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Stability and stabilization of polymers under irradiation

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FOREWORD

Considering the beneficial uses of high energy radiation in health care and polymer processing industries, two major applications can be seen to be emerging and becoming well established. These are sterilization of single use medical disposables and modification of polymer properties. Both involve extremely small chemical changes applied to macromolecules yet resulting in new systems with very considerable physical and biological advantages. The major challenge of every radiation processing application where macromolecules are involved is the inhibition of unwanted material property changes which often occur when materials are irradiated and to predict useful lifetimes. Stability and stabilization of polymers under irradiation environments thus has become a key issue in the extensive and still growing use of radiation processing in polymer processing and modification.

During the last decade a number of meetings have been organized under the auspices of the IAEA in order to elaborate recent developments in the application of radiation chemistry in polymer based industries.

The Co-ordinated Research Project (CRP) on Stability and Stabilization of Polymers under Irradiation was initiated in 1994 based on the recommendation of the final Research Co-ordination Meeting on Radiation Damage to Organic Materials in Nuclear Reactors and Radiation Environment (IAEA-TECDOC-351) and the Advisory Group meeting organized in 1991 at the University of Maryland, United States of America.

The CRP was established for the purpose of focusing the attention of technical experts on the complex task of establishing a better understanding and attacking problems of radiation degradation of polymers. The group interactions have been designed to achieve a synergistic interaction among the research groups for the purpose of identifying degradation problems, exchanging ideas and results on the solution of these problems. It was clearly pointed out during the active discussions that important new approaches are developing for the stabilization of materials to ionizing radiation. The Research Co-ordinated Meetings (RCMs) held during the CRP provided the forum for exchange of research ideas, which otherwise is not occurring very effectively in this field.

The present publication includes the contributions presented at these meetings. Collectively, they describe the progress in understanding and controlling the radiation induced changes, and most extensively degradation, in polymeric materials. It is hoped that it will provide a useful overview of current activities and of future trends in this field. The work and efforts of all contributors and expert editing of this TECDOC by R. Clough is gratefully acknowledged. The IAEA officer responsible for this publication is O. Güven of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

CONTENTS

SUMMARY OF THE CO-ORDINATED RESEARCH PROJECT

1. BACKGROUND

The contributions presented in this technical publication describe progress in understanding and controlling the degradation of polymeric materials induced by exposure to ionizing radiation. This subject area is of widespread importance to industrial use of radiation for two classes of applications: 1) the processing and production of polymeric materials by means of irradiation facilities, and 2) the use of polymeric materials in applications for which they must withstand irradiation throughout the course of their useful lifetimes.

Due to the extensive and still-growing use of polymeric materials for technological applications of immense variety, and the fact that radiation-processing has the potential to play an expanding role in polymer manufacturing (current uses include crosslinking, curing, sterilization, surface modification, lithography, etc.), the ability to inhibit unwanted material property changes which often occur when materials are irradiated, and to predict useful lifetimes, remains a limiting factor in a number of existing radiation technologies. Additionally, the ability to control unwanted degradation will be necessary for successful implementation of future, more advanced, radiation processing schemes.

The phenomena involved in radiation-degradation are exceedingly complex. In some instances, suitable stabilization technology is yet to be developed. In other cases, a functional stabilization scheme may exist, but its fundamental basis as well as its details are solely in the hands of one or more private firms, who keep the information proprietary. Despite the needs of both developing and developed nations for radiation stabilization methodologies, there exist only fragmented and widely scattered research efforts in this area, and the results are often not well communicated. Similarly, in the case of materials needed in the construction of radiation-related facilities (nuclear power plants, particle-physics experimental facilities, radiation processing plants, nuclear waste storage technologies, space vehicles, future fusion reactors, etc.), the ability to develop radiation-resistant materials will continue to be a key capability of widespread importance.

This co-ordinated research project was established for the purpose of focusing the attention of appropriate technical experts on the complex task of establishing a better fundamental basis for understanding and attacking problems of radiation degradation of materials. The group dynamics have been designed to achieve a synergistic interaction among worldwide research facilities for the purposes of identifying degradation problems, exchanging ideas and results on the solution of these problems, and making the emerging information available in an organized and accessible format. From this meeting, it is clear that much remains to be learned in terms of understanding degradation mechanisms and phenomena. It also appears that important new developments may be possible in stabilization techniques.

2. OBJECTIVES OF THE MEETINGS

Two meetings were convened by the IAEA with the main objectives of reviewing problems and progress in the stability and stabilization of polymeric materials towards exposure to ionizing radiation. Participants of the group have come together to share and to document cutting-edge research on new approaches to enhancing the radiation-stability of polymeric materials. Participants are also working to develop and test practical means of implementing radiation-resistant material formulations for commercial applications in the radiation processing industry (sterilization, crosslinking of polymers); such technology is presently not fully available due to the proprietary nature of many details of formulations and test procedures.

3. SHORT SUMMARY OF INDIVIDUAL CONTRIBUTIONS

Nine of the important contributions presented at the meetings are reported here. They demonstrate that the occurrence of degradation problems remains an important impediment to the commercial implementation of radiation-processing of polymeric materials in many applications and in many countries, and that the aging of polymers in long-term applications in nuclear-related facilities remains an ongoing problem. The contributions also demonstrate that there is significant progress in understanding degradation processes and in development of new approaches to enhancing the stability of polymers to radiation-induced effects.

Sun of the Chanchun Institute of Applied Chemistry, China, has made a series of important advances in demonstrating new approaches to improving radiation resistant properties of polymers. Both the phenomena and ideas are new. One approach is by formation of network structure (crosslinking) in polymers which inherently undergo chain scission. Fluorinated polymers can be crosslinked by irradiation at high temperature. When the crosslinked material is subsequently exposed to radiation at or near room temperature in the course of its intended application, it exhibits dramatically enhanced resistance to radiation-induced changes in properties from degradation (scission) effects. For pre-crosslinked PTFE, the radiation resistance is increased by 2 orders of magnitude. For a copolymer of C_2F_4 and C_2F_6, the pre-crosslinking improves the radiation stability by 10–50 times. Radiation-crosslinking of fluoro-polyimide at elevated temperature also greatly increases its stability, including its resistance to hydrolysis.

Another novel technique for enhancing polymer stability is through blending a crosslinkable polymer with a scissioning polymer. For example, when the scissioning polymer, polymethylmethacrylate (PMMA), is blended with the crosslinking polymer, polyisobutylene (PIB) in a ratio of 70:30, the resultant material retains its mechanical properties at high absorbed dose (such as 370 kGy), whereas the pure PMMA undergoes dramatic degradation at a similar dose.

Related work on the beneficial application of the technique of chemiluminescence, for examining the radiation-oxidation of stabilized polymeric materials, is summarized in a recent publication.

Clough of Sandia National Labs in the United States of America has reported on stability of polymers to radiation-induced degradation in mechanical properties and in optical properties (discolouration). A key finding is the occurrence of post-irradiation annealing (recovery) of properties in certain cases.

Many reports in the literature describe post-irradiation degradation effects in polymeric materials when irradiated samples are subjected to elevated temperature or held at room temperature for an extended time period. They have now found several examples of materials which exhibit the opposite effect: a post-irradiation recovery of mechanical properties when the irradiated sample is subsequently exposed to elevated temperature. The recovery can be dramatic in some cases. Samples which show this effect also exhibit another surprising phenomenon: the extent of degradation is larger when the sample is irradiated at room temperature than when it is irradiated at elevated temperature (e.g. 60°C).

They conclude from the large increase in gel content that occurs upon annealing that these phenomena result from a thermally-activated crosslinking reaction that counter-balances the chain scission which occurs upon low temperature irradiation, and which greatly reduces the effect of the scission on the macroscopic mechanical properties. Polymers which show this effect are all partially crystalline elastomers, having significant melting behaviour over the temperature range of the experiments. The annealing effect occurs only in the case of irradiation in the presence of air, indicating that the crosslinking is initiated by an oxidative species.

In related work, a collection of about 15 important optically-transparent polymer types were surveyed; most showed strong radiation-discoloration. Two types of color centers were formed: annealable color centers (shown by ESR to be connected to residual free radicals), and permanent color centers. The annealable color centers disappear via slow diffusion of oxygen into the sample, as it sits in air. The annealing rate, which is related to the oxygen permeability coefficient for the material, increases strongly at elevated temperatures. The recovery is dramatic in some materials; for example, in Nylon, PMMA and PET, the original degree of optical transmittance is almost fully restored after annealing. Tables of relative stability of polymers to radiation-discoloration, both before and after annealing, have been produced; a summary of the results are available in a recent publication.

The future potential of utilizing annealing phenomena for application to commercial/industrial purposes was discussed. Further work to understand and potentially control the annealing phenomena is necessary.

Feldman of the Karpov Institute of Physical Chemistry, Russian Federation, reported on fundamental aspects of the selectivity of radiation-induced chemical effects in polymers, in terms of localization of primary damage in macromolecules, real polymers and organized polymer systems. A specific feature of the approach used was a combination of ESR and IR spectroscopic studies of irradiated samples at low and super low (cryogenic) temperatures (down to 10 K). This made it possible to assign the localization and spatial distribution of primary events in the systems of various structure. Analysis of the radiation-induced species trapped in model hydrocarbons in low-temperature matrices, and in related polymers irradiated at low temperatures, revealed a remarkable correlation between the properties of the prototype ionized molecules and the selectivity of primary bond rupture in the corresponding macromolecules in the cases of polyethylene, polystyrene and some unsaturated hydrocarbons. This implies that the structure of ionized molecules, which is sensitive to conformational defects, weak intermolecular association etc., may control the mode of initial damage in the macromolecules.

It is suggested that using hole scavengers rather than "energy" (excitation) scavengers may provide a new way to stabilizing hydrocarbon polymers against radiation. On the other hand, electron scavengers (even in trace amounts) proved to have a sensitizing effect. New experimental data concerning primary localization of the radiation-induced effects in other polymers (polycarbonate, poly(alkylene terephthalates)) were also presented, and relevant mechanisms were discussed.

Another aspect of the studies reported was concerned with the specific features of the radiation-induced chemical effects in bicomponent microheterogeneous systems (block copolymers, interpolymers, polymer blends). It was shown that the interphase electron migration might result in both positive and negative non-additive effects in the formation of the radiolysis products in the polystyrene-based microheterogeneous systems. This may be used for designing a specific approach to stabilization and sensitization of these systems. The mechanisms of radiation protection were also analyzed for the case of microheterogeneous polycarbonate-based blends and copolymers of various structure.

Baccaro, of the ENEA Casaccia Laboratories, Italy, reported that the radiation induced effects (measured by infrared and ESR techniques) on ethylene-propylene copolymers are strongly influenced by oxygen and dose rate. In particular the oxidative degradation increases at low dose rate values due to increased time for oxygen diffusion. The IR profile is a good method to monitor the nonhomogeneous oxidation inside the sample. The good agreement between IR data and the theoretical model proposed by Gillen and Clough confirms the same scheme of reactions also for a polymer with added antioxidant. The theoretical model parameters are independent of antioxidant content, suggesting that antioxidant is oxidized in place of the polymer, but that this does not change the reactions involved in the oxidation process, or the oxygen distribution within the sample. Moreover, the analysis of the different components in the ESR spectrum of ethylene-propylene containing antioxidant, irradiated in the presence of oxygen, confirms that during post-irradiation storage in air two different processes take place: i) the partial disappearance of the polymer radicals and ii) the start up of a bimolecular process leading to the formation of the $R\text{-}NO^{\circ}$ radical. Furthermore, the recombination and production processes of the involved radicals are concomitant, and the $R\text{-}NO^{\circ}$ production as a function of the absorbed dose is non linear with radical concentration. High Performance Liquid Chromatography allowed them to determine the amount of antioxidant not consumed in the oxidation reaction, as a function of the total absorbed dose.

The stabilizing effects, with respect to gamma radiation, of different curing agents for epoxide resins, and of fly ash as filler, were also investigated through monitoring the mechanical properties of such composite materials. They can conclude that the samples are made globally more resistant to radiation by means of a "tailored" curing agent containing aromatic units. It can be finally noted that, during irradiation, the particulate composite always shows the best mechanical properties (hardness, impact and tensile strength) except for flexural strength.

Co-operation with participating institutes: ENEA collaborated with the CERN group to perform irradiation tests (^{60}Co source Calliope -ENEA Casaccia Center) of polymer-alanine and radio-photoluminescent dosimeters at low and room temperature with the aim to realize a comparison among different kinds of dosimeters, and it is possible to continue with the collaboration for particular aspects of the irradiation tests.

Ranogajec, of the Ruder Boskovic Institute, Croatia, considered the problem with widely used low-molecular-weight organic stabilizer molecules which are simply incorporated into the polymer matrix for improving resistance towards ionizing radiation as well as other environments. These can be lost during long use due to evaporation. Ranogajec proposed that the problem can be eliminated by radiation grafting of a stabilizer onto the polymer backbone. By a simultaneous gamma irradiation method, 2-hydroxy-4(3-methacryloxy 2-hydroxypropoxy) benzophenone (HMB) (HMB) was shown to be readily grafted to polyethylene from a solution. Surface grafting occurs from a methanol solution of monomer, while in benzene and tetrahydrofuran, solution grafting proceeds more or less in the inner parts of the polymeric films as well. LDPE films grafted with HMB under different conditions, LDPE films blended with HMB, and non-grafted LDPE films, were all exposed to accelerated ageing and natural weathering, and their IR spectral changes, expressed as the carbonyl index, were than compared. Changes in elongation at break and tensile strength were also measured in the course of ageing. The results demonstrate that the proposed approach to increase the stabilizer persistence in the polymer by radiation grafting is very efficient, the lifetime of the grafted LDPE being several times higher than that of nongrafted LDPE.

Tavlet, of the European Organization for Nuclear Research (CERN), reported on the extensive programme at that institution on evaluating the radiation resistance of materials and components. The next challenge for CERN is that, for the purpose of particle physics research, future multi-TeV detectors and accelerators like the CERN large hadron collider (LHC) will use super conducting magnets where organic materials will be exposed to high radiation levels at temperatures as low as 2 K. Electrical and thermal organic insulators will have to be selected for these application conditions. It had also to be checked that the present dosimetry methods (based on alanine and on radio-photo-luminescent (RPL) glasses) can be used for absorbed dose measurements at cryogenic temperature, for the purpose of studying materials degradation effects. About this latter point, it has been shown that for integrated doses below 1 kGy, both types of dosimeters are suitable: a temperature coefficient of 0.2%/K has been found for alanine-based dosimeters, and the RPL signal is not affected by the irradiation temperature. Above the level of 1 kGy, the response of alanine has to be calibrated at each temperature, and RPL dosimeters should not be used because their response saturates at cryogenic temperature.

For the selection of organic materials, some representative insulating films, cable insulations and epoxy-type impregnation resins were exposed to neutron and gamma radiation of nuclear reactors, both at room temperature and 77 K. Mechanical tests on the materials irradiated at low temperature were carried out without warming the materials. The results show that while cables based on polyolefin materials cannot be used, a number of other polymer-based materials are suitable for use in the radiation environment of superconducting machines. The data show that the radiation degradation of thermoplastic materials can be much less pronounced in a cryogenic fluid than in air. No significant influence of irradiation temperature is observed on the radiation degradation of thermosets and composites.

González, of the Polymer Laboratory of Ezeiza Atomic Center, Argentina, evaluated the stability of polypropylene and flexible polyvinylchloride medical products, composed of locally-available materials, which were subjected to ionizing radiation as the means of sterilization. Stability after a period of post-irradiation aging was established, when irradiated with the current sterilizing dose. The possibility of anticipating shelf life either by irradiating the products to a higher dose or by storing the irradiated products at a temperature higher than room temperature was examined; in both cases a negative result in the accelerated aging indicated non-stability for the real-time aged product. Radiation discoloration of polypropylene was eliminated by the addition of a hindered amine type light protector, in a formulation that will be available to small producers of medical products. PVC tubing of local origin was found acceptable after real time aging, according to the chemical test performed; discoloration was found not to interfere with the intended use of the product. Irradiation with a dose higher than sterilizing dose was found to give an indication of long term performance of the product treated with the sterilizing dose.

