2.5. They also had electric response behavior although it was not typical. The hydrogels were used in controlled release at different pH, temperature, and electric voltage. The release rates of methylene blue (MB) from the gels at 52°C and pH=1.24 were faster than those at 20°C and pH=10.56, respectively. In addition, the release rate at a field voltage of 5.0 was also faster than that of no electric field.

1. CHARACTERISTICS OF POLYDMAEMA HYDROGEL

The polyDMAEMA hydrogels obtained in this work show good mechanical properties and high swelling capacities in water. The equilibrium degree of swelling was 900% approximately. The hydrogels also display temperature and pH-sensitivity at 38~40°C and pH=2.5.

2. RELEASE STUDIES

For the release studies, Methylene Blue (MB) solution (~1g/l) was prepared first. Then the polyDMAEMA hydrogels were put in it. The release studies would begin after they got equilibrium swelling.

2.1. MB release at different pHs

MB release experiments were performed in deionized water at pH=1.24 and 10.56 and at room temperature. The release rate of MB at pH=1.24 was faster than that at pH=10.56. At pH=1.24, it leveled off after about 13 h while at pH=10.56 the time was about 60 h.

2.2. MB release at different temperatures

Since the polyDMAEMA hydrogel showed temperature sensitivity at 38~40°C, the release experiments were conducted at 20°C and 52°C, respectively. The results are shown in Fig.1. It was found that the release rate at 52°C was greater than that at 20°C, which could be attributed to the size of MB molecules. Even though the gel shrank at high temperature, MB molecules still could pass through the gel and its release rate was fast due to the fast diffusion of MB molecules at high temperature.
FIG. 1. The release of MB at different pH. **temperature** = 20°C.

2.3. MB release in electric field

Fig. 2 shows the release rate of MB at different electric voltage. The release rate at a field voltage of 5.0V was much higher than that without electric field. For example, it took 3 h to reach equilibrium at a field voltage of 5.0V. Without the electric field, it needs 23 h. However, the amount of MB in hydrogel could not be completely released at 5.0 V.

FIG. 2. Pulsatile electric field as a function of MB release.
PREPARATION OF POLY (ACRYLAMIDE-CO-METHACRYLIC ACID) HYDROGELS
BY GAMMA RADIATION. INFLUENCE OF THE ABSORBED DOSE ON THE
SWELLING PROCESS, 5-FLUOROACIL RELEASE

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²Center of Biomaterials, University of Havana,
Havana,
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Abstract

In this report gamma radiation performs the double functioning of copolymerization and crosslinking with the advantage of avoiding the use of chemical crosslinkers to obtain the poly (acrylamide -co-methacrylic acid) hydrogels (AA/MA). For these hydrogels the influence of absorbed dose on the swelling ratio as a function of pH has been presented. The swelling studies indicate that swelling decreases with the increase of the absorbed dose from 10 to 50 kGy. It was confirmed that at the first stages (100-150 min) the diffusion studies were in accordance with Fickian behavior and the diffusion coefficients were obtained, whereas the latest stages were in good agreement with the second-order diffusion kinetics proposed by Schott. These new hydrogels have a higher degree of swelling, and thus, assure high biocompatibility because the similarity with living tissues is enhanced. The drug delivery was followed by HPLC. The behavior of 5-FU migration from polymeric network followed the Iguchi equation.

1. INTRODUCTION

One of the most important physical properties affecting the behavior of the hydrogels under use conditions is their swelling in aqueous solutions. Swelling can be described in terms of rate and maximum uptake at equilibrium. Swelling defines the capacity of penetration of the molecules of the solvent in a main polymeric chain, and depends on the cross-linking degree of the polymer, and the nature of the solvent amongst others. Analysis of the mechanism of diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of these polymers in biomedical, pharmaceutical, environmental, and agricultural engineering [1,2]. The processes of formation of hydrogels by means of gamma radiation are essentially due to the polymerization of monomers and cross-linking of created polymer, as a result of the mutual recombination of macroradicals [3,4]. The aim of this paper is to determine the influence of the absorbed dose upon the swelling degree and the kinetic behavior at different pH solutions for hydrogels from AA/MA, in order to obtain a matrix with different diffusion characteristics, to allow for the release of some drugs such as the 5-fluorouracil (5-FU); this is an antimitabolic drug used in cancer chemotherapy [5].

2. EXPERIMENTAL

2.1. Materials

Acrilamide from BDH Chemicals Ltd, assay 98.5 % and methacrylic acid for synthesis from MERCK were used as received.

The antineoplastic drug, 5-FU (C₄H₃N₂O₂F) was supplied by CIDEM as a crystalline powder.

2.2. Monomer preparation and polymerization procedure

The polymerization of the feed mixture of acrylamide (AA) (75 %) and methacrylic acid (MA) (25%) in water solution was induced in sealed glass ampoules without degassing, with ⁶⁰Co gamma source. The gamma ray dose was 10, 30 and 50 kGy. The dose rate was 4.3 kGy/h, according to Fricke and ceric sulfate dosimetry [6].
2.3. Buffer solutions

The swelling experiments were carried out in different water buffer solutions in order to work with different ion strength at pH 2 (0.01M HCl, glycine and sodium chloride); at pH 7.4 (0.05 M phosphate buffer); and at pH 10, (sodium carbonate and sodium dihydrogen carbonate 0.1 M).

2.4. Disc preparation

In order to obtain thin xerogel disc, ready disks of 1.5 ± 0.2 mm of thickness and 15.1± 0.5 mm of diameter were prepared from the starting hydrogel. After polymerization, the discs were immersed in water for two weeks to remove any possible residual monomers and then were dried at environmental temperature with reduced pressure up to its constant weight. The disc measurements were carried out with a micrometer.

2.5. Swelling study

The swelling study was followed gravimetrically by measuring the weight gain of the prepared disks with the time of immersion in 20 mL of different saline solutions of well-known pH (2, 7.4, 10) at 37°C. Measurements were carried out until the equilibrium was reached; which was considered when three consecutive measurements gave the same weight. The equilibrium weight-swelling ratio W was followed according to the following relationship:

\[ W = \frac{(W_t - W_o)}{W_o} \]  

where

- \( W_t \) is the hydrogel weight at equilibrium swelling,
- \( W_o \) is the weight of the dry gel (xerogel).

For swelling calculation, the differential of Fick's law was used as a function reduced from \( W_t/ W_{max} \) of \( t^{1/2} \) according to the following equation [7]:

\[ \frac{W_t}{W_{max}} = 4 \left( \frac{Dt}{\pi l^2} \right)^{1/2} < 0.6 \]  

where

- \( W_t \) is the gain of water uptake at a t time
- \( W_{max} \) is maximal water solution uptake at equilibrium,
- \( D \) is diffusion coefficient,
- \( t \) is time,
- \( l \) is film thinness.

2.6. Trapping of 5-fluorouracil in the copolymers

5-FU was trapped in the similar hydrogels discs with 1.5 ± 0.2 mm of thickness and 15.1± 0.5 mm of diameter; irradiated at 10, 30 and 50 kGy. The discs were immersed in drug solutions containing 40 mg of drug in 10 ml of saline physiological salt solution at pH 7, 4 for each disc, until the total absorption of 5-FU took place. The discs were optically transparent. Finally discs were dry in vacuum until constant weight.

2.7. 5-fluorouracil release

The preliminary 5-FU release experiments were carried out by placing each hydrogel disc with drug on a holder in a vessel containing 50 ml of the same saline solution employed in the swelling experiments at a temperature of 37°C. The drug release was followed during the first 8 hours. At
intervals of one hour aliquots of 50 µl samples were drawn from the solution to follow 5-FU release. Sink conditions were maintained during drug release.

The concentration of 5-FU was measured by high-performance liquid chromatography (HPLC) KNAUER, SP ultraviolet detector with EUROCHRON computing integrator. The flow rate was 1 ml/min, and the detector wavelength was at 266 nm. The external standard method was employed. The 5-FU standards 100 µg ml⁻¹ were run for the calibration curve.

3. RESULTS

3.1. Synthesis

In this work we applied the method of radiation-induced simultaneous polymerization and crosslinking for hydrogel preparation by means of irradiating the mixture of monomers starting from a water solution of acrylamide and methacrylic acid. The mixture of AA and MA was selected by taking previous experiments into consideration [8], in which such a reaction could be accounted for in a simplified form, according to the following equation:

\[
\text{CH}_2=\text{CH}\cdot\text{C} \text{OOH} + \text{CH}_2=\text{C} \cdot \text{C} \text{NH}_2 \rightarrow \text{CH}_2=\text{C} \cdot \text{C} \text{NH}_2 \cdot \text{CH}_2=\text{C} \cdot \text{C} \text{OOH}
\]

The samples which received greater doses, ranging between 30–50 kGy took a hard consistency, were not very elastic, opaque and of an off-white color, while samples which had received minor doses of less than 10 kGy also were of an off-white color, but they were softer and more elastic. In the hydrate state, opaque hydrogels became transparent.

3.2. Swelling behaviour (kinetics)

In this work special emphasis was made on the study of the equilibrium swelling and their kinetics due to it being a thermodynamical process of great importance for the hydrogel characterization as a drug release system [9]. The following data show experimental values of the swelling related to the immersion time at temperature of 37°C for different absorbed doses (10, 30, 50) kGy, and for the maximum equilibrium swelling represented in Figs 1 and 2. As we can see the absorbed dose in the previous figures can influence the degree of swelling as a function of the pH solution, for instance, at the absorbed dose of 10 kGy, and pH 10 the equilibrium swelling was reached at 60 %, for 30 kGy 45 % and for 50 kGy, 35%, while at physiologic pH, (7.4) for doses of 10, 30 and 50 [kGy] it drops from 50, 40 to 25%; already for pH 2, the swelling values descended from 10 to 5% at the absorbed doses of 10, 30 and 50 kGy respectively. These results evidence dependence between the absorbed dose from the swelling degree and the ion strength of the medium. This proves that by increasing the absorbed dose the copolymer is more crosslinking. This effect makes the penetration of the solvent in the inside of the polymer change more difficult, due to the increase of elastic-retractile forces. In our case this effect is stressed in proportion to the absorbed dose increase in 10 to 50 kGy while the swelling in the equilibrium diminishes with the increase of the cross-linking degree.

It is worth noting that with an increase of the ionic strength at lower pH, the sensitivity on hydrogel swelling is restricted. As we can see, the maximal swelling degree increases with a pH variation from 2 to 10. This effect can be explained as follows: at greater pHs, the carboxylate anion of the methacrylic acid residues which have a delocalized charge between the oxygen atoms could accept more water buffer molecules, while at lower pHs, (e.g. pH 2) the methacrylic acid is in non dissociated form and it could only be bound with hydrogen bound links with water molecules in a lower degree.

A criterion of the Fickian behavior [10] considers that the diagram of Wt/Wmax with the square root of the time should be lineal. In Fig 3, the results obtained in these diagrams are shown for the
copolymer of AA/MA. The treatment of Fick's low fixes well for the first immersion times, since for upper stages deviations of the linear behavior occurred and were appreciated in all the cases.

The water sorption kinetics of these hydrogels was satisfactorily fitted to the Fick's law for the first 100-150 minutes. The good fit is also clearly shown in Fig.3; where the calculated curves seem to reproduce satisfactorily the experimental points at this time. As swelling depends on the thickness of the films, several measurements were carried out in order to minimize the errors in the calculations of diffusion coefficients of the hydrogel disks. The diffusion coefficients of these copolymers were determined through the slopes of the studied curves at pH 7.4. In Table I the values obtained through this method are shown.

**TABLE I. DIFFUSION COEFFICIENTS OF HYDROGELS FROM AA/MA DETERMINED FOLLOWING FICK’S LAW**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Diffusion Coefficients (cm²/s) x 10⁻⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH / Adsorbed Dose (kGy)</td>
<td>10 kGy</td>
</tr>
<tr>
<td></td>
<td>30 kGy</td>
</tr>
<tr>
<td></td>
<td>50 kGy</td>
</tr>
<tr>
<td>7.4</td>
<td>1.54 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.37 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>0.27 ± 0.04</td>
</tr>
</tbody>
</table>

Thus, with an increase of the absorbed dose we obtain a higher degree of cross-linking factor that leads to reduce the apparent diffusion coefficient; in this way, the transport of water saline solution into the gel will be more difficult.

It is well known that Fick's laws of diffusion to one-dimensional swelling of films considers the constant of the diffusion coefficient of penetrating solvent during the entire swelling process (Zaldívar, et al., 1993). In our case we have rigid polymeric films, considering that the film thickness does not remain constant. Taking into account the deviations of Fick's behavior, once the first 150 minutes passed we could check the studies referred by Schott [11] for the extensive swelling of polymers in the form, where the reciprocal of the average rate of swelling (t/w) is related to the time of treatment by linear equation

\[
\frac{t}{W} = A + Bt
\]  

(3)

where

\[ W \] is the swelling at time \( t \)
\[ B = 1/W_{\infty}, \] representing the inverse of maximum swelling,
\[ A = 1/(dW/dt)_{t=0}, \] is the reciprocal of the initial swelling rate.

It has been shown that equation (3) implies second-order swelling kinetics expressed as:

\[
\frac{dW}{dt} = K(W_{\infty} - W)^2
\]  

(4)

Schott's equation was satisfactorily applied to our system (see Fig 4), in all cases straight lines with good correlation were obtained. The linear behavior demonstrates that our system follows a kinetic of second-order for the later swelling states.

Thus, the equilibrium degree of swelling is determined by the balance between the network elastic forces on the hydrated chains. This balance is strongly dependent on the crosslinking density of the hydrogel network

**3.2. Kinetic study of the 5-FU in vitro release**

The preliminary survey of application of a new copolymer of AA/MA, on entrapped 5-FU was made. The drug delivery was followed by HPLC. The release profiles of 5-FU release are shown in Fig.5.
This results are in accordance with the diffusion coefficients reported at pH 7.4. Thus, an increase of the absorbed dose results in a slower release process similar to the behavior of the swelling process. Note that the samples with a higher release rate for 10 kGy are the AA/MA networks with the minor degree of cross-linking to which corresponds the greater diffusion coefficient \( D = 1.54 \pm 0.04 \times 10^{-9} \text{ cm}^2/\text{s} \) so a decrease of the diffusion coefficient values with and increase of the degree of cross-linking can be observed. Similar results were obtained in recent works of Zaldivar et. al (1993), for hydrogels of the same composition; cross-linking by thermal process employing redox initiators.

The behavior of the migration of the 5-FU from these networks is described by the Higuchi equation [12]:

\[
M_t = A_t \left(2 D Cs Co t\right)^{1/2}
\]

where

- \(M_t\) is the percentage of drug release at time \(t\),
- \(A_t\) is total surface of the hydrogel film,
- \(D\) is the diffusion coefficient of the drug in the hydrogel network,
- \(Cs\) is the solubility of the hydrogel network,
- \(Co\) is the total concentration of the drug in the matrix.

Thus, when the release rate is plotted against the time \(t^{1/2}\) (see Fig. 6), a linear relationship is clearly developed for each hydrogel obtained at different absorbed dose. These results support the view that cumulative amount of drug released from AA/MA hydrogels is proportional to the square root of time and follows the equation developed by Higuchi. The release rate of 5-FU decreased from 16% (for the absorbed dose of 10 kGy) to 5.6% (for the absorbed dose of 50 kGy) in the first 8 hours.

4. CONCLUSIONS

1. The irradiation of the water solutions of the acrylamide and methacrylic acid brings about the network formation (hydrogel).
2. The swelling degree in the studied system decreased, with an increase of the absorbed dose in the range of studied absorbed doses.
3. It was confirmed that for the first stages (100-150 min), the diffusion studies were in accordance with Fickian's behavior, and the diffusion coefficients were obtained, whereas the later stages were in good agreement with the second-order diffusion kinetics proposed by Schott.
4. Considering the above mentioned results, these hydrogels exhibit a higher degree of swelling, a factor that can be controlled by changing the degree of cross-linking by means of changing the value of absorbed dose.
5. The behavior of 5-FU migration from polymeric network followed the Higuchi equation.
FIG. 1. Equilibrium swelling isotherms (37°C) of discs prepared from the irradiated AA/MA hydrogel samples at 10 kGy.

FIG. 2. Equilibrium swelling ratio $W_{\text{max}}$ of hydrogel as a function of pH at 37°C for samples irradiated at 10, 30 and 50 kGy.

FIG. 3. The Plots of swelling ratio $W_t/W_{\text{max}}$ of AA/MA hydrogels versus square roots of immersion time at 37°C for absorbed dose 50 kGy.
FIG. 4. The plots of the reciprocal rate of swelling $t/W$ defined as a function of the swelling time of AA/MA hydrogels for absorbed dose 50 kGy.

FIG. 5. Profiles of the in vitro 5-FU release as a function of time for absorbed dose of 10, 30 and 50 kGy.

FIG. 6. Release rate of 5-FU as a function of $t^{1/2}$ for AA/MA hydrogels for adsorbed dose of 10, 30 and 50 kGy.
REFERENCES


RADIATION SYNTHESIS AND APPLICATION OF N-VINYL 2-PYRROLIDONONE BASED HYDROGELS CONTAINING MONO-, DI-, TRI-PROTIC ACID MOIETIES

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3 Department of Chemistry, Faculty of Science and Art, University of Gazi, Besevler, Ankara, Turkey

Abstract

Hydrogels containing mono-, di-, tri-protic acid moiety were prepared from the ternary systems of N-vinyl 2-pyrrolidone/acrylic, itaconic, tartaric, citric acid/water by irradiation with gamma rays at ambient temperature. The average molecular weight between cross-links, $\bar{M}_c$ and polymer-solvent interaction parameter, $\chi$ of these hydrogels were determined according to equations derived by authors for the characterization of network structure of poly-electrolytes. The effect of gel composition on the uranyl ions and enzyme adsorption capacity were found depending on the content of carboxylic acid in these hydrogels.

1. INTRODUCTION

Hydrogels are polymeric materials, which are able to swell but not dissolve in aqueous media and retain large volumes. According to their origin, they may be natural or synthetic and may be anionic, cationic or amphiphilic which can be classified as a polyelectrolytes. These gels usually contain pendant acidic and basic groups such as carboxylic acids and primary amines, or strong acid and bases, such as sulphanic acids and quaternary ammonium salts which change ionization in response to changes in pH, thus changing the properties of the gel. The equilibrium degree of swelling of electrolyte type hydrogel is mainly influenced by the charge of the ionic monomer, dissociation constant, $pK_a$ of the ionizable group, degree of ionization, concentration of ionizable monomer in the network, cross-linking density, structure of the polymer backbone, pH, ionic strength and composition of the swelling solution. The concentration of ionizable monomer in the hydrogel is important for the swelling and pH-sensitive of gel. This effect is a result of relative hydrophilicity of the ionizable monomer to the neutral monomer. One basic parameter that describes the structure of a hydrogel network is the molecular weight between the cross-links. This describes the average molecular weight of polymer chains between two consecutive functions. Their functions may be chemical cross-links, physical entanglements, crystalline regions, or even polymer complexes. In the more recent years, a series of articles have been published by Kantoğlu, Çaykara, Şen, and Güven who synthesized new hydrogels from the copolymers of N-vinyl 2-pyrrolidone and mono-, di-, tri-protic acids such as acrylic, itaconic, tartaric and citric acid [1-3]. These authors are also published that these hydrogels are potential adsorbents for biological agents and heavy metal ions from aqueous solution [4]. In this study, N-vinyl 2-pyrrolidone based hydrogels containing mono-, di-, tri-protic acid moieties were prepared by gamma rays. The hydrogels thus prepared were characterized in view of network properties and the application to the adsorption of uranyl ions and enzymes.

2. EXPERIMENTAL

2.1. Chemicals

N-vinyl 2-pyrrolidone (VP), and acrylic acid (AA), itaconic acid (IA), tartaric acid (TA), citric acid (CA) were purchased from Merck and Carlo Erba, respectively. The invertase and $\alpha$-amylase used for the adsorption studies were obtained from Fluka. Uranyl nitrate and uranyl acetate was purchased from Fisher. Sucrose (Sigma) was used as the substrate as received. Chemicals used in the preparation of buffers (Merck) were used without further purification. Glucose (Fluka) was of biochemical grade.
1.2. Preparation of hydrogels

Aqueous solutions of the monomer VP and AA, IA, TA, and CA were prepared in different compositions in 1 mL of distilled water (VP/AA) mole ratios: 100.0/0.0, 72.6/27.4, 55.5/44.5, 39.0/61.0; (VP/IA) mole ratios: 100.0/0.0, 97.6/2.4, 96.4/3.6, 95.3/4.7, 93.2/6.8; (VP/TA) mole ratios: 100.0/0.0, 97.9/2.1, 96.9/3.1, 95.9/4.1, 04.0/6.0; (VP/CA) mole ratios: 100.0/0.0, 98.4/1.6, 97.6/2.4, 96.8/3.2. The prepared solutions were irradiated with a dose of 1.85 kGy (VP/AA) and 25 kGy (VP/IA, TA, CA) in air at ambient temperature in a gamma irradiator at a fixed dose rate of 3.87 kGy/h.

1.3. Composition of gels

Irradiated mixtures were dried in vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction with water as solvent. Uncross-linked polymer and/or residual monomer were removed with this extraction from the gel structure. Extracted gels were dried again in vacuum oven at 315 K to constant weight. Percentage gelation, i.e. percentage conversion of monomers into insoluble network, was based on the total weight of acid and monomer in the initial mixture. The amount of carboxylic acids and VP in monomer, polymer and/or copolymer form was determined by titration of extract against NaOH (0.05 M) to phenolphthalein end point. The mole percentages of monomers in the initial mixtures and in the hydrogel systems are summarized in Table I.

1.4. Adsorption

1.4.1. Uranyl ions adsorption

A weighted of N-vinyl 2-pyrrolidone based hydrogels (~1.0g) was added to 50 mL of uranyl nitrate solution and was allowed to equilibrate for 48 hours at 25 °C. The adsorbent was removed by decantation uranyl ions were complexed with sodium salicylate (10%w/w) and measured at 466 nm by UV-Visible spectrometer.

1.4.2. Invertase adsorption

For the adsorption of α-amylase onto these N-vinyl 2-pyrrolidone based hydrogels, 0.1 g of the dry gel was placed in 20 mL solution of 400 mg dl⁻¹ invertase, and adsorption was carried out at 30 °C for 8 h. Hydrogel were separated and enzyme not adsorbed was removed by washing with phosphate buffer (15 mL). The adsorbed enzymes were used freshly or stored at 4 °C.

1.4.3. α-Amylase adsorption

For the adsorption of α-amylase onto these N-vinyl 2-pyrrolidone based hydrogels, 0.1 g of the dry gel was placed in 20 mL solution of 100 mg dl⁻¹ α-amylase in phosphate buffer (10 mM, pH=7.0) and allowed to equilibrate for 48 h. The enzymatic activities of free and adsorbed α-amylase were determined by an enzyme reaction using starch as substrate and starch-iodine method.
3. RESULTS AND DISCUSSIONS

In this study, synthesis of new sorbents, determination of co-polymerization reaction, investigation of their swelling behaviors and adsorption capacities were studied. For this purpose, VP monomer was copolymerized with acrylic, itaconic, tartaric and citric acid. The reaction mechanism between N-vinyl 2-pyrrolidone and carboxylic acids (acrylic, itaconic, tartaric and citric acids) is shown in Scheme 1.

Scheme 1. Polymerization reaction of N-vinyl 2-pyrrolidone/acrylic, itaconic, tartaric and citric acid by irradiation.
As it is seen from polymerization reaction scheme, the carboxylic acids containing double bonds (AA, IA) were polymerized by random radicalic polymerization reaction. Due to the hydrogen abstraction, non-double bond containing carboxylic acids (TA, CA) were entangled on PVP by grafting. An increasing mole percentage of TA and CA in the initial mixture increases the amount of TA and CA in the gel system, but causes a decrease in the conversion from monomer to gel. These results indicate TA and CA typical properties of chain transfer agent being grafted on the PVP backbone.

3.1. Determination of $\bar{M}_c$ and $\chi$ values of hydrogels

The following equations derived by the authors [5-8] for swelling behavior of charged polymeric networks were used for the determination of $\bar{M}_c$ and $\chi$ parameters of N-vinyl 2-pyrrolidone based hydrogels containing mono-, di-, tri-protic acid moieties.

\[
\left[ \frac{K_a}{10^{-pH} + K_a} \right]^2 \frac{V_1 X^2 a}{4I V^2} - v_{2m}^{-2} \ln(1-v_{2m}) - v_{2m}^{-1} = \chi + \frac{(1-2/\phi) V_1 v_{2m}^{2/3} v_{2m}^{-5/3}}{V M_c} \tag{1}
\]

\[
\left[ \frac{2K_aK_{a2} + 10^{-pH} K_{a2}}{2(10^{-pH})^2 + 10^{-pH} K_{a1} + K_{a1}K_{a2}} \right]^2 \frac{V_1 X^2 a}{4I V^2} - v_{2m}^{-2} \ln(1-v_{2m}) - v_{2m}^{-1} = \chi + \frac{(1-2/\phi) V_1 v_{2m}^{2/3} v_{2m}^{-5/3}}{V M_c} \tag{2}
\]

\[
\left[ \frac{3K_{a1}K_{a2}K_{a3} + 2(10^{-pH}) K_{a1}K_{a2} + (10^{-pH})^2 K_{a1}}{(10^{-pH})^3 + (10^{-pH})^2 K_{a1} + 10^{-pH} K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} \right]^2 \frac{V_1 X^2 a}{4I V^2} - v_{2m}^{-2} \ln(1-v_{2m}) - v_{2m}^{-1} = \chi + \frac{(1-2/\phi) V_1 v_{2m}^{2/3} v_{2m}^{-5/3}}{V M_c} \tag{3}
\]

The relevant parameters to be used with eq.1, 2 and 3 are as follows: ionic strength, $I=0.1$, M, molar volume of solvent, $V_f=18$ g cm$^{-3}$ and the number of branches originating from a cross-linking site, $\phi=3$. In the preparation of hydrogels, no cross-linking agents were used in this work. Cross-linking has been achieved by high-energy radiation. It has been determined and known for sometime that the radiation induced cross-linking produced is either H or Y types. If the swelling data of gel is used to plot the left hand side of Eq. 1, 2, 3, (A) against the coefficient of $1/\bar{M}_c$ on the right hand side (B) a linear relation must be obtained with $\chi$ and $\bar{M}_c$ values as the intercept and inverse slope, respectively.

\[
A=\chi+B/\bar{M}_c \tag{4}
\]

The effect of presence of carboxylic acid groups on the network properties and polymer-solvent (water) interaction parameter is obvious from these results. With increasing amount of carboxylic acid groups in the network, the hydrogel becomes less swollen and the network properties change accordingly.
in the copolymer structure the average $\bar{M}_c$ values increase, whereas $\chi$ values changed between 0.32 and 0.64 which are very close to the $\chi$ parameter of pure PVP. The former effect indicates that carboxylic acid unit does not act as a cross-linking agent; furthermore, it shows chain transfer agent properties. The $\chi$ parameter of the pure PVP has been found to be 0.49 [3]. The $\chi$ values in Table I are very well in accordance with this reported value of interaction parameter.

### TABLE I. THE MOLE PERCENTAGE OF CARBOXYLIC ACID IN FEED AND GEL, $\bar{M}_c$ AND $\chi$ OF HYDROGEL SYSTEMS

<table>
<thead>
<tr>
<th>Gel Name</th>
<th>Mole of carboxylic acid$^a$</th>
<th>In feed</th>
<th>In gel</th>
<th>$\bar{M}_c$ $^b$</th>
<th>$\chi$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VP-g-AA)</td>
<td>27.0-61.0</td>
<td>27.0-61.0</td>
<td>3100-19200</td>
<td>0.54-0.64</td>
<td></td>
</tr>
<tr>
<td>P(VP-g-IA)</td>
<td>2.4-6.8</td>
<td>2.0-3.0</td>
<td>9100-16200</td>
<td>0.44-0.48</td>
<td></td>
</tr>
<tr>
<td>P(VP-g-TA)</td>
<td>2.1-6.0</td>
<td>1.7-3.1</td>
<td>6100-11700</td>
<td>0.32-0.51</td>
<td></td>
</tr>
<tr>
<td>P(VP-g-CA)</td>
<td>1.6-3.2</td>
<td>1.1-2.7</td>
<td>62000-97000</td>
<td>0.51-0.53</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Min. and max. carboxylic acid contents are presented in feed and gel systems.