Evaluation of locally formulated commercial polyvinylchloride wire insulations similar to the ones employed in the gamma facility of Ezeiza Atomic Center, by testing of samples irradiated during a period of 100 days, showed that the reduction in the elongation at break to 50 % of the original value was reached much earlier than could be estimated according to the actual performance of wires installed in the facility's conveyor system. This result suggests relating the elongation test to other functional tests for this type of insulation.

As a result of the last meeting, co-operation with Australia in relation to studies on natural rubber latex, with Croatia in relation to grafting processing and with Pakistan in relation to the development of new radiation resistant polymer formulations, is under discussion.

Perera of the Polymer Materials and Radiation Group in Queensland, Australia, reported on the primary events that occur when a range of polymers, including rubbers, methacrylates and polyesters, interact with high energy radiation. The primary mechanisms of radiation degradation of these polymers, including the radiation yields, were reported. The results confirm that mainly a Y-linking mechanism for crosslinking occurs in butyl rubbers, and the main cause for more main chain scission in chlorobutyl rubber compared to bromobutyl rubber is the ability of the chlorine radical to abstract hydrogen from the main chain isobutylene units. The radicals formed from such hydrogen abstraction are known to undergo rearrangements with chain scission.

The group also presented evidence for chain reactions and crosslink clustering when some diene polymers such as polybutadiene, polyisoprene, and nitrile rubber are exposed to high energy radiation. When nitrile rubber is irradiated, primary radicals are formed in acrylonitrile units and they then undergo intramolecular hydrogen abstraction and form allylic radicals in butadiene units. However, there are no such reactions and structures in polychloroprene. The presence of changes in tacticity in PMMA when irradiated above Tg, and a certain amount of G(X) in methacylates with longer side chains, were reported. This results in gel formation in some methacrylates such as 2-methyl heptyl methacrylate. The group also reported the structures of the new saturated and unsaturated chain ends formed in poly-Lactic acid and poly-Glycolic acid. The suitability of techniques such as ESR and NMR to study degradation reaction mechanisms was demonstrated, and precautions necessary in using solid state NMR techniques in these studies were reported.

Co-operation with Participating Countries: The Queensland Polymer Group has had interactions with the group of J. Sun in China and R. Clough in USA with exchange of students and visits. Such interactions will be continued and new collaboration work with Argentina and Croat will be commenced.

Ahmed, of the Pakistan Institute of Nuclear Science and Technology, reported on the development of radiation crosslinkable formulations of insulators for PE- based, flame-retardant and radiation resistant wires, using Co-60 as irradiation source. The work includes the evaluation of stabilizer additives and of various means of providing inert atmosphere during irradiation, as means of enhancing stability. Ahmed also carried out a program to develop a polypropylene material having enhanced radiation resistance and clarity, as well as other properties. This work examined the use of ethylene as a copolymer, as well as the addition of nucleating agents to the material. This work is likely to hasten transfer of technology of radiation processing of wires to local industry in Pakistan and other developing countries, for which the implementation of radiation processing is hampered by the proprietary nature of many of the details of radiation-stabilizing technology for polymers.

Collaboration with the participating institutes: The work on the development of PVC based flame retardant thin wires was carried out in collaboration with the Changchun Institute of Applied Radiation, Changchun, China.

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STUDIES ON RADIATION STABILITY OF POLYMERS

JIAZHEN SUN, XIAOGUANG ZHONG
Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences,
Changchun, China

Abstract

Fluoropolyimide (FPI) is crosslinked by gamma-irradiation at high temperature. After crosslinking, the glass transition temperature is increased with increasing dose. High temperature tensile strength is also increased with increasing dose. The high temperature water resistance property is improved markedly. XPS results show that the fluoro-atom in the CF_3 group is decreased during radiation crosslinking of PFI, so the crosslinking reaction of PFI is thought to proceed through defluorination.Likewise, certain common polyolefins, such as polytetrafluoroethylene, which undergo primarily chain scission when irradiated at room temperature, can be crosslinked by irradiation at high temperature. This dramatically improves their subsequent radiation resistance. We have also been able to achieve improved radiation resistance by irradiation of certain blends of a predominantly scissioning polymer with a predominantly crosslinking polymer.

SECTION-A: RADIATION CROSSLINKING OF FLUORO-POLYIMID AND RADIATION STABILITY IN HIGH TEMPERATURE WATER

1. INTRODUCTION

Fluoropolyimid (FPI) is well known for its good resistance to high temperature and hydrolysis. Until now, no research work on the radiation included crosslinking of FPI has been done. In this paper, we studied the radiation crosslinking of FPI and its properties before and after irradiation. In addition, we also characterized its crosslinking density with XPS (X-rays Photoelectron Spectroscopy).

2. EXPERIMENTAL

Irradiation was carried out in 2×10^{15} Bq Co-60 source. Mechanical properties were measured by an Instron test machine, and dynamic mechanical properties were measured by SJH-751 which is made by our institute. Gel content of FPI was measured as follows: extraction in DEF for 24 hr, then washed with acetone and dried, repeating the above procedure until constant weight was obtained. The XPS spectra were measured with Shimidaz ESCA-450-B X-ray photo ESCA.

3 RESULTS AND DISCUSSION

3.1. Radiation crosslinking rule

In the past, we studied radiation crosslinking of a series of aliphatic fluoropolymers, such as F-30 *(copolymer of trifluoro chloroethylene and ethylene)*, F-46 *(copolymer of tetra fluoro* ethylene and perfluoro propylene), F-4 (polyvinylidene fluoride), and found that they could be crosslinked by irradiation only above their glass transition temperature [1]

In this paper, we also discover that no gel of FPI was found below its glass transition temperature (Tg), even when the radiation dose is higher than 3000 kGy This phenomenon is very similar to our previous work [1] It shows that a crosslinking reaction can not be achieved on account of the rigid molecular chain of FPI and its poor mobility Experimental results show that FPI can be crosslinked at 250-300°C, giving different gel content for different radiation dose From the Charlesby-Pinner Equation, we find that the dose of gelation of FPI(Rg) is 570 kGy, which is 30-40 times higher than that of ordinary fluoropolymers Rg for F-46 is 20 kGy, for F-30 it is 16 kGy The high Rg of FPI may be due to the protection effect of the phenyl ring in the polymer molecules, so that the free radical of FPI is more difficult to be produced under γ-rays Another reason is the steric hindrance of the phenyl ring, which makes the FPI molecular chain very rigid Therefore, even at high temperature, the mobility of the molecular chain is still very low With the decreased possibility of collision of radicals or its transition, the possibility of crosslinking reaction is reduced accordingly

3.2. The dynamic mechanical properties of FPI

With the Torsion Braid Analysis method, we studied the dynamic properties of FPI before and after γ-ray irradiation The results are shown in Fig. 1

From Fig 1, we can determine the glass transition temperature of FPI before and after irradiation Before irradiation, Tg of FPI is 280°C After being irradiated with 600 and 1800 kGy, the Tg increased to 295°C and 310°C respectively This means that after crosslinking, new connections between molecular chains are formed, which hinder the chain mobility and increase the Tg of FPI The higher Tg also indicates the increased crosslinking density

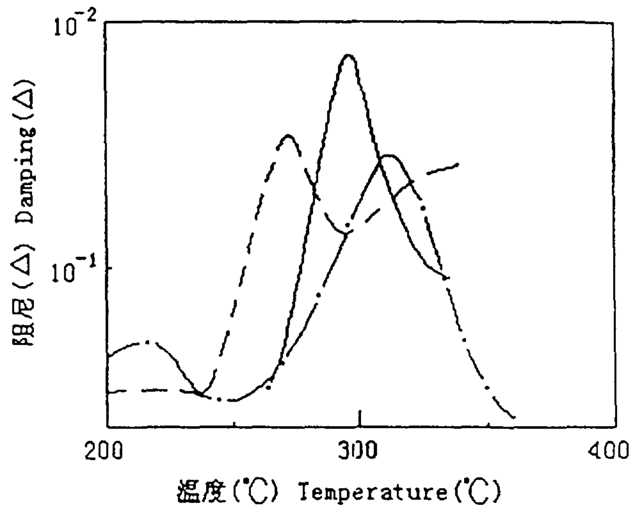

FIG 1 Dynamic mechanical property of FPI---Conventional sample, 60Mrad- - 180 Mrad

3.3. The mechanical properties of FPI

The mechanical properties of FPI before and after irradiation are shown as Table I. From Table I, we can find that after high dose irradiation, the tensile strength of FPI at room temperature becomes lower than that of unirradiated FPI. This fact may be due to the damaged crystal structure caused by irradiation. However, the tensile strength of FPI at 200°C increases with increasing dose, which shows that at high temperature the mechanical properties of network-structure polymer is superior to that of ordinary linear polymers.

TABLE I. MECHANICAL PROPERTIES OF FPI

Dose Mrad	Tensile Strength (kg/cm^2)	
D(Mrad)	Room temp.	200°C
0	860	167
60	1070	113
180	605	242
300	708	500

3.4. Thermostability of FPI

The thermostability of FPI before and after radiation have been studied with thermogravimetry. The results in Fig. 2 show that the decomposition temperature (Td) of FPI is influenced by radiation crosslinking, which may be due to the sensitivity of CF_3 radical in FPI to radiation.

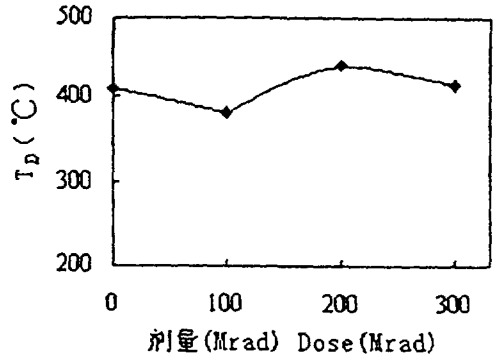

FIG. 2. The relationship of the decomposition temperature (Td) and radiation dose for FPI.

3.5. High temperature water resistant properties

The water resistance of polyimid is a very important property because in some nuclear power engineering systems, the polymer must be stable at high dose and to high temperature water vapors. The polyimid is easily hydrolyzed to low molecular weight polymer, and loses its mechanical properties. Thus, in this case, polyimid can not used. We find after radiation crosslinking that the water resistance properties of polyimid are higher.

TABLE II. THE IMPROVEMENT OF HIGH TEMPERATURE WATER RESISTANCE OF CROSSLINKED FPI

Treatment condition	FPI control	FPI 320,10days	FPI radiation crosslinked
250 water 4Mpa 6hrs	Powdering	Powdering	Keeps good strength

From this result, we can see the hydrolysis of FPI is improved. It is due to the radiation crosslinking induced structure change of FPI. After crosslinking, new bonds formed are stable under hydrolysis. Although we do not know the crosslinking mechanism of FPI, from XPS study the CF_3 group was destroyed after crosslinking, so maybe C-C bonds are formed. C-C bonds are hydrolysis-resistant, so the high temperature water resistant property is improved.

3.6. The characterization of crosslinking density of FPI with XPS

Fig. 3 shows the ESCA spectrum of FPI before and after radiation. From Fig. 3 we can see that the photoelectrical peak intensity of CF_3 (293.0 ev in the spectrum) in irradiated FPI is lower

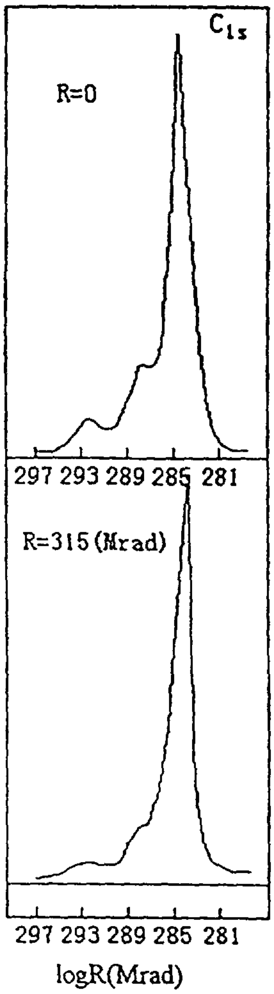

FIG.3. The ESCA spectrum of FPI.

than that of FPI before irradiation. The above results show that the crosslinking of FPI is conducted through defluorination. Therefore, the F/C value (ratio of fluorine to carbon atoms) must be decreasing with increasing crosslink density.

If we plot the Log F/C of irradiated FPI with Log R, we can get a straight line. We can also get another straight line, which is parallel to Log R axis, and its Log F/C is taken from that of unirradiated FPI We can consider the R in the intersecting point of the above two lines as the dose of gelation (Rg) of FPI, (see Fig.4) We can also discover that the Rg of FPI (500 kGy) is very close to 57 Mrad, which is obtained through the gel content method. Therefore, we can reach the conclusion that it is reasonable to characterize the crosslinking density of FPI under different radiation dose with XPS.

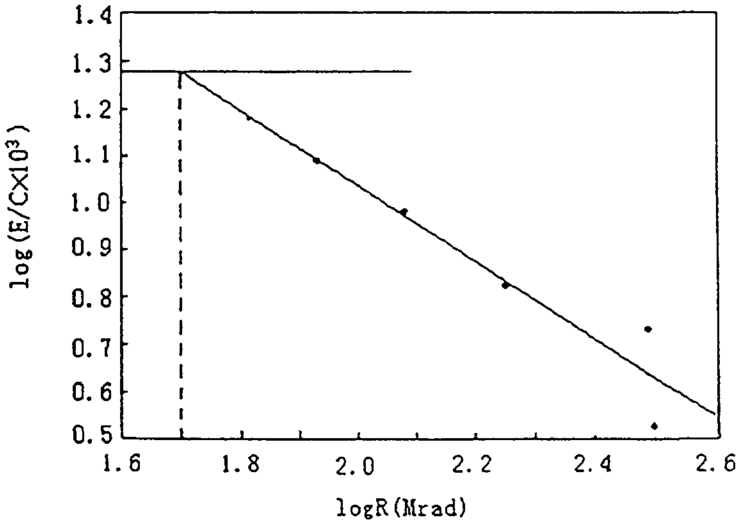

FIG.4 The relationship of log F/C and log R for FPI.

SECTION-B STABILIZATION OF POLYMERS BY RADIATION

1 INTRODUCTION

With the development of space science, the stability of polymeric materials against radiation has been drawing the attention of scientists. Polymers which contain aromatic groups are well known to have relatively good radiation stability, but are also very expensive. On the basis of previous work, we are trying to use common olefin polymers and special technology to improve their radiation stability and obtain cheap radiation-stable polymer composites.

2 RESULTS AND DISCUSSION

2.1. Increasing radiation stability of polymers by forming network structure

As we all know, the mechanical properties of polymers strongly depend on their molecular weight Thus, polymers with higher molecular weight generally show better mechanical properties In actual application, a commonly used method to prevent polymers from molecular chain fracture caused by aging is to incorporate an antioxidant In the case of exposure to ionizing radiation, however, besides crosslinking, some polymers will undergo predominant degradation of molecular weight. For these polymers, the molecular structure makes them very sensitive to radiation, and even small amounts of radiation dose lead their molecular chain to fracture and thus poor mechanical properties. For radiation crosslinkable polymers the molecular weight increases with increased radiation dose, and thus their mechanical properties are improved markedly. These polymers can also be called radiation resistant polymers. The main purpose of the present work is to try to find a way by which the radiation stability of radiation degradative polymers can be improved greatly.

On the basis of previous experience in past decades of our investigation, it was found that even for radiation degradative polymers the formation of network structures could markedly increase their radiation stability. The reason for that is the relatively slow speed of molecular-weight degradation for a network structure. The following experimental data provide further evidence for the above explanation.

2.1.1 The radiation behavior of copolymer of hexafluoropropylene and tetrafluoroethylene (F-46)

As a perfluoropolymer, the radiation behavior of F-46 depends on the temperature at which it is exposed to ionizing radiation. When the polymer is irradiated at temperatures higher than its glass transition point (about 90°C), the predominant radiation behavior is crosslinking; otherwise the degradation of molecular weight is observed. Table I shows the difference of radiation stability for crosslinked and linear F-46.

Data shown in Table I indicate that for linear F-46, when irradiated in air at room temperature, degradation effects are clearly seen, and irradiation up to 20 kGy lead the polymer to show no elongation. For crosslinked F-46 however, the radiation stability shown by changes in mechanical properties is improved greatly.

TABLE III. PROPERTIES OF F-46 BEFORE AND AFTER RADIATION AGING

Dose of Radiation Aging 10 kGy	Linear F-46		Crosslinked F-46	
	TB MPa	EB %	TB MPa	EB %
0	3.3	350	4.0	300
0.5	3.0	225	-	-
1.0	2.5	105	-	-
2.0	1.7	0	2.8	270
3.0	1.0	0	-	-
4.0	-	-	2.6	250
8.0			2.3	200
10.0			2.2	180
15.0			1.7	110

* The condition of radiation crosslinking:
240°C , Vacuum 100kGy
TB: Tensible Strength, EB: Elongation
Test temperature : 200 °C

2.1.2 *The radiation behavior of polytetrafluoroethylene (F-4)*

F-4 is well known to be a radiation sensitive polymer Exposure to a small amount of radiation can make it lose most of its mechanical properties Our previous work has shown that when F-4 is irradiated at a temperature above its melting point (327°C) under vacuum, a crosslinked polymer can be obtained Fig 5 and 6 show the difference in radiation stability of crosslinked and linear F-4 The results illustrate that the radiation resistance of crosslinked F-4 is increased to a degree much higher than that of F-46

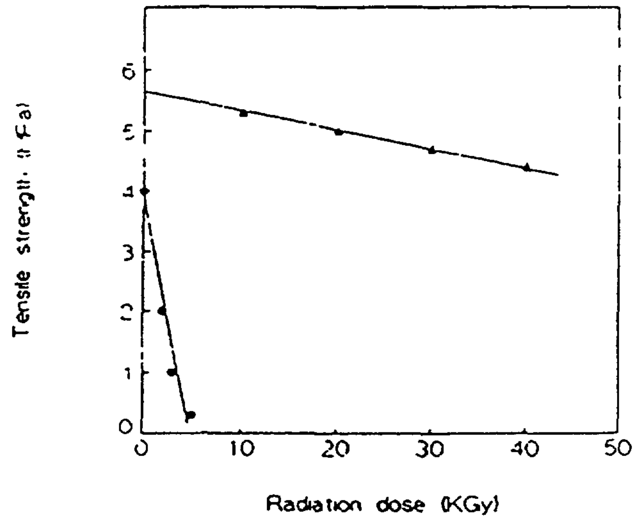

FIG 5 Effect of radiation on tensile strength on PTFE

- uncrosslinked PTFE

Δ crosslinked PTFE

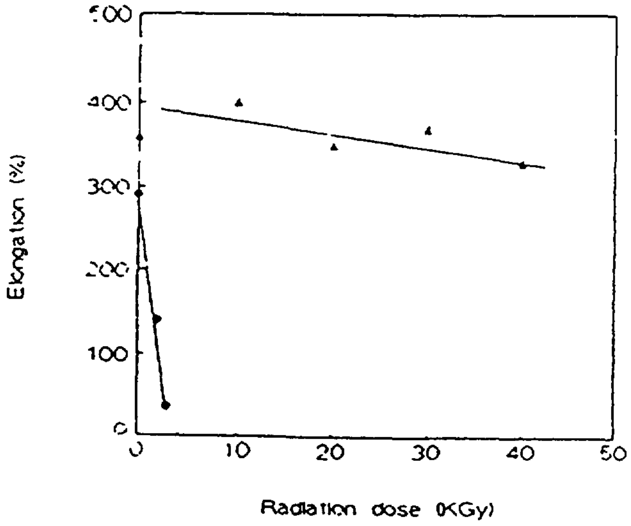

Fig 6 Effect of radiation on elongation of PTFE

- uncrosslinked PTFE

Δ crosslinked PTFE

2.2. Improving the radiation stability of radiation degradative polymers by blending

2.2.1 PMMA/PEO system

Our previous work showed that blending two kinds of polymers which have different radiation behavior is also an effective way to improve their radiation stability For example, upon blending a radiation crosslinkable polymer with a radiation degradative polymer, the radiation behavior of the composite system sometimes shows a protective effect to the degradative polymer, as in the case of the PMMA/PEO system In this case PMMA is a typical radiation degradative polymer, while PEO is a radiation crosslinkable polymer. Table IV gives the radiation stability, shown by mechanical properties, of the blended system with varying blend ratio.

TABLE IV RADIATION RESISTANT PROPERTY OF PMMA

dose of radiation 10 kGy	The content of PMMA in PEO/PMMA ,(%)					
	3 0		7 0		10 0	
	TB MPa	EB %	TB MPa	EB %	TB MPa	EB %
0	20.7	50.1	31	223	81.1	2.4
1	-	-	-	-	60.5	1.2
3	20.0	22	32 6	226	52 4	0 9
6	19.8	20	33	222	45 6	0.9
10	19.4	18.8	33.2	226	-	-
15	19.3	12 5	33.6	219	-	-
30	17.9	6.6	29 0	225	38.6	0.8

It can be seen that the radiation stability of the blended system is improved. Particularly the PMMA/PEO = 70/30 system, the mechanical properties are observed to be little changed with irradiation dose, while for pure PMMA, the same dose results in the loss of tensile strength and elongation

2.2.2 PMMA/PVDF system

The similar protective effect is also observed in the blending of PMMA/PVDF Table V shows the change of mechanical properties of the system with various blending ratio with radiation dose. The reasonable explanation for the observation is obviously the radiation induced grafting of fractured chains from radiation degradative polymer to molecules from radiation crosslinkable polymers

TABLE V RADIATION RESISTANTANCE PROPERTIES OF PMMA

Dose of Radiation 10 kGy	The content of PMMA in PVDF/ PMMA, (%)							
	2 0		5 0		7 0		10 0	
	TB MPa	EB %	TB MPa	EB %	TB MPa	EB %	TB MPa	EB %
0	22	373	58	112	69	25	81	2 4
1	25 6	399	58 8	108	70 5	25	60 5	1 2
3	25 1	408	57 1	110	68 9	35	52 4	0 9
6	32 4	500	56 9	111	64 9	35	45 6	0 9
15	33 0	499	54 5	107	63.2	24	-	-
37	-	-	51 6	100	53.3	23	35*	0 8*

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ANNEALING PHENOMENA IN THE RADIATION DEGRADATION OF CROSSLINKED POLYOLEFINS

M. CELINA, K.T. GILLEN, R.L. CLOUGH
Sandia National Laboratories,
Albuquerque, New Mexico,
United States of America

Abstract

The radiation-thermal degradation of several types of commercial cable insulation materials (semi-crystalline crosslinked polyolefins) was investigated. Annealing at elevated temperatures of samples that had been previously irradiated at or near room temperature led in some cases to significant recovery of mechanical properties (elongation at break) and concurrent changes in gel content (additional crosslinking) and density. A comparison of degradation in samples irradiated at different temperatures (in the range of 22°C to 120°C) showed that mechanical property deterioration surprisingly occurred most rapidly at the *lowest* temperatures. The importance of molecular mobility in the semi-crystalline materials and the nature of the additional crosslinking reaction as contributors to these anomalous behaviors are evaluated and discussed. The observed temperature effects are due to a combination of the semi-crystalline morphology of the materials, and a specific crosslinking reaction, which can act as a repair mechanism at elevated temperatures, but is dormant at ambient conditions. The beneficial thermal annealing which can result in substantial recovery of useful mechanical properties in this type of material is reminiscent of the beneficial annealing phenomenon that results in the recovery of optical transmittance properties of glassy polymers, which we have reported on recently.

1. INTRODUCTION

For the accurate prediction of polymer material lifetimes it is necessary to develop a detailed understanding of the relevant degradation behaviors and mechanisms. A common approach to predict aging is the Arrhenius methodology [1], which requires that there be no temperature-dependent changes in the dominant degradation mechanism. The current understanding of polymer aging, however, suggests that in most cases a valid Arrhenius description of polymer aging over a wide temperature range should not be expected [2]. To improve predictive models it is important to identify why and how degradative mechanisms can be affected by temperature. There is considerable evidence that in some cases polymer lifetimes can easily be overestimated by extrapolations from high temperature aging [3,4,5]. This is related to the complex nature of polymer degradation, which is dependent on morphological features and their related transition temperatures [6], diffusion-limited oxidation effects occurring at elevated temperature [1,7,8,9,10], solubility and volatility of stabilizers [11,12,13], and other kinetic heterogeneities [14,15].

The complexity of polymer degradation under combined radiation and thermal conditions has been reviewed in detail [16,17,18]. Diffusion-limited oxidation can lead to anomalous effects in radiation-temperature environments [19,20], although a viable predictive approach, referred to as time-temperature-dose rate superposition, has been developed and successfully tested [19,20,21]. Complications which can occur during the irradiation of semi-crystalline polyethylene were summarized by Chapiro [22]. Crystallinity and density changes were found to depend on temperature and some competing processes, i.e. the destruction of crystalline regions, or the formation of double bonds and crosslinking [23]. Increased crystallinity [24] and density [25] resulted during irradiation, this has been ascribed to "chemi-crystallization" due to morphological rearrangements of polymer fragments after chain scission events In general, mechanical properties [26] are governed by morphological features such as degree of crystallinity, crystallite thickness, or structure and relative amount of amorphous and interfacial region [27] Radiation-induced changes in polyolefins [28] may occur preferentially at crystalline surfaces and defects, or as a selective degradation of tie molecules between crystallites [29] This would explain why mechanical degradation may not always be directly related to the absolute extent of oxidation [30]

In a recent study we presented evidence of mechanistic changes with temperature in the combined radiation-temperature aging of a crosslinked polyolefin (XLPO) insulation material [31]. We observed an anomalous aging situation, with **faster** degradation at the **lower** temperatures, indicating an inverse temperature effect This behavior is most easily recognized in a dose to equivalent damage (DED) plot (see Fig. 3 of ref. [31]), a convenient approach to represent combined-environment data [20,21], as well as in the loss of mechanical properties (elongation) at the two selected temperatures shown in Fig. 1 It was also noticed that the mechanical properties of the XLPO insulation that had been aged at ambient conditions could recover during a subsequent annealing step (i e 140°C).

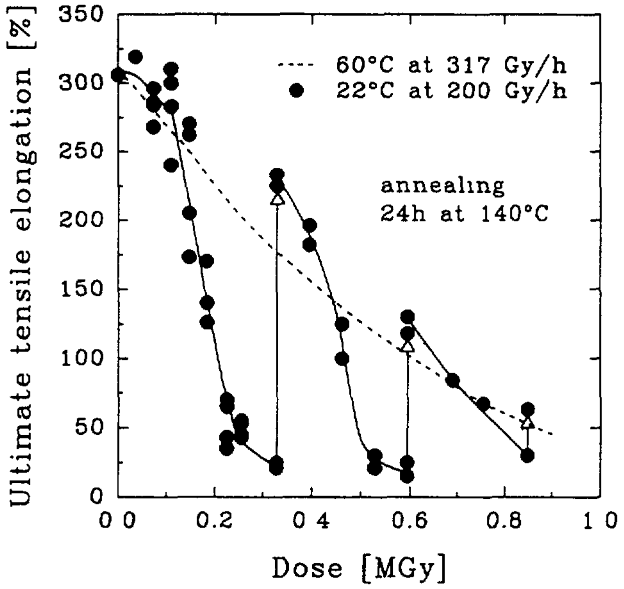

FIG 1 Decrease in ultimate elongation for material A during degradation at 22°C and 200 Gy/h and the recovery of mechanical properties upon annealing at 140°C for 24 hours after 328, 594 and 849 kGy Note the slower degradation for the material when aged at 60°C

Trends in network properties (gel content) were distinctly different in the two temperature regions (above and below 60°C) and showed a dramatic jump during the annealing step suggesting a chemical crosslinking reaction taking place (Fig 2) An increase in the gel content during annealing was not observed for samples aged under nitrogen, indicating that oxidation products are involved in the crosslinking The most obvious conclusion, that common hydroperoxide species, formed during the aging, are responsible for the crosslinking, could not be confirmed Both infrared analysis and deactivation experiments with reactive gases suggested that any hydroperoxides were either too low in concentration to be detected or were protected from deactivation at morphological boundary regions (i.e immobilization/inaccessability at crystalline interfaces). Alternatively, other more stable or less reactive peroxide species may be involved. We concluded that the extended life time of the material above a certain threshold temperature is related to some damage-compensation or recovery behavior which is inactive or extremely slow at the lower temperature regime. Chemical reactivity as well as morphological mobility of crystalline or pseudo-crystalline material in spherulitic boundary regions are required for this effect [31].

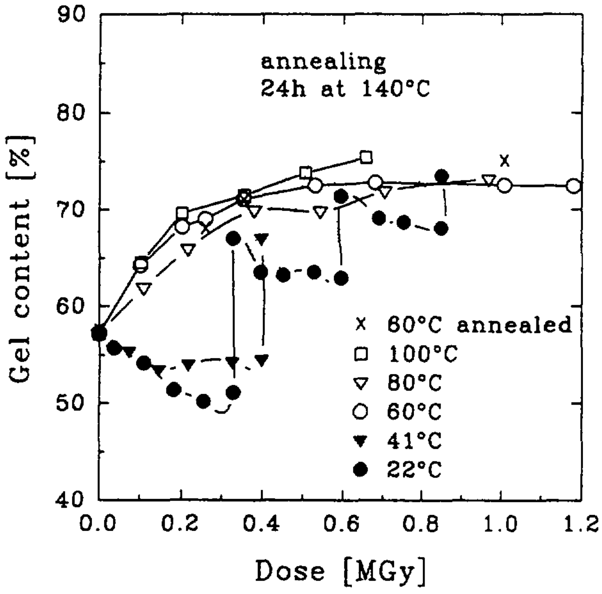

FIG. 2. Changes in the gel content of material A during combined radiation-temperature exposures as a function of temperature showing predominantly scission at lower temperatures and crosslinking at higher temperatures as well as a marked increase in the gel content during annealing of samples aged at 22 °C and 41 °C.

In the current study we have attempted to identify and evaluate similar anomalies in other elastomers and to investigate whether the observed aging characteristics are of generic nature or specific to a certain polymer type.

2. EXPERIMENTAL

2.1. Cable insulation materials

All polymer samples investigated are commercial insulation materials, removed from electrical cables used for power and control applications in nuclear power plants. Some of the cables are offered by the industry as radiation-resistant and flame-retardant materials. Specific details of the polymer composition and manufacturing process are, however, proprietary. All materials are of crosslinked semicrystalline nature as shown by differential scanning calorimetry (DSC) (Fig. 3) and gel content analysis with major melting peaks in the range 90-125°C These data are consistent with those expected for crosslinked polyolefins (XLPO) and polyethylene (XLPE) Partial melting occurs down to ambient temperatures An overview of the IR absorption features of the unaged samples is shown in Fig. 4 All insulation materials (~1 mm wall thickness) were removed from the conductor core, tested and aged in the tubular form which results after the stripping operation

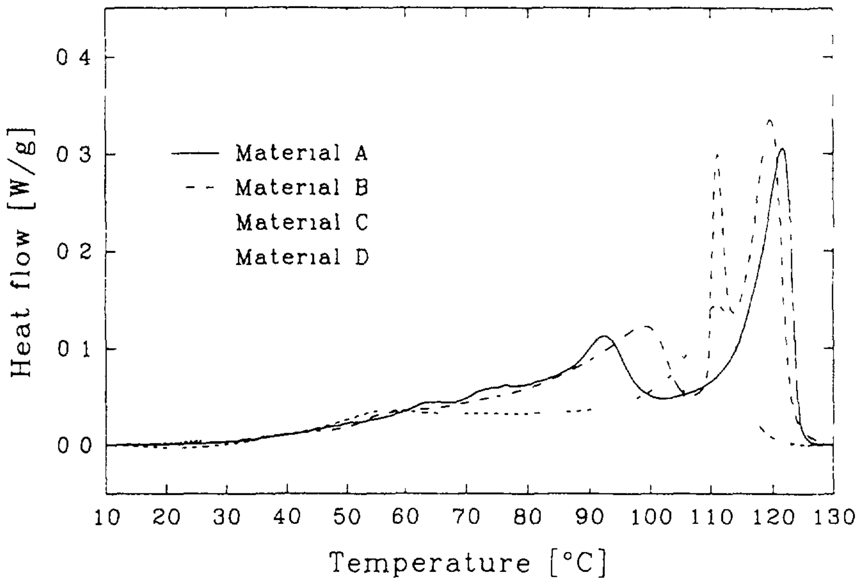

FIG. 3. DSC-scans (first) of the original XLPO insulation materials.