$^b$ Min. and max. $\bar{M}_c$ and $\chi$ values are presented for each gel systems.

In Eqs 1, 2, 3; $K_{a1}$, $K_{a2}$, $K_{a3}$ are dissociation constants of the mono-, di-, tri-protic carboxylic acids. $\bar{M}_c$ and $\chi$ denote molecular weight between cross-links and Flory-Huggins polymer-solvent interaction parameters. $\chi$ denotes the weight fraction of ionizable polymer in the gel system. $\nu$, $\nu_2$, $\nu_{2m}$ represent specific volume of polymer, the polymer volume fraction in relaxed state, that is, after cross-linking but before swelling, the volume faction of polymer network, respectively. In equation 1, $a$ is the correlation factor, which was found by try and error method. By using these equations $\bar{M}_c$ and $\chi$ were calculated and presented in Table I.

### 3.1. Determination of adsorption capacity of hydrogels

The adsorption capacities of hydrogels were presented in Table II. As can be seen from Table II, the total amount of uranyl ions and enzyme depends on the mole percentage of carboxylic acid in the gel system. The reason of increase can be thought of an increase in specific interactions between positively charged molecules (uranyl ions or enzyme) and ionized carboxylic acid in the hydrogel as well as an increase of free volume of gel available for diffusion.

### TABLE II. THE URANYL IONS AND ENZYME ADSORPTION CAPACITY OF HYDROGELS$^a$

<table>
<thead>
<tr>
<th>Gel Name</th>
<th>$\text{UO}_2\left(\text{NO}_3\right)_2$ (mg/g dry gel)</th>
<th>$\text{UO}_2\left(\text{CH}_3\text{COO}\right)_2$ (mg/g dry gel)</th>
<th>$\alpha$-Amylase (mg/g dry gel)</th>
<th>Invertase (mg/g dry gel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VP-g-IA)</td>
<td>27.2-70.0</td>
<td>-</td>
<td>2.3-3.4</td>
<td>4.4-18.4</td>
</tr>
<tr>
<td>P(VP-g-TA)</td>
<td>7.0-76.0</td>
<td>10.0-133.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P(VP-g-CA)</td>
<td>18.0-144.0</td>
<td>22.0-156.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Min. and max. adsorption capacity of each hydrogel systems have been presented.
REFERENCES


RADIATION PREPARATION AND CHARACTERISTICS OF SODIUM CARBOXYMETHYL CELLULOSE HYDROGELS

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Abstract

Sodium carboxymethyl cellulose (CMC) is a kind of degraded polymer under irradiation. However, in this work, it can be found that CMC crosslink partially to form hydrogel by radiation technique at more than 20% CMC aqueous solution. The gel fraction increases with the dose. The crosslinking reaction of CMC is promoted in the presence of N₂ or N₂O due to the increasing of free radicals on CMC backbone, but gel fraction of CMC hydrogel isn’t high (less than 40%). Some important values related to this kind of new CMC hydrogel synthesized at different conditions, such as radiation yield of crosslinking G(x), gelation dose Rg, number average molecular weight of network Mn is calculated according to Charlesky-Pinner equation. The results indicated that although crosslinked CMC hydrogel can be prepared by radiation method, the rate of radiation degradation of CMC is faster than that of radiation crosslinking due to the character of CMC itself. Swelling dynamics of CMC hydrogel and its swelling behavior at different conditions, such as acidic, basic, inorganic salt as well as temperature is investigated, too. Strong acidity, strong basicity, small amount of inorganic salts and lower temperature can reduce swelling ratio. Because of no toxicity and good biocompatibility of natural polymer, CMC based hydrogel will have wide application in biomedical materials.

1. INTRODUCTION

CMC is an anionic water-soluble natural polymer. It is widely used in detergents, oil exploration, and in the food, paper and textile industries because of its viscosity-increasing properties [1]. Recently, some natural polymers, such as carrageenan [2], and chitosan [3] have been used in radiation preparation of hydrogels as a biomaterial due to their nontoxicity, degradability and good biological compatibility, but few study on CMC used in radiation preparation of hydrogels. CMC similar to other natural polymers is a degraded polymer under irradiation [4]. In this work, crosslinking of CMC using ⁶⁰Co gamma radiation technique to form the hydrogel was studied. Effect of prepared conditions on crosslinking of CMC and swelling behaviors of the hydrogel at different conditions was discussed detailedly.

2. EXPERIMENTAL

2.1. Materials

Sodium carboxymethyl cellulose was supplied by Suzhou Yiming Chemical Plant. NaCl, CaCl₂ used was of an analytical grade and distilled water was used for the preparation of hydrogels.

2.2. Preparation of CMC hydrogel

20% even CMC jelly was prepared by dissolving CMC in distilled water at 40 °C for 2d. N₂ or N₂O was bubbled beforehand into CMC solution for 30min to eliminate the influence of O₂ on the crosslinking of CMC. The samples were cooled and irradiated at room temperature by ⁶⁰Co gamma source.
2.3. Gel fraction of CMC hydrogel

The hydrogel samples were extracted by distilled water for 24h to remove the sol and then dried to a constant weight at 50 °C. The gel fraction was calculated as follows:

\[ \text{Gel fraction (\%)} = \frac{W_g}{W_o} \times 100 \]

where

- \( W_g \) is the weight of dry gel after extraction,
- \( W_o \) is the initial weight of dry gel.

2.4. Swelling behavior of CMC hydrogel

Gel samples dried to a constant weight were immersed in distilled water at room temperature. The swelling ratio of the hydrogel can be calculated as:

\[ \text{Swelling ratio} = \frac{W_t}{W_o} \]

where

- \( W_t \) is the weight of swelling hydrogel at different time,
- \( W_o \) is the initial weight of dry gel.

Effect of some factors such as acid, base, inorganic salt as well as temperature on swelling behavior of CMC hydrogel also were performed by determining the swelling ratio of CMC hydrogel at above condition for 24h.

3. RESULTS AND DISCUSSION

3.1. Radiation preparation of CMC hydrogel

When the concentration of CMC jelly is more than 20%, after irradiation, CMC crosslinked partially to form hydrogel. Effect of dose, \( N_2 \) or \( N_2O \) on the crosslinking of CMC is shown in Fig.1. The gel fraction increases with the dose, the crosslinking reaction of CMC is promoted in the presence of \( N_2 \) or \( N_2O \) due to the increasing of free radicals on CMC backbone (Fig.1). Fig.1 also manifests that gel fraction of CMC hydrogel isn’t high (less than 40%).

Some important values related to this kind of new CMC hydrogel synthesized at different conditions, such as radiation yield of crosslinking \( G(x) \), gelation dose \( R_g \), number average molecular weight of network \( M_c \) is calculated according to Charlesky-Pinner equation from the results in Fig.1 (Table I). According to the results in Table I, it isn’t difficult to found that although crosslinked CMC hydrogel can be prepared by radiation method, the rate of radiation degradation of CMC is faster than that of radiation crosslinking due to the character of CMC itself. (\( p_o \) is more than \( q_o \)). \( G(x) \) increase, both \( M_c \) and \( R_g \) decrease in the presence of \( N_2 \) or \( N_2O \), which also manifest further that the crosslinking reaction of CMC is promoted by \( N_2 \) or \( N_2O \).
TABLE I. SOME IMPORTANT VALUES RELATED TO CMC HYDROGEL

<table>
<thead>
<tr>
<th></th>
<th>p_o ×10^5</th>
<th>q_o ×10^5</th>
<th>M_c ×10^-5</th>
<th>G(x)</th>
<th>R_g (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in air</td>
<td>6.91</td>
<td>4.84</td>
<td>1.03</td>
<td>0.93</td>
<td>27.3</td>
</tr>
<tr>
<td>in N_2</td>
<td>7.14</td>
<td>5.41</td>
<td>0.92</td>
<td>1.04</td>
<td>20.6</td>
</tr>
<tr>
<td>in N_2O</td>
<td>8.84</td>
<td>6.88</td>
<td>0.73</td>
<td>1.32</td>
<td>15.4</td>
</tr>
</tbody>
</table>

p_o is the ratio of main chain scissions per unit dose to chain units; q_o is the proportion of chain units crosslinked per unit dose; M_c is number average molecular weight of network; G(x) is radiation yield of crosslinking; and R_g is gelation dose.

3.2 Swelling behavior of CMC hydrogel

In this work, swelling dynamics of CMC hydrogel and effect of some inorganic salt such as NaCl, CaCl_2 on the swelling behavior of CMC hydrogel is shown in Fig.2.

**FIG.1. The change of gel fraction of CMC hydrogel with dose.**
25% CMC solution, 3.15Gy/s, A: in air, B: in N_2, C: in N_2O

**FIG.2.** A: The change of swelling ratio of CMC hydrogel in distilled water with the time
B: Effect of the content of NaCl on swelling behavior of CMC hydrogel, swelling time: 24h
C: Effect of the content of CaCl_2 on swelling behavior of CMC hydrogel, swelling time: 24h
25% CMC solution, 50kGy, 3.15Gy/s, in N_2, swelling temperature: 40°C
It can be found that the swelling rate of CMC hydrogel is very big at the beginning, after 12h, the swelling is basically to equilibrium (curve A). At the following experiment on swelling behavior at different conditions, 24h are used as a swelling time. Inorganic salt has an obvious influence on the swelling of CMC hydrogel, and inorganic salt with higher valence (such as Ca\(^{2+}\)) has a bigger influence on the swelling of CMC hydrogel than that with lower valence (Na\(^{+}\)) (curve B and C).

Effect of pH value of the solution and temperature on the swelling of CMC hydrogel is shown in Fig. 3. The optimum pH for swelling of CMC hydrogel is about 7. When pH is bigger than 8 or smaller than 5, the swelling of CMC hydrogel decreases obviously (curve B). The swelling ratio of CMC hydrogel also increases with the increasing of temperature (curve A). Because of no toxicity and good biocompatibility of natural polymer,\(^2\) CMC based hydrogel will have wide application in biomedical materials.

![FIG.3. A: Effect of temperature on swelling behavior of CMC hydrogel in distilled water B: Effect of pH on swelling behavior of CMC hydrogel, swelling temperature: 40°C 25% CMC solution, 50kGy, 3.15Gy/s, in N\(_2\), swelling time: 24h](image)

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RADIATION PROCESSING OF STIMULI-RESPONSIVE HYDROGELS AND MEMBRANES BASED ON VINYL ETHERS

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Abstract

Different stimuli-responsive hydrogels and membranes were synthesized using gamma-radiation. The synthesis regularities as well as some possible applications of these polymers in different areas are considered.

1. INTRODUCTION

Stimuli-responsive polymers that exhibit transitions in response to changes in pH, temperature, presence of different substances in solution have been considered as candidate materials for development of controlled release systems, selective membranes and sorbents.

Vinyl ethers of glycols and monoethanolamine are perspective monomers for synthesis of various kinds of stimuli-responsive water-soluble and water-swelling polymers by radiation polymerization [1-3].

\[
\begin{align*}
\text{VEEG} & \quad \text{VBE} & \quad \text{VEMEA} \\
\text{CH}_2=\text{CH} & \quad \text{CH}_2=\text{CH} & \quad \text{CH}_2=\text{CH} \\
\quad \text{(CH}_2\text{)}_2 & \quad \quad \text{O} & \quad \quad \text{O} \\
\quad \quad \text{OH} & \quad \quad \text{CH}_2 & \quad \quad \text{CH}_2 \\
\quad \quad \quad \text{CH}_2 & \quad \quad \quad \text{CH}_3 & \quad \quad \quad \text{NH}_2
\end{align*}
\]

In the present work we have developed the methodology for radiation processing of stimuli-responsive hydrogels and membranes based on vinyl ethers.

2. EXPERIMENTAL PART

The \(\gamma\)-irradiation polymerization was conducted using the facility \(^{60}\text{Co} \) “MPX-gamma-25M” at an irradiation dose rate 1 Gy/s. The synthesized linear polymers were purified by three-fold precipitation and dried in a vacuum dessicator at 30 °C until constant weight was achieved. The composition of terpolymers was determined by using elemental analysis and potentiometric titration.

Hydrogels were synthesized by three-dimensional polymerization in the presence of divinyl ether of ethyleneglycol as cross-linking agent. After synthesis they were cut into cylinders and placed into distilled water, washed periodically by replacement of the distilled water during 2-3 weeks.
The films were prepared by casting the aqueous solution of interpolymer complexes (IPC) on the polyethylene surface and drying them on air. The \( \gamma \)-irradiation treatment of dry IPC films was carried out with the help of \(^{60}\)Co "MRX-gamma -25M".

The equilibrium swelling degree of hydrogels and IPC films was calculated according to the formulae: \( \alpha = (m - m_0)/m_0 \), where \( m_0 \) is the weight of dry film and \( m \) is the weight of swollen film.

3. RESULTS AND DISCUSSION

3.1. Hybrid pH- and thermo-sensitive linear and cross-linked polymers

Hybrid polymers which simultaneously sensitive to both temperature and pH are of great interest for development of novel drug delivery systems and materials for biotechnology.

Earlier it was shown that copolymers of vinyl butyl ether (VBE) with vinyl ether of ethyleneglycol (VEEG) possess thermo-sensitivity [3]. In order to obtain the polymers which simultaneously sensitive to pH and temperature we introduced ionic groups into the structure of the thermosensitive polymers.

Novel hybrid pH- and thermosensitive linear terpolymers and hydrogels were synthesized by \( \gamma \)-irradiation terpolymerization of hydrophilic VEEG, hydrophobic vinyl butyl ether (VBE) and anionic acrylic acid (AA) or cationic VEMEA. The general regularities of terpolymerization have been studied. Linear terpolymers VEEG-VBE-AA and VEEG-VBE-VEMEA possess lower critical solution temperature (LCST) in aqueous solutions. The LCST of terpolymers strongly depends on pH and ionic strength of the solution, because of the decrease of the charge density for the former polymer and its increase for the later one. An increase of pH decreases the LCST for VEEG-VBE-VEMEA and increases for VEEG-VBE-AA. An increase of ionic strength of solution considerably decreases LCST in both cases due to the deterioration of the solvent quality. Terpolymers, which contain higher amounts of hydrophobic VBE groups are characterized by lower values of LCST.

The swelling behavior of prepared networks has been studied in dependence of temperature at different pH and ionic strength values of solutions. Fig.1 shows the dependence of equilibrium swelling degree of VEEG-VBE-AA hydrogels on pH.

\[ \text{FIG. 1. Dependence of equilibrium swelling degree of VEEG-VBE-AA hydrogels on pH (} \mu =0.1 \).} \]

\[ [\text{AA}]=17 \text{ mol} \% , [\text{VEEG}]:[\text{VBE}]=63:15 (1), 58:20 (2), 53:25 \text{ mol} \% (3). [\text{Cross-linking agent}]=5 \text{ mol} \% \]
An increase of VBE content in hydrogel shifts the inflection point to the higher pH region because of the additional contribution of hydrophobic VBE groups to the stabilization of compact conformation of hydrogels.

For terpolymer hydrogels VEEG-VBE-AA the complex swelling behavior in response to temperature increase was detected. It includes the swelling, shrinking and reswelling with increase of temperature. The qualitative model that predicts the existence of structural inhomogeneity (hydrophobic and hydrophilic domens) in hydrogels owing to the different reactivities of monomers has been developed [4]. It was shown that the heterogeneity of the synthesized hydrogels can be varied by changing the synthesis conditions. The highly heterogeneous gels show the ability of volume oscillating behavior upon the temperature increase.

3.1. Interpenetrating networks

Interpenetrating networks (IPN) were prepared by γ-irradiation of thermosensitive network VEEG-VBE swollen in the mixture of acrylic acid and cross-linking agent. It was found that the equilibrium swelling degree of the IPN depends on concentration of cross-linking agent, swelling degree of initial VEEG-VBE gel, content of water in feed mixture and irradiation dose. The swelling degree of IPN is higher than the swelling degree of pure gel VEEG-VBE because of the additional contribution of electrostatic component AA to the common swelling pressure of hydrogels. Due to the presence of AA the IPN are simultaneously sensitive to both pH and temperature. The pH interval of phase transition for IPN can be regulated by varying the VEEG-VBE composition and PAA content.

3.2. Cationic and amphoteric hydrogels

Cationic and amphoteric hydrogels were synthesized by γ-irradiation copolymerization of VEMEA with VEEG as well as with sodium acrylate in the presence of crosslinking agent. The general regularities of copolymerization have been studied. In both cases the increase of VEMEA content in the feed mixture leads to a decrease of gel-fraction yield and increase of sol-fraction yield. The observed phenomena are due to the less activity of VEMEA in comparison with VEEG and sodium acrylate.

The influence of water on the kinetics of three-dimensional copolymerization of VEMEA with VEEG has been studied. It was found that the dilution of the feed mixture leads to the anomalous acceleration of polymerization with increase of gel-fraction and cross-linking density and decrease of equilibrium swelling degree in water.

The influence of pH and ionic strength of solution on the swelling behavior of cationic and amphoteric hydrogels was studied. It was shown that for cationic hydrogels the decrease of pH is accompanied by increase of equilibrium swelling degree.

Polyampholyte hydrogels are characterized by dependence of swelling properties on pH with minimum in isoelectric point. It was shown that at isoelectric point the increase of ionic strength slightly increases the swelling degree of the gels.

We have studied the complex formation of VEMEA-VEEG hydrogels with cooper ions (Fig.2).

It is seen that in the first stage the hydrogel undergoes contraction, then it starts to swell again. The similar “reversive” swelling behavior was found earlier by Tanaka, et al. [5]. The same gel, which was immersed into KCl solution, undergoes contraction because of the decrease of thermodynamic quality of the solvent indicating the absence of complexation.

Thus, the synthesized cationic and amphoteric hydrogels can be successfully used as sorbents for sorption of transition metals.
FIG. 2. Swelling of VEMEA-VEEG hydrogels in CuCl$_2$ (1) and KCl (2) solutions. [VEMEA]:[VEEG] = 13:87 mol. %. [Salts]=0.05 mol/L.

3.3. Membranes based on interpolymer complexes

Interpolymer complexes and blends of polycarboxylic acids with hydroxyl-containing non-ionic polymers due to their valuable physicochemical properties are perspective for development of different hydrophilic film composite materials.

Earlier it was shown that polymers of vinyl ethers of glycols are able to form interpolymer complexes stabilized by hydrogen bonds with polycarboxylic acids in aqueous and organic solutions [6-8].

In the present work the hydrophilic films were prepared from mixtures of polyvinyl ether of ethyleneglycol (PVEEG) and polyacrylic acid (PAA). The films are clear and elastic materials. The solubility of the films in aqueous solutions with different pH has been studied. It was shown that the films are insoluble at pH < 2.4 due to the formation of interpolymer complexes stabilized by hydrogen bonds.

Hydrogel membranes were obtained by $\gamma$-irradiation treatment of solid interpolymer complexes of PAA and PVEEG. The swelling behavior of the synthesized membranes has been studied in water, ethanol and their mixtures. It was shown that an increase of irradiation dose considerably decreases the equilibrium swelling degree of composite membranes in water. The maximal swelling of cross-linked IPC films is realized in water-ethanol mixture (1:1) due to the simultaneous solvation of hydrophilic groups of the polymer by water and organophilic ones by ethanol. The cross-linked composite films possess typical polyelectrolyte hydrogels properties such as pH- and ionic strength responsive swelling behavior.

4. CONCLUSIONS

The synthesized stimuli-responsive hydrogels and membranes are very perspective for application in medicine, biotechnology, sorption and separation technologies.

ACKNOWLEDGEMENTS

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Invited Paper

INDUSTRIAL PLANT FOR ELECTRON BEAM FLUE GAS TREATMENT

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Abstract

The electron beam flue gas treatment technology after in pilot plant scale came into industrial applications. Industrial installation is under operation at Chengdu Electric Power Station in China another is under construction in EPS Nagoya in Japan. The Polish industrial installation is examined for continuous operation. In the paper Polish experiences in design and construction of EB plants is presented.

1. INTRODUCTION

The electron beam flue gas treatment technology was invented many years ago [1]. Research on the process has been carried out in Japan [2], USA [3], Germany [4] and Poland [5]. However, the recent findings, based on the experiments performed at pilot plant at Electric Power Station Kawęczyn, led to developments that made the process mature just at the dawn of the 21st century [6]. The process is being implemented in full industrial scale at Electric Power Station Pomorzany (Dolna Odra EPS Group) [7]. Other developments are reported in Japan and, after Nagoya’s pilot plant experiments [8], an industrial plant has been built in China and another one is constructed in Japan [9]. There are remarkable differences in technological and design solutions applied in all these installations. The developments achieved at EPS Kawęczyn pilot plant [10] and the INCT laboratory unit [11] were the basis for the project realized at EPS Pomorzany.

2. PILOT PLANT AT ELECTRIC POWER STATION KAWĘCZYN

The pilot plant with a capacity of 25 000 Nm³/h was constructed at the Electric Power Station Kawęczyn. It was installed on a bypass of the main flue gas stream from boiler WP-120. Two accelerators ELV-3a (50 kW, 700 keV) were installed in series on a reaction vessel. For the first time in an industrial pilot installation, cascade double gas irradiation was applied [5, 10, 12, 13, 14].

The flue gases are cooled in a spray cooler working with „dry-bottom” conditions and then irradiated in two steps in the reaction vessel being a cylinder 7 m long and 1.6 m in diameter. The double titanium window system was employed. An „air curtain” was used to separate the secondary window from corrosive flue gas. Gaseous ammonia is injected by nozzles upstream of flue gas irradiation. Aerosol particles formed in the process are small with a diameter less than 1 micron and sticky. Three types of filters were tested — bag filter, gravel bed filter [15, 16] and electrostatic precipitator. Electrostatic precipitator constructed by ELWO SA Pszczyna factory presented its good performance in the process.

The pilot plant is equipped with a modern monitoring and control system [17, 18]. Manual sample grab methods were also used for results verification [19].

The fact that NOₓ removal efficiency depends mostly on dose and inlet NOₓ concentrations, SO₂ is mostly removed via thermal reaction which imposes interesting observations concerning ammonia consumption in both reactions.

Therefore, high enthalpy water and steam were used for flue gas conditioning. The humidity of flue gases can be increased to 15% vol. and the gas inlet temperature reduced to 55-60°C. At the conditions SO₂ removal efficiency as high as 98% can be achieved. Due to a thermal reaction very low dose is required to obtain high removal efficiency. In the case when moderate NOₓ removal efficiency is
required the economical competitiveness of eb process with conventional technologies increases further (Fig. 1).

![FIG. 1. Dose dependence on SO₂ and NOₓ removal efficiency.](image)

Additional energy consumption for NOₓ removal can be achieved by a scavenger application [20].

The most important problem to be solved in process upscaling is irradiation vessel construction. In the Kawęczyn’s pilot plant longitudinal, double irradiation of the flue gases has been applied. Further optimization can be achieved by adequate dose distribution between irradiation stages [21].

3. BYPRODUCT APPLICATION

Average composition of byproduct obtained during e-b purification of flue gases is: (NH₄)₂SO₄ - 95%, NH₄NO₃ - 5%. In principle the byproduct with small fly ash content (less then 2%) is equivalent to commercial fertilizer - ammonium sulfate.

Another possibility is to use byproduct as a component of NPK fertilizer. A test performed in Poland has proven that a blend obtained with the application of the byproduct meets the standards established for this kind of fertilizers.

Agriculture tests have been performed for pure byproduct and byproduct with different fly-ash content. Results are very positive [22].

The content of heavy metals is much lower than the values allowable for commercial fertilizers.

4. INDUSTRIAL PROJECT IN POLAND

The experience gathered during laboratory and pilot plant tests has allowed for the preparation of the fullscale industrial plant design.

The electron dry scrubbing process is will be employed at the Pomorzany Electric Power Station - Szczecin in Poland for the simultaneous removal of SO₂ and NOₓ from flue gases emitted by Benson boilers [23].

After a detailed analysis it was decided to design and construct the electron-beam installation treating a maximum 270 000 Nm³/h flow of flue gas.
High concentration of NOx and relatively low content of SO2 in flue gas emitted from Benson boilers establish the specific conditions for flue gas treatment. The parameters of e-b process are chosen so as to guarantee efficiency of removal of NOx up to 80% and of up 70% SO2 in continuous operation of the installation. For intermittent operation up to 80% removal of NOx and 90% reduction of SO2 are expected.

The conceptual system arrangement is shown in Fig. 2.

![Process flow diagram of EB installation at the EPS Pomorzany, Szczecin.](image)

**FIG. 2. Process flow diagram of EB installation at the EPS Pomorzany, Szczecin.**

5. VOLATILE ORGANIC COMPOUNDS (VOCS) REMOVAL

Combustion of fossil fuel is one of the largest sources of volatile organic compounds emission also. Emitted VOCs belong to aliphatic hydrocarbons, aldehydes, chlorinated hydrocarbons, aromatic hydrocarbons and the most dangerous polyaromatic hydrocarbons (PAHs) groups. Many of them are involved in the formation of photochemical smog as well as depletion of stratospheric ozone. In addition some of them are toxic and carcinogenic. These compounds are emitted from combustion process with various concentrations, ranged from few ppm up to hundreds ppm, the volume of emission depends on process conditions and kind of used fuels simultaneously [24].

The pilot plant tests for influence of electron beam on the chosen polyaromatic hydrocarbons during simultaneous SO2 and NOx removal has been carried out at EPS Kawęczyn. Concentration of 5 polyaromatic hydrocarbons have been measured before and behind of the irradiation chamber. After filtration, the sample gas have passed through the adsorbants (activated coal and XAD- 2resin) PAHs trapped on the adsorbant material have been extracted by solvents and analysed by GC/MS technique. The experimental work has been carried out in 2 series: in the both of irradiation dose was 7 kGy, in series 2 ammonia was injected into combustion gases. The removal efficiencies obtained in the pilot plant test are presented in Fig. 3 in the case of ammonia presence higher removal efficiencies for all PAHs are observed. Simultaneously high removal efficiencies of SO2 (89%) and NOx (72%) were obtained [20].
FIG. 3. Removal efficiencies of PAHs from flue gas by electron beam irradiation at pilot plant at EPS Kawęczyn. The experimental conditions: gas flow – 10 000 m³/h, gas humidity – 6.5% (V), D – 7 kGy, \( \alpha_{\text{NH}_3} = 0.83 \).

6. CONCLUSIONS

The tests performed in the laboratory installations and the pilot plant resulted in the preparation of the industrial plant design. All the technical and economical analyses prove the advantages of this technology over present day conventional technologies. The pilot plant test for polyaromatic hydrocarbons suggests that electron beam treatment is promising technology for emission control of organic compounds as well.

ACKNOWLEDGMENT

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REFERENCES


ELECTRON BEAM PURIFICATION OF FLUE GAS WITH HIGH CONCENTRATION OF SULFUR DIOXIDE

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Abstract

In order to apply the electron beam purification method to the flue gas containing high concentrations of SO2, a basic study was done with a simulated flue gas containing 4800 ppm of SO2. Removal efficiencies of SO2 and NOx were satisfactorily achieved to reach 97 and 88%, respectively, at 70°C with the dose of 10.3 kGy without any NH3 leakage. The higher concentrations of SO2, H2O, and added NH3 were found to be effective to oxidize NO to form NO2 and to oxidize SO2 to form SO3 in the process. The results obtained by the study clearly show that the electron beam processing will have high potential for the treatment of the flue gas containing a high concentration of SO2 such as that of the Bulgarian plant being constructed now.