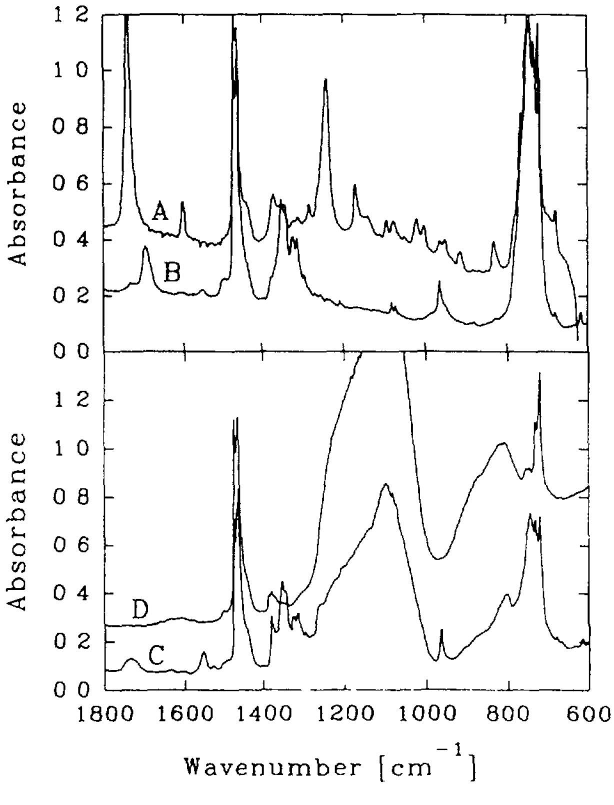

FIG. 4. IR absorbance spectra of the original XLPO insulation materials.

Material A

DSC (Fig. 3) and infrared (IR) spectroscopic analysis (Fig. 4) indicates a medium to high density ethylene vinylacetate-copolymer (dominant carbonyl band at 1740cm^{-1}) with double melting peaks at 93°C and 122°C. Additional compositional elemental analysis with microprobe X-ray fluorescence and with IR revealed the presence of some flame retardants as antimony oxide in combination with chlorinated and brominated organics (dodecachloro-dodecahydro-dimethano-dibenzo-cyclooctene and decabromo-diphenylether), and a small amount of TiO_2. The polymer content of the insulation is estimated to be approximately 65%.

Material B

DSC analysis (Fig. 3) shows major peaks at approximately 100, 110 and 120°C. This is the most complex melting behavior of the four polymers studied and indicates a block-copolymer structure with distinct LDPE and MDPE units. IR analysis reveals a material which is similar to XLPE with a possible minor conjugated carbonyl band (preoxidation) in the spectrum at 1695cm^{-1} (Fig. 4). Compositional elemental analysis using microprobe X-ray fluorescence and IR analysis identified flame retardants as antimony oxide in combination with a brominated organic (decabromodiphenylether) as well as a small amount of TiO_2. The polymer content of the compound is estimated to be approximately 67%.

Material C

This material according to manufacturer information is based on an EPDM copolymer. DSC (Fig. 3) analysis shows a major melting peak at ~110°C and a weak response at ~55°C. There is no DSC melting at approximately 160°C (expected for crystalline PP) which suggests a statistical random copolymer structure.

Material D

This material is a true crosslinked polyethylene (XLPE). DSC analysis (Fig. 3) shows a major peak at ~105°C and a weaker response at ~55°C. Peak integration between 20 to 120°C yields approximately 84 J/g and thus indicates a crystallinity of approximately 30% (when using the melting energy of 280 J/g to 290 J/g of an ideal polyethylene crystal [32,33]). Analysis of major bands in the IR correlates with an XLPE material.

2.2. Radiation-thermal aging

The combined radiation-thermal aging was carried out under flowing air conditions in an underwater cobalt-60 aging facility using water-tight aging canisters [20,21] and dose rates ranging from ~17 to 5200 Gy/h (1.7 to 520 krad/h) at temperatures from ambient (22°C) to 120°C (see Fig. 3 of ref. [31]). The samples investigated here in detail were exposed to dose rates ranging from approximately 200 to 300 Gy/h. These dose rates are sufficiently low that complications due to diffusion limited oxidation and the resulting highly heterogeneous degradation behavior are precluded.

2.3. Annealing of samples

Annealing refers to a thermal treatment at elevated temperatures. Our standard annealing process was to hold the sample at 140°C for 24 hours in a circulated air oven and then allow it to cool by natural convection at ambient temperature The temperature of 140°C was chosen because it is above the main crystalline melting peak of the elastomers in the study

2.4. Mechanical testing

Tensile tests were performed with an Instron Table Model Testing Machine (Model 1000) equipped with pneumatic grips and an extensometer The strain rate was 12 7 cm/min for an initial crosshead separation of 5 1 cm.

2.5. Differential Scanning Calorimetry (DSC)

The melting characteristics were investigated using a Perkin Elmer Model DSC-7 after calibration with an indium standard Sample weights of approximately 5-10 mg were analyzed at a scanning rate of 5°C/min. Crystallinity determination from DSC melting is complicated by the fact that most of the materials are ethylene-copolymers and melting energies can therefore not easily be referenced to an ideal polyethylene crystal, unless all side groups are rejected into the amorphous phase

2.6. Infrared spectroscopy

Microtomed specimens (~10μm) were analyzed by transmission FTIR-microscopy using a Biorad Model FTS-40 spectrometer with microscopy attachment and a liquid-nitrogen-cooled MCT detector, 64 scans were averaged at a resolution of 4 cm^{-1}

2.7. Gel content analysis

Gel content (often incorrectly referred to as crosslink density) determinations were carried out by solvent swelling and extraction of the sample with refluxing p-xylene (Bp 133°C in Albuquerque) [34,35,36,37]. Samples of 10-20 mg (w_0) of the XLPO were accurately weighed to ±0 01 mg and placed in approximately 50 ml of p-xylene using a 100 ml round bottom flask with water cooled condenser and heating mantle After extraction for a minimum of 8 hours, the samples were quickly recovered from the hot solvent with the help of a funnel and filter paper Drying was carried out in a vacuum oven at 80°C for a minimum of 4 hours and the weight of the final insoluble fraction (w_{gel}) was obtained The gel content was calculated as the ratio of $(w_{gel}/w_0)*100\%$

2.8. Density measurements

The density of some samples was determined using Archimedes principle by accurately (±0 01mg) determining the weight of a sample specimen in the range of 10-20 mg in air (w_{air}) and comparing it with its weight (w_{liquid}) when immersed in a liquid This approach has been described before ([31] and ASTM Standard D792-91 [38])

3. ANOMALOUS AGING BEHAVIOR

3.1. Gel content

The insoluble fraction of a material, as well as network swelling in solvent equilibrium, depend on initial crosslinking and material changes during degradation [37]. In general, scission and crosslinking both occur during aging; an increase in the gel content relates to degradation dominated by crosslinking, whereas a decrease indicates a process controlled mainly by scission. For material A we noticed a distinct difference in the gel content data during aging at ambient and elevated temperatures [31]. The gel content decreased only at the lower temperatures (see Fig. 2) and recovered during thermal annealing to levels similar to those observed when the aging is carried out at higher temperatures. The changes in the gel content for materials B, C and D during irradiation at different temperatures are presented in Figs. 5-7. Analogous to the results found for material A (Fig. 2) we observe for all samples a more pronounced decrease in the gel content during aging at the lower temperatures, and a tendency towards increases (material B in Fig. 5) or considerably less reduction (material C and D in Figs. 6 and 7, respectively) in the gel content at the higher temperatures. For samples aged extensively at the lower temperatures and subsequently annealed at 140°C for 24 hours there is a marked increase in the gel content to similar levels as when aged directly at elevated temperatures. Only a minor change in the gel content occurs for samples which were aged at the higher temperatures and subsequently annealed.

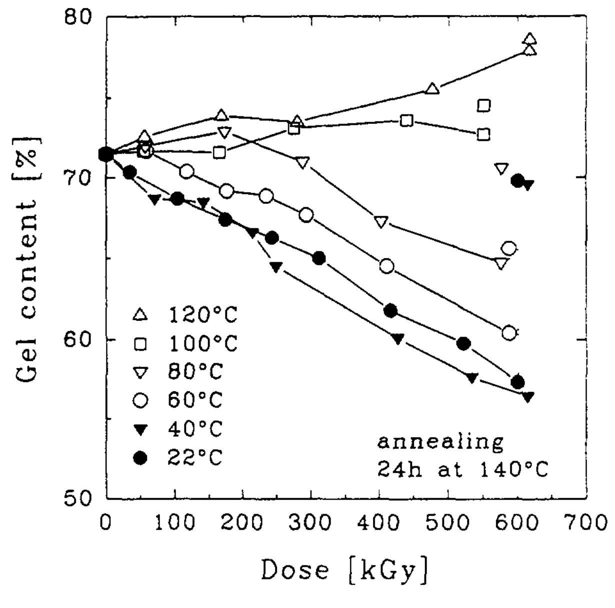

FIG. 5. Changes in the gel content of material B during aging at different temperatures and dose rates ranging from 0.21-0.35 kGy/h.

These data suggest that 1) the degradation at the lower temperatures is dominated by scission, 2) chemical crosslinking occurs during the annealing step and 3) a similar degree of crosslinking is involved during aging at elevated temperatures, but is inactive or extremely slow below a threshold temperature. Previous studies indicated that this crosslinking potential is related to oxidative degradation, since it does not develop under inert atmosphere [31]. The temperature-dependent changes in the gel content clearly suggest that there is a fundamental difference in the degradation mechanism at the two temperature regimes. The transition temperature between the two mechanisms appears, however, to be material specific and is lower, for example, for material A than for material B (Figs. 2 and 5).

3.2. Mechanical aging

The monitoring of the gel content during degradation clearly demonstrates that there is a consistent change in the prevailing degradation mechanism with temperature for all four XLPO materials. The influence on the loss of mechanical properties can, however, be more complex and depends on changes in morphological features (crystallinity, density) [24,25] as well as selective damage to the amorphous, interfacial region and the tie molecules [26-29]. Tie molecules are important for the tensile properties of polymers [39,40]; it has been concluded that annealing can in fact reestablish mechanical properties via a rearrangement of tie molecules [41]. In agreement with the results previously reported for material A (Fig. 1), we notice a more rapid loss in tensile elongation for both materials B and C (Figs. 8 and 9) when irradiation is carried out at ambient conditions. Thus, there is a pronounced inverse temperature dependence where the mechanical aging occurs faster at the lower temperatures, contrary to the established routines of increasing temperature to achieve accelerated aging.

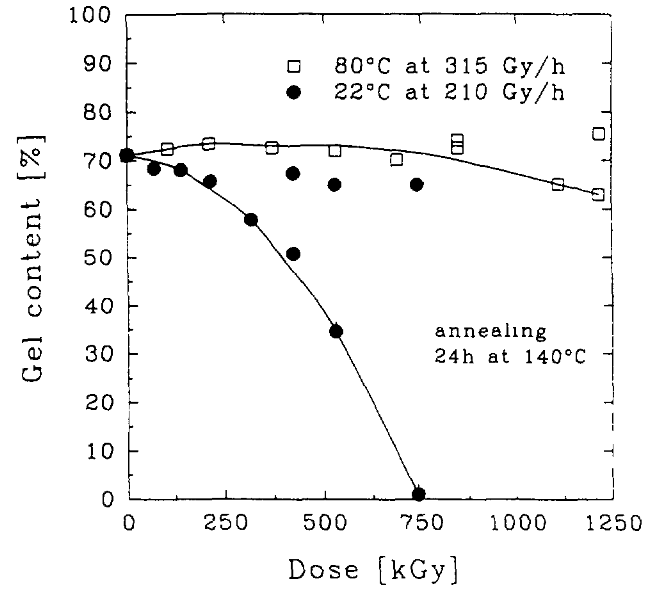

FIG. 6. Changes in the gel content of material C during aging at 22°C (0.21 kGy/h) and 80°C (0.315 kGy/h).

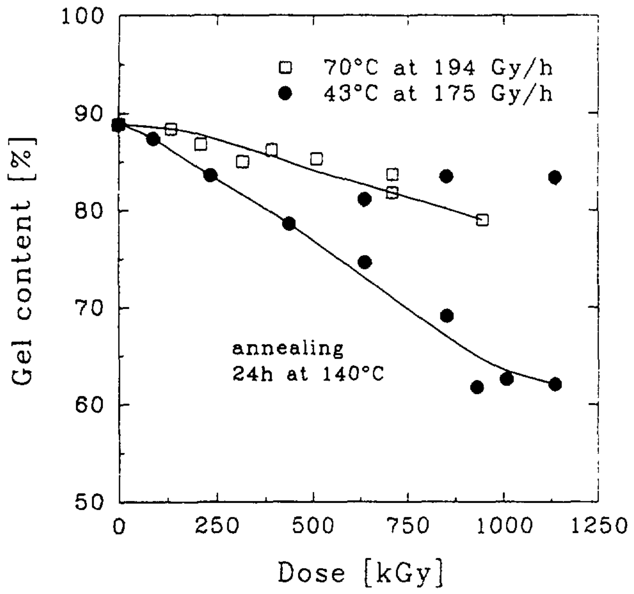

FIG. 7. Changes in the gel content of material D during aging at 43 ℃ (0.175 kGy/h) and 70 ℃ (0.194 kGy/h).

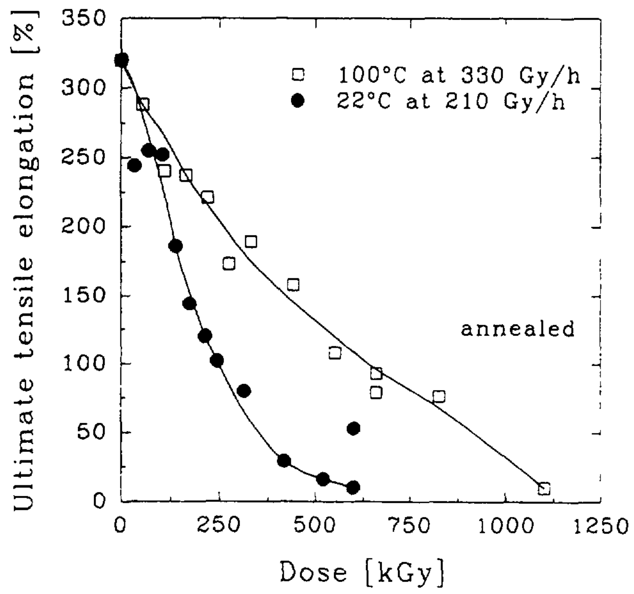

FIG. 8. Decrease in mechanical elongation of material B aged at 22 ℃ (0.21 kGy/h) and 100 ℃ (0.33 kGy/h).