1. INTRODUCTION

Damages of forests and human health originating from acid rain by sulfur oxide (SO2) and nitrogen oxides (NOx) cause a serious problem in the world. Emission of pollutants to the environment is increasing with increase of energy used in the society. Energy is produced in large amounts by firing oil or coal at thermal power stations, where the pollutants may be released from the flue gas. A conventional method for removing SO2 and NOx from the flue gas was almost established technologically and applied to thermal power stations. In this method a wet system is used for SO2 removal. This system is complicated and the wastewater must be purified in another facility. Furthermore, although NOx is treated with a catalyst, the catalyst is very expensive and must be changed periodically.

In order to avoid these defects, a noble method of removing SO2 and NOx from the flue gas by electron beam irradiation was proposed, and a fundamental research on the method was started in 1970’s under a joint programme of Japan Atomic Energy Research Institute (JAERI) and Ebara Corporation. The research made clear that the method was sophisticated and very promising to applying for practical use [1]. Various efforts have been made later for the development of the technology [2,3]. At a large scale, a plant has been operating since 1997 in China [4] and three plants are being constructed in Poland [5], Japan [6] and Bulgaria. The main performances of the plants are shown on Table I.

<table>
<thead>
<tr>
<th>Place</th>
<th>Scale</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nishi-Nagoya Thermal Station (Japan)</td>
<td>620,000 m³/h, Oil (1,500 ppm SO2)</td>
<td>2001 (Scheduled)</td>
</tr>
<tr>
<td>Chengdo Thermal Power Station (China)</td>
<td>300,000 m³/h, Coal (1,800 ppm SO2)</td>
<td>From 1997</td>
</tr>
<tr>
<td>Pomorzany Thermal Power Station (Poland)</td>
<td>270,000 m³/h, Coal (400 ppm SO2)</td>
<td>2000 (Scheduled)</td>
</tr>
<tr>
<td>Maritsa-East Thermal Power Station (Bulgaria)</td>
<td>10,000 m³/h, Coal (5,000 ppm SO2)</td>
<td>2000 (Scheduled)</td>
</tr>
</tbody>
</table>

Value is presented in NPT.
The flue gases released from three plants except the Bulgarian plant contain the concentrations of SO₂ less than 1800 ppm. Also, some fundamental studies on the plants have been done [4-6].

This paper presents a fundamental study for applying to the flue gas containing high concentration of 4800 ppm SO₂ to be released from the Bulgarian plant.

2. EXPERIMENTS AND RESULTS

The compositions of simulated flue gas used in this work was 4800 ppm SO₂, 320 ppm NO, 12% CO₂, 7.5% O₂, 80% N₂, and 22% H₂O. The gas is almost the same as that obtained from the Bulgarian plant where lignite coal is burned. After the addition of NH₃, simulated flue gas was irradiated at 70°C with an electron beam (1.5 MeV, 2.3 mA) from a Cockcroft-Walton type electron accelerator. The concentrations of NH₃ added were 6900-9000 ppm, which correspond to 0.7-0.91 NH₃ stoichiometry, where NH₃ stoichiometry is defined by the initial concentration of NH₃, SO₂ and NOₓ, namely, \([\text{NH}_3]/(2[\text{SO}_2]+[\text{NO}_x])\). By-products produced by electron beam irradiation were collected by the electrostatic precipitator. Experiments were carried out using a flow system with simulated flue gas with the flow rate of 0.9 m³h⁻¹. The flow diagram of experimental apparatus is shown in Fig. 1.

![Flow diagram of experimental apparatus.](image)

Fig. 2 shows the experimental results of the dose dependence of SO₂ and NOₓ removals and NH₃ leakage at 70°C, together with the results by coal-fired flue gas (800 ppm SO₂) used at Nagoya Pilot Plant [3].

![Dose dependence of NOx and SO2 removals and NH3 leakage at 70°C.](image)
Open marks above shows values obtained in the condition of 0.86 NH₃ Stoichiometry and closed ones in the condition of 0.9 NH₃ stoichiometry.

Removal rates of NOₓ increased with increasing dose, and reached 88% at 10.3 kGy irradiation. Conversely, removal rates of SO₂ were almost saturated (>97%) at each dose higher than 2.5 kGy, while the rates without irradiation were less than 58%. In spite of containing higher SO₂ and NOₓ concentrations, the removal rates of SO₂ and NOₓ were higher than in coal-fired flue gas. Although the removal rates of SO₂ and NOₓ were almost independent to the amount of ammonia added, the amount of leaked ammonia was strongly affected by inlet concentration of ammonia. At 0.86 NH₃ stoichiometry, almost no leakage of ammonia was detected; however, at 0.9 NH₃ stoichiometry, rather large amount of NH₃ leakage was observed.

Furthermore, the mechanism on removal of SO₂ and NOₓ by electron beam irradiation of the simulated flue gas was discussed [7] from “radical” reactions and their branching ratios related to the removal of SO₂ and NO in the flue gas. Fig. 3 shows the main reaction pathways to remove SO₂ and NOₓ. Dotted lines indicate “thermal” reactions. Oxidizing processes of SO₂ and NO to form (NH₄)₂SO₄ and NH₄NO₃ through H₂SO₄ and HNO₃ are most important pathways to produce by-product.
Based on these studies, a pilot plant for treating the flue gas containing a high concentration of \( \text{SO}_2 \) is under construction in Bulgaria and the test will begin in 2000.

3. CONCLUSION

The basic study on removal of \( \text{SO}_2 \) and \( \text{NO}_x \) was carried out by electron beam irradiation of the simulated flue gas in order to evaluate the applicability of the process to the flue gas containing high concentrations of \( \text{SO}_2 \). Removal efficiencies of \( \text{SO}_2 \) and \( \text{NO}_x \) were 97% and 88% at 70°C, respectively, with a dose of 10.3 kGy without \( \text{NH}_3 \) leakage. The high removal efficiencies of \( \text{SO}_2 \) and \( \text{NO}_x \) were due to the effective radical reactions of \( \text{OH} \) and \( \text{HO}_2 \) to the oxidization of \( \text{SO}_2 \) and \( \text{NO} \) to \( \text{SO}_3 \) and \( \text{NO}_2 \), respectively. The reducing reactions of \( \text{NO}_x \) to produce \( \text{N}_2 \) and \( \text{N}_2\text{O} \) with \( \text{N} \) and \( \text{NH}_2 \) radicals also contributed to high removal efficiency of \( \text{NO}_x \) in the flue gas. The by-product was determined to be the mixture of \( (\text{NH}_4)_2\text{SO}_4 \) and \( \text{NH}_4\text{NO}_3 \) containing a small amount of \( \text{H}_2\text{SO}_4 \). The acid could be neutralized by ammonia, with engineering modification, in a large scale plant. The results obtained by the studies clearly show that the electron beam processing will have high potential for the treatment of such flue gas containing high concentrations of \( \text{SO}_2 \) that Maritsa-East Thermal Power Station in Bulgaria releases.

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Invited Paper

ELECTRON BEAM TREATMENT OF TEXTILE DYEING WASTEWATER

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Abstract

A pilot plant with e-beam for treating 1,000 m³/day of dyeing wastewater were constructed and started in operation from 1998, together with the biological treatment facility. The wastewater from various stages of the existing purification process can be treated with electron beam in this plant, and it will give rise to elaborate the optimal technology of the electron beam treatment of wastewater with increased reliability at instant changes in the composition of wastewater. Installation of the e-beam treatment results in decolorizing and destructive oxidation of organic impurities in wastewater, appreciable to reduction of chemical reagent consumption, in reduction of the treatment time, and in increase in flow rate limit of existing facilities by 30-40%. Commercial plants for treating over 10,000 m³/day each, based upon this pilot experimental result, will start in construction from 2001 by the support of IAEA and Korean Government.

1. INTRODUCTION

The treatment of municipal and industrial wastewater becomes a more important subject in the field of environment engineering. The treatment of the industrial wastewater containing refractory pollutant with electron beam is actively studied in Samsung Heavy Industries (SHI). Electron beam treatment of wastewater often leads to their purification from various pollutants. It is caused by the decomposition of pollutants as a result of their reactions with highly reactive species formed from water radiolysis (hydrated electron, OH free radical and H atom). Sometimes such reactions are accompanied by the other processes, and the synergistic effect upon the use of combined methods such as electron beam with biological treatment, electron beam and adsorption and others improves the effect of electron beam treatment of the wastewater purification.

In the Central Research Institute of Samsung Heavy Industries, many industrial wastewater including wastewater from papermill, dyeing complex, petrochemical processes, etc. are under investigation with electron beam irradiation. For the study of treating dyeing wastewater combined with conventional facilities, an electron beam pilot plant for treating 1,000 m³/day of wastewater from 78,000 m³/day of total dyeing wastewater has constructed together with Korea Dyeing Technology Center (DyeTech) and operated in Taegu Dyeing Industrial Complex (TDIC).

2. WASTEWATER FROM TDIC

Taegu Dyeing Industrial Complex (TDIC) includes about hundred factories occupying the area of 600,000 m² with 13,000 employees in total. A majority of the factories has equipment used for dip dyeing, printing, and yarn dyeing. The production requires high consumption of water (90,000 m³/day), steam, and electric power, being characterized by large amount of highly colored industrial wastewater. Therefore, intensive and effective purification of the wastewater is one of the most complicated and actual problems of TDIC’s current activities.
Purification of the wastewater is performed by union wastewater treatment facilities in Fig.1 using conventional methods (chemical treatment and 2 steps of biological treatment). Current facility treats up to 80,000 m³ of wastewater per day, extracting thereby up to 750 m³ of sludge. Rather high cost of purification results from high contamination of water with various dyes and ultra-dispersed solids.

3. LABORATORY-SCALE FEASIBILITY STUDY

Because of increase in productivity of factories and increased assortment of dyes and other chemicals, substantial necessity appears in re-equipment of purification facilities by application of efficient methods of wastewater treatment. The existing purification system is close to its limit ability in treatment of incoming wastewater.

The studies have been carried out regarding the possibility of electron beam application for purification of wastewater. With the co-works of SHI Central research Institute, DyeTech and IPC, the experiments on irradiation of model dye solutions and real wastewater samples (from various stages of current treatment process) have been performed.

**FIG. 1. Wastewater treatment facility in Taegu Dyeing Industries Complex.**
TABLE I. TYPICAL CHARACTERISTICS OF WASTEWATER

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>BOD₅ (mg/l)</th>
<th>CODₘₙ (mg/l)</th>
<th>Suspended (mg/l)</th>
<th>Color units (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td>12</td>
<td>2,000</td>
<td>900</td>
<td>100</td>
<td>1,000</td>
</tr>
<tr>
<td>After chemical treat</td>
<td>6.8-7.5</td>
<td>1,700</td>
<td>450</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>After 1st Bio-treat</td>
<td>7.0-8.0</td>
<td>1,300</td>
<td>250</td>
<td>50</td>
<td>400</td>
</tr>
<tr>
<td>After 2nd Bio-treat</td>
<td>7.0-8.0</td>
<td>30</td>
<td>60</td>
<td>50</td>
<td>250</td>
</tr>
</tbody>
</table>

The results of laboratory investigations of representative sets of samples showed the application of electron beam treatment of wastewater to be perspective for its purification (Fig. 2). The most significant improvements result in decolorizing and destructive oxidation of organic impurities in wastewater. Installation of the radiation treatment on the stage of chemical treatment or immediately before biological treatment may results in appreciable reduction of chemical reagent consumption, in reduction of the treatment time, and in increase in flow rate limit of existing facilities by 30-40%.

4. CONSTRUCTION AND OPERATION OF PILOT PLANT

A pilot plant for a large-scale test (flow rate of 1,000m³ per day) of wastewater has constructed and is now under operation with the electron accelerator of 1MeV, 40kW (Fig. 3). The size of extraction window is 1500mm in width and Titanium foil is used for window material. The accelerator was installed in Feb. 1998 and the technical lines are finished in May. For the uniform irradiation of water, nozzle type injector with the width of 1500mm was introduced. The wastewater is injected under the e-beam irradiation area through the injector to obtain the adequate penetration depth. The speed of injection could be varied upon the dose and dose rate. Once the wastewater has passed under the irradiation area, then directly into the biological treatment system. The Tower Style Biological treatment facility (TSB), which could treat up to 1,000m³ per day, was also installed in October 1998. TSB is composed of an equalizer, a neutralizer, and 6 steps of contact aeration media. The aeration basins are filled with floating or fixed bio-media to increase the contact area and removal efficiency.

![FIG.2. Combined effect of e-beam and biological treatment.](image-url)
5. RESULTS AND DISCUSSION

Pilot plant inlet flow is a mixture of two flows: raw wastewater from dyeing process and wastewater from polyester fiber production enriched with Terephthalic acid (TPA) and Ethylene glycol (EG); relative flow rate of the latter being 6-8% of total inlet flow rate. TPA concentration of influent is about $2 \times 10^{-2}$ mol/l that is much higher than total concentration of all other dissolved pollutants. This concentration corresponds to electron fraction of TPA about 0.2% that makes direct action of radiation on TPA (or other pollutant) be negligible when treating the wastewater by electron beam. On the other hand, this concentration is high enough to prevent recombination of radical products of water radiolysis in the bulk of solution, taking into account high rate constants of reactions of both reducing (hydrated electrons, hydrogen atoms) and oxidizing (hydroxyl radicals) particles with terephtalate anion:

$$
e^{-}_{aq} + 1,4-C_{6}H_{4}(COO)^{-}_{2} \rightarrow R^{1} \quad k = 7.3 \times 10^{9} \text{ mol}^{-1} \text{ s}^{-1}
$$

$$
H + 1,4-C_{6}H_{4}(COO)^{-}_{2} \rightarrow R^{2} \quad k \equiv 1 \times 10^{9} \text{ mol}^{-1} \text{ s}^{-1}
$$

$$
OH + 1,4-C_{6}H_{4}(COO)^{-}_{2} \rightarrow R^{3} \quad k = 3.3 \times 10^{9} \text{ mol}^{-1} \text{ s}^{-1}
$$

Besides, because of high relative concentration of TPA comparing to other polluting compounds, competition between listed reactions and reactions of radical products from water with other compounds appears to be much in favor of the former ones. It follows from above mentioned that the main (if not the only) result of electron-beam treatment of pilot plant influent would be radiolytical transformations of TPA which can improve its removal by biological treatment. Radiolytical transformations of other initially present compounds, if those take place at all, can proceed via radical or molecular products from TPA.

FIG. 3. Schematic diagram of pilot plant with e-beam.

FIG. 4. Electron accelerator and wastewater under injection.
Figure 4 shows that TPA enriched wastewater can be efficiently purified by biological treatment. However, preliminary electron-beam treatment improves the process, resulting in more significant decreasing TOC, CODCr, and BOD5. As concerns changes in TOC, CODCr, and BOD5 during biological treatment, from the data presented in Fig. 5 it follows that preliminary electron-beam treatment make it possible to reduce bio-treatment time twice at the same degree of removal. Coincident results were obtained in a separate set of experiments on the same pilot plant but with reduced wastewater flow rate (~130 l/day). In this case inlet flow was divided into two flows: the first one passed only biological treatment while the second one passed electron-beam treatment, then biological treatment with reduced hydraulic retention time (HRT). Averaged for one month’s period decrease in TOC values amounted 72%, for the first flow (48h HRT biotreatment), and 78%, for the second flow (1 kGy electron-beam treatment followed by 24 h HRT biotreatment).

Usually, increase in biodegradability after radiation treatment of aqueous-organic systems is due to radiolytical conversions of non-biodegradable compounds. In present experiments the improvement of biological treatment of wastewater after preliminary electron-beam treatment was found to be caused by radiolytical transformations of biodegradable compound. Electron-beam treatment should not appreciably affect total biodegradability of pollutants if the main pollutant is biodegradable, but can improve biodegradation process at initial stages. In other words, irradiation at comparatively low doses (several Greys) for this case does not change total amount of biodegradable substance characterized by BOD5, but convert part of it into easier digestible form. This is confirmed, also, by the data presented in Fig. 5 where one can see that decrease in TOC, CODCr, and BOD5 during biological treatment is close to linear one for non-irradiated wastewater, while for electron beam treated wastewater the decrease is faster at the beginning of biological treatment and decelerates during the process.

**FIG. 5. Effect of irradiation and biological treatment on wastewater parameters:**

- a-TOC; b-CODCr; c-CODMn; and d-BOD. 1- after EB treatment; 2- without EB treatment.
6. SUMMARY AND PLAN FOR FUTURE

(a) A pilot plant with electron beam for treating 1,000m³ per day of dyeing wastewater was constructed and has been operating continuously since October 1998.

(b) For industrial wastewater with high impurity levels such as dyeing wastewater, electron beam treatment combined with biological system shows the reduction of chemical reagent consumption, and also, retention time with the increase in removal efficiencies of CODₐ and BOD₅ up to 30–40%.

(c) On the basis of data obtained by the pilot plant, construction of actual plant that will treat 10,000m³ of dyeing wastewater per day started in January 2001, and finished by 2002.

This project is financially supported by the IAEA and the Korean Government, and will be open to scientists and engineers as a demonstration and training facility for commercialization of wastewater treatment with ionizing radiation.

ACKNOWLEDGEMENT

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Radiation processing of seawater for COD reduction

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Abstract

Radiation processing of seawater in the presence of ozone reduced COD and eliminated nitrite, which were contained in concentrations of 30 mg/L and 1 mg/L, respectively. 4-Chlorobenzoic acid and glucose were used as surrogates for COD. The goal of a residual COD < 5 mg/L together with nitrite elimination could be met only with a combined ozone/γ-irradiation treatment. Electron beam irradiation proceeds too fast for sufficient ozone introduction during irradiation. However, a dose requirement of 2 kGy together with an ozone demand between 90-120 mg/L is certainly much too high to consider a technical application.

1. INTRODUCTION

There is still an increasing market for marine aquaculture products all over the world. Accordingly intensive fish culture systems have been installed worldwide in order to satisfy the demand for these products. As a consequence of these activities a negative environmental impact was noticed that is already causing considerable concern for the international environmental protection agencies. The main input originates from fish feed which is partly released into the water as suspended organic solids or as dissolved matter from excess food, faeces and excretions [1]. Most of the dissolved substances are biodegradable. However, biodegradation in seawater often proceeds rather slowly. It likewise produces biomass, which would again burden the marine environment and impede a re-use of the treated water in a cycle process. Consequently there is an interest in residual free water purification technologies, e.g. Advanced Oxidation Technologies (AOPs).

AOPs are those that involve generation of the highly reactive hydroxy free radical OH as an intermediate, and its subsequent reaction with the targeted pollutant. Advanced oxidation is supposed to have the potential to mineralize organic pollutants. Such a complete mineralization would represent a single stage process without any residual to dispose of. In the present case of contaminated seawater from fish culture systems advanced oxidation could be considered for removal of dissolved organics and nitrite.

The simplest method to generate OH free radicals in water is its irradiation with ionizing radiation. However, along with the OH free radicals some reducing species are formed which often induce undesired side reactions [2] and may reduce, moreover, the economy of the irradiation process considerably [3]. Therefore, ozone is added to the water before or during irradiation, which often converts the “hybrid” irradiation process into an almost pure AOP [4]. Accordingly radiation processing of seawater with and without addition of ozone has been performed in order to elucidate the potential for COD and nitrite removal. Since experiments with original samples were not possible because of uncontrollable biodegradation of some organics during transportation, 4-chlorobenzoic acid and glucose were selected and used as surrogates for COD. Both components react very fast with OH free radicals but very slowly with molecular ozone.

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2. EXPERIMENTAL

4-Chlorobenzoic acid (Merck-Schuchardt) and glucose (Merck) were dissolved in various waters in concentrations corresponding to a COD of 30 mg/L. For experiments with seawater beside original seawater, synthetic seawater was also used. Its salt concentration is given in [1]. Tapwater used contained 268 mg/L bicarbonate, 44 mg/L nitrate, 51 mg/L chloride and 143 mg/L sulfate. Moreover, a so-called “chloride-free” seawater containing 142 mg/L bicarbonate, 67 mg/L bromide, 1 mg/L nitrite and 2 mg/L nitrate was prepared for the experiments with glucose as COD surrogate. COD measurements were performed with Merck Spectroquant COD cell test, in the experiments with 4-chlorobenzoic acid the u.v. absorption at 235 nm measured with a CARY 3C UV-visible spectrophotometer was used to determine the COD. Ozone was prepared from pure oxygen using a laboratory ozonizer (E. Sander Ltd., Germany). Ozone concentrations were determined routinely by measuring the u.v. absorption at 259 nm, calibrated against indigotrisulfonate method. Electron beam irradiations were performed with an ICT-accelerator (500 kV, 25mA) manufactured by High Voltage Eng., USA. Gamma irradiations were performed in an AECL Gammacell 220 at an average dose rate of 0.9 Gy/s.

3. RESULTS AND DISCUSSION

![FIG. 1. Decomposition of 4-chlorobenzoic acid (given as COD) in various waters by γ-irradiation.](image)

4-Chlorobenzoic acid and glucose which have been chosen as COD surrogates are rather different in chemical structure but similar in their reactivity to OH free radicals (the corresponding bimolecular rate constants are $5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $1.5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) as well as to molecular ozone ($1.2 \pm 0.2 \text{ M}^{-1}\text{s}^{-1}$ and $0.45 \pm 0.05 \text{ M}^{-1}\text{s}^{-1}$). Accordingly under the conditions given the reaction with molecular ozone can be neglected for both components.

Fig. 1 shows the COD reduction by means of γ-irradiation in various waters. The more pronounced COD reduction in tapwater was firstly attributed to the lack of bromide as compared with seawater. However, addition of analogous bromide quantities to tapwater did not result in the same COD reduction as was recorded with seawater. Most likely the high chloride concentration of the seawater acts like a shielding for the organics present in the water. Furthermore noticeable is the identical COD
reduction obtained in original and synthetic seawater. As a consequence all further experiments with seawater were performed with synthetic seawater.

The seawater to be polished usually contains about 30 mg/L COD together with 1 mg/L nitrite. The treatment goal is a COD reduction to < 5 mg/L together with an almost total nitrite elimination. The latter is not possible with just an irradiation treatment [2] in case the water contains nitrate. The seawater usually contains 2 mg/L nitrate. Therefore, the irradiation has to be performed in the presence of sufficient ozone in order to eliminate nitrite [3, 4].

Due to the results presented in Fig. 2 addition of ozone during irradiation resulted in a better COD reduction. It is noticeable that in these experiments doubling of the ozone supply did not have an effect on COD reduction. Accordingly a radiation dose of 2 kGy together with an ozone demand of about 90 mg/L reduces COD down to < 5 mg/L and eliminates nitrite. Using glucose instead of 4-chlorobenzoic acid gave similar results (see Fig. 3) However, in this case COD reduction increases with increasing ozone supply. More ozone (about 120 mg/L in combination with 2 kGy) was necessary to reach the treatment goal.

![Graph](image)

**FIG. 2.** Decomposition of 4-chlorobenzoic acid (given as COD) in various waters by a combined ozone/γ-irradiation treatment. Ozone added gaseously during irradiation: 10 L O₂/h-flow (○; %) and 20 L O₂/h-flow (●). Ozone concentration about 10 mg O₃/L O₂.

Please note: in the experiments with glucose, a “chloride free” seawater was used. The reason is the rather laborious work necessary for COD determination in the presence of high chloride concentrations. In neutral or weak alkaline aqueous solutions chlorides (and sulfates as well) virtually are inert for the radiation induced reactions in the system. It seems to be justified, therefore, to omit them in these experiments in order to make the COD determinations much less time consuming. However, there is a certain shielding effect at high chloride concentrations as described in Fig. 1. Accordingly these results cannot directly compared with the results obtained in seawater with 4-chlorobenzoic acid as COD surrogate.
FIG. 3. Decomposition of glucose (given as COD) in “chloride-free” seawater by various treatment processes as a function of radiation dose and ozone supply. Ozone added gaseously during irradiation. Ozone concentration between 10 and 24 mg O₃/L O₂.

FIG. 4. Decomposition of glucose (given as COD) in “chloride-free” seawater by various treatment processes.

The experiments with electron beam irradiation (Fig. 4) clearly indicated that γ irradiation in any case is more efficient and, moreover, that the short irradiation time of less than 1 second limited the maximum ozone concentration in water to about 33 mg/L. Under such conditions a COD<5 mg/L can never be realized.

If no radiation is applied ozone may react directly with glucose despite of the very low reaction rate constant. This is due to the high initial concentration of both glucose and ozone. Consequently
ozonation with 120 mg O$_3$/L applied in the pH range 7.7 up to 11 resulted in a COD of about 17 mg/L independent of the pH adjusted. This is less than a factor of 2 for COD reduction. The corresponding combined γ/ozone treatment resulted in a COD reduction by a factor of 6.

In conclusion, a treatment process based on a combined ozone/γ-irradiation (90-120 mg/L together with 2 kGy) would reduce the COD from 30 mg/L down to about 5 mg/L and would also eliminate the 1 mg/L nitrite. However, the treatment cost of such a process is most likely too high especially when large amounts of water have to be treated.

REFERENCES

THE IMPORTANCE OF RADIATION MICROBIOLOGY ON ENVIRONMENTAL AND HEALTH CARE APPLICATIONS

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Abstract

In certain application of radiation technology (radiation sterilization of health care products, radiation preservation of food, radiation treatment of waste water) the main objectives are to sterilize the products or to eliminate the pathogenic microorganisms. For the calculation of required dose we should obtain reliable information about the radiosensitivity of microorganisms. The sensitivity of microorganisms towards high energy radiation varies widely: different types, species and strains exhibit greatly different sensitivities. Certain environmental factors are also able to influence the actual radiation response. The basic principles of radiation damage, radiosensitivity of microorganisms and physical, chemical and biological dose modifying factors are reviewed in this paper.

1. RADIATION DAMAGE

The radiation induced inactivation of cells under a given test condition is a resultant effect of a series of complex physical, chemical and biological processes [1]. Traditionally, it has been a practice to consider two quite distinct mechanisms. These have been called direct and indirect actions. The alteration in the molecule occurring as a result of absorption of radiation is said to be due to the direct action. The target may be ionized or excited, initiating the chain events that lead to a biological change. On the other hand, when energy is absorbed in a certain molecule and transferred to a second molecule in which the chemical change takes place, it is called the indirect action.

Generally the damage to cells produced by ionizing radiation can be divided into three categories:

Lethal damage – is irreversible, irreparable, and by definition leads to cell death.

Sublethal damage – under normal circumstances can be repaired unless additional sublethal damage is added.

Potentially lethal damage – this component of radiation damage can be influenced by environmental condition (oxygen, temperature, chemicals, etc.)

Radiation action occurs over a broad timescale, which extends from the very early physical processes to the very late biological effects, such as mutagenesis. The earliest event is the physical stage, which occurs between $10^{-18}$-$10^{-12}$ second. The most important reaction of this stage is the ionization of water, which leads to the formation of radical ions.

The chemical stage occurs between $10^{-12}$-$10^{5}$ seconds. The most important parts of it are the different reactions between primary radicals and biochemical processes.

The timescale of biological stage can range from hours up to several years (mutagenesis, carcinogenesis).

2. THE RADIOSENSITIVITY OF MICRO-ORGANISMS

The relationship between dose and effect can be demonstrated by different kinds of survival curves. It is a common practice in the radiation biology to present results in the survival curves, where surviving
fractions of organisms plotted semilogarithmically against dose of radiation. Originally, three types of survival curves were described, namely exponential, sigmoidal and composite.

For the practical application of radiation effects, the $D_{10}$ value (decimal reducing dose) was introduced, which is the dose required to reduce the population by a factor of ten. The radiosensitivity of microorganisms is conventionally expressed in term of $D_{10}$ value.

The sensitivity of microorganisms towards high energy radiation varies widely: different types, species and strains exhibit greatly different sensitivities. Certain environmental factors are also able to influence the radiation response (temperature, oxygen, water, soluble chemical agents).

2.1. Viruses

In general it is accepted that viruses are more resistant than bacterial spores. Single-stranded simple viruses are more sensitive than double-stranded complex structures. Radiosensitivity of 30 viruses was studied by Sullivan, et al. The $D_{10}$ values of viruses suspended in Eagle’s minimum essential medium containing 2% foetal bovine serum ranged from 3.9 kGy to 5.3 kGy. Radiosensitivity was significantly affected by suspending media. At least threefold difference was noted when the $D_{10}$ values of the same virus suspended in distilled water and in Eagle’s MEM were compared. The fully dry viruses are more resistant; as hydration proceeds, radiosensitivity increases.

2.2. Bacteria

The bacteria show more complexity than viruses. From a series of radiation microbiology studies, it can be concluded [3]:

- Among the vegetative bacteria, Gram-negative organisms ($D_{10}$ ranging between 29 Gy-240 Gy) are more radiosensitive than the Gram-positive species ($D_{10}$ ranging between 180 Gy - 890 Gy).
- Bacterial spores are considerably more resistant than vegetative species. Some micrococci (Micrococcus radiophylus, Deinococcus radiodurans) can survive surprisingly high doses due to the effective reparation of DNA double strand breaks. The $D_{10}$ values of these bacteria can reach 10 kGy.
- The anaerobic spore formers like Clostridium ($D_{10}$ values ~ 2.2-3.4 kGy) are more radioresistant than aerobic Bacillus spores ($D_{10}$ ranging between 1.2 and 3.3 kGy). Besides the differences between the species, there are a number of factors concerned with the environmental conditions that can greatly influence actual radiosensitivity. The $D_{10}$ values of Salmonella typhimurium were significantly different, when the suspending medium was phosphate buffer ($D_{10} = 210$ Gy) or fish meat, where $D_{10}$ value reached the 1.74 kGy. The different supporting surfaces can also alter the radiosensitivity of bacteria.

2.3. Fungi

Most studies of the inactivation of fungi by irradiation have been made on asexual spores. Germinating spores, mycelia and other morphological structures of fungi might have different radiation responses. The radiation sensitivity of fungi is influenced not only by genetic factors but also by the number of cells in a spore (effect of multicellularity), the number of nuclei per cell (effect of multinuclearity). The haploid yeast cells are more sensitive than diploid ones (effect of ploidity). Ten species of fungi representing the genera Alternaria, Aspergillus, Cladosporium, Curvularia, Fusarium and Penicillium were examined by Saleh, et al. [4]. $D_{10}$ values of fungal conidia in water were for Aspergillus niger 420 Gy, for Cladosporium cladosporoides 300 Gy and for Curvularia geniculata 290 Gy. $D_{10}$ values for dematiaceous fungi (in agar medium!) ranged from 6 to 17 kGy and for moniliaceous fungi were less than 3 kGy. Yeasts appear to be about as sensitive as non-spore forming bacteria.

At present an immense quantity of data is available in the literature. Unfortunately, most of these data were obtained under different experimental conditions. Regarding the considerable influencing effect
of environmental condition to the actual radiosensitivity, to achieve a correct comparison is very difficult.

3. DOSE MODIFYING FACTORS

Radiosensitivity of microorganisms can be influenced by some factors other than genotype of species. The responses of cells to a given dose can be altered in different ways. This is possible because response depends on physical factors (quality of radiation, dose rate, temperature, etc.), on chemical factors (oxygen, water content, chemicals, etc.) and biological factors (growth phase, amount of DNA, etc.).

3.1. Physical dose modifying factors

Radiation damage is highly dependent on the quality of radiation. Radiation quality can be characterized by the Linear Energy Transfer (LET). LET is defined as the energy lost by particle per unit length of medium. To describe the difference between high LET (fast neutrons, accelerated heavy ions, etc.) and low LET (γ ray, X ray, etc.) radiation, Relative Biological Effectiveness (RBE) was introduced. RBE is a ratio of absorbed dose of a reference irradiation to the absorbed dose of test irradiation to produce the same level of biological effect. The value of RBE depends on the radiation dose, dose rate and biological system.

The radiobiological importance of high LET particles:

- relative biological effectiveness is increased,
- oxygen enhancement ration is reduced,
- repair of radiation damage is less,
- age response function is suppressed.

Dose rate differences between γ rays are too small to be of any significance with respect to microbial inactivation, but clearly a large difference between 60Co gamma ray and accelerated electron. It was also recognized that the radiation response was usually reduced if the total dose was delivered in fraction rather than single shoot. In the case of dose fractionation a second shoulder appears in the survival curve. Manifestation of a second or more shoulders assumed to be the evidence that radiation damage must accumulate within the cell before a final event becomes lethal. This sublethal damage during the so-called “recovery interval” can be restored. The size of the shoulder depends on the repair capacity of cells and the recovery interval.

The temperature is also an important physical dose-modifying factor. A number of investigations reported that relatively mild doses of ionizing radiation sensitized microorganisms very significantly to subsequent heat treatment. Combined heat and radiation treatment of microorganisms yields a lethal effect greater than the additive rates of independent agents. Maximum synergism occurs at those conditions where heat and radiation are equally effective as destructing agents.

3.2. Chemical dose modifying factors

Oxygen has received the greatest attention of all chemical agents known to modify radiation damage in cells. Oxygen has been found to increase the sensitivity to radiation of almost all types of cellular systems and even higher organisms, and this phenomenon has been generally known as the “oxygen effect”.

The sensitizing effect of oxygen can be expressed by the Oxygen Enhancement Ratio (OER), which is the ratio of dose required under anoxic condition to that under condition of air to produce the same level of effect.
Gray [5] considered at first the possibility that the action of oxygen is mediated through reaction with products of the radiolysis of water. These reactions can be presented in a simplified formula, as follows:

\[
\begin{align*}
    H^\cdot + O_2 & \rightarrow HO_2^\cdot \\
    e^-_{aq} + O_2 & \rightarrow O_2^\cdot
\end{align*}
\]

Secondary \( ^\cdot OH \) radicals can be produced from superoxide anion and hydrogen peroxide through the Haber-Weiss reaction:

\[
O_2^\cdot + H_2O_2 \rightarrow ^\cdot OH + OH^- + O_2
\]

Later Howard-Flanders proposed that irradiation creates two types of damage [6].

\[
\begin{align*}
    R - \frac{\text{radiation}}{} - R^\cdot (\text{lethal}) \\
    R - \frac{\text{radiation}}{} - R^\cdot (\text{potentially lethal}) \\
    R^\cdot + O_2 & \rightarrow R^\cdot O_2 (\text{lethal})
\end{align*}
\]

The potentially lethal damage is not lethal to the cells unless it reacts with oxygen. Later three distinct responses were obtained by altering the gaseous environment [7].

**Class I.** Damage is seen when the cells are in anoxic condition during and after the irradiation. This damage is independent of oxygen.

**Class II.** Damage is oxygen dependent and is referred to as “immediate oxygen dependent damage”. It occurs when oxygen is present during and after irradiation. It is believed to result from interaction of oxygen with short-lived radicals.

**Class III.** Damage is the post irradiation oxygen dependent damage, which occurs when the cells are in anoxic condition during irradiation and oxic condition after irradiation. This damage is known to occur as the result of interaction of oxygen with long-lived free radicals, formed by irradiation in the absence of oxygen.

The oxygen dependent sensitization is quite similar in the cellular radiobiology, the OER values varying between 2-4.

Nowadays, for the radiation chemical mechanisms of oxygen effect, two hypothesis have been proposed [8], namely: “the oxygen fixation” and “activated oxygen” hypothesis.

Regarding the whole natural environment, many chemicals can enhance the radiation response. Within the last decade various classes of chemical agents have been found to increase the efficiency of radiation induced cellular damage. These include inorganic and organic chemicals with various properties.

Some ideas on the different modes of action can be gained from the following classification.

(a) Radiosensitizers specific for hypoxic cells
- electron affinic agents
- membrane-specific agents
(b) Analogues of DNA processors
- incorporated into DNA
- non-incorporated into DNA
(c) Radiation-activated cytotoxic compounds
- Agents which modify cellular regulatory processes
  - inhibitors of repair,
  - DNA binding and intercalating compounds,
  - inhibitors of natural radioprotectors.

*Protective agents* are chemicals that reduce the lethal effect of radiation. The most remarkable groups of protectors are the sulfhydryl compounds, which were discovered many years ago [9]. Agents such as cysteine, mercapto-ethyl-amine and amino-ethyl-isothioronium were among the most effective. Favoured hypotheses are the hydrogen donation from the SH (as a reaction competing with damage fixation) and the ability to quench free radicals and their products.

*Water content* of the microbial cell at the instant of radiation is also known to affect greatly its radiation response. In most cases progression from dry to wet results in an increase in response. Regarding the presence of chemical dose, modifying factor is very important for the calculation of required dose in wastewater treatment and food preservation.

### 3.3. Biological dose modifying factors

Effect of radiation on cells can be modified not only by agents present during irradiation but also by biochemical processes occurring over a much longer time. Profound changes in radiation response may be altered to progress of cell through different phases and stages of growth. These may be associated with changes in the intercellular environment. The literature on the radiation response of bacteria in different growth phases reveals some contradictory results. Unfortunately a general rule concerning the influencing effect of growth phase is not available. Sometimes survival curves are deeper in exponential than in stationary phases, sometimes the reverse is true.

In this paper we tried to describe the extent of radiosensitivity of microorganisms and factors other than the genotype of microbes influencing radiosensitivity.

**REFERENCES**


STUDIES FOR RADIATION TREATMENT OF POLLUTED WATER IN SHANGHAI

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3Environmental Protection Research Institute, Menfeng Group Corporation, China

Abstract

The basic point is controlling stage before 2000 and improving stage after 2000 in Shanghai. Therefore, refined process with high efficiency of removal, low operating energy and no-second pollution was needed. Some studies on radiation treatment of aqueous solution and polluted water were conducted and some projects were suggested: radiation-induced degradation and decoloration of dye wastewater, radiolytic decomposition of bleached pulp-mill effluents, radiation regeneration of polluted activated carbon, application of radiation technique to sewage sludge treatment and to emulsifier breaking. Pulse radiolysis was also carried out for the typical dye of Rhodamine.

1. INTRODUCTION

Shanghai is situated in the fringe of the Yangtze River Delta. The water resources in Shanghai come from the Huangpu River mostly, which is 113.4 km long. Water for domestic and industry consumption 66% comes from the Huangpu River, 9.5% from the Yangtze, 30% from the branch of the Huangpu River, and 3.5% from groundwater [1]. There are not plentiful water resources in Shanghai, drinkable quality source is especially less and less. Shanghai is a typical city where there is short supply of good quality water.

Pollution of the surface water in Shanghai is of organic type and main pollution consists of variables chemical oxygen demand (COD), unionized ammonia, total phosphorus and petroleum, etc. The main water body is at the standard limits of Category II or III, which is mainly from Huangpu River. The worsening water quality at Suzhou Creek has eased up due to the function of the Shanghai sewerage Projects I and II [2]. New balance was reached and life in creek has appeared to be, in spite of the quality, still out of the standard limit of category IV. The water quality of creek has been becoming better since 1999.

Water contamination comes from industrial effluent (about 3 million tons per day or chemical oxygen demand discharged about 120 thousand tons a year), domestic wastewater (organic matter of about 170 thousand tons per annual). The pollution of agriculture and livestock accounts for 15% of the total load. Another important pollution source is raining rush [3].

The target of environmental protection in Shanghai for the year 2000 and 2010 was formulated. The basic point is controlling stage before 2000 and improving stage after 2000. Therefore, refined process with high efficiency of removal, low operating energy and no-second pollution was needed. Some studies on radiation treatment of aqueous solution and polluted water were carried out in Shanghai: radiation-induced degradation of dye wastewater, radiolytic decomposition of bleached pulp-mill effluents, radiation regeneration of polluted activated carbon, application of radiation technique to sewage sludge treatment and to emulsifier breaking. Pulse radiolysis was also carried out for the typical dye [4].

2. TREATMENT OF DYE SOLUTION AND WASTEWATER

One cause of water contamination is effluent containing dye from dyeing and textile industry. Anthraquinone dye and azo dyes cannot be degraded easily by traditional methods. Electron beam (EB) irradiation in combination with biological treatment was identified to be promising for dye effluent treatment. Acid Blue 40, Acid Red 265, Cation Blue (Astrazon Blue), BG, disperse dye
yellow, RGFL, and disperse black, 2BL were selected for the samples in aqueous solution. The acid blue 80 and acid red 265 are the anthraquinone and azo dye, respectively. The BG is the anthraquinone dye with oxygen and nitrogen. RGFL and 2BL are diazo and blended configuration, respectively. The concentration of the sample solution was for 20 – 1000 mg/l. The industrial wastewater contains azo dye, sulfide dye, ion dye, reactive dye and other surfactants.

All the sample solutions were irradiated at low energy (0.3 MeV) EB accelerator. The sample solutions were aerated during irradiation. The dose ranged from 1 to 100 KGy. Spectrum measurements were conducted for the dye solutions. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) measurements were carried out for the most dye solution and industrial effluent.

The value of COD/CODth (theory COD) is smaller for the non-irradiated samples, which means that the molecular structure of the dye BG was not easily degraded. It is more difficult for the higher concentration (Table I). The removal can reach 65% when the samples were irradiated at dose of 3KGy. Removal of the pollutant in the samples increased due to irradiation. The changes of COD, degradation and decoloration are shown in Table II when the samples at concentration for 25–100mg/l were irradiated.

Measurement of UV-visible spectra for the GB aqueous solution at concentration of 25-100 mg/l indicated that aromatic rings and color-generated group were affected by irradiation. Decoloration and degradation of the sample solution increased with increasing of the dose. The amount of aromatic rings degraded is proportional to amount of oxygen consumption. Therefore, aqueous solution should be kept in certain oxygen concentration for decoloration and decomposition of dye solution during irradiation.

2Bl and RGFL dye solutions at high concentration of 1000 mg/l were selected for biological treatment before and after irradiation. The results of COD indicated there was little effect of biological treatment on 2BL and RGFL dyes for non-irradiation dye solutions. COD value was still at over 1200mg/l. However, COD of 2BL and RGFL increased at first and then decreased with bio-treating time for the RGFL and 2BL dye solution irradiated at the doses of 30KGy. Increasing ratio of BOD/COD for 2BL and RGFL dye solution irradiated indicated that irradiation had made pollutants biodegradable.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CODth</th>
<th>CODm1</th>
<th>CODm1/CODth (%)</th>
<th>CODm2 at 3KGy</th>
<th>Removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>72</td>
<td>43</td>
<td>59.7</td>
<td>15</td>
<td>65.5</td>
</tr>
<tr>
<td>B</td>
<td>143</td>
<td>67</td>
<td>46.9</td>
<td>33</td>
<td>50.7</td>
</tr>
<tr>
<td>C</td>
<td>286</td>
<td>106</td>
<td>37.1</td>
<td>55</td>
<td>48.3</td>
</tr>
</tbody>
</table>

TABLE I. RATIO OF MEASURED COD_m TO THEORY COD_th AND REMOVAL OF POLLUTANT IN THE BG SAMPLE SOLUTIONS AFFECTED BY IRRADIATION.
CONCENTRATION (MG/L): A 25, B 50, C 100
TABLE II. CHANGES OF COD, DEGRADATION AND DECOLORATION AS FUNCTION OF IRRADIATION DOSE. THE CONCENTRATION OF THE BG DYE SOLUTION: 100 MG/L

<table>
<thead>
<tr>
<th>Irradiation dose (KGY)</th>
<th>0</th>
<th>1.5</th>
<th>3</th>
<th>7.5</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD&lt;sub&gt;cr&lt;/sub&gt; (mg/l)</td>
<td>106</td>
<td>63</td>
<td>55</td>
<td>35</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>Degradation (%)</td>
<td>40.8</td>
<td>48.3</td>
<td>63.0</td>
<td>70.4</td>
<td>92.6</td>
<td></td>
</tr>
<tr>
<td>Absorptance</td>
<td>41.0</td>
<td>0.102</td>
<td>0.01</td>
<td>little</td>
<td>little</td>
<td>little</td>
</tr>
</tbody>
</table>

The wastewater was bio-treated effluent, that was still beyond national standard, from the Hangtai Textile Ltd. However, COD in the effluent was decreased down by less than 100 mg/l at irradiate dose of 2 KGY. Ratio of BOD/COD was increased and the refractory pollutant became biodegradable. Therefore, an opinion was suggested that combination of biological process with irradiation is promising in technology and cost for dye effluent.

3. TREATMENT OF PULP MILL WASTEWATER

Pulp-making materials are mainly grass-like fiber in China. Pulp is made using alkaline method. For making pulp of 1 ton, 10 m³ black liquid was produced and 300 m³ wastewater was generated with BOD of 300 – 500 mg/l, COD of 1200 – 2000 mg/l, ss of 500 – 1000 mg/l, in preparing and bleaching process. Biochemical treatment and chemical coagulation are often used for the effluent. Organic compound in pulp-mill effluent accounts for about over 65% of total pollutants. High color effluent resulted mainly from a great deal of lignin, tannic acid and chloroorganic compounds, which were generated, in the bleached process. Some compounds such as tannic acid were easily oxidized and caused color-generated reaction.

The effluent from Minfeng Pulp-Mill Group Corp. was taken as the samples, which was acid with PH3. The effluent before and after biological treatment was irradiated at low energy (0.3MeV) electron accelerator. It was found that the COD value of the samples went down to 1/2 of the original effluent at the dose of 10KGY and then slowly declivous with dose increasing. It suggested that irradiation-caused decomposition of the pollutants and obvious deposition of suspended particles in the solutions and color degree decreased.

TABLE III. REMOVAL EFFICIENCY OF EFFLUENT IS AS FUNCTION OF IRRADIATION DOSE. THE EFFLUENT COMES FROM MINFENG PULP-MILL GROUP CORP. WASTEWATER A: BEFORE BIO-TREATMENT, AND EFFLUENT B: AFTER BIO-TREATMENT

<table>
<thead>
<tr>
<th>Irradiated doses (KGY)</th>
<th>0</th>
<th>6</th>
<th>15</th>
<th>30</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater A COD (mg/l)</td>
<td>1664</td>
<td>1020</td>
<td>863</td>
<td>482</td>
<td>302</td>
</tr>
<tr>
<td>Wastewater A removal (%)</td>
<td>38.9</td>
<td>48.3</td>
<td>71.1</td>
<td>81.9</td>
<td></td>
</tr>
<tr>
<td>Effluent B COD (mg/l)</td>
<td>492</td>
<td>370</td>
<td>230</td>
<td>158</td>
<td>63</td>
</tr>
<tr>
<td>Effluent B removal (%)</td>
<td>24.8</td>
<td>53.3</td>
<td>67.0</td>
<td>87.2</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV. RESULTS (COD MG/L) OF BIO-TREATMENT BEFORE AND AFTER IRRADIATION FOR THE EFFLUENT FROM MINFENG PULP-MILL GROUP CORP. WASTEWATER A – BEFORE IRRADIATION, WASTEWATER B – AFTER IRRADIATION

<table>
<thead>
<tr>
<th>Bio-treated time (hr)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>10</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiated wastewater</td>
<td>863</td>
<td>532</td>
<td>422</td>
<td>382</td>
<td>259</td>
<td>214</td>
</tr>
<tr>
<td>Non-irradiated wastewater</td>
<td>1669</td>
<td>1279</td>
<td>977</td>
<td>721</td>
<td>617</td>
<td>503</td>
</tr>
</tbody>
</table>

There is a better removal for the non-bio-treated wastewater than that for biochemical treated effluent at low doses (Table III). However, different situation appeared, that is, there was higher removal for the bio-treated effluent than that for non-bio-treated effluent. The cause probably may be due to measurement error. Further studies should be carried out. It took 24 hours using bio-treatment for decreasing the COD of the non-irradiation wastewater from 1669 to about 500 (Table IV). However, it only took 5min (about 15Kgy) using irradiation for the same kind of wastewater. The effluent can be improved with decreasing of COD from 492 to 63 mg/l if the bio-treated effluent was irradiated (Fig.1). That effluent can be discharged out directly. The spectra of irradiated tannic acid showed that the molecular structure was changed. The absorption at 207.4nm suggested that ester bond was broken and -COOH bond formed and π-π* transition took place at conjugation structure. Breaking of C=C, C=O bonds of tannic acid was brought about at the high dose. The results supported the opinion that the effluent from pulp-mill is irradiated at low dose and followed by biochemical treatment and then irradiation again. The advantage of this process is that refractory compounds become biodegradable and the effluent from pulp-mill could be discharged out.

4. OTHERS

Wastewater containing emulsifier is commonly industrial effluent. Oily substances as three kinds of states exist in wastewater, floating oil, emulsifier and soluble oil. The size of emulsified oil particle, which disperses in wastewater, is about 6 – 7 µm. the soluble oil concentration is less than 5-15 mg/l. In fact emulsifier is colloidal solution. It is stable and difficult to be separated. In general oil concentration in emulsified solution, 15000 – 30000 mg/l, CODcr, 18000 – 35000 mg/l and BOD5, 5000 – 12000 mg/l, pH9 – 12. Emulsifier will become gray-black with bad smell from milky white [5]. It is a problem for environment. Treatment of the emulsified oily wastewater was studied using EB. CaCl2 and 98% H2SO4 was taken as breaking emulsion agent to pre-treat the wastewater samples and then the samples were irradiated using EB. The results indicated that adding the breaking emulsion agents can break emulsified oily wastewater effectively and oil can be separated from the solution. The oil concentration of the treated effluent was reduced down and removal of COD reached 80% after irradiation. Comparison of the treating effect of the two kinds of agents was carried out. The results indicated that combination of adding the breaking emulsion agents with irradiation is more useful (Fig. 2).

In general, activated carbon is used as a significant step for removal of organic pollutants from different wastewater. However, the polluted activated carbon is too burden to absorption capacity when over working time. Regeneration should be undertaken for re-exciting. The experimental results indicated that the polluted activated carbon was highly regenerated under the condition of process concentration, 3%, treating time 30min, radiation dose of 5Kgy. Stable property was obtained for the regenerated activated carbon [6].

Pulse radiolysis was also conducted for typical dye Rhodamine B (RDM). The mechanism of decolorization of RDM was studied, and reaction rate was measured using three different conditions: N2O saturated solution, t-BuOH-N2 solution, and aerated solution. For each condition, the pulse radiolysis spectrum was determined at 300 – 600 nm. The spectrum was characterized with adsorption maximal at 430 nm and the background bleach effect of RDM was observed at 520 – 540 nm. In N2O and t-BuOH-N2 systems, the adsorption rate was determined to be 5.5 x 109 l/mol-s and 5.2 x 109 l/mol-s, respectively (Bao, et al., 2000).
Suzhou creek is one of the important river through Shanghai center. Sewage sludge in the creek bed must be treated if water of the creek needs cleaning-up. Radiation process will play a rule for the sewage sludge treatment. Cleaning water supply had been major items for Shanghai with population of 13 million. Several decades of resident areas in which about 100 thousands people live. These areas are good models. Cooperation between a resident zone and the university is being designed for the radiation process of drinking water in such a zone.

ACKNOWLEDGEMENT

Support for this research was provided by the Shanghai Education Committee, United Nuclear Analysis Laboratory and Shanghai Ion Beam Laboratory of the Chinese Academy of Sciences.

REFERENCES

FIG. 1 Removal of pollutant in wastewater (a and b) from Mingfeng Pulp-Mill Group Corp. and removal of tannic acid (c and d)

a. Wastewater before bio-treatment, b. Wastewater after bio-treatment, c. Tannic acid at concentration of 200 mg/l, d. Tannic acid at concentration of 800 mg/l.

FIG. 2. Removal of emulsifier affected by adding breaking emulsion agents and irradiation
a. adding CaCl2     b. adding H2SO4 (98%).
CONSISTENCY IN EVALUATION OF A FEW MeV ELECTRON DOSE AND Co-60 GAMMA RAY DOSE IN RADIATION PROCESSING

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²Ion Beam Irradiation Service, Co., Ltd., Takasaki, Japan

Abstract

The uncertainty components in evaluation of absorbed dose in water were reviewed for 2-MeV electron dosimetry based on the on-line electron calibration system, which consists of a total-absorption calorimeter, an electron current density meter and cellulose triacetate film dosimeters. Dose comparison was performed for 2-MeV electrons employing cellulose triacetate and alanine film dosimeters which were independently calibrated for 2-MeV electrons and ⁶⁰Co gamma rays using the calorimeter and the ionizing chamber systems, respectively. Agreement of two different dose evaluations was better than 2.0%(1σ). While combined uncertainties in two different dose evaluations are estimated to be within 3.0%(1σ). Consistency of electron dose evaluation with gamma ray dose evaluation was confirmed from these two values.

1. INTRODUCTION

As use of radiation processing using high-energy electrons grows, accurate evaluation methods of electron energy and absorbed dose become vital to the purpose of quality assurance of irradiated products. Electron dose evaluation should have consistency with gamma ray dose evaluation that is traceable to national or international standards.

A reference level ⁶⁰Co gamma ray dosimetry at JAERI has maintained its high quality metrological performance through periodical calibration checks at the Electrotechnical Laboratory, the primary standard dosimetry laboratory in Japan, and gamma ray dose intercomparison studies with the National Physical Laboratory in UK [1,2]. Total uncertainty in evaluation of gamma ray dose in water is 1.7% (1σ) employing a parallel-plate ionization chamber and alanine rod dosimeters [2].

While an on-line electron calibration system has been developed for calibration of electron energy and absorbed dose in the electron energies of 1.0-5 MeV under passing the system successively through the irradiation zone of broad-scanned electron beams using a conveyor [3-5]. The system consists of three detectors of a total absorption calorimeter, an electron current density (ECD) meter and a stack of cellulose-triacetate (CTA) film dosimeters. The absorbed energy per unit area and electron fluence measured respectively by the calorimeter and the ECD meter provide calibration of energy of incident electrons. The measured absorbed energy and the depth dose profile in relative value measured by the calorimeter and a stack of CTA film dosimeters provide calibration of dosimeter responses. The on-line electron calibration system, therefore, allows simultaneous calibration of energy of incident electrons and the dose responses of un-calibrated film dosimeters [4].

Consistency of electron dose evaluation with gamma ray dose evaluation was checked experimentally employing CTA and alanine film dosimeters. The former and latter dosimeters were independently calibrated for electrons and gamma rays on the basis of calorimeter and ionizing chamber systems, respectively. Reviewing uncertainties in calibration procedures of CTA and alanine film dosimeters, electron doses evaluated using these dosimeters were compared under the same irradiation condition of 2-MeV electron beams.
2. UNCERTAINTIES IN ELECTRON DOSE EVALUATION

The CTA dosimeters were calibrated using the total-absorption calorimeter and the ECD meter. The ECD meter is a kind of compact Faraday cup usable in air. Both the calorimeter and the ECD meter have a main graphite core (absorber) of 20 mm diameter and 19 mm thick, surrounded by a sufficient graphite guide ring with a 0.3-mm air gap for each. The temperature of the calorimeter core is measured by a thermistor. Integrated current value of the ECD meter is measured in terms of total charge at main absorber and sub-absorbers placed under the air gap. The detailed procedures of two measurements are described in elsewhere [3-5].

Uncertainties in electron dose evaluation employing CTA film dosimeters was estimated on the basis of uncertainty components in calibration procedure of CTA film dosimeters using the calorimeter and the ECD meter taking into account of non-uniformity of fluence and influences of current instability even under scanning electron beam irradiation using a conveyor.