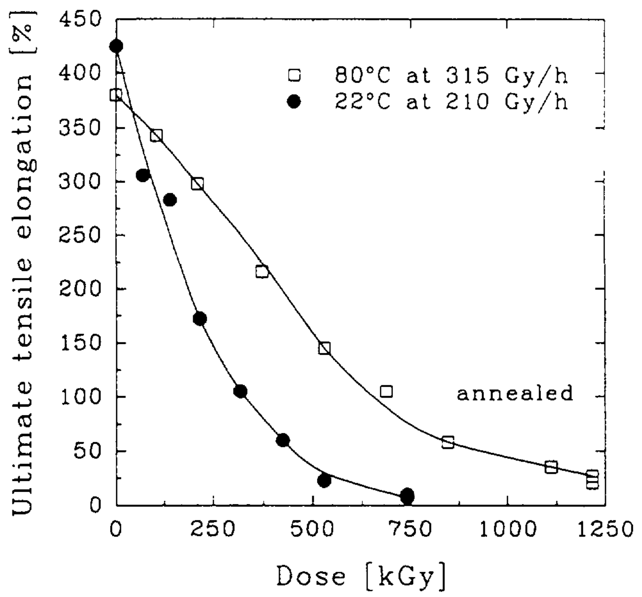

FIG. 9. Decrease in mechanical elongation of material C aged at 22 °C (0.21 kGy/h) and 80 °C (0.315 kGy/h).

The extent of loss in tensile elongation for material D is nearly the same at 70°C and 43°C, although the gel content analysis (Fig. 7) clearly indicates comparable differences in the degradation mechanism.

3.3. Density

A more complex situation is encountered when studying the changes of density during degradation. An increase in density will normally indicate a higher crystallinity [23] (chemi-crystallization [25,42] of scission products resulting from chain scission events [24,25]), although severe oxidation and crosslinking can result in similar changes [31,43,44]. Density changes are controlled by chain mobility, network properties and morphological composition, and can be highly material specific. For material A we observed an increase in density during aging at ambient conditions [31], presumably related to chemi-crystallization. Similar increases exist for material C and D (Figs. 10a and 10b), both at ambient and elevated temperatures. There is no increase in density for annealing of unaged materials. We also notice strong fluctuations in density for annealed samples consistent with important compositional changes (morphology, chemistry) associated with the annealing process.

3.4. Deactivation of possible hydroperoxides

The treatment of oxidized and degraded polymers with reactive gases, such as phosphine (PH_3) [45], sulfur tetrafluoride (SF_4) [46], sulfur dioxide (SO_2) [47,48] and nitric oxide (NO) [49,50] is an appealing approach to identify functionalities via selective derivatization. This method has been particularly useful to identify hydroperoxides and alcohols [49,50]. The gases can diffuse quickly into the polymer and undergo chemical reaction, thus allowing for identification of specific groups via characteristic absorption bands in the infrared spectrum, often with higher

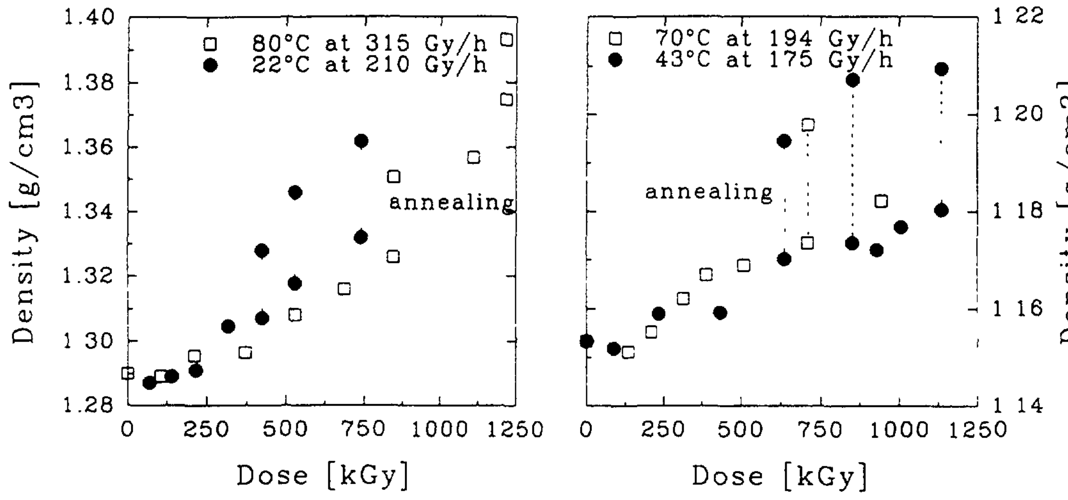

FIG. 10. Density changes of (a) material C during aging at 22 °C (0.21 kGy/h) and 80 °C (0.315 kGy/h) and of (b) material D during aging at 43 °C (0.175 kGy/h) and 70 °C (0.194 kGy/h).

molar absorptivity than the original species. Previously, we treated microtome cuttings of the degraded material A with nitric oxide and used IR-spectroscopy to evaluate whether secondary hydroperoxides (transformed into secondary nitrates with specific absorption bands at 1630, 1273, and 860 cm^{-1}) are involved in the crosslinking reaction which occurs during the annealing step at 140°C. Since these bands could not be identified we concluded that either the concentrations of hydroperoxides were below the detection limit, which would also suggest that the quantities are insufficient to induce the observed crosslinking, or are physically protected (crystalline boundaries) from a reaction with the nitric oxide gas [31]. We also noticed that extensive exposure to reactive and hydroperoxide destroying gases, such as PH_3, SO_2 and NO could not prevent a crosslinking reaction during subsequent annealing [31]. To identify whether any hydroperoxide species are indeed protected from deactivation with gases at ambient temperatures we repeated a NO treatment of material A at 60°C. Additional crosslinking during annealing still occurred as summarized in Fig. 11. Similarly, phosphine treatment of material C (considerable crosslinking potential), both at ambient and elevated temperature (60 and 125°C) could not prevent subsequent crosslinking (Fig. 12). These results suggest that common hydroperoxides species do not initiate the crosslinking reaction. Other peroxidic (or related radical-generating species) that are rendered less reactive due to their molecular structure are a possible source of the crosslinking chemistry.

3.5. Annealing kinetics

One approach which may provide further understanding on the crosslinking reaction which occurs during annealing, is the study of the kinetic behavior of this thermal-induced reaction. If the morphology and chain mobility (melting) have a decisive influence on this reaction we would expect a considerable difference depending on whether the crosslinking occurs at temperatures below or above the main crystalline melting peak. This should also result in different activation energies, if molecular mobility becomes a determining factor in the solid state. Hence, we studied some annealing aspects of the Material A and C above and below the melting point.

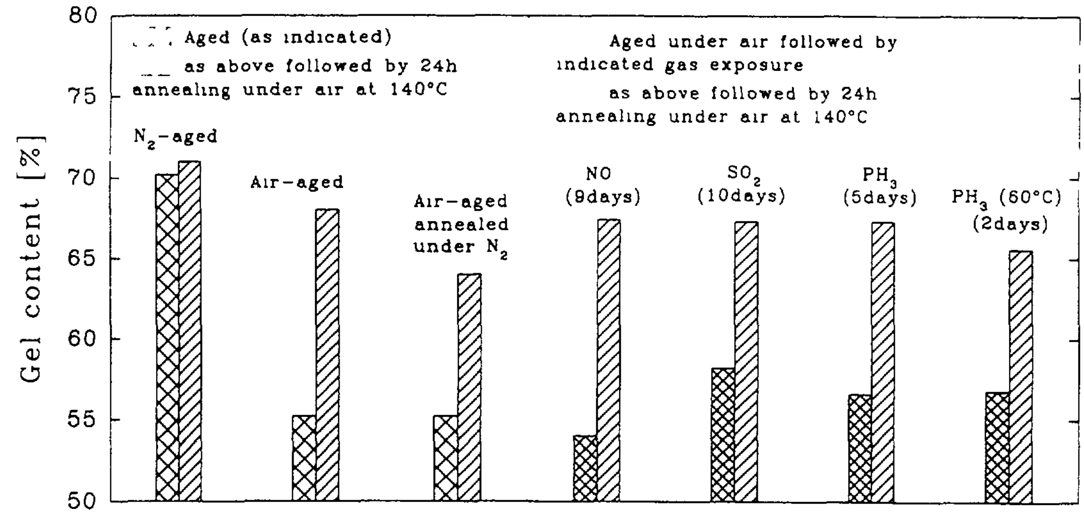

FIG 11 Gas treatment of material A, aged at 22°C to 400 kGy at 485 Gy/h, and its influence on subsequent crosslinking during annealing at 140°C (deactivation of any hydroperoxides)

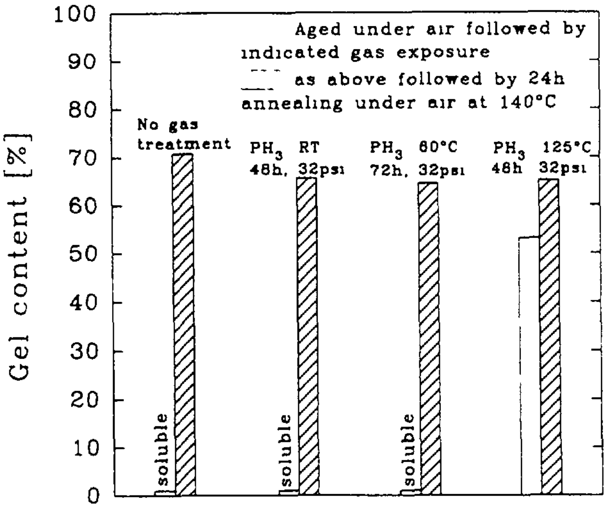

FIG. 12. Phosphine treatment of material C, aged at 22°C to 740 kGy at 210 Gy/h, showing no significant influence on subsequent crosslinking during annealing at 140°C.

3.5.1. Annealing kinetics in the melt

The amount of crosslinking which can occur in the degraded material C (aged at 22°C for 740 kGy at 210 Gy/h) is considerable and is therefore well suited to be analyzed during isothermal annealing at different temperatures with time The increase in the gel content at temperatures ranging from 125-170°C was superposed to a reference temperature of 125°C, by multiplying the data at each temperature by a constant factor (a_T) chosen to give the best overlap, and is shown in Fig. 13a. The crosslinking is described by a reaction with an activation energy of approximately 85 kJ/mol obtained from the superposition a_T factors (Fig. 13b) A more detailed analysis of the data indicates that the crosslinking does not follow simple first or second order kinetics. A similar superposition was obtained from the data measured for the degraded material A (aged at 22°C for 400 kGy at 485 Gy/h) over the same temperature range (Fig 14a). We observe more scatter in the data, but the analysis of the temperature shift factors (a_T values, Fig. 14b) results in a similar activation energy of 84 kJ/mol. This suggests that the underlying chemistry responsible for the crosslinking in both materials A and C is most likely the same. Absolute yields of the gel formation are, however, material specific.

3.5.2. Annealing kinetics in the solid state

Samples of the degraded material A (aged at 22°C for 328 kGy at 200 Gy/h) were annealed at temperatures of 50-110°C and the increase in gel content as well as recovery in tensile elongation determined. These results are summarized in Fig. 15a-b The gel content data appear to be primarily time dependent at each annealing temperature and can easily be superposed (Fig. 16a), resulting in an activation energy of 129 kJ/mol. This is considerable larger than the 84 kJ/mol which was obtained when the crosslinking was carried out at temperatures above the melting point (see above). For the recovery in tensile elongation (Fig. 15b) we observe that the maximum recovery which can be reached is limited depending on the annealing temperature. This indicates that the recovery of this property is more dependent on partial melting and mobility than the concurrent increase in the gel content. However, it also results in difficulties when attempting to superpose the data to determine an activation energy. This is shown in Fig. 16b, in which an apparent leveling off occurs at maximum recovery, thus preventing an overall superposition. A superposition of the initial data (straight line in Fig. 16b), however, is easily possible and yields an activation energy of 191 kJ/mol; considerably larger than the two values obtained for the gel content increase, both above and below the melting point.

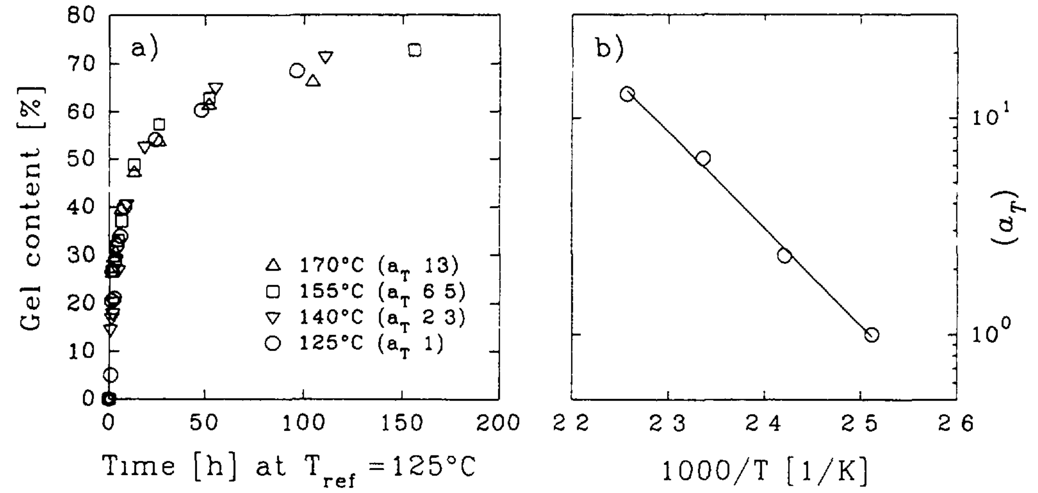

FIG. 13. (a) Empirical time/temperature superposition of the crosslinking behaviour of material C at T_{ref}= 125°C and (b) Arrhenius plot of the corresponding a_T factors resulting in an activation energy of 85 kJ/mol.

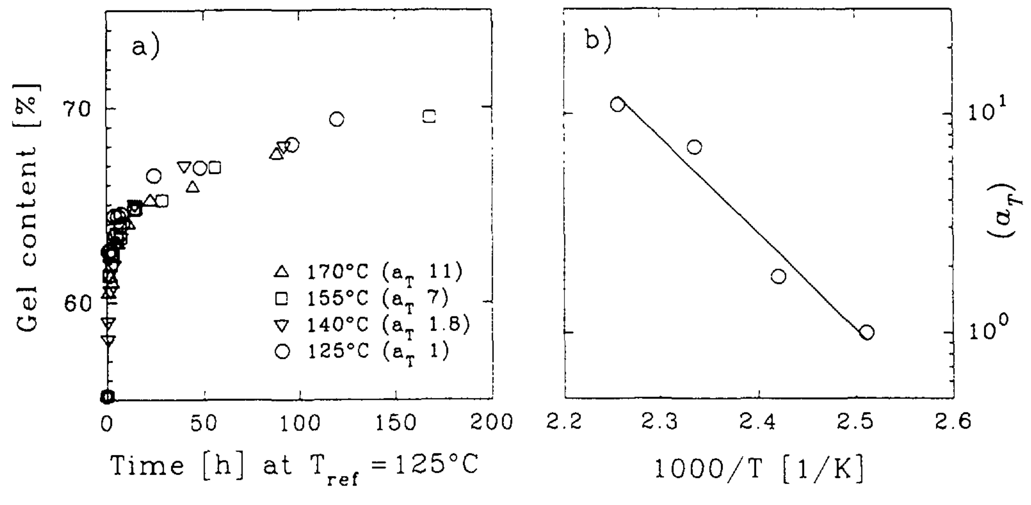

FIG. 14. (a) Empirical time/temperature superposition of the crosslinking behaviour of material A at T_{ref}= 125 °C and (b) Arrhenius plot of the corresponding a_T factors resulting in an activation energy of 84 kJ/mol.

We also studied the gel formation kinetics for material C (aged at 22°C for 740 kGy at 210 Gy/h) during annealing at temperatures below the main melting region (75-110°C). [Note that this is not accompanied by a recovery in mechanical properties (Fig. 9)]. The data of these experiments are presented in Fig. 17a and give excellent superposition with an activation energy of 123 kJ/mol, again larger than the 85 kJ/mol observed for this material when the crosslinking was initiated above 125°C. The same set of experiments was also used to repeat the analysis for material A which resulted in 128 kJ/mol for the crosslinking over this temperature range (Fig. 17b), consistent with the 129 kJ/mol found before (Fig. 16a).

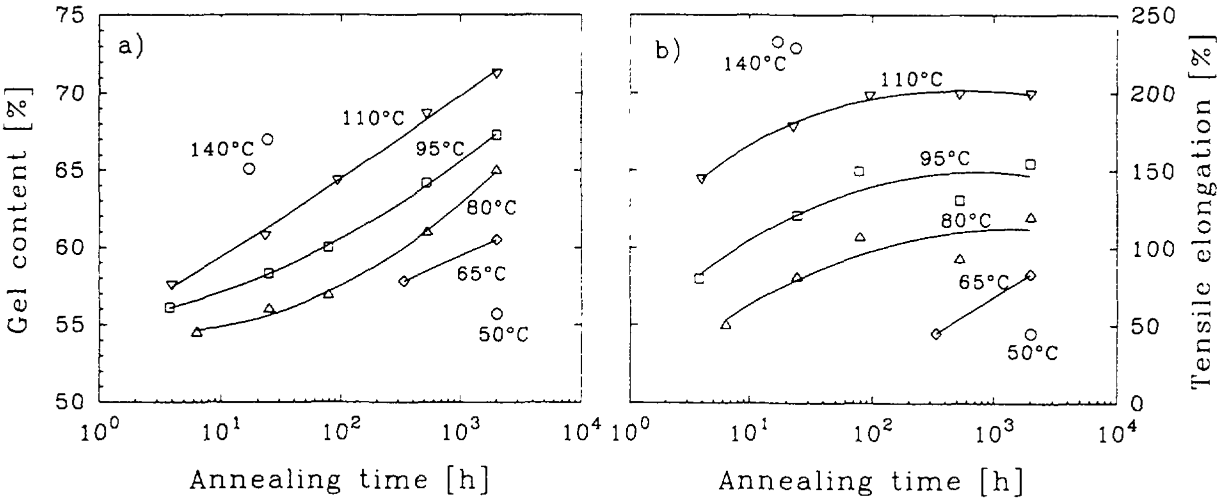

FIG. 15. Annealing of material A below the main melting point (~122 °C); (a) increase of gel content, (b) recovery of tensile elongation.

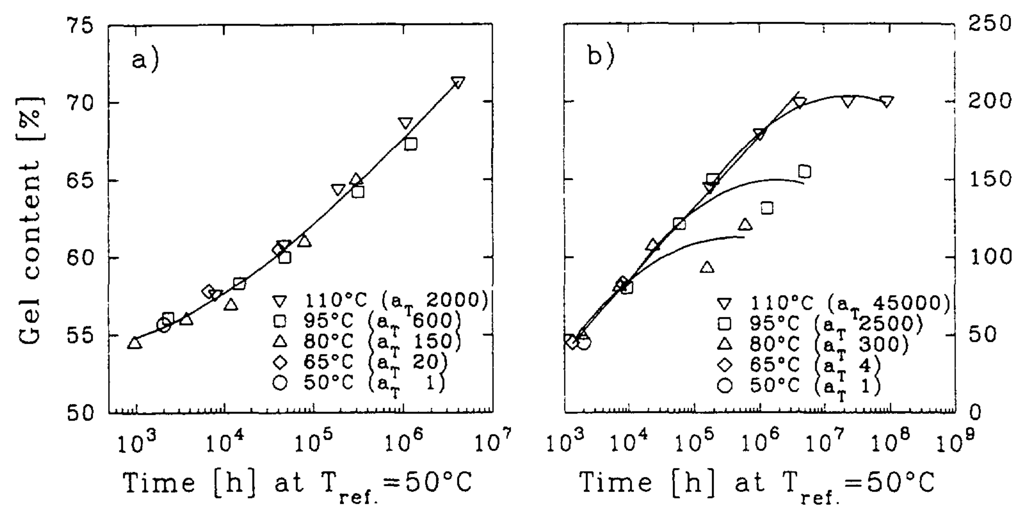

Fig.16. Empirical time/temperature superposition for material A at T_{ref}= 50°C of the (a) crosslinking (shown in Fig. 15a) yielding 129 kJ/mol and (b) tensile elongation (shown in Fig. 15(b) resulting in 191 kJ/mol.

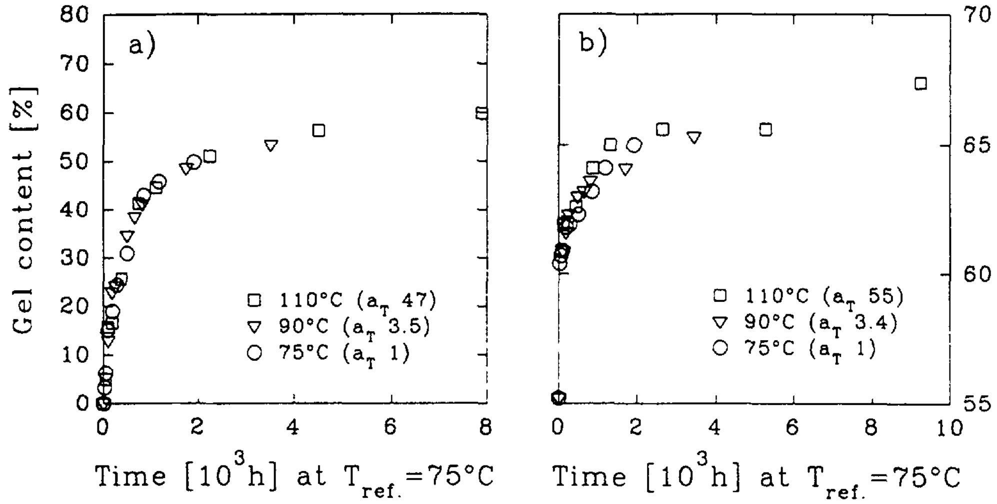

FIG. 17. Empirical time/temperature superposition of the crosslinking at T_{ref}= 75°C for (a) material C resulting in 123 kJ/mol and (b) material A resulting in 128 kJ/mol.

The activation energies describing the annealing reactions for the two materials at the two temperature regimes are summarized in Table I. We observe larger activation energies when the annealing is carried out below the main melting of the materials (50-110°C). At these temperatures only partial melting of the semicrystalline material will occur and it is expected that this limitation will severely impair molecular mobility and thus interfere with the chemical crosslinking reaction taking place. When the temperature is further lowered (i.e. aging at ambient conditions), mobility will become severely restricted and may ultimately lead to a complete inhibition of the reaction. Such restrictions for the efficiency of this reaction would normally relate to higher activation energy, which is indeed observed.

TABLE I. ACTIVATION ENERGIES OBTAINED FOR THE ANNEALING BEHAVIOR

	Activation energy [kJ/mol] Material A	 Material C
Gel content (125-170°C)	84	85
Gel content (75-110°C)	128	123
Gel content (50-110°C)	129	-
Tensile elongation (50-110°C)	191	-

3.6. Repair mechanism at elevated temperatures

The kinetic behavior of the crosslinking reaction for the two materials (Figs. 16 and 17) further indicates that the reaction is fast enough to lead to considerable crosslinking within a reasonable time frame over the temperature range of ~60-110°C. The actual duration of the combined thermal-radiation aging experiment (normally more than 100 days) at the elevated aging temperatures allows for much of the crosslinking reaction to take place. At the lower temperatures (i.e. ambient to ~50°C) the reaction becomes too slow to result in any significant crosslinking during the time period of the aging experiment. Thus we conclude that the crosslink potential is generated at all aging temperatures. At the elevated temperatures the reaction is fast enough to lead to a degradation mechanism where crosslinking plays a major role in counter balancing the effects of chain scission. This is equivalent to an active repair mechanism at these temperatures. At the lower temperatures, however, the reaction is too slow or entirely inhibited (complete mobility restriction) to result in any crosslinking. The responsible reagents are produced nevertheless and result in a dormant reactivity which is expressed during any subsequent annealing step.

3.7. DSC melting

We previously concluded (for material A) that a considerable morphological rearrangement occurs when the aging is carried out at elevated temperatures. This was shown by an analysis of the DSC melting behavior which revealed the development of new melting peaks (i.e. 45°C and 80°C) for samples aged at 60°C, but no significant changes when aged at ambient temperature [31]. During annealing (140°C) of the latter samples significant recrystallization could also occur. We now find similar effects in all of the investigated materials. This is shown, for example, in Figs. 18 (a) and 18 (b) for material B and C, respectively. We notice a considerable change in the melting, with the formation of new melting peaks and a decline in the amount of material which melts at the relevant aging temperature.

The observed changes in the melting behavior for samples aged at the elevated temperatures, however, do not necessarily relate to radiative damage. Similar recrystallization tendencies and annealing effects are frequently observed in these semicrystalline XLPO materials when held for long time periods at elevated temperatures [51]. It does, however, reveal that molecular mobility at the those temperatures is sufficient and that tie molecules, as well as amorphous and crystalline material, can easily be exchanged. It also provides enough mobility for the crosslinking to occur and for the observed repair mechanism to be active at these temperatures.

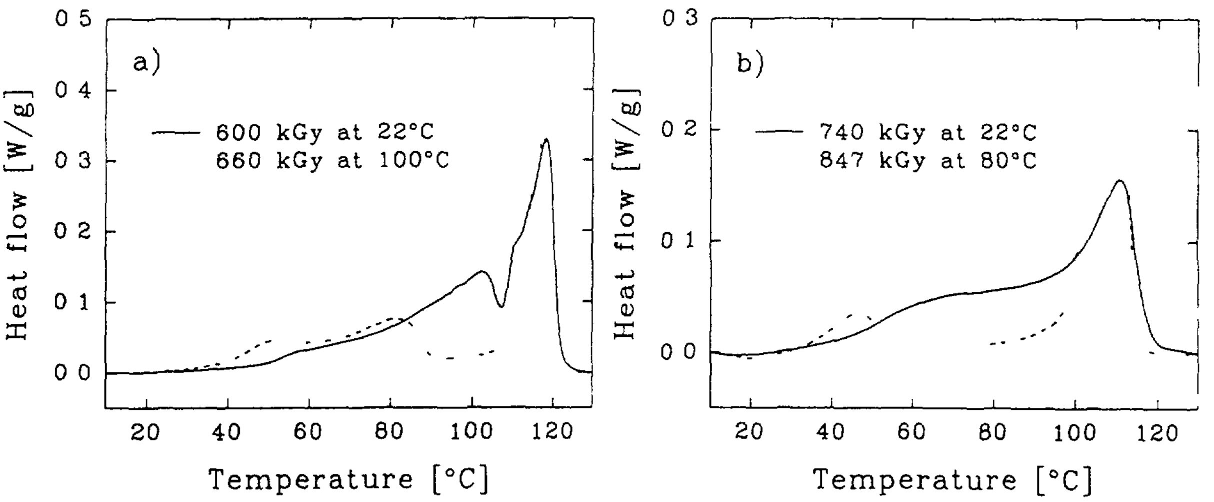

FIG. 18. DSC scans (first) showing considerable crystallinity changes at the higher temperature for (a) material B aged at 100 °C and 22 °C and (b) material C aged at 80 °C and 22 °C.

4 CONCLUSIONS

The combined radiation-thermal degradation of some crosslinked polyolefin based cable insulation materials was studied over a wide temperature range Surprisingly, the materials were found to age considerably *faster* at ambient conditions than at elevated temperatures Thus, we identified an inverse temperature effect which is contrary to expectation and which defies established procedures for carrying out accelerated aging experiments

The aging carried out at elevated temperatures clearly differs (the extent is material specific) from that at ambient conditions with regard to changes in mechanical properties, dose to equivalent damage, gel content, density, crystallinity and morphological changes Following their rapid loss at ambient temperature, however, useful mechanical properties of some materials can be recovered during a subsequent annealing step above the main melting temperature of the XLPO or partially recovered at temperatures within the materials melting range This annealing is characterized by a dramatic increase in the gel content of the polymer network Recovery does not occur for samples aged at the higher temperatures or under nitrogen Oxidation chemistry is clearly involved in both the rapid loss of mechanical properties at low temperatures and in the subsequent crosslinking during annealing, since oxygen during the radiation aging is required for these anomalous effects to occur

The thermally-induced changes in the XLPO clearly involve chemical crosslinking reactions, as evidenced by the dramatic increase in the gel content during annealing at elevated temperatures Attempts to deactivate any hydroperoxides by chemical treatment gave only negative evidence on the participation of hydroperoxides Of particular significance is the observation that for aging carried out at the elevated temperatures, or when samples aged at ambient temperature are subsequently annealed at temperatures above the main melting point, the melting of the XLPO compound imparts enough mobility for the latent chemical crosslinking reaction to occur When the annealing is carried out at temperatures below the main melting point (partial melting) a reduction in crosslinking rate occurs, as well as a reduction in the overall extent of mechanical property recovery that is achieved. We also notice distinctly different activation energies describing the crosslinking during annealing in the melt or solid state. Thus the semi-crystalline nature and morphology of the polymers are important for these anomalies to occur. All evidence suggests that the observed crosslinking reaction is highly dependent on partial melting of the material. During elevated-temperature aging the reaction is fast enough to act as a repair mechanism for scission damage. At the lower temperatures the reaction is effectively inactive or too slow, and the responsible species produced stay dormant or can lead to crosslinking during a subsequent annealing step.

This anomalous aging behavior is of generic nature, since it was observed in very different polymers (XLPE to XLPO vinylacetate copolymers), and is not dependent on a certain copolymer type or additive component. Such an anomalous aging dependence will lead to complications in the applicability of the Arrhenius methodology to predict material aging and life times. While the chemical species responsible for the crosslinking have not yet been specifically identified, we do conclude that these anomalous aging phenomena require the participation of some specific oxidative species as well as an appropriate environment, which is the semicrystalline morphology of these materials.

The recovery of useful mechanical properties in irradiated samples of these materials, which occurs upon thermal treatment, is of potential interest for commercial applications involving radiation processing of polymers, if this phenomenon can be more fully understood and controlled, and possibly be enhanced or made more widely applicable. In that regard, the situation is similar to strong recovery of optical transmission (i.e., reduction of discoloration) which has been found to occur upon annealing of irradiated samples of many types of glassy polymers [52].

ACKNOWLEDGMENTS

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SELECTIVITY OF RADIATION-INDUCED PROCESSES IN HYDROCARBONS, RELATED POLYMERS AND ORGANIZED POLYMER SYSTEMS

V. I. FELDMAN, F.F. SUKHOV, A.A. ZEZIN, A.Yu. ORLOV
Karpov Institute of Physical Chemistry,
Moscow, Russian Federation

Abstract

Fundamental aspects of the selectivity of radiation-induced events in polymers and polymeric systems were considered: (1) The grounds of selectivity of the primary events were analyzed on the basis of the results of studies of model compounds (**molecular aspect**). Basic results were obtained for hydrocarbon molecules irradiated in low-temperature matrices. The effects of selective localization of the primary events on the radical formation were examined for several polymers irradiated at low and super-low temperatures (77 and 15 K). A remarkable correlation between the properties of prototype ionized molecules (radical cations) and selectivity of the primary bond rupture in the corresponding polymers were found for polyethylene, polystyrene and some other hydrocarbon polymers. The first direct indication of selective localization of primary events at conformational defects was obtained for oriented high-crystalline polyethylene irradiated at 15 K. The significance of dimeric ring association was proved for the radiation chemistry of polystyrene. Specific mechanisms of low-temperature radiation-induced degradation were also analyzed for polycarbonate and poly(alkylene terephthalates). (2) Specific features of the localization of primary radiation-induced events in microheterogeneous polymeric systems were investigated (**microstructural aspect**). It was found that the interphase processes played an important role in the radiation chemistry of such systems. The interphase electron migration may result in both positive and negative non-additive effects in the formation of radiolysis products. The effects of component diffusion and chemical reactions on the radiation-induced processes in microheterogeneous polymeric systems were studied with the example of polycarbonate - poly(alkylene terephthalate) blends. (3) The effects of restricted molecular motion on the development of the radiation-chemical processes in polymers were investigated (**dynamic aspect**). In particular, it was found that kinetics of radical decay was affected strongly by local molecular dynamics of polymeric chains in specific microphases. These features are especially important at low temperatures and for “well-organized” polymeric systems, such as highly oriented and highly crystalline polymers or microheterogeneous bicomponent systems. The results obtained show that the radiation-induced chemical events in solid polymers are far more selective than it might be expected from formal energetic reasons. The localization of primary events is controlled by conformation, weak molecular interactions, and microstructure of polymeric system. Some important mechanisms of this selectivity could be understood taking into account the properties of prototype ionized molecules. Significance of the concept of “selective radiation chemistry” for prediction and improvement of the radiation resistance of polymers and polymeric materials is discussed.