<table>
<thead>
<tr>
<th>Source of uncertainties</th>
<th>Type A (%)</th>
<th>Type B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorimetry</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Electron current density measurement</td>
<td>1.5</td>
<td>0.4</td>
</tr>
<tr>
<td>CTA dosimeter system</td>
<td>1.0</td>
<td>---</td>
</tr>
<tr>
<td>Correction for geometry/timing</td>
<td>0.5</td>
<td>---</td>
</tr>
<tr>
<td>Correction for depth-dose distribution in CTA</td>
<td>---</td>
<td>1.0</td>
</tr>
<tr>
<td>Mass collision stopping power conversion</td>
<td>---</td>
<td>0.5</td>
</tr>
<tr>
<td>Type A and Type B components combined in</td>
<td>1.66</td>
<td>1.83</td>
</tr>
<tr>
<td>quadrature separately</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Both components combined in quadrature</td>
<td>(1σ)</td>
<td>2.47</td>
</tr>
<tr>
<td>Total uncertainty</td>
<td>x 2 (2σ)</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Uncertainty components specified in the calorimeter measurement were estimated as concerning the effective areas of the core, evaluation of specific heat of graphite absorber, precision of temperature rise measurement at the graphite absorber. Uncertainties in ECD measurement were estimated relating to the effective area defined by the core and the gap to the graphite guard ring taking account of backscattering and bremsstrahlung. Uncertainties in CTA film dosimeter system were estimated relating to spectrophotometry, thickness measurement, linear fitting of dose response curve, and correction of depth-dose distribution in one CTA film. Through uncertainty estimation for each measurements considering correction for geometry/timing and mass collision stopping power conversion between carbon and CTA, total uncertainty in electron dose evaluation employing CTA film dosimeters is 2.5% (1σ) by means of summation of Types A and B in quadrature, as summarized in Table I. Uncertainties of Type A and B used here correspond to the ones estimated from repeated experiments and others [6].

Alanine film dosimeters (DL-α-alanine 60wt%, low-density polyethylene 40wt%) of 0.22 mm in thickness have been developed and applied to dosimetry for MeV electrons and MeV/u ion beams [7,8]. Total uncertainty in dose evaluation using alanine film dosimeters was estimated to be 1.7% (1σ) by addition of an uncertainty in correction of dose-response using weight, 0.1% (1σ), to the uncertainty of the alanine rod dosimeters calibrated using the ionizing chamber system [4].
3. DOSE COMPARISON BETWEEN CTA AND ALANINE FILM DOSIMETERS

Doses given by CTA and alanine film dosimeters were compared under the same condition of 2-MeV electron irradiation except for difference in irradiation pass number. Two-MeV electron irradiation was made in air using Dynamitron (RDI, IEA3000-25-2) with the 60 cm wide scanning beams at a current of 2 mA with the conveyor speed of 3.46 m/min, ultimately at a dose rate of about 10 kGy/pass. Three films for each dosimeter were separately placed side by side and irradiated on the graphite block covered with the 500-µm thick CTA sheets as backing material. The doses given by different pass numbers of 1 to 12 were correspondent to doses from 10 to 120 kGy. This dose range covers the overlapping dose region 20-60 kGy of CTA and alanine film dosimeters. The differences in mass energy absorption coefficients and mass stopping power values of relevant dosimeter materials were properly taken into account for evaluation of dose in water. The doses estimated by these dosimeters are shown in Fig.1 as a function of ‘nominal dose’, which is preliminarily estimated on the basis of irradiation parameters. The ratios of dose given by CTA film dosimeters to dose given by alanine film dosimeters were 0.5, 1.7, 0.6 and 1.4 % for doses of 20, 30, 40 and 60 kGy, respectively. The agreement of respective dose evaluations is, therefore, better than 2.0% (1σ).

![Graph showing dose comparison between CTA and alanine film dosimeters](image)

**FIG. 1.** Comparison of absorbed doses in water given by CTA film dosimeters with those given by alanine film dosimeters. These dosimeters were independently calibrated for 2-MeV electrons and 60Co gamma rays, respectively. Here, ‘nominal dose’ is expressed by means of doses estimated from different irradiation pass numbers assuming at a dose rate of about 10 kGy/pass.

This agreement level demonstrates its consistency with the uncertainty value of 3.0% (1σ), a combination of uncertainties in gamma ray dose evaluation 1.7% (1σ) and those in the electron dose evaluation 2.5% (1σ) in quadrature.

4. SUMMARY

Gamma ray and electron doses evaluated experimentally using CTA and alanine film dosimeters were in agreement, better than 2.0% (1σ) difference. While uncertainty value of 3.0% (1σ) was calculated by a combination of uncertainties in gamma ray and electron dose evaluations using these film dosimeters. Consistency of two dose evaluations was confirmed by comparing these values.
Dose intercomparison experiments using 4-MeV electrons are in progress between NPL and JAERI to support the above consistency study. These results should enable us to achieve highly reliable dosimetry for the quality assurance in electron radiation processing on the basis of gamma ray dose standards.

REFERENCES


IRRADIATION OF FROZEN BIOLOGICAL MATERIAL — DOSE MAPPING, PROCESS CONTROL, TRACEABILITY AND UNCERTAINTY IN MEASUREMENT

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Abstract

An overview of the technique used for dose-mapping frozen biological material prior to routine irradiation at ANSTO is given. The methods used for calibrating reference standard dosimeters with measurement traceability to a national standard are described. Values for measurement uncertainty for the calibration and use of the dosimeters are tabulated and combined with the uncertainty in measuring the extreme doses to the product. This uncertainty value is used to set process control limits for subsequent routine processing to ensure regulatory compliance.

1. INTRODUCTION

The Radiation Technology Group at ANSTO is part of the Physics Division and provides services and advice in the areas of gamma irradiation and high-dose dosimetry.

The Group maintains and operates a number of irradiation facilities. ANSTO’s pond facility consists of seven cobalt-60 sources configured in annular arrays with a range of activities and dose rates. The main irradiation facility is GATRI – the Gamma Technology Research Irradiator – a research and small scale batch irradiator commissioned in 1970. The source is a cobalt-60 plaque source with a maximum capacity of 3.7 PBq (100 kCi).

Materials commonly irradiated at ANSTO include medical and other materials requiring processing for sterilization or verification of sterilization dose, items requiring decontamination and disinestation for quarantine purposes, frozen bone and tissue samples for transplant surgery, monomers and polymers for modification of properties, virus samples, and Queensland fruit fly pupae used in the Sterile Insect Technique. The GATRI facility has been loaded with cobalt-60 to provide the largest possible uniform radiation field, rather than for efficiency, so that we can provide the required doses as precisely as possible. We can offer irradiations at a range of dose rates and at frozen and elevated temperatures. During the past twelve months, client demand for target doses ranged from 10 Gy to 2000 kGy, at temperatures from –80°C to 300°C.

Radiation Technology is licensed by Australia’s Therapeutic Goods Administration (TGA) and the Australian Quarantine and Inspection Service (AQIS), which requires maintenance of a Quality System complying with the ISO 9000 series of standards. In addition, the GATRI facility is required to comply with the National Health and Medical Research Council’s (NH&MRC) Code of Practice for the Design and Safe Operation of Non-medical Irradiation Facilities. In addition to independent internal safety approval, the GATRI facility is regulated by an external body, the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA), which is responsible for licensing government nuclear and radiation facilities.

Radiation Technology makes and sells reference and transfer standard dosimeters that are purchased by users and suppliers of commercial irradiation services in Australia and the Asia-Pacific Region. A calibration service is also provided for dosimeters made by or purchased from other organisations. ANSTO’s dosimetry practices are based on the standards published by the American Society for Testing and Materials (ASTM). Dosimetry systems in use are Fricke (Ferrous Sulfate), Ceric-Cerous Sulfate, Harwell Red and Amber Perspex and Alanine/ESR.
2. DOSE MAPPING


Before any materials can be submitted for routine irradiation, the parameters required to ensure the irradiation process meets the stated specifications must be determined. The outcome of this process qualification step is the loading pattern and corresponding processing parameters, which are unique to the particular irradiation facility.

Tissue grafts and other biological materials are often irradiated as frozen materials and must be packaged and irradiated in dry ice at all times. Most commercially available and commonly used dosimetry systems are either not suitable for, or not calibrated at, low temperatures. Therefore these dosimeters cannot be placed directly on or inside the samples during process qualification or routine processing. Consequently, dose mapping is performed using material at ambient temperature that simulates the bulk density of the frozen sample and dry ice.

At ANSTO, frozen material is irradiated in dedicated thick walled polystyrene foam boxes, chosen to provide maximum insulation to the material and minimise the loss of dry ice during the irradiation process. The weight of the boxes filled with samples and dry ice is measured immediately before and after a typical processing time, and the average weight chosen as that to be used when filled with simulated product, which in this case are polyethylene beads.

Dosimeters are located throughout the simulated product in a three-dimensional array and the whole is irradiated in the predetermined loading pattern. A map of the dose distribution in the boxes is thus obtained, in particular the maximum and minimum dose zones and the respective dose rates. During the dose-map, positions on the external surface of the boxes are identified as locations to be used for reference dosimeters to be sited during routine processing. Measurements made in these locations allow a numerical relationship to be derived between the reference dosimeter reading and the maximum and minimum doses to the product.

This procedure is repeated at least three times to demonstrate reproducibility and allow statistical calculations to be made regarding the process. Reference standard dosimeters (currently ceric-cerous sulfate) are used to establish all critical processing parameters.

3. CALIBRATION OF DOSIMETERS

All dosimetry calibrations performed at ANSTO, either for internal use or for external clients, are carried out in the known radiation field of the Underwater Calibration Facility (UCF). Calibration of this radiation field is described in Section 4.

The source consists of 12 cobalt-60 pencils in an annular arrangement, stored at the bottom of ANSTO’s pond facility. All items for irradiation are loaded into a water-tight stainless steel canister which is in series with a continuous stainless steel roller chain driven by an electric motor which lowers it reproducibly into the centre of the source. The dosimeters for calibration are mounted onto a turntable fitted with a polyethylene holder with locations for up to 12 dosimeters. The turntable is sited in a fixed position within the irradiation canister and the dosimeters are continuously rotated to ensure an even dose.

The facility is controlled by a computer that provides for independent confirmation of irradiation time, irradiation temperature and rotation of the turntable. Temperature is monitored using a thermocouple.
4. TRACEABILITY

At ANSTO, measurement traceability to the national standard is obtained by the following approach. The Australian Standard for Absorbed Dose consists basically of a cobalt gamma source whose dose rate at a fixed point is measured using a graphite calorimeter. This primary standard is then disseminated by the Secondary Standard Dosimetry Laboratory or SSDL. The SSDL ionisation chamber is calibrated against the primary standard and this chamber is then used to calibrate a collimated beam from a teletherapy gamma source. ANSTO’s Fricke dosimeters are then irradiated in this calibrated beam to a range of doses so that the response of this solution is well characterised. This dosimeter solution is then used to determine the dose rate in a fixed geometry on the turntable in the Underwater Calibration Facility. Routine and transfer standard dosimeters are then calibrated as required in the UCF, with the dose rate calculated according to the decay of the cobalt-60 source. Doses are routinely expressed in terms of the dose absorbed in water.

In conjunction with this calibration process, ANSTO has confirmed the dose rate in the UCF through irradiation of dosimeters supplied and measured by the National Physical Laboratories in the UK and via the IAEA’s International Dose Assurance Scheme (IDAS). The dose rate measured in these instances agrees within 1% with ANSTO’s calibrated dose rate.

5. MEASUREMENT UNCERTAINTY

As with the result of any analysis, the absorbed dose measurement obtained after reading a dosimeter is meaningless without an expression of the uncertainty associated with the result. In principle ANSTO follows the guidelines set out in ISO’s 1993 “Guide to the Expression of Uncertainty in Measurement” [1] and ASTM Standard E 1707 [2].

Components of uncertainty are classified as Type A or Type B and are given as the percent standard deviation. Components of uncertainty are combined in their simplest form, that is, they are assumed to be uncorrelated and are added in quadrature by type before a combined uncertainty is obtained. The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor of \( k = 2 \), providing a level of confidence of approximately 95%. Table I shows the components of uncertainty in the calibration, analysis and use of ANSTO ceric-cerous dosimeters.

<table>
<thead>
<tr>
<th>Component of uncertainty</th>
<th>Type A (per cent)</th>
<th>Type B (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>absorbed dose rate measurement (UCF)</td>
<td>0.37</td>
<td>1.17</td>
</tr>
<tr>
<td>timing of irradiations; transit dose</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>decay corrections</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>random uncertainty of dosimeter readings</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>curve fitting</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Routine use</td>
<td></td>
<td></td>
</tr>
<tr>
<td>random uncertainty of dosimeter reading</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>measurement temperature</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>irradiation temperature</td>
<td></td>
<td>0.69</td>
</tr>
<tr>
<td>Type A &amp; B components combined in quadrature separately</td>
<td>1.07</td>
<td>1.37</td>
</tr>
<tr>
<td>Both components combined in quadrature</td>
<td></td>
<td>1.74</td>
</tr>
</tbody>
</table>

When adequate care is taken in the set-up and use of the electrochemical cell, the overall uncertainty of absorbed dose measurement by a single dosimeter is estimated to be ±3.5% at the 95% confidence level.
If $R_{\text{min}}$ (the dosimeter factor) is the ratio of dose at the minimum position ($D_{\text{min}}$) to dose at the reference position ($D_{\text{ref}}$), then the uncertainty in this factor can be calculated from its variance that is approximated by the first two terms of a Taylor series expansion using the variances of $D_{\text{min}}$ and $D_{\text{ref}}$.

The uncertainty in the reference dosimeter reading is combined with the uncertainty associated with the calculation of minimum dose from the dose in the reference position. See Table II.

### TABLE II. OVERALL UNCERTAINTY IN MEASUREMENT OF MINIMUM DOSE TO PRODUCT

<table>
<thead>
<tr>
<th>Component of uncertainty</th>
<th>Type A (percent)</th>
<th>Type B (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference dosimeter reading</td>
<td>1.07</td>
<td>1.37</td>
</tr>
<tr>
<td>dosimeter factor</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>Type A &amp; B components combined in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>quadrature separately</td>
<td>1.83</td>
<td>1.37</td>
</tr>
<tr>
<td>Both components combined in quadrature</td>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>

The overall uncertainty in the measurement of minimum dose during processing is therefore $\pm 4.6\%$ at the 95% confidence level. This uncertainty estimate does not take into account any differences in product positioning and radiation absorption characteristics between the dose-mapping exercise and routine processing.

### 6. PROCESS CONTROL

Once the overall uncertainty in the measurement of minimum dose during routine irradiation of the frozen material has been established, target doses and lower process limits can be set. The desired level of confidence that a defined dose has been exceeded in all the product must be stated – for example, 95%.

If, for example, the required minimum dose is 25 kGy and the overall uncertainty in the measurement of minimum dose is $\pm 4.6\%$ at the 95% confidence interval, then the minimum measured dose allowable for acceptance of the material having received the required dose would be 26.2 kGy. To allow for small variations in the nature of the material being irradiated and minimise the occurrence of below-limit results, it is normal to set the target dose for processing somewhat higher than this lower process limit. A similar procedure is followed in the case of any specified maximum limits.

### ACKNOWLEDGEMENT

The author would like to acknowledge the assistance and support provided to him by his colleagues in the Radiation Technology Group, and to thank ANSTO for providing funds to make attendance at this Symposium possible.

### REFERENCES

THE STUDY ON DOSE CHECK IN IDAS AT SSDL SHANGHAI

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Abstract

Using alanine/ESR dosimetry technique, the dose check service provided by IAEA/IDAS plays an important role for assuring quality of irradiation products and facilitating industrialization of radiation processing. Since 1985 SSDL Shanghai has participated in the activities of the International Dose Assurance Service (IDAS) once a year. The dose check technique is investigated and discussed in this paper. It refers to basic concept, phantom, traceability, action level and some technical details of quality control, etc. in dose check.

1. INTRODUCTION

Ionizing radiation can effectively accelerate chemical reactions, improve quality of natural and synthetic material, preserve food and sterilize medical products. Radiation processing on industrial scale has already been made a reality and produced marked economical benefit. In view of the increasing trend in industrial application and advanced research in radiation processing, it is necessary to standardize high dose measurement since legal and quality assurance requirements in radiation processing are primarily based on reliable dosimetry.

International Dose Assurance Service (IDAS) is the principal ingredient of the high-dose dosimetry programmer of IAEA. It performs dose quality audit for secondary standard dosimetry laboratories (SSDL) and for user’s irradiation facilities. The alanine/ESR dosimetry system is used as transfer dosimeter (i.e. one of reference dosimeters) in IDAS, which was calibrated over the full range of the IDAS, namely from 0.1 to 100 kGy of absorbed dose to water. It is based on the electron-spin-resonance (ESR) of the radiation-induced free radicals in alanine. IDAS results can be used for confirmation of dosimetry as well as quality control of radiation technology. Furthermore, standardization of dosimetry provides a justification for the regulatory approval of irradiated products and the basis of international clearance for free trade [1].

The Ionization Radiation Division under the Shanghai Institute of Measurement and Testing Technology (SIMTT) is a standard laboratory engaged in the research and service in the field of ionizing radiation metrology, under the Network of Secondary Standard Dosimetry Laboratory (SSDL) under IAEA/WHO. It is essential for us that the performance of our reference and routine dosimetry systems are checked by the IAEA in the framework of IDAS. Also, it is significant that we carefully review the dosimetry system and entire procedures us, in order to provide the wide industrial users with better measurement service.

2. RESULTS AND DISCUSSIONS

2.1. Basic concepts

Some technical terms such as calibration, check and quality audit are often used for measurement of high dose in activities of IDAS. Following ASTM standard E170, terminology relating to radiation measurement and dosimetry, calibration is defined as the process whereby the response of a measuring system is characterized through comparison with an appropriate standard that is traceable to, and consistent with, a nationally or internationally recognized standards. This definition has a strict meaning in metrology [2].
Check means an examination in order to learn whether something is correct. When we use it for dose check it has the meaning of inspection and comparison in dose measurement rather than a group of operations of calibration.

The term Dose Quality Audit has been used in IAEA/IDAS documents since 1998. Quality audit (assessment) is defined as an independent review of the quality assurance programme and the results achieved by it. The essential point is that it is to be performed by an independent person who is not responsible for the results achieved [3].

2.2. Results

Since 1985, six sorts of dosimeters in SSDL Shanghai had been selected for γ ray dose check, they are separately Fricke, ceric-cerous sulfate, alanine/ESR, ion chamber, blue cellophane and FWT-60 radiochromic thin film dosimeters. A mean of absolute value of 15 items on relative deviation of dose check is about 2.2% and standard deviation is 2.0%. The data show that about 60% of the measured values have the relative deviation within 2.0%, among them the maxim item of relative deviation was 6.65%, and the minim one was 0.2%, the range of dose level is from 0.12 to 12 kGy.

Here relative deviation is defined, as follows:

\[
\text{Relative deviation} = \frac{\text{SSDL reported dose - IAEA estimated dose}}{\text{IAEA estimated dose}}
\]

The results show that agreement between high dose dosimetry systems in SSDL Shanghia and IAEA transfer dosimeter (alanine/ESR) is within the acceptance limit 5% of IDAS dose quality audit.

2.3. Phantom

The geometry of irradiation is very critical to dose check, so it is important that the reference dosimeter (alanine) set and own dosimeters are irradiated under identical conditions, so as not to introduce a source of uncertainty in the results. Ideally, this may be achieved by irradiating these dosimeters in a phantom specifically designed for this purpose. The phantom should minimize the difference between the absorbed doses received by the routine and transfer dosimeters, and should hold two types of dosimeter for γ rays and for electron beams, so that they do not significantly shield each other, that they are as close together as possible and that the geometry is separately suitable for the radiation source used.

For γ or χ ray, the phantom should provide a sufficient thickness of water-equivalent material to achieve approximate electron equilibrium conditions. When thick and thin dosimeters are irradiated together, surround the thin dosimeters by sufficient polymeric material to ensure that the attenuation characteristics are similar and that the dosimeters receive same dose.

In the cavity of phantom, the absorbed dose variation should be within specified limits of about 1%. When the transfer dosimeters could not be irradiated simultaneously with own routine dosimeter, sometimes substitution method is still a better way for dose check. Scanning the results of our dosimeters checked in standardized water phantom or solid Perspex phantom separately, it seems that standardized phantom should be developed at first for cobalt-60 γ ray irradiation.

2.4. Other details

— Considering the characteristics of dosimeters, the action level of dose should be chosen to get a suitable response; otherwise there could be some discrepancy at higher dose level.
— Radiation field should be uniform at the dose of interest.
— Since the response of the alanine dosimeters depends on the temperature during irradiation, it is essential that the temperature of the dosimeter be monitored as good as possible.
— Before and after irradiation the dosimeters should be stored at a temperature between 20°C and 25°C, also exposure to humidity extremes should be avoided.
— The procedure of dose check should carefully follow the IDAS instructions, for example, even though alanine dosimeters are considered stable after irradiation, there is some fading of ESR signal, thus irradiated dosimeters as well as the control dosimeter should be immediately returned to IAEA.
— User’s dosimeters should keep traceability to national standard, that is, they should be calibrated periodically in an accredited standard laboratory in order to keep high dose dosimetry system at a good quality level.

2.5. Uncertainty

Variations in absorbed dose rate, temperature and energy spectrum and geometry, etc. are dependent on the location and characteristics of dosimeter and practical environment condition. These factors have to be considered in evaluating uncertainties during dose check.

Overall accuracy achievable with reference dosimeters is of the order of 3% (2σ), and the overall accuracy of the order of 5% (2σ) is achievable with routine dosimeters [4]. In general the environmental influence factors can not be taken properly into account in the field of plant, so phantom and check procedures are very important; especially using three alanine can get a reasonable mean value, but it needs more uniform radiation field to suit the requirements of IDAS in irradiation at the same dose at the same time.

There is another error source yet, i.e. the non-equivalence of irradiation geometry between the alanine transfer dosimeter to be calibrated and the user’s dosimeter.

Both relative deviation and specific value (user stated dose to IAEA estimated dose) are all evaluated in dose check; relative deviation would be preferable to be applied, because this term is more directly perceivable.

3. CONCLUSION

Presently the IDAS is limited to 60Co γ-rays; however, a field test for electron beams using the same transfer dosimetry system is in progress [5]. It is possible that IDAS can be expanded by the IAEA dosimetry laboratory. Along with a QA programme, the annual dose quality audit service will be continued and enhanced in the form of IDAS. IDAS assures the accuracy of dosimeters used in irradiation facilities and promotes the worldwide standardization of high dose dosimetry. Dose check will bring more benefit to vast industrial users using radiation processing technology.

REFERENCES

ION BEAM TECHNOLOGY FOR BIOLOGICAL APPLICATIONS IN TIARA

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Abstract

The JAERI AVF cyclotron and electrostatic accelerators in TIARA (Takasaki Ion Accelerators for Advanced Radiation Application) have been applied to biological studies covering cell surgery technique for plant breeding, high-LET specific mutation induced by ion beam, the repair of DNA damage on radiation resistant bacteria, and the analytical technique of living organisms using secondarily produced radiations such as X rays, gamma rays and positrons. The paper summarizes technical and research progress in application of ion beams to biological studies in TIARA.

1. INTRODUCTION

Energetic heavy charged particles transfer their energy to living organisms with high-density ionization and excitation along the particle trajectory, which results in microscopically non-uniform dose delivery, expected to induce unique mutation and local inactivation in living organisms. For relatively low energy ions, the small energy loss struggling allows high resolution control of the penetration depth, which may also induce local structural damage due to the atomic displacement. These are in contrast to relatively uniform dose delivery in gamma ray or electron beam irradiation.

Ion beam handling such as microbeam irradiation and single ion hit is also available for the localized irradiation, which can be applied to inactivation of microscopic region, cell surgery technique, and estimation of radiation risk for human space flight. Ion beams are becoming useful for analysis of living organisms using secondarily produced radiations such as X rays, gamma rays and positrons, which are applied to particle induced X ray emission (PIXE) analysis, nuclear reaction analyses (NRA) and positron emission tomography (PET), respectively.

The ion beam irradiation research facility, TIARA, was completed in 1993. Extensive applications of ion beams have been conducted mainly for R & D in materials science and biotechnology under full-scale operation of the AVF cyclotron and three electrostatic accelerators. A wide range of LET, giving different biological effectiveness and relatively deep penetration for heavy ions with high LET, could be covered by various ion beams from the four accelerators [1].

The present paper summarizes technical and research progress in application of the ion beams to biological studies in TIARA.

2. FACILITIES FOR BIOLOGICAL APPLICATIONS

The layout of TIARA facilities is shown in Fig. 1. Main characteristics of four accelerators are also shown in the figure.

2.1. Cyclotron facility

The JAERI AVF cyclotron provides many kinds of ion species from proton to xenon in a wide range of beam energies from 10 to several hundreds MeV. The cyclotron is equipped with nine horizontal beam courses and four vertical branch beam courses. In a vertical beam course, the cyclotron beam is two dimensionally scanned over an area up to 50×50 mm² for uniform high energy beam irradiation to
biological samples in the atmosphere. A number of different samples can be irradiated continuously by passing through the radiation field using a conveyor system.

At the end of another vertical beam course, an apparatus for local irradiation of a single living cell is installed, in which very low current high-energy heavy-ion microbeam is formed by a three step collimation system and finally extracted into the air through a bottom micro aperture. The position of the sample cell is adjusted just under the final aperture by an optical microscope. Each particle extracted is detected for hit verification after sample penetration.

Another research activity in biological application is dynamical study of physiological function of plants \textit{in vivo} using positron emission tomography. A positron emitting tracer imaging system has been developed together with the production methods of labeled compounds as short-lived positron emitters [2].

\begin{figure}
\centering
\includegraphics[width=\textwidth]{schematic_layout}
\caption{Schematic layout of four accelerators and beam lines in TIARA.}
\end{figure}

2.2. Electrostatic accelerator facility

Three electrostatic accelerators, a tandem and a single-ended accelerator with a maximum terminal voltage of 3 MV and an ion implanter with 0.4 MV make a combined beamline network [3]. The feature of the facility is that two or three accelerators can be operated simultaneously, providing triple or dual beam irradiation into a sample.

The facility has 10 beam courses, two of which are equipped with apparatus exclusively for biological studies. One is an apparatus for heavy ion irradiation to cells in the air with penetration control installed at a beam course end of the tandem accelerator. Another is a light ion microbeam apparatus for biological study, which was installed at a course end of the single-ended accelerator.
3. TECHNICAL AND RESEARCH PROGRESS IN ION BEAM TECHNOLOGY FOR BIOLOGICAL APPLICATION

In TIARA a couple of microbeam apparatus was developed by using the 3MV electrostatic accelerators; one is the light ion microbeam apparatus connected with the single-ended accelerator and another is the heavy ion one connected with the tandem accelerator. Fig. 2 shows technical achievements which have been accumulated in the microbeam development using electrostatic accelerators so far and their application fields. We evaluated a beam size of a quarter-micron meter with a beam current of more than 10 pA for light ions and have developed a high sensitivity in-air micro-PIXE camera for trace element mapping of cells. For accurate beam positioning without radiation damage even to biological cells, we introduced a scanning transmission ion microscopy (STIM) technique using a very low current (less than femto-A level) [4].

The in-air micro-PIXE camera has been applied to bovine aortic endothelial cells, which were cultured in culture medium containing bromodeoxyuridine (BrdU) used in the DNA synthesis, resulting in reasonable elemental mappings of uniformly distributed main elements such as phosphorus, potassium and sulfur in the cell, and localized trace element of Br from BrdU in nucleus in the cell [5]. We are now developing a high-sensitivity X-ray multi-detector system with a large solid angle and a high-speed signal analyzing system to minimize the difficulty without increasing the time for analysis.