1. INTRODUCTION

The problem of selectivity of the radiation-induced events in solid polymers is basically important for prediction and improvement of the radiation stability of polymeric materials as well as for radiation-chemical modification of polymers. Generally speaking, it is this factor that determines efficiency of the use of radiation energy for specific transformations of the material. The primary radiation-induced chemical events (e. g., bond rupture) are often treated as non-selective; this implies that any heterogeneity in the radiation-induced damage of the material results from secondary processes, such as microscopic and macroscopic diffusion of the radiolysis products. This concept is rather intuitive than physical. It originates from a simple idea that the energy of ionizing radiation is too high, so the differences between the energies of specific chemical bonds and even more "subtle" structural differences (e. g., resulting from conformation, weak interactions etc.) become unimportant. Actually, it is known for a long time that the model of random primary bond rupture does not work well (one illustrative example is that main chain scission is negligible in the radiolysis of n-alkanes and polyethylene, whereas the yield of C-H bond rupture is rather large, see, e. g., [1]). Nevertheless, this point of view is still wide-spread, especially in applied researches.

An alternative approach is concerned with the concept of "weak bonds". This implies simply that the weakest bond in the molecule is favorably ruptured in radiolysis, like that in conventional thermal processes. This approach provides reasonable description of the distribution of final radiolysis products of some liquid hydrocarbons [2], which may be partially due to rapid secondary thermal radical reactions; however, it is at least questionable for primary events in solid polymers.

A common problem of both of these concepts results from the fact that they ignore physical mechanisms of the degradation of energy of ionizing radiation in the condensed phase, that is, the properties of ionized and excited macromolecules are not taken into account. Furthermore, previous studies of primary radiation-induced events often disregarded real microstructure of the polymers used, which may be very important in terms of defects, microdomain sizes etc. Several years ago we started extensive experimental studies in order to obtain direct information concerning basic factors determining selectivity of radiation-induced events in hydrocarbons, polymers and organized polymeric systems. These studies [3 - 5] revealed remarkable selectivity of primary events, which could not be explained in the frame of simple intuitive concepts mentioned above. The present report describes some basic results and tentative interpretation, and analyzes possible consequences of the selective radiation-chemical effects for practical applications.

2. EXPERIMENTAL APPROACHES

In the course of our studies, we used several techniques for evaluation of the radiation-induced effects in polymeric systems (ESR, IR-spectroscopy, sol-gel analysis, mechanical testing, X-ray scattering). Meanwhile, the most important feature of our approach is concerned with using a combination of ESR and IR spectroscopy at low and super-low temperatures (down to 10 K) for analysis of the localization of primary radiation-induced events in model hydrocarbons, polymers and organized polymeric systems.

Application of spectroscopic techniques is very useful since we are interested in the precise nature of the primary radiation-induced defects and their spatial distribution. ESR and IR spectroscopy are very informative tools for determining the chemical nature of radiolysis products; moreover, both ESR and IR spectra are sensitive to the local environment of the radiation-induced defects. These methods are intersupplementary. ESR spectroscopy provides unique information concerning structure and distribution of paramagnetic species (radicals, radical ions), which is of primary significance to determine the selectivity of bond rupture at early stages. IR spectroscopy makes it possible to study the radiolysis products regardless of their magnetic properties. In particular, this method allows one to reveal unambiguously the formation of many common degradation products (e. g., unsaturated bonds, methane, carbon monoxide, carbon dioxide, etc.) promptly after irradiation of solid samples at low temperature.

On the other hand, identification of the IR spectra of primary species is often not straightforward, and in some cases ESR spectroscopy may serve as a reference tool. It should be noted that the approach based on combination of low-temperature ESR and IR spectroscopy, in spite of its great potential, is still not widely used to probe the radiation chemistry of organic and polymeric materials. We believe that this is partially due to technical difficulties, which were overcame in our laboratory.

Using low temperatures is basically important in our spectroscopic studies. In terms of the radiation chemistry of organic solids and polymers, low temperature means, first of all, restriction of molecular motion, which reduces the probability of secondary reactions. This makes it possible to analyze not only chemical identity of primary radiolysis products, but also their initial distribution. A typical low-temperature experiment in radiation chemistry is carried out at liquid nitrogen temperature (77 K). However, it was shown [6 - 9] that some local processes in polymers (e. g., radical site migration) may occur even below 77 K. For this reason, in some cases it is necessary to use super-low, or “helium-range” temperatures (4-77 K). In our studies we used an original homemade complex of continuos-flow helium cryostats for spectroscopic studies of electron-irradiated samples at 8-300 K. The complex consists of three cryostats: (1) cryostat for ESR spectroscopic studies of film polymeric samples (including oriented films) irradiated in cold helium flow at 8-20 K; (2) cryostat with vacuum resonator cavity for ESR spectroscopic studies of matrix deposited samples irradiated in vacuum at 8-20 K; (3) cryostat for IR spectroscopic studies of polymeric and deposited samples irradiated in vacuum at 10-20 K (the latter cryostat is also suitable for UV/visible optical spectroscopic studies of irradiated samples). In all cases, irradiation with fast electrons is carried out through thin aluminum foil windows in the cryostats (a commercial EG-2.5 Van-de-Graf accelerator was used; electron energy was typically 1-1.5 MeV; dose rate 20-150 Gy/s). The spectra were measured in the same cryostats without intermediate heating; it was possible to follow the post-irradiation processes occurring upon annealing the samples at any temperature up to 300 K. More detailed description and schemes of the cryostats are given in a recent review [10]. To the best of our knowledge, no other research group in the world possess such a complex of equipment for the low-temperature radiation-chemical studies. It appears that, in addition to basic mechanistic significance, the studies of radiation-induced effects in organic and polymeric materials at super-low temperatures are important for some specific applications.

The experiments at 77 K were carried out with commercial and homemade [10] cryostat equipment. Both fast electron irradiation (see above) and ^{60}Co γ-ray irradiation (dose rate 8-16 Gy/s) were used in this case.

The polymeric samples used were characterized by various techniques (IR spectroscopy, X-ray scattering, DSC, HPLC). Detailed description of the materials used and sample preparation is given elsewhere [4, 11-16].

3. RADIOLYSIS OF HYDROCARBONS IN LOW-TEMPERATURE MATRICES

First of all, we have investigated the **molecular aspect** of the problem. This implies analysis of the selectivity of primary chemical events (e. g., chemical bond rupture) in ionized and excited macromolecules. Special attention was paid to the elucidation of the structure and reactivity of ionized molecules since ionization appears to be the most important primary process in the radiation chemistry of molecular materials in condensed phases. In general, our studies revealed the very important role of primary ionic species in the radiolysis of most hydrocarbon polymers.

Actually, in many cases it is not possible to follow the fate of primary ionization and excitation at the molecular level in real solid polymers. For this reason, it is necessary to use model systems. The primary ionized aliphatic molecules are highly reactive, so they are not trapped in pure organic substances even at super-low temperatures (down to 4 K). Since at this stage we are interested in the basic properties of isolated ionized molecules it is relevant to use the matrix isolation technique, which implies irradiation of organic molecules in rigid inert environment at low temperatures.

Recent progress in the studies of ionized hydrocarbon molecules in low-temperature matrices is associated with two main approaches. The first approach, rather simple and elegant, deals with the so-called "Freon matrix technique" [17, 18] using frozen dilute solutions of hydrocarbons in specific halocarbons (Freons). Trapping of ionized organic molecules (radical cations) in Freon matrices is efficient because of the high electron affinity of the matrix, which scavenges electrons resulting from radiolysis. The application of Freon matrices made it possible to get unique information about the properties of reactive ionized molecules. In particular, the ESR studies in Freon matrices revealed remarkable selectivity of bond rupture in ionized hydrocarbon molecules, which was determined by their electronic structure and geometry. We used the Freon matrix technique for the studies of selective reactivity of the radical cations of alkenes [19] and aromatic hydrocarbons [20]. The limitations of this approach result from rather strong cation-matrix interactions and unknown matrix microstructure in most cases.

The second approach was introduced by us very recently [10]. It is concerned with using solid rare gas matrices (argon and xenon), which seems to be more rigorous from the point of view of the classic formulation of matrix isolation. The advantages of this approach are due to inertness, low polarizability and optical transparence of solid rare gas matrices; the latter factor makes it possible to carry out not only ESR, but also IR spectroscopic studies in the same environment. The main difficulty is concerned with technical problems of designing the complex apparatus for radiation-chemical studies at super-low temperatures required for using solid rare gas matrices; our way of solving these problems is described in the previous section of the report.

We present here some details of the most recent studies of hydrocarbon radiolysis in solid rare gas matrices.

The experiments were carried out with linear alkanes (butane - heptane); longer alkanes are less suitable for these studies because of low volatility. Heptane appears to be an appropriate model molecule to probe the selectivity of the rupture of various C-H and C-C bonds in ionized and excited alkanes. Irradiation of heptane in solid rare gas matrices doped with electron scavengers allows us to obtain the information concerning trapping and degradation of primary ionized molecules. On the other hand, experiments with heptane/matrix systems without electron scavengers shed light on the primary mode of degradation of excited molecules resulting from ion-electron recombination. Variations of the matrix nature makes it possible to follow "low-energy" or "high-energy" paths of the reactions of primary ions. Indeed, using a xenon matrix (ionization potential 12.13 eV) results in predominant formation of ground-state alkane cations, whereas using an argon matrix (ionization potential 15.75 eV) leads to formation of excited alkane cations because of highly exothermic positive hole transfer [11].

Fig. 1a shows the ESR spectra of irradiated heptane/xenon systems. The multiplet signal with a characteristic splitting of ca. 2.2 mT is due to secondary heptyl radicals. In addition, intense signals from trapped hydrogen atoms (a doublet with the splitting of 51.0 mT and well-defined superhyperfine structure due to interaction with xenon magnetic isotope nuclei) are observed [10].

IR spectra of the same irradiated system show a rather large radiation-chemical yield of the total degradation of parent alkane molecules ($\geq$ 1.4 molecule per 100 eV [11]), which demonstrates high efficiency of energy transfer from matrix to isolated molecules. The most intense new absorptions resulting from irradiation of the sample at 15 K are due to *trans*-vinylene olefins and some unidentified intermediates (probably, radicals). The intensity of the absorption bands of methane and vinyl olefins are lower. Thus, both ESR and IR spectroscopic data show that C-H bond rupture is the most important primary process for excited isolated alkane molecules resulting from ion-electron recombination. The efficiency of the C(1)-C(2) bond rupture is lower, whereas other processes of C-C bond rupture were not detected [11].

Irradiation of heptane/xenon systems containing an electron scavenger results in trapping of primary ionized heptane molecules (radical cations). The intensity of the signals from trapped hydrogen atoms drops dramatically because of ceasing ion-electron recombination. The ESR spectrum of the radical cations (Fig. 1b) is a characteristic triplet with a coupling constant of a(2H) = 3.1 mT due to the interaction of the unpaired electron with two in-plane chain-end protons [21] (the spectrum is similar to those observed earlier in halocarbon and related matrices [22, 23]). The spectrum corresponds to the extended-chain conformer (planar zigzag) of ionized heptane molecules. It should be noted that the spectra of gauche conformers of the radical cations are remarkably different, which also results in different site-selective reactivity of these species [24 - 26]; this peculiarity is very important when considering the selectivity of reactions of ionized macromolecules (see discussion below). IR spectra of the irradiated systems heptane/xenon/electron scavenger show a low-frequency-shifted feature in the C-H stretching region (maximum at ca. 2770 cm^{-1}) [11]. This feature may be due to selectively weakened specific C-H bonds in the radical cations; this appears to be the first indication of the vibrational spectra of such species. Further studies are necessary to prove the identification.

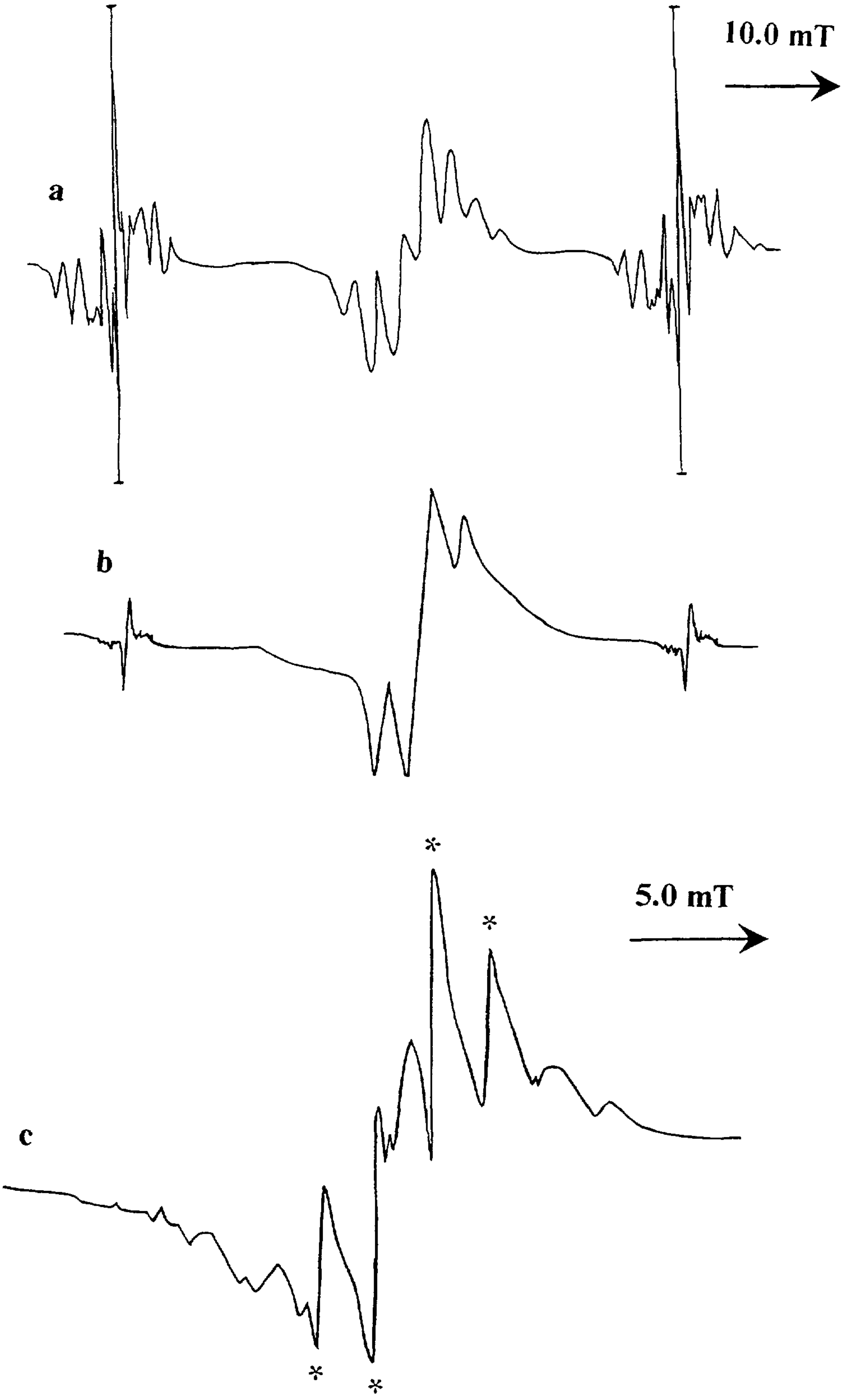

FIG 1 ESR spectra of the products of heptane radiolysis in xenon and argon matrices at 15 K (a) heptane/xenon = 1/400, (b) heptane/xenon/Freon-113 = 1/400/2, (c) heptane/argon/Freon-113 = 1/400/2 The signals from methyl radicals are marked with asterisks

The isolated radical cations of alkanes are quite stable in inert matrices at low temperatures. However, they react with parent neutral molecules to yield alkyl radicals at elevated temperatures or at higher alkane concentrations [3, 24-26]. In the cases of neat alkanes or polymers, such ion-molecule reactions may occur even at super-low temperatures [27]. This reaction has proved to be *proton transfer* of the type

$$RH^{+\bullet} + RH \text{-------->} RH_2^{+} + R^{\bullet} \quad (1)$$

An important feature of proton transfer is its selectivity, which correlates with the spin density distribution in the radical cations. The proton transfer occurs from the maximum spin density site, i. e., the protons showing the largest coupling constants in the ESR spectra are the most "acidic" (weakly bound). Thus, for extended-chain conformers, primary deprotonation occurs at the chain-end position yielding terminal alkyl radicals, whereas for *gauche* conformers deprotonation may occur from the gauche position [25-27]. This is the reason for *conformational selectivity* of the bond rupture in ionized alkane molecules and related macromolecules. Although the correlation between spin density distribution and selective reactivity of the radical cations was known for several years [25-27], the theoretical grounds of this rule were not completely clear. Our IR spectroscopic observations of bond weakening in the radical cations in a xenon matrix appear to shed light on this issue.