In energetic heavy ion beams, only a single particle may cause severe local damage to living organisms. Therefore we have developed a single ion hit system for heavy ion microbeams from the tandem accelerator and have so far achieved a hit control within an accuracy of hit positioning of 1 µm to make a single hit or a small number of ion hits to an aimed local area at the target. We are now extending this single ion hit technique for higher-energy heavy ion microbeams from cyclotron. The final goal of the beam size is a few µm, although the beam size less than 10 µm was already achieved.
using extremely weak collimated beams from the cyclotron. A recent study of local irradiation effects of heavy ion microbeam on the embryogenesis in silkworm clearly shows that the microbeam can be used as a new surgical tool to analyze cell determination and differentiation mechanism in various organisms, since it can inactivate them effectively and reliably without destroying the structure [6].

Linear energy transfer (LET) is the most important and universal parameter that characterizes the radiation effects in application of energetic ion beams to biology. At JAERI cyclotron, cocktail beam acceleration technique has been developed to obtain a series of ion species with required LET values without time-consuming magnet excitation process. This technique is based on the principle that a series of ions with almost identical mass to charge ratio (M/Q) can be accelerated using the same isochronous magnetic field and acceleration frequency just like cocktail ions. By use of this technique it takes only several minutes or less for switching ion species in cocktail beam acceleration operation mode [7]. The cocktail ions available at TIARA are $^{15}$N$^{3+}$, $^{20}$Ne$^{4+}$, $^{40}$Ar$^{8+}$ and $^{84}$Kr$^{17+}$ for the M/Q 5 cocktail ions and $^4$He$^+$, $^{12}$C$^{3+}$, $^{16}$O$^{4+}$, $^{20}$Ne$^{5+}$, $^{40}$Ar$^{10+}$ and $^{84}$Kr$^{21+}$ for the M/Q 4 ones, respectively.

In addition to these above mentioned technical activities, related technologies have been also developed to support research activities, which are ion beam dosimetry techniques using physical/chemical dosimeters [8], visual beam adjustment technique for accurate and efficient operation of cyclotron [9], ion source technologies [10] for the specific ion production such as cluster ions and highly charged ions, and so on.

**TABLE I. PLANT BREEDING USING ION BEAMS IN TIARA**

<table>
<thead>
<tr>
<th>Mutation induced by ion beams</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ultraviolet (UV-B) resistant mutants of Arabidopsis</td>
</tr>
<tr>
<td>2. Bacterial leaf blight (BLB) resistant mutants of rice</td>
</tr>
<tr>
<td>3. Disease resistant mutants of barley</td>
</tr>
<tr>
<td>4. Potato virus Y (PVY) resistant mutants of tobacco</td>
</tr>
<tr>
<td>5. Flower color mutants of Chrysanthemum</td>
</tr>
<tr>
<td>6. Flower form mutant of Arabidopsis</td>
</tr>
</tbody>
</table>

| Interspecific Hybrid produced by the cross with ion beam irradiated pollen |

| 1. Inset resistant hybrids of tobacco plant                        |

Application of ion beams to plant breeding is one of the main research topics at TIARA. Callus proliferation of leaf and floral petals of chrysanthemum irradiated with 220 MeV carbon ion beam resulted in the mutants with huge variety of flower colors, while the variety of colors induced by gamma ray was limited [11]. This characteristic of ion beam was observed in other plants as well. The observed different spectra in mutation between ion beam and gamma rays can be explained by the LET dependence of the characteristics of microscopic energy delivery. Uniform dose delivery from gamma rays may cause a large number of point mutations, while nonuniform and highly localized dense dose delivery from ion particles may allow to produce a few but large deletions, translocations and so on, which are resulted in the various mutations. Table I lists typical examples of new and improved plant varieties induced by ion beam irradiation in TIARA [12-15].

4. SUMMARY

It is clearly shown that ion accelerator beam is very useful as a new experimental tool for wide fields of biological and biotechnological studies. The tool has two functions, which are an analytical probe and a surgical tool for microscopic inactivation. In TIARA much efforts have been so far concentrated on the technical improvement of the facilities for their advanced applications and also their efficient utilization to meet various requirements.
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HIGH POWER ELECTRON ACCELERATOR FOR ENVIRONMENTAL APPLICATIONS

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Abstract

At present, the world market of electron accelerator is saturated with the reliable and efficient plants of 0.3-3 MeV energy range and the power of the beam extracted into air up to 150 kW. However, such accelerators cannot satisfy the demand of new energy-intensive technologies (mainly referred to as ecological), which require accelerators with the power of an electron beam ranging from a few hundreds of kilowatts to tens of megawatts. In its turn, the megawatt power complexes require modules with a minimum unit power of hundreds of kilowatts.

1. INTRODUCTION

At the Budker INP SB RAS, the high voltage accelerators of a new generation with the required power of an electron beam extracted have been developed. One of these accelerators is the ELV-12 accelerator, with a power of electron beam of 400 kW at energy of 0.6-1.0 MeV.

2. DESIGN OF ELV-12 ACCELERATOR

The ELV-12 accelerator compiled all the design and technological solutions found and checked in the process of development and manufacture of the ELV-type accelerators. General vies of the ELV-12 accelerator is shown in Fig. 1.

Inside the vessel there is the tandem-type high voltage source, where two high voltage rectifiers placed one above the other are operated in parallel with the common load. Each rectifier consists of a set of rectifying sections connected between each other by the series-parallel circuit. Rectifying sections do not comprise filtering capacitors. The low rippling of the output voltage is provided by an increase of the operating frequency up to 1000 Hz, by the phase shift of the feeding voltage in the primary winding of the accelerator and by the presence of large constructive capacities in the accelerator (mainly capacities of gas feeders). At the point of connection, there is a special coil providing the power supply of electron injectors of accelerating tubes.

With the gas feeders the rectifying module is connected to the accelerating modules. The accelerating module is a separate vessel with the accelerating tube and beam current control system inside. The beam extraction device is connected to the bottom of the vessel. In addition, one accelerating tube can be placed in the rectifier vessel. The beam current in each accelerating module is controlled independently. The beam is controlled through the optic control system. The maximum beam current of a separate module is 200 mA. In this case, the maximum total current of the accelerator is 400 mA.

The accelerating tubes are the same as for all the ELV-type accelerators. As was already tested at the “Torch” accelerator, such tubes of the INP design and production enable the long time operation with the electron beam current of up to 0.8 A. Emission of electrons is performed with the thermo-emission LaB₆ cathode. The beam current is regulated by the cathode temperature at the same value of control voltage. This provides the stability of an electron beam at the entrance of the extraction device.
FIG. 1. ELV-12 accelerator common view.

1- rectifying module
2- accelerating module
3- rectifying column
4- high voltage feeder
5- injector control unit
6- accelerating tube
7- extraction device.

In the extraction device of the accelerating module shown in Fig. 2, two parallel foils are used for the beam extraction. An approximate trajectory of the beam along the extraction foils is also given in Fig. 2. The beam is scanned with the bending magnets standard for the ELV type accelerators. The only difference is the presence of a toggle magnet for a fast shift of a beam from one extraction window to another. In the toggle magnet, the current is synchronized with the scanning system so that the shift of the beam is performed at the maximum deviation of a beam in the extraction window (at its ends). At the time of the shift, the beam power is absorbed by the water-cooled protection cylinder, which is also the element of construction rigidity. The beam shift control system is completely automated based on PC within the limits of the accelerator general control program.

Extraction Titanium foils are cooled by the high speed air jets formed by two independent high pressure fans. The average current density in the foil does not exceed 100 µA/cm², which is two times less than the maximum admissible value of the current density for such rates of jets for foil cooling. This enables a manifold increase in the foil lifetime. The total beam power loss in such a two-window extraction device does not exceed 6%.

The long term and reliable work of the two-window extraction device was checked earlier on the ELV-6M accelerator. The beam current for this accelerator makes 200 mA for want of energy of accelerated electrons 0.75-1 MeV.
The high voltage insulation of ELV-12 is SF₆-gas as in other accelerators of the ELV-series. The rectifier module vessel and accelerating module vessels are filled with the SF₆-gas under high pressure.

**FIG. 2. Two-window extraction device.**
1- ion pumps
2- beam scanning system
3- protection water cooling cylinder
4- foil blow pipes
5- foil fastening frames
6- extraction titanium foils.

The primary winding of the high voltage rectifier is power supplied from static frequency converter thus providing high conversion coefficient of the electric energy into the electron beam energy.

The ELV-12 accelerator is controlled by a similar PC-based system for compatibility and flexibility over a broad range of operation. This system is fully automated and capable of operation without an operator. Its software provides all the necessary interfaces within the accelerator and between the accelerator and under-beam technology equipment. These are monitored continuously during the operation.

3. CONCLUSION

The ELV-12 accelerator is designed as a module type accelerator. It allows, using the single high-voltage rectifier and gang of accelerating modules over a wide range, to adjust distribution of a absorbed doze power. Besides that, because the designed high-voltage rectifier would provide the power of 1 MW, it is possible increase the power of electron beam extracted into air up to this level by magnification of a number of accelerating modules.

Now the ELV-12 accelerator is in the assembly stage; its main systems have already been checked early in work on other accelerators.
ALLANCE™ — THE NEW MULTI-MODAL FLEXIBLE IRRADIATION SYSTEM

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2MDS Nordion, Inc., Kanata, Ontario, Canada

Abstract

As the rapid progress of gamma irradiation markets, many developing countries eagerly want to own an irradiator that can adapt to a range of low-to-high-dose applications, and hope the facility is cost efficient. But few of them can afford the irradiators supplied by the developed countries. Maybe the Allance irradiator is a solution. The engineers from Beijing Institute of Nuclear Engineering (BINE) in China and from MDS Nordion in Canada, worked together for more than two years, presented a new irradiator named Allance in June. 2000. Allance is a single source-rack facility based on the design of MDS Nordion’s JS series carrier irradiators, its source capacity is 1.5 million curies Co-60. The dimension of the shield is:19 meters(L)×12 meters(W)×6meters(H). The distance between the center of the source rack and the inner pass carriers can be about 88mm. Each irradiator comes with a total of 50 product carriers. The dimension of each carrier is 1077mm(L)×663mm(W)×2950mm(H). The DUR (dose uniformity ratio) is less than 1.7. The source efficiency ratio can be 40% or more. The facility has three operational modes: Two Inner Pass Batch Mode, Two Outer Pass Automatic Mode and Four Pass Automatic Mode. It can satisfy various requirements of irradiation processing. The system is designed for manufacture and component sourcing in China, which partners high quality Canadian design with cost-efficient Chinese assembly.

1. INTRODUCTION

Gamma radiation is the preferred method used to sterilize single-use medical products. High-energy gamma ray penetrates all product parts. Varying densities, sealed cavities, foils, films and laminates can be sterilized through and through. Even products in hermetically sealed packaging and final shipping cartons can be treated. International companies depend on gamma for safe, effective processing with minimum turnaround time. When validated process procedures are established, products can be released for use immediately after processing.

Radiation processing has many other valuable applications including the treatment of various herbal and traditional medicines, consumer products and spices. Food can be treated to extend shelf life, reduce bacterial contamination and disinfection. Even automotive parts can be made stronger by radiation cross-linking. The list of products and applications just keeps growing.

In developed countries, because the products to be irradiated are normally in large quantity but few types, most of the new irradiators are large-scale special industrial facilities (10 million curies or more).

The radiation processing needs of developing countries have their own characteristics. Developing markets for gamma irradiation require irradiators that can adapt to a range of low-to-high-dose applications. Because the kinds of the products are various, the quantity of each product is small, and the absorbed dose is quite different. It will be ideal if one irradiator can have several operational modes, and it must be flexible and convenient to switch from one mode to another. Some developing countries, including China, keep working on this, and gain some achievements. But there are still many efforts needed to gain rationality and reliability.

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In 1998, engineers from China Beijing Institute of Nuclear Engineering (BINE) and Canada MDS Nordion Inc. began the co-operation to design a new irradiator. The design is based on the JS series industrial irradiators of MDS Nordion and the technology of BINE. In June 2000, they successfully presented the Allance irradiator. This innovative system is specifically designed and developed to address the radiation processing needs of developing countries. The Allance system satisfies the requirements with its three, flexible operational modes that adapt and grow with the changing gamma processing needs, from batch processing to fully automated irradiation.

2. THE FACILITY

This irradiator treats pre-packed materials by exposure to a controlled dose of gamma radiation emitted from a large cobalt-60 plate source. The boxed product is loaded into metal carriers and then conveyed automatically along a predetermined path past the source to ensure that a required dose is received. The entire arrangement is enclosed within a biological shield of thick concrete, see Fig. 1.

![Allance TM](image.png)

2.1. Product conveyors system

This system automatically transports the product to and from the radiation room. It consists of three main components: Source Pass Conveyor, Interim Transfer Conveyor and Storage Conveyor.

2.1.1. Source pass conveyor

Inside the irradiation room, carriers are conveyed along parallel monorails on each side of a rectangular rack containing the cobalt-60 sources. Pneumatic cylinders mounted on the source pass rails are used to move the product carriers forward. At each end of the source pass rails, a cross-transfer mechanism transfers the carriers from one pass to the next.

Guide rails are located on the floor to guide the keel on the bottom of the carriers in each pass. The carriers are thus guided top and bottom to maintain proper clearance between each pass.

Three modes of operation are available. In each mode, the product is irradiated on both sides of the source at two levels, the upper and lower shelves of the carrier, to ensure good cobalt utilization and radiation dose uniformity. The absorbed dose depends on the processing mode selected, product density and length of exposure time.
(a) Batch mode (Fig. 2)

This is ideal for batch processing of smaller lot quantities of product. Nine product carriers circulate around the source along the inner monorails and are then automatically transferred to a product interchange station outside the radiation shield where products on the two levels are interchanged. While the changing of the product levels is being performed, another batch is being processed. The product then re-enters the irradiator for completion of the cycle.

(b) Two-outerpass mode (Fig. 3)

For irradiation of many food products and other low to medium dose applications within a narrow dose range, the irradiator can be operated in an automatic mode which utilizes only the 2 outer monorails. In this mode 16 carriers are in the irradiator at any time. The changing of the product between the two product levels is performed at the product interchange station outside the radiation shield. Depending on this mode, the operators can accurately control the dose that the products received. Many foods and low dose products or narrow-dose-range products can be treated in this mode.

(c) Four-pass mode (Fig. 4)

For sterilization of medical products or other high dose applications, continuous irradiation of product source on both the inner and outer monorails provides the highest cobalt utilization. In this multi-pass mode, 22 carriers are automatically transported past the source, providing economical processing of large volumes of product in high dose applications. Again, the pallets are upper and lower shelves of the carrier at the interchange station outside the radiation shield.

The irradiator can be in any one of a number of modes, or states, that are mutually exclusive and limited as to the methods to reach each state. When switching from one mode to another, the operator needs to select the desired mode on the control console. The corresponding mechanism also needs tuning. The conversion operation is very simple and convenient.

In addition, the irradiator has two modes for maintenance: Maintenance Auto Mode and Maintenance Manual Mode. The source rack is in the safe position during maintenance mode. The workers can check and test the equipment in the radiation room.

2.1.2. Interim transfer conveyor

The Interim Transfer Area consists of two maze passages conveying carriers on overhead rails forming the connection between the source pass and the “irradiated” and “non-irradiated” storage conveyors. Carriers are indexed through the maze passages by pneumatic cylinders that move the carriers from the “non-irradiated” storage to the Source Pass Conveyor, and from the Source Pass Conveyor to the “irradiated” storage.
2.1.3. Storage conveyor
This is an arrangement of overhead tracks each with its own pneumatic movement mechanism. Carriers will be automatically conveyed into the radiation room from the “non-irradiated” storage conveyor, and from the radiation room, into the “irradiated” storage area. The product interchange station is in the storage area, where products on the two levels of each carrier are interchanged with a forklift.

2.2. Source rack
The source rack of *Allance* is a multi-level, vertical source rack with several doors. It takes advantage of the source racks design of *MDS Nordion* and that of *BINE*. Source pencils can be easily installed in it. A shroud for additional safety protects the sources rack. The source hoist mechanism is driven by a pneumatic system. When the air supply is shut off, the source returns by gravity to the safe position. A safety chain across the maze just inside the personnel access door is interlocked with the air supply to the source hoist. Unless this chain has been hooked across the maze, air cannot be supplied to the source hoist to raise the source.

2.3. Control system
*Allance*’s Control System consists of a Control Console with a Programmable Logic Controller (PLC) and a Computer. The Control Console with all of its functional operators and indicators is designed to operate the irradiator safety and efficiently. The PLC controls operation of the irradiator through the use of solid state relays, and various input/output devices it is the core of the control system and the safety system.

The Computer provides the operator with complete irradiator status including safety and logic conditions. The *Irradiator Management System (IMS)* (running in *Windows NT*) is installed in the computer. This application is used to monitor each procedure and record data in the *SQL Server Database*. During the processing, all abnormal events are recorded, and the on-line analysis system will give solution methods for the events.

In the power supply failure situation, the *Uninterrupted Power Supply (UPS)* can ensure the power supply to the control system lasting more than 10 minutes. This will allow the source rack return to the bottom of the Pool, and the operators can reset all the equipment to their safe condition.

2.4. Product carrier
The carrier is constructed of steel. It has two closed sides, a partially open back and an open front with swinging doors that encloses the product. The carrier is suspended by trolley assemblies that are attached to the top frame, and run on overhead rails. A keel is attached to the bottom frame and is used as a guide to keep the carrier in a vertical attitude.

3. PARAMETERS
*Allance* is a single source rack Co-60 γ Irradiator, its source capacity is C-188 type Co-60 55.5PBq (1.5 million curies). The dimension of the Shield is: 19 meters(L) × 12 meters(W) × 6 meters(H). External Shield Thickness: 2 meters (concrete wall and ceiling). The Source Storage Pool is 6.8 meters deep, and utilizes a stainless steel liner.

Co-60 C188 sources are held in a multi-level vertical framed source rack with several doors. The distance between the center of the source rack and the inner pass carriers can be about 88mm. Each irradiator comes with a total of 50 product carriers. The dimension of each carrier is shown in Table 1. DUR (dose uniformity ratio) of some main products: Red Meat <1.7, Medical Products <1.5, Shrink Material <1.4. The source efficiency ratio can be 40% or more.
Positions in Source Pass area are 32 (4 Passes). The facility has three operational modes: *Two Inner Pass Batch Mode*, *Two Outer Pass Automatic Mode* and *Four Pass Automatic Mode*. In addition, it has two maintenance modes: *Maintenance Auto Mode* and *Maintenance Manual Mode*.

**TABLE I. THE DIMENSIONS OF A CARRIER**

<table>
<thead>
<tr>
<th></th>
<th>Carrier outside size (mm)</th>
<th>Compartment size (mm)</th>
<th>Maximum size (mm)</th>
<th>Pallet size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>1077</td>
<td>1020</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Width</td>
<td>663</td>
<td>612</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Height</td>
<td>2950</td>
<td>1360</td>
<td>1200*</td>
<td>40</td>
</tr>
</tbody>
</table>

*excluding pallet.

4. CONCLUSION

The *Allance* Irradiation System stems from a winning combination of two companies with distinct strengths in irradiation and gamma processing. Steadfast processing, reproducibility, together with programmable logic controls, monitoring and safety systems are essential components of the *Allance* Irradiator. MDS Nordion design expertise brings to this system a history of safe and reliable operations worldwide. The system is designed for manufacture and component sourcing in China. BINE and MDS Nordion believe that the *Allance* is an important development in the expansion of radiation technology in the developing countries. It provides a flexible, cost-efficient solution that is tailored specifically for developing markets, and meets with the most rigorous safety and quality standards.
NEW PROGRESS ON RADIATION PROCESSING IN CHINA

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Abstract

This paper expounds the new progress on radiation processing in the 1990’s in China. The exposition covers the detailed materials, tables and drawings representing the development of radiation processing technology, progress of the radiation processing technology facilities, scale and capability of radiation processing products which have been industrialized, etc.

In the last ten years of the 20th century, radiation processing technology has developed rapidly in China. In this period we achieved the development from the stage of research test to the stage of industrialization, and the field has been developed as a new industry. It has brought about activity contribution for the economy of China.

1. RADIATION PROCESSING TECHNOLOGY HAS DEVELOPED INTO THE INDUSTRIALIZATION STAGE

At the end of 1999, total radiated product sales and technology service income was two billion Yuan (2,000,000,000.). The total production value (radiated foods, medical product, electronic elements and other radiated products) is 5 billion Yuan (5,000,000,000.) per year. The total capital fund has achieved 7 billion Yuan (7,000,000,000.). The growth rate per year is 25% (see Table I and Fig. 1.).

2. IRRADIATION PROCESSING TECHNIQUES HAVE BEEN RIPE FOR MANY KINDS OF IRRADIATION PRODUCTS

In the 1990’s, irradiation processing techniques have been ripe in China. Before that, academies, institutes and universities co-operated to do a long term and a systematic study and test of irradiation processing techniques for many radiation products, for example: heat shrink materials, chemical product, cross link wire and cable, irradiation food, medical products, etc. They depended on the support and money invested by national and local governments and industrial enterprises. Now national standards have been established for each kind of product.

2.1. Irradiation of food

There are six series and 18 kinds of irradiated foods that established national hygienic standards; there were several irradiated foods in the markets (see the Table II).

In addition, the national hygienic standard for seafood is being drafted. A publication on “Hygienic Administration Regulation for Irradiated Food” was issued on 5 April 1996 by the Public Health Department of the Government.

Irradiated food — for example: garlic, dried vegetables, spices, health food, red meat and its products, rice, beans, wines and dried fruits, etc. have been put into the market in batches.

In the 1999, the quantity of irradiated food in the market was more than 86 kilotons.
2.2. Radiation sterilization

Several medical products and hundreds of hygienic products have been treated by irradiation, were put into the market in batches and established the national standards (see the Table III).

(a) Standards for $\gamma$ ray radiation sterilization of disposable medical appliances GB16352-1996, issued on May 23, 1996

(b) Standards of Quality control for radiation sterilization of medical and hygienic products, GB16383-1996.

2.3. Radiated chemicals

Irradiated chemical materials have gone into the market and provided larger economic and social benefits. We are establishing national standards of irradiated wires and cables (see the Table IV).

2.4. Radiation treatment of environmental pollutants

Recently, China has further studied the treatment of city rubbish, wastewater and gas from burning coal by radiation technology. Especially relating to flue gas treatment by electron beam, the study of the technology was finished in the laboratory, and it underwent pilot and industrial tests. For example, the pilot test at the Chengdu Sichuan province has been in operation for two years.

3. PROGRESS OF IRRADIATION FACILITIES TECHNOLOGY IS RAPID

Along with development of radiation technology into industrialization, the technology and construction of industrial irradiation facilities developed speedily.

A batch of a new type, safe, high effect, advanced $\gamma$ irradiators and accelerators used for industrial irradiation were put into use (see the Table V).

3.1. Industrial $\gamma$ irradiator

Preliminary statistics show that at present there are 120 sets of $\gamma$ irradiators that are in operation. The industrial $\gamma$ irradiators designed capacity of loading Co-60 Source $1.11\times10^{16}$ Bq(300 kCi) number 55 sets (including 3 irradiators imported from abroad). The largest capacity irradiator designed loading source is $1.48\times10^{17}$ Bq(4 MCi), Shenzhen Irradiation Centre. The largest capacity irradiator designed by China is $3.7\times10^{16}$ Bq(1 MCi). The total of capacity loading source is $1.48\times10^{18}$ Bq(40 MCi). At the end of 1999, the total of loading source is $5.18\times10^{17}$ Bq(14 MCi). Irradiators are located in more than 40 cities in 25 provinces. In the period of ten years, the quantity of irradiators increased by 2.5 times; and the quantity of loading source increased by 3.5 times.

The features of development of industrial irradiators are, as follows:

(a) Using ways: multipurpose is more, special is less.
(b) Scale of design: most irradiators in China are $1.11\times10^{16}$ Bq(300 kCi) $3.7\times10^{16}$ Bq(1 MCi), many are of $1.85\times10^{16}$ Bq(500 kCi).
(c) Developing to standardization.
(d) The level of automation and mechanization of irradiator is largely increased.
(e) Issued and enforced the national standard “Regulations for design, construction and use of gamma radiation facilities”, GB17568 (1998).

3.2. Industrial accelerator

Within a period of ten years, development of accelerators used for industrial irradiation was great. Until to the end of 1999 the total of accelerators used for irradiation was 49 sets, the total power was
2830 kW (see the Table VI). The increase in quantity is 4 times; total power has increased 13 times (see the Fig. 2).

Table VII indicates the countries from where China imported accelerators. Of the 49 sets of accelerators, 22 sets were made in China, i.e. 45% with total power of 693 kW 24.5%, 17 sets were made in Russia, i.e. 35% with total power of 687 kW 24.3%, 8 sets were made in Japan and the USA, i.e. 16% but with total power of 1260 kW 44.5%, almost half of the overall total.

To see the scale and power, most of the accelerators are 1～3 MeV and 50～75 kW; at present these are main types accelerators used in China.

The industrial standard is “General Regulations for Accelerators used for Radiation Processing”, EJ/T 971-95.

3.3. Radiation processing and technological measures

3.3.1. Radiation protection and safety: the level of technology has been greatly increased and national standards were established

(a) Regulations for Radiation Protection of Radioisotope and Radiation Facilities, No.44 State, issued in October 1989.
(b) Administrative Regulations for Radiological protection of \( \gamma \) Ray Radiation Processing Assembly, issued on 26 April 1991.
(c) Standards for Radiation Protection and Safety of Co\(^{60} \) irradiation facility, GB10252-1996, issued on 19 December 1996.

3.3.2. Dosimetry system has been completed and established NDAS, IDAS and national standards

(a) Examination Rules for \( \gamma \) Ray Source (used for irradiation processing), JJG591-89, issued in 1989.
(b) Examination Rules for Electron Beam (used for irradiation processing), JJG772-92, issued in 1992.
(c) Practical Guide of Dosimetry in a Gamma Irradiation Facility for Food Processing, GB16334-1996, issued on 1 September 1996.
(d) 17 Standards of Dosimetry.

4. TECHNICAL FORCE WORK IN THE IRRADIATION INDUSTRY HAS BEEN GREATLY INCREASED

Radiation processing technology has been developed to reach the industrialization stage. The technicians who work directly in the study and development of irradiation technology and production increased greatly from 1000 people before 1990 to 10000 people by the end of 1999. They are from the food industries, chemical industries, medical and hygienic industries, etc. and moved to the radiation technological industries.

5. PROSPECTS OF DEVELOPMENT OF RADIATION PROCESSING TECHNOLOGY INDUSTRY IN CHINA

In the 21\(^{st} \) century, radiation processing technology industry in China is undergoing more development. It will be faster, along with the Chinese economic development.

(a) Further studies and development of radiation processing technology techniques will be made to spread the scale of radiation processing industries. First, big achievement is on hand which is being used on food, sterilization, and chemical industries, especially to intensify industrial using on sterilization of medical and hygienic products by radiation technology, as quick as possible instead of ETO by \( \gamma \) Ray, working hard for achieving an objective: 70 80% of medical and hygienic products
adopting radiation technology to sterilize, as well as spreading actively into the industrial sector applying in the environment protection industries; first to do best is industrial use of flue gas treatment by EB. Until 2010 at least 20 sets of industrial plant for EB flue gas treatment will be operated.

(b) To intensify management of design, construction and operation of irradiation facilities implementing strictly national standards issued, a management organization has been established led by the China Isotope and Radiation Association and supported by the Government to regulate and design the construction and use of irradiation facilities.

To elaborate amply the latent capacity of irradiation, facilities have been built and to create more economic benefits.

At present efforts are made to increase construction of $1.85 \times 10^{16}$ Bq–$3.7 \times 10^{16}$ Bq(0.5–1 MCi)type $\gamma$ irradiator and make further study; to develop $1.11 \times 10^{17}$ Bq (3–5 MCi)type $\gamma$ irradiator; until 2010 total of loading source of Co-60 will be $3.7 \times 10^{18}$ Bq(100 MCi). Regarding the accelerator used for industrial irradiation at present, efforts are made to spread 1–3 MeV 50–80 kW type, speed up the study and development of 3–4 MeV, 250–320kW type accelerator used for flue gas treatment, working hard for commercial usage from 2 to 3 years. And until 2010, total accelerator power will be 10000kW.

(c) To increase co-operation by radiation industries

Elaborating large scale's economic benefits, and in order to avoid low level, small, repeated study and construction, the Radiation Processing Special Committee of China Isotope and Radiation Association will encourage co-operation and collaboration by radiation industries. This co-operation is a guide of the market. The dominant factor for irradiation products is promoting and developing fully the large plants — deemed very important in order to form the large radiation industrial groups and fields such as in radiation sterilization, irradiation food, radiation chemical and environmental protection, etc. If all work goes well, production value of irradiation processing industry will achieve more than 100 billion Yuan until 2010 per year.
**FIG. 1. Growth of radiation processing technology.**

**FIG. 2. Development of accelerators used for industrial irradiation.**
**TABLE I. RADIATED PRODUCT SALES INCOME**

<table>
<thead>
<tr>
<th>Kind of product</th>
<th>Heat shrink materials</th>
<th>Wire and cable</th>
<th>Radiation chemical</th>
<th>Radiation food</th>
<th>Radiation medical products</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sell income</td>
<td>764</td>
<td>584</td>
<td>338</td>
<td>78</td>
<td>90</td>
<td>146</td>
</tr>
<tr>
<td>Ratio (5)</td>
<td>38.2</td>
<td>29.2</td>
<td>16.9</td>
<td>3.9</td>
<td>4.5</td>
<td>7.3</td>
</tr>
</tbody>
</table>

**TABLE II. IRRADIATED FOODS THAT ESTABLISHED NATIONAL HYGIENIC STANDARDS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of kinds</th>
<th>No. of standard</th>
<th>Irradiation dose</th>
<th>Name of food</th>
<th>Issue time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Irradiated cooked meat of livestock and poultry</td>
<td>GB14891.1-1997</td>
<td>8.0kGy</td>
<td>Pork, beef, lamb, rabbit, duck, chicken</td>
<td>1997.6.8</td>
</tr>
<tr>
<td>2</td>
<td>Irradiated dried nuts and preserved fruits</td>
<td>GB14891.3-1997</td>
<td>0.4-1.0kGy</td>
<td>10 series</td>
<td>1997.6.8</td>
</tr>
<tr>
<td>3</td>
<td>Irradiated dried spice</td>
<td>GB14891.4-1997</td>
<td>10.0kGy</td>
<td>All of spice</td>
<td>1997.6.8</td>
</tr>
<tr>
<td>4</td>
<td>Irradiated fresh fruits and vegetables</td>
<td>GB14891.5-1997</td>
<td>1.5kGy</td>
<td>Potato, onion, garlic, tomato, apple, etc. – 17 kinds</td>
<td>1997.6.8</td>
</tr>
<tr>
<td>5</td>
<td>Irradiated frozen packaged meat of livestock and poultry</td>
<td>GB14891.7-1997</td>
<td>2.5kGy</td>
<td>Pork, beef, lamb, rabbit, duck, chicken, frozen packaged</td>
<td>1997.6.8</td>
</tr>
<tr>
<td>6</td>
<td>Irradiated beans, grains and their products</td>
<td>GB14891.8-1997</td>
<td>Beans: 0.2kGy, Grains: 0.4-0.6kGy</td>
<td>Beans, grains and their products</td>
<td>1997.6.8</td>
</tr>
</tbody>
</table>
### TABLE III. KINDS OF IRADIATED MEDICAL PRODUCTS IN THE MARKET IN CHINA

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of product</th>
<th>Package material</th>
<th>Raw materials</th>
<th>Situation in market</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liquid transfusion device</td>
<td>Plastics</td>
<td>Plastics PVC</td>
<td>Big batch</td>
</tr>
<tr>
<td>2</td>
<td>Injection needle</td>
<td>Paper</td>
<td>Stainless steel, plastics</td>
<td>Big batch</td>
</tr>
<tr>
<td>3</td>
<td>Blood transfusion device</td>
<td>Plastics</td>
<td>Plastics PVC</td>
<td>Big batch</td>
</tr>
<tr>
<td>4</td>
<td>Blood transfusion tubes</td>
<td>PE</td>
<td>Polypak, silicon rubber</td>
<td>Big batch</td>
</tr>
<tr>
<td>5</td>
<td>Bandage and dressing</td>
<td>Paper/plastics</td>
<td>Plastics, cotton yarn, non-woven cloth</td>
<td>Big batch</td>
</tr>
<tr>
<td>6</td>
<td>Medical gloves</td>
<td>Paper</td>
<td>Emulsion, talcum powder</td>
<td>Big batch</td>
</tr>
<tr>
<td>7</td>
<td>Surgical clothes</td>
<td>Paper/plastics</td>
<td>Non-woven cloth, cotton yarn</td>
<td>Big batch</td>
</tr>
<tr>
<td>8</td>
<td>Nutriments</td>
<td>Paper box/glass box</td>
<td>Liquid, solid, Powder</td>
<td>Big batch</td>
</tr>
<tr>
<td>9</td>
<td>Chinese medicine</td>
<td>Paper box/glass box</td>
<td>Chinese herbal medicine</td>
<td>Big batch</td>
</tr>
<tr>
<td>10</td>
<td>Herbs</td>
<td>Paper/plastics</td>
<td>Herbs</td>
<td>Developing and spreading</td>
</tr>
<tr>
<td>11</td>
<td>Cosmetics</td>
<td>Plastics/glasses</td>
<td>Chemical materials</td>
<td>Spreading</td>
</tr>
<tr>
<td>12</td>
<td>Woman’s Napkins</td>
<td>Paper/plastics</td>
<td>Plastics/non-woven cloth</td>
<td>Spreading</td>
</tr>
<tr>
<td>13</td>
<td>Children’s napkins</td>
<td>Paper/plastics</td>
<td>Plastics/non-woven cloth</td>
<td>Spreading</td>
</tr>
<tr>
<td>14</td>
<td>Hygienic towel</td>
<td>Paper/plastics</td>
<td>Paper, non-woven cloth</td>
<td>Spreading</td>
</tr>
<tr>
<td>15</td>
<td>Furs</td>
<td>Paper/plastics</td>
<td>Furs</td>
<td>Spreading</td>
</tr>
</tbody>
</table>

### TABLE IV. IRRADIATED CHEMICAL PRODUCTS IN THE MARKET IN CHINA

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of product</th>
<th>Raw materials</th>
<th>Situation in market</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heat shrink materials and their products</td>
<td>Plastics</td>
<td>Big batch</td>
</tr>
<tr>
<td>2</td>
<td>Wires and cables</td>
<td>Plastics, copper, aluminium</td>
<td>Big batch</td>
</tr>
<tr>
<td>3</td>
<td>Catalytic agent of printing and dyeing</td>
<td>Chemical materials</td>
<td>Big batch</td>
</tr>
<tr>
<td>4</td>
<td>PAA (Polyacrylamide)</td>
<td>Chemical materials</td>
<td>Big batch</td>
</tr>
<tr>
<td>5</td>
<td>Crystal and gems get or change color</td>
<td>Crystal and gems</td>
<td>Batch</td>
</tr>
<tr>
<td>6</td>
<td>Medical silicon rubber tubes</td>
<td>Rubbers</td>
<td>Big batch</td>
</tr>
<tr>
<td>7</td>
<td>Rubbers sulphurate</td>
<td>Rubbers</td>
<td>Batch</td>
</tr>
<tr>
<td>8</td>
<td>Lack of mutual of battery</td>
<td>Plastics</td>
<td>Batch</td>
</tr>
<tr>
<td>9</td>
<td>Coat curing</td>
<td>Plastics, paint</td>
<td>Batch</td>
</tr>
</tbody>
</table>
### TABLE V. SITUATION OF DEVELOPMENT OF IRRADIATORS IN CHINA

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sets</td>
<td>31</td>
<td>37</td>
<td>68</td>
<td>36</td>
<td>172</td>
</tr>
<tr>
<td>Use</td>
<td>Study</td>
<td>Study, development</td>
<td>Study, industrial</td>
<td>Industrial irradiation</td>
<td></td>
</tr>
<tr>
<td>Source/set (Bq)</td>
<td>$3.7 \times 10^{13}$ - $3.7 \times 10^{14}$</td>
<td>$3.7 \times 10^{14}$</td>
<td>$&gt;3.7 \times 10^{15}$</td>
<td>$&gt;11.1 \times 10^{16}$</td>
<td></td>
</tr>
<tr>
<td>Co-60 source</td>
<td>SSSP, Canada</td>
<td>Canada, China</td>
<td>China, Canada, UK</td>
<td>Canada, Russia, UK</td>
<td></td>
</tr>
<tr>
<td>Way of source storage</td>
<td>Dry</td>
<td>Water pool</td>
<td>Water pool</td>
<td>Water pool</td>
<td></td>
</tr>
<tr>
<td>Construction of source rack</td>
<td>Point, rod</td>
<td>Flower basket type</td>
<td>Plate type</td>
<td>Single plate</td>
<td></td>
</tr>
<tr>
<td>Hoist</td>
<td>By hands</td>
<td>Electric</td>
<td>Electric</td>
<td>Electric and hydraulic</td>
<td></td>
</tr>
<tr>
<td>Control system</td>
<td>By hand</td>
<td>Electric</td>
<td>Electric, PC</td>
<td>PC and computer</td>
<td></td>
</tr>
<tr>
<td>Interlock system</td>
<td>Not</td>
<td>Electric</td>
<td>Electric and electron</td>
<td>Electric, electron mechanism</td>
<td></td>
</tr>
<tr>
<td>Conveyor system</td>
<td>By person</td>
<td>By person</td>
<td>Suspending conveyor</td>
<td>Automatic suspending</td>
<td></td>
</tr>
</tbody>
</table>

*a More than 50 of small γ irradiators have been closed, indeed 120 sets of γ irradiators are operating.
*b Total of loading source capacity is $1.48 \times 10^{18}$ Bq (40 Mci). Until the end of 1999, total of loading source is $5.18 \times 10^{17}$ Bq (14 MCi).

### TABLE VI. ACCELERATORS USED FOR INDUSTRIAL IRRADIATION (IN THE 1990s)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total quantity</td>
<td>10</td>
<td>13</td>
<td>18</td>
<td>29</td>
<td>30</td>
<td>36</td>
<td>40</td>
<td>44</td>
<td>46</td>
<td>49</td>
</tr>
<tr>
<td>Total power</td>
<td>225</td>
<td>400</td>
<td>650</td>
<td>935</td>
<td>955</td>
<td>1295</td>
<td>1436</td>
<td>1950</td>
<td>2690</td>
<td>2830</td>
</tr>
</tbody>
</table>

### TABLE VII. SUPPLIERS OF INDUSTRIAL IRRADIATION ACCELERATORS

<table>
<thead>
<tr>
<th>Country</th>
<th>Quantity</th>
<th>Share %</th>
<th>Power (kW)</th>
<th>Share %</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>22</td>
<td>45</td>
<td>693</td>
<td>24.5</td>
</tr>
<tr>
<td>Russia</td>
<td>17</td>
<td>35</td>
<td>687</td>
<td>24.3</td>
</tr>
<tr>
<td>USA</td>
<td>5</td>
<td>10</td>
<td>490</td>
<td>17.3</td>
</tr>
<tr>
<td>Japan</td>
<td>3</td>
<td>6</td>
<td>770</td>
<td>27.2</td>
</tr>
<tr>
<td>France</td>
<td>2</td>
<td>4</td>
<td>190</td>
<td>6.7</td>
</tr>
</tbody>
</table>
IMPLEMENTATION OF EB RADIATION STERILIZATION PROCESS IN POLAND

Z. ZIMEK, I. KALUSKA
Department of Radiation Chemistry and Technology,
Institute of Nuclear Chemistry and Technology,
Warsaw,
Poland

Abstract

Radiation sterilization has been applied at the Institute of Nuclear Chemistry and Technology (INCT) since 1973. INCT facilities and activity in the field of radiation sterilization commercial service were described.

1. INTRODUCTION

The first accelerator installed at INCT was UHF linac LAE 13/9 with electron energy adjustable in the range 5-13 MeV and 9 kW of average beam power [1]. Electrons in this accelerator are accelerated in the field of a traveling electromagnetic wave. A regulated microwave power divider and regulated microwave phase shifter are the principal components of the waveguide line between accelerating section. Regulation of UHF power and phase at the input of second section makes it possible to vary the electron energy in the wide range including the case when electrons are deaccelerated in second accelerating section. The accelerator was equipped with two output windows for horizontal beam used for pulse radiolysis experiments and vertical scanned beam for radiation processing. Electron beam current densities up to 80 µA/cm² are extracted horizontally into the air through a 50 µm titanium window. The vertical beam is formed by a 270° electromagnet and scanning device. The electron beam is directed down towards the conveyor through a 50 µm titanium window 60 cm long. That multipurpose facility equipped with LAE 13/9 electron accelerator were used for pulse radiolysis experiments, radiation sterilization of medical devices, polymer and semiconductors modification and other radiation technologies applied on laboratory and industrial scale.

Radiation sterilization was the first radiation technology implemented on industrial scale at INCT. It was proceeded with research works and testing of radiation tolerance of different plastic materials, microbiological studies on sterilization effectiveness, elaboration of suitable dosimetric systems for routine dose and dose-depth determination. The research and commercial irradiation was made using linear electron accelerator LAE 13/9. The detailed research program where performed in 1973-1977 period to developed methods and procedures and evaluate suitable materials for industrial application of the process. The commercial irradiation was started in 1974. Since that continuous progress has been observed in quantity of sterilized products. The nominal electron beam parameters 10-13 MeV and 9 kW of average beam power can provide approximate capacity of 10 million pieces of sterile product per year and allowed to perform regular radiation sterilization service [2]. The increasing demands for radiation processing (polymer and semiconductors modification), experimental work in the field of radiation chemistry (basic study) and R&D activity heave been observed in second decade of LAE 13/9 accelerator exploitation. Accordingly, other electron accelerator facilities were planned and built at INCT as dedicated, more specialized units.

Van de Graaff electrostatic accelerator type AS-2000, which was installed in 1988, is used as a laboratory tool in the field of radiation physics and radiation chemistry. The dose distribution measurements in the gas phase were performed using this facility in preliminary stage of flue gas treatment technology development. Low energy, high power accelerator ILU 6M2 type was installed in 1988 to be applied as a pilot plant for radiation processing of polymers and a large scale irradiation unit. A laboratory unit for flue gas treatment with gas flow capacity of 400 Nm³/h has been constructed later on. The composition of the flue gas coming from two natural gas fired boilers can be adjusted by dosage with different gaseous pollutants like SO₂, NOₓ and VOCs (volatile organic compounds) for farther investigation. Pilot facility for food irradiation localized at INCT was equipped with two electron accelerators installed in 1990 (PILOT) and 1993 (ELEKTRONIKA). A pilot plant
with a flue gas flow capacity of up to 20 000 Nm$^3$/h (by-pass of main gas stream from the boiler) was constructed according to INCT project at the Kaweczyn Electric Power station (EPS) located in Warsaw. Two accelerators in step by step configuration was applied first time in large scale flue gas treatment facility. Construction and successful operation of the pilot plant provided the data base for industrial demonstration plant design. Vertically installed ELEKTRONIKA 10/10 type accelerator was applied in facility for radiation sterilization of medical devices (1993). The newest electron accelerator LAE 10 has been constructed at Department of Radiation Chemistry and Technology (INCT) and put into operation in 1999. This facility is dedicated to pulse radiolysis and related experiments in the field of radiation chemistry (basic study). The main parameters of accelerators installed at INCT and currently used are shown in Table I.

### TABLE I. ELECTRON ACCELERATORS INSTALLED AT INCT

<table>
<thead>
<tr>
<th>Type of accelerator</th>
<th>Year of installation/producer</th>
<th>Energy and beam power</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAE 13/9 UHF linac</td>
<td>1971 NIIFA, Russia</td>
<td>5 – 13 MeV, 9 kW</td>
<td>Multipurpose facility, basic research, R&amp;D, processing</td>
</tr>
<tr>
<td>AS 2000 Electrostatic</td>
<td>1988 HVEC, Holland</td>
<td>0,1 - 2 MeV, 0,2 kW</td>
<td>Radiation chemistry and Radiation physics</td>
</tr>
<tr>
<td>ILU 6 HF resonator</td>
<td>1988 INF, Russia</td>
<td>0,5 - 2 MeV, 20 kW</td>
<td>Pilot plant for polymer process,, flue gas treatment lab. unit</td>
</tr>
<tr>
<td>PILOT UHF linac</td>
<td>1990 IPJ, Poland</td>
<td>10 MeV, 1 kW</td>
<td>Pilot plant for food irradiation</td>
</tr>
<tr>
<td>ELW 3A Transformer</td>
<td>1991 INF, Russia</td>
<td>0,5 - 0,7 MeV, 2 x 50 kW</td>
<td>Pilot plant for flue gas treatment, Power Station Kaweczyn</td>
</tr>
<tr>
<td>ELEKTRONIKA UHF linac</td>
<td>1993 TORIJ, Russia</td>
<td>10 MeV, 10 kW</td>
<td>Radiation sterilization</td>
</tr>
<tr>
<td>ELEKTRONIKA UHF linac</td>
<td>1993 TORIJ, Russia</td>
<td>10 MeV, 10 kW</td>
<td>Pilot plant for food irradiation</td>
</tr>
<tr>
<td>LAE 10 UHF linac</td>
<td>1999 INCT, Poland</td>
<td>10 MeV, 10 ns</td>
<td>Basic research in the field of radiation chemistry</td>
</tr>
</tbody>
</table>

2. EB INDUSTRIAL FACILITY FOR RADIATION STERILIZATION

Dedicated electron beam facility for radiation sterilization of single use medical devices was designed and introduced into the operation to increase sterilization capacity of INCT facilities [3]. A UHF linear electron accelerator, with traveling wave and 10 MeV electron energy, 10 kW average beam power was placed vertically to avoid a bending magnet and related beam power losses. A high average power magnetron is used as a source of microwave energy. Accelerator ELEKTRONIKA 10/10 and the auxiliary equipment are located in a separate building. The storage area is divided into two separate parts; one for untreated and the other for irradiated products. A microprocessor controlled roller and belt conveyors systems are used to carry irradiated boxes of a typical size of 46 x 58 x 20 cm. The speed of the conveyor located in the irradiation chamber, where a stainless steel belt has been applied, can be varied continuously within the range 0.3 - 7 m/min. The program of capacity upgrading by use more powerful source of microwave energy (up to 15 kW of average beam power) is being started now [4]. The main facility parameters are shown in Table II.
Traceability of the product being sterilized in both accelerators (LAE 13/9 and ELEKTRONIKA 10/10) is achieved by computer recording data of the irradiation parameters. An adequate software was designed by INCT staff to collect automatically readings of such parameters as beam current, energy, scan parameters, conveyor speed and allow to enter the data about customer and product. The data are printing on the label which is put on each sterilized package. To increase the total capacity of the facility an additional accelerator installation in the same building is being considered.

3. REGULATION CONCERNING RADIATION STERILIZATION PROCESS

Till today above described facilities are the only ones in Poland where the radiation sterilization of medical devices is performed on a commercial scale. The amount of customers varied through that long period of our activities. In early 80’s this method of sterilization was a new challenge of Polish manufactures and they took a great interest on it. In centralized economy several factories under government administration have established the production of limited number single use medical devices. The amount of irradiated medical products has shown the continuos grow what can be seen on Fig. 1; to such extent that Polish authorities have decided to provide suitable funds to build dedicated facility only for radiation sterilization process. When arrangements associated with a new facility were in progress political changes in Poland influenced economical situation of the country. In market economy the prices of any goods were released including the price of energy, which was increased tremendously. For this reason we have lost at that time our customers and the total time of the service calculated for one year was reduced dramatically in the beginning of 90’ what is reflected on Fig. 2. Nowadays instead of several factories around 50 private manufactures have signed a contract on irradiation service. The continuos grow of radiation sterilization service is observed again. Over 40 different types of single use medical devices are being sterilized among them: bimedical implants and tissue grafts, burn pads, cannulas, catheters, dialysis unit, drains, Petri dishes and labware, pharmaceutical ingredients, surgical gloves, talc and powders, towels, urine collection kits and many others.

For many years the internal sterilization procedures were fine enough for INCT as the contractor and for customers, the manufacturers of medical devices. The standards concerning radiation sterilization appeared in mid 90’s (EN 552:1994 and ISO 11137:1995). The content of those standards gives the requirements regarding validation procedures and routine control of sterilization using ionizing radiation that should be performed. Taking into account manufacturers requirements and different regulation about sterility it became obvious that national regulations concerning radiation sterilization should be introduced to every day practice. To have a worldwide picture of above mentioned subject Polish Committee of Standardization (PCS) have decided that Polish representative would participate in ISO/TC 198 Working Group 2 concerning Radiation Sterilization as an observer. Later on PCS has appointed a Standardization Working Group for Sterilization, Dezinfection and Antiseptics with mentioned above observer as one of the members. Although ISO 11137 covers wider range of products which can be sterilized by radiation and it is obvious that it implementation should cause that
sterilization process would be less expensive than after implementation of EN 552, it was decided that the Polish translation of EN 552 would become the national standard. The one of the main reason why EN 552 was chosen as a Polish standard was the joining process to European Committee. EN 552 has become a Polish Standard in 1999 [5].

**FIG. 1.** Continuous growth shown by the amount of irradiated medical products.

**FIG. 2.** Reduced time of service due to political and economic changes.

4. REMARKS AND CONCLUSIONS

EB radiation sterilization facilities installed at INCT can be recognized as part of the total device manufacturing process where GMP (good manufacturing practices), GIP (good irradiation practices), total quality management system are being applied. To meet such demands the validation of accelerator and handling equipment has been performed and routine control of sterilization process are being done according to established procedures. The growing interest in electron beam sterilization
process provides substantial base for future progress in terms of capacity of provided service and facility development. Although at the beginning stage of the sterilization process implementation the facility throughput level usually is not a critical the regular established contract irradiation service should be based on two independent irradiators (limited accelerator reliability) to provide smooth operation. The average beam power of INCT facilities devoted to radiation sterilization will be increased to 30-50 kW level in few years time. It should be noticed that to achieve substantial unit cost reduction electron beam power should be adequate to capacity of the provided irradiation service. Product handling capabilities will establish practical limit of electron beam power applied for the sterilization process.

REFERENCES

STATE AND PROSPECTS OF RADIATION PROCESSING TECHNOLOGIES IN TUNISIA

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1Centre National des Sciences et Technologies Nucléaires, Tunis,
2Institut Préparatoire aux Ecoles d’Ingénieurs de Monastir, Monastir, Tunisia

Abstract

The state and prospects of radiation processing technologies in Tunisia with emphasis on prospective research and development activities are discussed. Cobalt 60 Irradiator of the National Centre of Sciences and Nuclear Technologies (CNSTN) at Sidi – Thabet is the newest and the first radiation processing demonstration plant in the country, commissioned in May 1999, will play a great role in enhancing research and development work in the areas of food irradiation, sterilization of medical devices, sterile insect technique, radiation processing of plastics and conservation of art objects. However, the radiation processing technology will be reinforced in the near future with the installation of an Electron Beam machine to be set in proximity of the gamma irradiator at CNSTN. This paper presents an overview of the current and prospective industrial applications of radiation processing technologies utilising gamma radiation and Electron Accelerator in Tunisia.

1. INTRODUCTION

In Tunisia the use of the process of ionizing radiation on an industrial scale began in May 1999 with the setting up of the pilot unit, equipped with a radioactive source of cobalt 60. This gamma irradiator of maximal activity of 100 000 curies, is geared to the promotional activities of the radiation processing technology in the fields of agriculture, health industry and environment.

It is worth mentioning that Tunisia has a large agricultural vocation but the industry for medical devices and pharmaceuticals is performing very well and it is contributing increasingly in the national economy.

2. INDUSTRIAL APPLICATIONS OF RADIATION PROCESSING

2.1. Food irradiation

Tunisia is an important agricultural country and exports several agro-food products. Knowing that techniques of storage and conditioning not being always satisfactory, the technique of treatment by ionizing radiation produced profitable alternative therefore to improve the food availability destined to the self-consumption and to assure a better chain of distribution. Several tests of treatment by ionizing radiation have been undertaken in Tunisia in the domain of the agro-food on several products. Studies of economic feasibility undertaken before the installation of the pilot unit of Sidi Thabet proved and demonstrated that this technology could be applied safely and cost-effectively.

Dates constitute an important export commodity, Tunisia ranks third in export after Iraq and Saudi Arabia [1]. National production is averaging 100,000 tons per year [2]. Deglet Nour, the best variety on the market occupies 30% of the world exchange value and satisfies more than 40% of the needs of the European Community. Unfortunately, dates are frequently subjected to microbial contaminations as several works [3] (also: Mahjoub, 1986) and [4] showed that dates are contaminated regularly by molds.

According to work done in Tunisia on the irradiation of dates, it is noticed that an important decrease of the microbial load is observed and proportional to the doses applied (Table I), indeed, from the dose of 4 kGy the microbial load disappear. Thus, this technique of irradiation could be used to control of microorganisms after packaging.
Other tests had also been made on sea products such as fishes and shrimps. The fishery industry constitutes a key sector of the national economy, which generates good revenues from exports of shrimps, fishes and octopus.

In 1997, the shrimp production of Tunisia was estimated at 89027 tons [5].

The impact of five increasing doses of ionizing radiation on the decontamination and the increase of the storage length of shrimp wrapped and refrigerated at 4°C has been studied, it proved that doses of 4 and 5 kGy constitute the optimal doses of shrimp irradiation since they permitted to destroy the total and faecal coliforms completely and to maintain the total germs to a very low level [5].

**TABLE I. EFFECT OF THE IRRADIATION ON THE REDUCTION OF THE NUMBER OF DATE MICROORGANISMS, VARIETY DEGLET NOUR**

<table>
<thead>
<tr>
<th>Irradiation Dose (kGy)</th>
<th>Microorganisms</th>
<th>Total germs</th>
<th>Vegetative forms</th>
<th>Spores</th>
<th>Molds</th>
<th>Yeast</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>4.1 x 10⁴</td>
<td>4.0 x 10⁴</td>
<td>5.4 x 10²</td>
<td>3.7 x 10³</td>
<td>7.8 x 10²</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>2.4 x 10³</td>
<td>2.0 x 10³</td>
<td>4.0 x 10²</td>
<td>2.6 x 10²</td>
<td>5.5 x 10¹</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1.6 x 10²</td>
<td>8.7 x 10¹</td>
<td>7.3 x 10¹</td>
<td>1.4 x 10¹</td>
<td>1.3 x 10¹</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3.2 x 10¹</td>
<td>2.0 x 10¹</td>
<td>1.2 x 10¹</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE II. POTATOES, GARLIC AND ONION PRODUCTION (TONS)**

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Potatoes</td>
<td>200 000</td>
<td>210 000</td>
<td>233 000</td>
<td>270 000</td>
<td>289 000</td>
<td>295 000</td>
</tr>
<tr>
<td>Onion</td>
<td>270 000</td>
<td>262 000</td>
<td>254 000</td>
<td>238 000</td>
<td>246 000</td>
<td>245 000</td>
</tr>
<tr>
<td>Garlic</td>
<td>6 600</td>
<td>5 600</td>
<td>6 000</td>
<td>8 000</td>
<td>7 300</td>
<td>10 000</td>
</tr>
</tbody>
</table>

Other tests have also been carried on the ionisation of almonds, strawberries, refrigerated red meats and cheese. All experiments showed good results for longer storage periods with acceptable organoleptic quality. Currently, tests are underway for protocole setting for local varieties of potatoes, onions and garlic to inhibit germination during long storage periods.

Tunisia produced in 1998, 295 000 tons of potatoes (Table II) with losses due to storage of about 10 to 15% per year, considering the price of the ton of potatoes that is equal to 200 dinars, losses would be annually 2 000 000 to 3 000 000 dinars [2]. The near totality of the production is sold at the national market for local consumption.

Locally produced potatoes is under testing for a cost effective protocol combining Irradiation with storage at low temperatures (10 and 15°C).

**2.1. Technique of the sterile insect**

A lot of works have been made on the estimation of economic advantages of medfly management on fruit crops using the sterile insect technique in the Maghreb countries.

The use of the sterile male insect became a technique which use is urgent due to damages caused by the devastating flies.
According to evaluations of the AIEA in 1995 [6] losses owed to these insects especially medfly are of the order of 9.24 thousand tons for citrus, 7.25 thousand tons for pome fruits and 14.7 thousand tons for stone fruits in Tunisia.

Two tests using the sterile male technique have been carried out in Tunisia and results proved to be encouraging.

CNSTN is actually implementing a project for the construction of an insect factory for exclusive production of fruit fly males that will be sterilised and released in fields of the citrus areas.

The technique of the sterile insect became a technique whose use is urgent since damages caused by this pest are tremendous and widespread to many fruit varieties.

2.3. Sterilization of medical devices

In this domain, all advantages of the sterilization process by the ionizing radiation on using gamma radiation of Cobalt 60, or, electron beam accelerator had been put forward and were well documented.

During the year 1999, the Tunisian export trade showed a decrease of 72 % at the level of the pharmaceutical product in comparison to 1998 (Table III). No single cause could explain this regression, but it is worth mentioning that our products are not Gamma sterilized which could have hampered our export in these items. the application of Gamma irradiation for the medical devices will certainly promote the business export toward the European countries, where stringent regulations are applied [7].

2.3.1. Single-use surgical material

2.3.1.1. Probes, catheters, perfuseurs, transfuses, extra-bodily lines of circulation, tubules diverse, blood bags, etc.

These items generally represent an important volume of consumption; the indication of National industrial production for the pharmaceutical industry recorded a progression of the order of 60 % between 1993 and 1998 (Table IV). There are manufactured especially in PVC, plastic matter that rests a problem of deterioration under radiation. It is the reason for which these PVC articles are in principle sterilized by oxide of ethylene. This being, the radio - steady material choice becomes today possible to costs that permit to consider medium-term a transfer of the market of the ETO sterilization toward the radio - sterilization. Otherwise, this transfer will require experimentation and tests that can constitute a non-negligible load plan for the irradiation unit of CNSTN. The sterilized volume can reach 4000 m$^3$/year [1].

2.3.1.2. Hypodermic syringes

Syringes represent a very thick market for the sterilization. In general, Europe uses of the order of 4 syringes per year and per person, what would represent a market extrapolates to Tunisia of $36 \times 10^6$ syringes/year [1]. The hypodermic syringes are manufactured in polypropylene, that can especially pose problems of supporting to the gamma radiation and may turn yellow in color. Experimentation must be undertaken on this topic with close cooperation with the manufacturers. If this problem is solved, the market is very attractive for the CNSTN, which means: 1050 m$^3$ of products at short-term and 2100 m$^3$ at long-term, with a fast saturation load of the Cobalt 60 unit, which has a total yearly capacity of treatment of 800 m$^3$ [1].

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Products</td>
<td>13.0</td>
<td>24.0</td>
<td>12.0</td>
<td>5.8</td>
<td>15.9</td>
<td>18.8</td>
<td>5.8</td>
</tr>
</tbody>
</table>
TABLE IV. NATIONAL PRODUCTION FOR THE PHARMACEUTICAL INDUSTRY
(BASIS: 100 IN 1990)

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceutical industry</td>
<td>147.2</td>
<td>180.9</td>
<td>229.3</td>
<td>224.9</td>
<td>231.0</td>
<td>235.8</td>
</tr>
</tbody>
</table>

2.3.1.3. Compresses and bandages

These articles are generally sterilized by steam. Because of their weak density, electrons would be generally better placed economically than gamma. On the other hand, bandage items are more sophisticated than the classic gazes, and can not be sterilized by steam nor by ethylene oxide, such as: impregnated compresses, collagen, hemostatic, self adhesive bandages. Tunisia exported in 1998 about 80 tons of these products [2].

2.3.1.4. Surgical gloves

The market is very open for radiation sterilization for this product. The Tunisian manufacturers of gloves stopped their operation because of the stiff competition coming from Asian glove manufacturers, whose prices are much cheaper. Alternatively, bulk import of these articles can be foreseeable with final packaging and sterilization in Tunisia. Then, CNSTN will be in charge of the radiation sterilization of these articles.

2.4. Reticulation of thermoplastics

By free radical formation, treatments by ionizing radiation of polymers lead to the important modifications of macromolecular chains while conferring thus to the plastic matters irradiated of new physico - chemical and mechanical properties.

Three types of macromolecular modifications can be exploited industrially: The reticulation of thermoplastics, radiation grafting of a monomer on a polymer and radiation degradation of polymer. The Tunisian market has especially been prospected in the domain of the reticulation. The reticulation of thermoplastics is the transformation of a linear network non-branched out in a tridimensionnel network.

The new proprieties are very interesting: Better holding in temperature, insolubility, flame resistance, elastic properties, Stress - cracking resistance, resistance to the compression, superficial toughness. This radiation reticulation is applied for: ribbons, gains, insulation of cables, tubes for hot water, vulcanization of rubbers and silicones.

For the installation of its pilot unites of treatment by ionizing radiation (Cobalt60 and accelerator of electrons), the CNSTN undertook a survey of market and a technico - economic feasibility survey [1]. These studies showed that many Tunisian companies are strongly interested by radiation reticulation. Indeed, the electric cable domain recorded an important growth at the level of the export since 1993 (Table V). The value of the export can progress again during the next decade, if the Tunisian industry manages to solve several technical problems in order to improve some physic - chemical properties of cables, for example the problem of the heat resistance. Among these Industrials we can mention "ELECTRIC CABLE" and "TUNISIA CABLES".

TABLE V. EVOLUTION OF EXPORT OF ELECTRIC CABLE (MILLION DINARS)

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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Electric cable</td>
<td>103.3</td>
<td>121.6</td>
<td>142.1</td>
<td>178.0</td>
<td>241.7</td>
<td>302.7</td>
<td>361.0</td>
</tr>
</tbody>
</table>
In 1999, ELECTRIC CABLE produced with the new line 630 000 km/year of cable car with an increase of the production of 57 % (Table VI), of which 60 % are targeted to export. ELECTRIC CABLE is interested by radiation reticulation of electric cable to raise the temperature of utilization in continuous service and to increase the resistance to the accidental or occasional rises of temperature owed to a short - circuits (solely cables class 3 are produced: resistance to 125 ° C during 2000 hours in continuous). The radio - reticulate cables can resist temperatures of 300 ° C, what is going to permit development of the cable class 4 and 5 for cables close to the motor block. The laboratory of control of ELECTRIC CABLE arranges all means allowing him to test a radiated product and therefore to follow the development of these new products. It will be dealt with by a joint research group, CNSTN-ELECTRIC CABLE.

TUNISIA CABLE produces the electric cables of low and medium voltages and also for measurements. At the present time it produces about 500 Km of reticulate cable by year, by a chemical process. The chemical processes take place in coercive conditions because they require a mixture to about the fusion point of the polymer without thermal decomposition of the peroxide in the case of the treatment of a polymer saturated with a peroxide, or an elevated vulcanization temperature in the case of a treatment of a polymer with sulfur. In addition the length, the degree and the homogeneity of the reticulation are easier to control for a radiated polymer.

2.5. Coloration of glass articles

Submitted to the action of ionizing radiation , some articles in glass can be over valued by the development of colours. This simple technique permits to color the finished articles while avoiding to glassmakers of colourful glass the use of fusion.

Two types of coloration can be developed:

— Yellow color, brunette, and crotchet, through trapping of electrons and formation of unsteady colorful centres,
— Specific colors due to the types of mineral traces present in the glass: yellow, blue, green, orange, and purple, by oxide-reduction.

These colors are stable in the time. This process of coloration applies very well to the small bottles of perfume. The SOTUVERRE company, one of the most important Tunisians glassmakers, is interested by the coloration by ionizing radiation. This society even considers raising its manufacture to 50 million small bottles of perfume per year, with a demand in coloration of about 10 [%][1]. This technique of coloration will allow this company to avoid difficult coloration carried out by fusion and to get colouration in a more satisfactory quality than surface treatments.

The yearly National production of bottles in glass in 1999 is 19100 Tons [7]. Table VII shows the evolution of the yearly production of bottles in glasses in Tunisia between 1990 and 1999. In 1998, our country exported about 2779.108 Tons of bottles in glasses, about 16% of the National production. Bottles in coloured glasses only represent about 9% of the volume of the export.

### Table VI. Electric Cable Production of Car Cable (1000 Km)

<table>
<thead>
<tr>
<th>Year</th>
<th>1996</th>
<th>1997</th>
<th>1998</th>
<th>1999</th>
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<tr>
<td>Car cable</td>
<td>225</td>
<td>300</td>
<td>400</td>
<td>630</td>
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### Table VII. Glass Bottles Production (1000 Tons)

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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass bottles</td>
<td>17.2</td>
<td>17.5</td>
<td>18.9</td>
<td>15.2</td>
<td>19.0</td>
<td>14.2</td>
<td>17.8</td>
<td>16.7</td>
<td>17.4</td>
<td>19.1</td>
</tr>
</tbody>
</table>
2.6. Conservation of art objects

After the installation of the pilot unit of Sidi – Thabet, contacts had been done with the officials of the National Museum of Bardo, in order to benefit from this new technology for the conservation and the restoration of our cultural heritage.

3. CONCLUSION

It is difficult to state all the different applications that the Tunisian economy would benefit from this new radiation technology process. But, it is well clear that the products we mentioned in the paper will undoubtedly be advantageous, quality and quantity wise. The Cobalt 60 unit will be reinforced by an Electron Beam machine that will take in charge products more suitable to be treated with electrons and eventually fill the different gaps that Gamma irradiation will leave.

REFERENCES

PROMOTION STRATEGY AT MULTIPURPOSE IRRADIATION FACILITY –
IRASM, ROMANIA

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Bucharest,
Romania

Abstract

Multipurpose Irradiation Facility “IRASM” is the result of the Technical Co-operation Project
ROM/08/11 between the International Atomic Energy Agency and Romanian Government that started in 1993.
Official objective of the project was “to establish a demonstration facility”. IFIN-HH, the most important nuclear
institute of the country, received the responsibility of setting up the irradiator. The irradiator’s economic future is
logically related to this responsibility.

The real state of the art of radiation processing in Romania prompted us to integrate the promotion of
specific means in a broader approach, probably better covered by the word “acceptance”. To this aim, it was
defined as an interactive puzzle of related targets d to involve science, techniques, legislation and market.

This paper presents the strategy we followed to implement industrial radiation processing in Romania and
evaluates its achievements at the moment of facility commission.

1. INTRODUCTION

The Technical Co-operation Project ROM/8/011, “Multipurpose Irradiation Facility”, made between
the International Atomic Energy Agency and Romanian Government, 1993-2000, had the objective of
establishing a demonstration gamma irradiation facility. It is called IRASM and is the first industrial
irradiator in Romania. At the commissioning it was loaded with a 100 kCi Co-60 source, that means a
productivity of 50000 kGy x m³/year (2000 m³/year at 25 kGy as sterilizing dose). Biological
protection, source holder and hoist mechanism and auxiliary systems permit a source load 20 times
greater. Though it is specially designed for sterilization, the facility is flexible enough for other
irradiation technologies like food treatments or cultural heritage preservation.

IRASM, a compartment of IFIN-HH, is located near Bucharest, the capital and economically most
important city of Romania.

IFIN-HH, a national R&D institute, is an experienced operator of large nuclear facilities (research
reactor, cyclotron and tandem accelerators, waste treatment plant, radioisotope production). The
institute was considered to have proper knowledge and structure for establishing and operating this
first Romanian industrial irradiator.

Having a proper structure and organization at the company level could be favorable for setting up the
irradiator.

Having basic nuclear knowledge could be a good premise for safety and efficient everyday operation
and maintenance.

IFIN-HH noticed that these favorable premises only would not automatically assure the economical
success of the irradiator and of irradiation processing in Romania. Therefore, a project task force was
nominated in 1994. It was called Radiation Processing Team (RPT).
2. CONSTRUCTION THE PROMOTION STRATEGY

RPT first goal was to analyze all aspects involved in project implementation and to prepare a realistic promotion strategy in the view of having clients for IRASM’ activity at the facility commission.

RPT started its activity trying to ask good questions and thus hoping to find the best answers. Most important of them were the following:

(a) **Question:** What does it mean promotion of radiation technologies?

**Answer:** There is a high tech to be promoted whose efficiency and viability on the market depends on multiple interconnections between science, techniques, legislation and public acceptance. It was stated that this complexity is the reason why irradiation technologies slowly penetrate the market in countries with low or medium economic level, like Romania.

**Question:** How could look the most pessimistic general state of the art?

**Answer:** Objective and subjective reasons can be claimed for a pessimistic state of the art.

— Knowledge on radiation is confuse and considered unfriendly, even by educated people
— It is a lack of proper legislation and of established control methods
— Supposing these difficulties overcame, it is needed a previously adopted and audited GMP practice on clients’ production chain and GLP practice in health laboratories devoted to control and license medical products
— Last but not least, ignorance and fear, sometimes undeclared, makes promotion of radiation processing a complex and difficult task.

**Consequence:** This view is probably typical for a country unprepared for adoption a high tech like radiation processing

(b) **Question:** How much of mentioned general view is true for Romania?

**Answer:** The pessimistic view is partially true for Romania.

**Consequence:** Promotion by ordinary methods can hardly be successful. A successful approach must structure all involved aspects.

(c) **Question:** Which are additional specific characteristics for Romania?

**Answer:**

— Romania is on the way of changing the centralized economy by a free market economy. The process is accompanied by a general economic stagnation (the market is abruptly changing; big state companies shut the doors; export declined; legislation is changing)
— Some facts indicate the regulatory bodies and public opinion do not reject irradiation treatments (medical supplies - mostly parapharmaceuticals - coming from abroad were licensed, imported irradiated chicken meat was on the market)
— On academic level there is experience concerning radiation technologies and radiation facilities (some small facilities were set up in R&D institutes after original designs - they operated for long time; one can find specialists, even PhD theses on the subject)

— There is a general effort in the country for establishing a legislative system compatible with that of European Union

Consequences:

— One could hardly count on a pressure from industry to improve legislation problems

— Specialists could be gathered and involved in every aspects of project promotion

Based on briefly presented analyze, RPT designed a **Frame-Program (FP)** - a puzzle of needs, necessary not only for “establishing a demonstration facility” (ROM/8/011 official objective) but also for irradiator successful operation.

The Frame Program IRASM put together actions and final objectives - Fig.1.

![Diagram of the Frame-Program of IRASM project](image)

**FIG.1. The Frame-Program of IRASM project**

3. PROJECT PROMOTION

FP target was to prepare technical, technological and legislative bases for radiation processing promotion and the promotion itself.

The concrete actions necessary for facility establishment counted on dedicated services at the company (IFIN-HH) level: design and construction work supervision, radioprotection, and quality assurance.

The profile of IFIN-HH permitted to agglutinate an R&D team of different specialists in radiation chemistry, dosimetry and microbiology.

Specific actions’ resources came directly from the Government and from R&D national program “Orizont 2000”.

261
The main results of this approach were:

— a facility designed and constructed in conformity with strictly followed quality assurance prescriptions, offering confidence to Nuclear and Health Regulatory Bodies

— a Final Safety Report, in compliance with IAEA guide and USA regulations, convened with and agreed by National Nuclear Regulatory Body

— basic knowledge on radiation processing of different kind of products, packaging, international licensing procedures, alternative sterilization methods, dosimetry

— adoption in Romania of most important international standards for radiation microbiology, GMP rules in drug, medical devices and dry herbs manufacture; ISO standards for dosimetry and packaging will be adopted soon

4. PROMOTION METHODS AND ACHIEVEMENTS

Because promotion itself is based on: gaining confidence on scientific results, economic advantages for producers and benefit for common people, FP identified and used the following methods for end-user assistance:

4.1. Starting R&D projects in partnership with possible end-users

These projects are parts of newborn national R&D program “RELANSIN”, end-user oriented. RELANSIN is organized, as it is European Union Program FP 5. The industrial partner proves his interest by co-financing the project and has the benefit of the result.

Five projects are approved and financed (microbial control of dry herbs - a methodological project aiming to trace the licensing procedure, peat sterilization for agricultural needs - 3 different projects - and a project devoted to general promotion of IRASM and radiation processing).

4.2. Spreading information

(a) Three information booklets of general and specific interest were published and spread. They are dedicated to:

— Radiation sterilization of medical supplies (sterilization concept, industrial sterilization options for medical supplies, pharmaceuticals and cosmetics, microbiological validation procedure, packaging and constitution plastics, ETO-gamma conversion)

— IRASM facility and applications of radiation technologies (layout - design, nuclear safety, physical protection, licensing procedures in the different countries and European Union, Romanian legislation, applications)

— Preservation of cultural heritage by irradiation

The fourth one devoted to food treatment is in press. The fifth, concerning packaging, is previewed to be prepared in the frame of a RELANSIN project.

(b) Reference papers were sent to the Health Regulatory and Control Bodies concerning other countries’ experience in validation / utilization of radiation technologies.

(c) Important scientific papers, internal and European Union legislation and commented concepts on radiation treatment are handled to potential end-users (GMP code, EU Directives 2 and 3/1999, parametric release concept etc).

(d) A mini-library is organized and can be consulted free of charge.

262
4.3. Public meetings

Starting from 1997, RPT constantly organized or participated at national seminars and contacted end-users. To mention a few:

— 1997 — “Irradiation Technologies and IRASM facility” was a workshop that was oriented to legislators and end-users, organized by IFIN-HH and National Atomic Energy Agency (NAEA); 12 invited papers; a moving picture recorded at similar facilities in Hungary and Turkey; a round table discussion focused on legislation.

— 1998 and 1999 — Papers presenting IRASM at national seminars “NUCINFO 98” and “NUCINFO 99” organized by NAEA; press conferences.

— 2000 — “Basic and Practical Knowledge on Radiation Sterilization and Microbiological Validation”, a seminar organized by IFIN-HH, headed by Professor L. Gazso, IAEA expert in radiation microbiology. It was oriented to health regulatory bodies and end-users.

4.4. Lobby at governmental level

By Romanian Government Decision No. 400/1997, IRASM was nominated as a ‘Facility of National Importance’. It meant provision of a state financial support to partially cover the operation cost. Postponing the repayment of investment until the facility will reach sufficient demands for economic independence is under negotiation.

5. CONCLUSIONS

— Promotion and implementation of radiation processing in Romania started at the beginning of TC Project ROM/8/011. This activity was the charge of a task force - RPT. The members of the team had experience in R&D. Part of them became the operation personnel.

— Enlarging the meaning of term “promotion” by including scientific and legislative activities, RPT improved the legislation.

— At the operation start of the facility, an opinion favorable to radiation treatments dominates at the Health Regulatory Bodies level. The most important one - National Agency for Drugs - accepted to participate at a RELANSIN project.

— Four companies co-finance R&D projects that will end with a technology transfer, radiation treatment included. There are other companies expressing the intention of working with us.

ACKNOWLEDGEMENTS

The efforts of IAEA are highly acknowledged, not only for the financial support under the IAEA Technical Co-operation Project ROM/8/011, but also for the belief in our determination to finish the project in spite of various difficulties.

The authors wish to express their gratitude to the organizers of this Symposium that made possible the presentation of this paper.
<table>
<thead>
<tr>
<th>IAEA-SM-365/</th>
<th>Name(s)</th>
<th>Designating Member State/Organization</th>
<th>Title</th>
</tr>
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<tbody>
<tr>
<td>101 P</td>
<td>Doan, B.</td>
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<td>Determination of surface grafted structure of acrylic acid onto rubber-based thermoplastic elastomer</td>
</tr>
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<td>Abdel-Aziz, M.M.</td>
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<td>Radiation crosslinking of ternary polymer blends based on polyvinyl chloride, nitrile rubber and polychloroprene rubber. Part I: Physical and mechanical properties</td>
</tr>
<tr>
<td>103 P</td>
<td>Khan, M.A.</td>
<td>Bangladesh</td>
<td>Effect of structure and glass transition temperature (Tg) of monomers on the performance of radiation cured film</td>
</tr>
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<td>104 P</td>
<td>Sedlakova, Z.</td>
<td>Czech Rep.</td>
<td>Structure and physical properties of vinyllactame networks prepared by radiation</td>
</tr>
<tr>
<td>105 P</td>
<td>Zhai, Maolin</td>
<td>China</td>
<td>Radiation improvement of the melt flow property of polypropylene in the presence of bifunctional monomers</td>
</tr>
<tr>
<td>106 P</td>
<td>Xie, Hongfeng</td>
<td>China</td>
<td>Theoretical research of PTC properties of polymer/carbon black composite</td>
</tr>
<tr>
<td>107 P</td>
<td>Deng, Pengyang</td>
<td>China</td>
<td>Radiation effect of PLA and PCL polyblend system</td>
</tr>
<tr>
<td>108 P</td>
<td>Zhou, Yong</td>
<td>China</td>
<td>Study on oxygen inhibition effect of EB curing</td>
</tr>
<tr>
<td>109 P</td>
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<td>China</td>
<td>Grafting reactivity of pre-irradiated polypropylene film</td>
</tr>
<tr>
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<td>China</td>
<td>Radiation effects on the immiscible polymer blend of nylon 1010 and high impact polystyrene (hips): morphology and thermal behaviour</td>
</tr>
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<td>111 P</td>
<td>Zhang, G.X.</td>
<td>China</td>
<td>Formation of porous polymeric materials by polymerizing bicontinuous microemulsions</td>
</tr>
<tr>
<td>112 P</td>
<td>Ni, Yonghong</td>
<td>China</td>
<td>A novel route to prepare cadmium sulfide nano-rods</td>
</tr>
<tr>
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<td>Jia, Shaojin</td>
<td>China</td>
<td>Analysis of rheology and morphology of PP/SBS blends irradiated by gamma rays</td>
</tr>
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<td>China</td>
<td>Elastomer/flame retardant for insulation by gamma rays</td>
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<td>China</td>
<td>Study of plasma-polymerized deposition of C2H2/CO2/H2 onto ethylene-co-propylene rubber membrane</td>
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<td>Viet Nam</td>
<td>Study on the effect of in vitro plant growth promotion of oligochitosan produced by radiation technique</td>
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<tr>
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<td>Japan</td>
<td>Radiation processing of biodegradable polymer (3). Crosslinking of carboxymethyl starch at paste-like condition</td>
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<tr>
<td>120 P</td>
<td>Xing, Xiao Hei</td>
<td>China</td>
<td>The comprehensive radiation technique for improving the utilization rate of rice straw</td>
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<tr>
<td>121 P</td>
<td>Prieto Miranda, E.F.</td>
<td>Cuba</td>
<td>The radiation sterilization: a tool of the Cuban medical-pharmaceutical industry</td>
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<td>122 P</td>
<td>Muñoz-Burgos, R.A.</td>
<td>Ecuador</td>
<td>Study on the radiolysis of lignin contained in wood sawdust</td>
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<td>Borisenko, A.</td>
<td>Kazakhstan</td>
<td>Radiation technologies on industrial electron beam accelerator elv-4</td>
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<td>124 P</td>
<td>Gonzalez, M.E.</td>
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<td>Swelling behaviour and gel fraction of gamma irradiated polyvinyl alcohol films</td>
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<td>125 P</td>
<td>Wach, R.A.</td>
<td>Japan</td>
<td>Radiation processing of biodegradable polymer (2) hydrogel from cellulose derivatives</td>
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<td>126 P</td>
<td>Ren, Jing</td>
<td>China</td>
<td>Radiation synthesis and characteristic of IPN hydrogel composed of poly(diallyldiethylammonium chloride) and kappa-carrageenan</td>
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<td>127 P</td>
<td>Yi, Min</td>
<td>China</td>
<td>Radiation preparation of blend hydrogels composed of dadmac and nipaam</td>
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<td>Zhang, Yanqun</td>
<td>China</td>
<td>Effect of KC and KCl on strength and thermo-responsivity of KC/nipaam gel</td>
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<tr>
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<td>Mao, Benjiang</td>
<td>China</td>
<td>A pilot plant for flue gas desulphuration and denitrification with electron beam irradiation</td>
</tr>
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<td>130 P</td>
<td>Nitchipor, G.V.</td>
<td>Belarus</td>
<td>Theoretical study on decomposition of CH2Cl2 in nitrogen and dry air under influence of electron beam</td>
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<tr>
<td>131 P</td>
<td>Kostoski, D.</td>
<td>Yugoslavia</td>
<td>Charge trapping in gamma irradiated polyethylene</td>
</tr>
<tr>
<td>132 P</td>
<td>Lee, M.J.</td>
<td>Republic of Korea</td>
<td>Pilot plant test for reclamation of sewage by irradiation</td>
</tr>
<tr>
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<td>Republic of Korea</td>
<td>Surface modification of polypropylene film for blood compatibility by radiation induced grafting</td>
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<td>134 P</td>
<td>Takriti, S.</td>
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<td>The effect of gamma radiation on sewage wastewater of Damascus plant</td>
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<td>Trojanowicz, M.A.</td>
<td>Poland</td>
<td>Radiolytic degradation of 2,4-d herbicide for environmental purposes</td>
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<tr>
<td>137 P</td>
<td>Gao, De Yu</td>
<td>China</td>
<td>Absorption of chemicals by SAPC prepared by radiation polymerization</td>
</tr>
<tr>
<td>138 P</td>
<td>Bao, Borong</td>
<td>China</td>
<td>Study on decolourization of dye in water by pulse radiolysis</td>
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<tr>
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<td>Bao, Hua Ying</td>
<td>China</td>
<td>Application of irradiation in treatment of industrial wastewater</td>
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<td>Dodbiba, A.</td>
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<td>Dosimetry and irradiation technique of polyethylene film</td>
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<td>Salimov, R.A.</td>
<td>Russian Federation</td>
<td>New technological applications of elv type accelerators</td>
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<td>Auslender, V.L.</td>
<td>Russian Federation</td>
<td>Ilu electron accelerators with energy 5-10 MEV and beam power 50-100 kw for food product processing</td>
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<td>143 P</td>
<td>Makarovska, O.</td>
<td>Ukraine</td>
<td>Review of use of radiation technologies in the industry of Ukraine</td>
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<tr>
<td>144 P</td>
<td>Wang Guorong</td>
<td>China</td>
<td>Quality evaluation of the traditional Chinese medicine sterilized or decontaminated by $^{60}$Co gamma rays</td>
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<td>Method of measurement and calculation on absorbed dose to various dense irradiated products</td>
</tr>
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<td>148 P</td>
<td>Yan Aoshuang</td>
<td>China</td>
<td>Gamma ray radiation modifications on polymer materials</td>
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<tr>
<td>149 P</td>
<td>Wang Huaifa</td>
<td>China</td>
<td>Magnetic property modification of iron bearing minerals by electron beam irradiation</td>
</tr>
<tr>
<td>150 P</td>
<td>Nam, Irina</td>
<td>Kazakstan</td>
<td>Gamma-radiationally synthesized hydrogels of vinyl ethers with stimuli-sensitive behaviour</td>
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