Generally speaking, experiments in xenon matrices show that C-H bond rupture is the most important primary process for both ionized and excited isolated alkane molecules, and this process is site-selective in the case of ionized molecules. The C(1)-C(2) bond rupture also occurs for excited molecules, but the yield of this process is smaller.

As stated above, the studies in an argon matrix allow us to follow the fate of excited primary radical cations ("high-energy pathway") resulting from the large gap in ionization potentials between argon and hydrocarbons. Actually, it is not known whether such "high-energy pathway" is essential for the radiolysis of neat solid hydrocarbons. It depends on the energy degradation spectrum (not well defined at relatively low electron energies) and the efficiency of deactivation of excited ions in condensed phase. Nevertheless, it seems to be of interest to use this unique possibility to get some information concerning the properties of excited ions in a solid matrix.

Fig. 1c shows the ESR spectra of irradiated heptane/argon systems in the presence of an electron scavenger. The most important difference between xenon and argon matrices results from the fact that the excited radical cations undergo rapid fragmentation in argon; these species are not trapped in the presence of electron scavengers. Instead of this, rather large yields of methyl radicals (a quartet signal with coupling of 2.3 mT) are observed, independent of the presence of scavengers, which indicates the primary significance of the C(1)-C(2) bond rupture for excited radical cations. This result is in general accord of our IR spectroscopic observations [11] exhibiting favorable formation of methane and vinyl-type olefins in the radiolysis of the heptane/argon solid system at 15 K. The yields of the products of the C-H bond rupture (secondary heptyl radicals, *trans*-vinylene olefins) are relatively smaller than those observed in a xenon matrix. In addition, the products of deeper destruction (such as terminal allyl-type radicals) are observed in argon at relatively high doses, probably due to secondary processes. Detailed analysis of the products of heptane degradation in argon and the tentative radiolysis scheme are presented in [11]

Thus, the results of our studies of alkane radiolysis in solid rare-gas matrices, show that the primary degradation of isolated alkane molecules occurs mainly via C-H bond rupture, and, to a certain extent via C(1)-C(2) bond rupture No evidence for alkane chain scission at other positions was obtained so far These results contradict both "random scission" and "weak bonds" concepts, however, they match well the experimental results on the radiolysis of neat alkanes and polyethylene We may conclude that it is the electronic structure of primary ionized and excited molecules that determines the mode of primary bond rupture, and the weakest bonds in these species may be not the same as in parent neutral molecules In particular, the spin density distribution in the ionized molecules is very important

We have studied also the selectivity of the reactions of linear alkene radical cations [18, 28] These investigations were carried out using Freon matrices It was shown that deprotonation of ionized alkene molecules occurs predominantly at the maximum spin density site For this reason, the conformation of the ionized molecule may also affect the selectivity of the C-H bond rupture [18] On the other hand, the presence of p-p associates in alkenes prior to irradiation (rather weak in neutrals) may result in the formation of dimeric radical cations, which yield dimeric-type alkyl radicals [28] In terms of the radiation chemistry of unsaturated polymers, the latter process can be interpreted as the first step of *radical ionic crosslinking* [3] The results obtained show that both the molecular conformation and weak interactions may control the mode of formation of the radiolysis products Furthermore, it was shown that allyl radicals observed in the low-temperature radiolysis of alkenes (and probably of unsaturated polymers) resulted mainly from primary radical cations rather than from excited molecules [3, 29]

In the case of aromatic hydrocarbons (benzene and alkyl benzenes), our studies revealed two basic pathways of the reactions of primary ionized molecules [20] Benzene radical cations react with neutral molecules to yield dimeric species

$$C_6H_6{}^{+\bullet} + C_6H_6 \longrightarrow (C_6H_6)_2{}^{+\bullet} \quad (2)$$

These dimeric radical cations are quite stable in the presence of electron scavengers Neutralization of these species with electrons results in the formation of excimers, which mainly dissipate their energy without formation of any observable products On the other hand, toluene and other alkyl benzene radical cations yield benzyl-type radicals as a result of an ion-molecule reaction

$$C_6H_5\,CH_3{}^{+\bullet} + C_6H_5\,CH_3 \longrightarrow C_6H_5\,CH_2{}^{\bullet} + C_6H_5\,CH_3(H^+) \quad (3)$$

Reaction (3) is most likely proton transfer, i e , a particular case of general scheme (1)

It was suggested [20, 29] that for the molecules containing two or more phenyl rings and corresponding macromolecules (e g , polystyrene) both ways were possible depending on molecular organization (packing of aromatic rings) Thus, the proposed mechanism provides a basis for the correlation between aromatic ring packing and radiation stability of the corresponding solid system

4. LOCALIZATION OF PRIMARY EVENTS AND THE MECHANISMS OF RADIOLYSIS OF SOME SPECIFIC POLYMERS

4.1. Polyethylene

In spite of numerous studies of the radiolysis of polyethylene during the past 40 years (see, e. g., [30]), the mechanisms of early stages of the process are still not completely understood. In general, it is known that the C-H bond rupture strongly predominates over main chain scission (in accordance with the properties of ionized and excited molecules of prototype alkanes considered above). However, up to recently no direct evidences of the site selectivity of the C-H bond rupture related to structural defects was obtained. As shown in the previous section, deprotonation of ionized linear alkane molecules is highly selective and correlates with the conformation of these species. In particular, extended conformers undergo deprotonation at the chain-end position, whereas *gauche* conformers exhibit deprotonation at the defect position. Such a selectivity results in high primary yields of terminal alkyl radicals in alkane crystals (up to $C_{25}H_{52}$) irradiated at 4 K [27]. Alkane molecules in the crystals are packed as extended-chain conformers, so this result implies that the positive hole delocalizes over the extended chain resulting in large spin densities on the in-plane chain-end protons, which are the most acidic. Similar effects are expected for polyethylene, however, their direct observation is difficult because of the complex supramolecular structure of the polymer and the occurrence of secondary local radical site migration even at 77 K. Thus, in order to clarify this issue, it is necessary to use well-organized high-crystalline samples with low defect concentrations and to carry out the experiment at super-low temperatures.

Recently we obtained the first direct spectroscopic evidence for selective localization of primary radiation-induced events at conformational defects in high-crystalline polyethylene irradiated at 15 K [3, 4]. The most illustrative results were obtained for polyethylene with extended-chain crystals (ECC PE) obtained by high-pressure annealing (538 K, 686 MPa) of linear polyethylene (<0.05 CH_3 per 100 carbon atoms, molecular weight 150000). This sample has a very high degree of crystallinity (95 - 98%) and large perfect crystallites, so the concentration of conformational defects (*gauche* conformers) is extremely small. Nevertheless, the ESR spectrum of oriented ECC PE irradiated at 15 K (Fig. 2) shows well-defined features of alkyl radicals localized at *gauche* conformers (in addition, to "normal" *trans-trans* conformers of interior alkyl radicals). The fraction of radicals localized at *gauche* conformers was estimated to be as large as ca. 30%; the computer simulated spectrum agrees well with the experimental one [4]. This result clearly indicates favorable localization of primary bond rupture at conformational defects, which is consistent with the model of selective deprotonation of the primary ionized macromolecule at the *gauche* position (the scheme is shown in Fig. 2). In fact, this means that the delocalization of the primary positive hole terminates at a conformational defect, that is, *gauche* conformers act as "effective chain ends". In this case, actual fraction of radicals resulting from ion-molecule reaction (1) should be approximately ca 60% of the total radical yield the protonated ion RH_2^+ gives one more radical upon subsequent neutralization with an electron:

$$RH_2^+ + e^- \text{------->} R^{\cdot} + H_2 \quad (4)$$

The radical resulting from neutralization is most likely localized at the adjacent polymeric chain relative to the radical trapped at conformational defects. Indeed, trapping of correlated radical pairs was observed in high-crystalline polyethylene irradiated at super-low temperatures

[7, 8] Thus, the reactions of primary ionized molecules may account for the formation of a major part of the alkyl radicals trapped in irradiated polyethylene

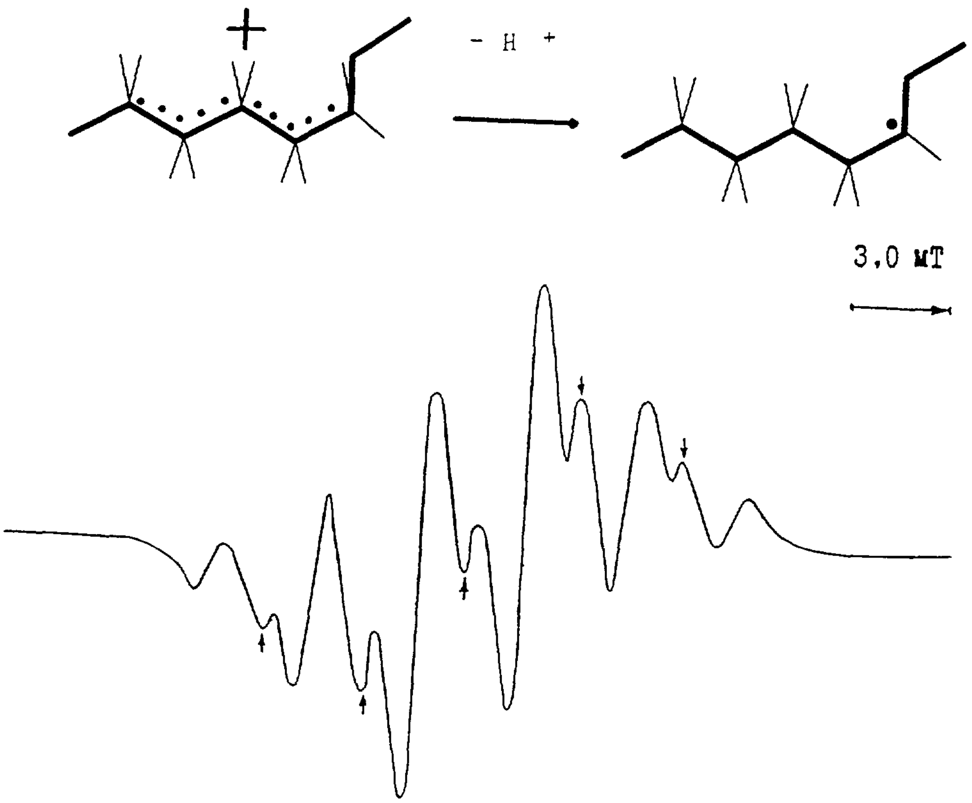

FIG. 2. First direct spectroscopic evidence for a favourable primary localization of radical site at conformational defects in macromolecules. The spectrum corresponds to oriented ECC PE (95- 98% crystallinity) irradiated to 36 kGy at 15 K; magnetic field was applied parallel to draw axis. The signals from alkyl radicals trapped at gauche conformers are marked with arrows.

4.2. Polystyrene

The radiolysis of polystyrene has been studied extensively from both mechanistic and practical viewpoints. Nevertheless, we failed to find in the available literature even a crude self-consistent scheme of the radiolysis mechanism, which met the balance requirements. Our studies made it possible to formulate such a scheme on the basis of an ionic mechanism of radical formation [14, 20, 29] The basic significance of the reactions of primary ionic species in the radiolysis of polystyrene is illustrated well by the effect of electron scavengers on the yield of paramagnetic species trapped in polystyrene irradiated at 77 K [20] Indeed, addition of even a small amount of chloroform (ca 0.1%) results in considerable increase in the yield of paramagnetic species (Fig. 3). This result is explained by electron scavenging and a corresponding increase in the yield of chemical reactions of primary cations. It should be noted that the remarkable effect of trace amounts of electron scavengers on the radiolysis implies formally very large radius of capture that means that electrons may travel rather long distances (several nanometers)

As mentioned in section 2 of this report, primary positive ions in polystyrene may appear as monomeric or dimeric aromatic radical cations Monomeric radical cations react to yield benzyl-type radicals via proton transfer to polystyrene matrix ("toluene-like behavior") Dimeric radical cations are stable in the presence of chloroform at low temperatures

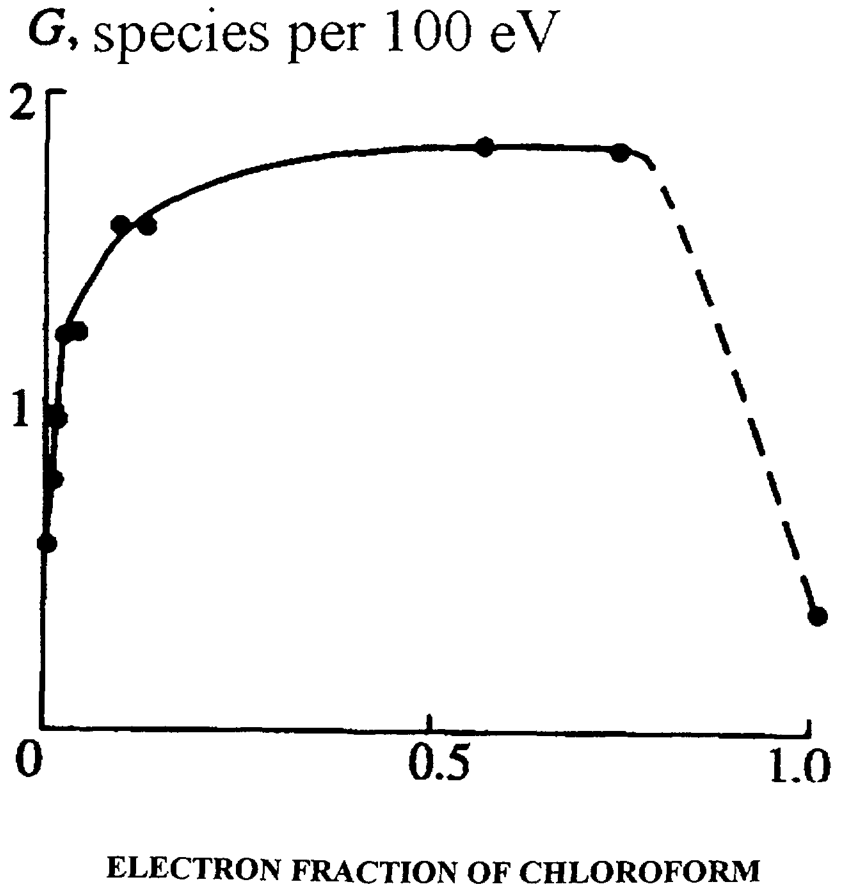

FIG 3 The effect of chloroform on the formation of paramagnetic species in the radiolysis of polystyrene at 77 K

This may be referred to as "benzene-like behaviour" Aromatic excimers are formed upon neutralization of these dimeric radical cations, these species probably do not yield radicals because of their efficient deactivation (both light emission and radiationless relaxation) Thus, the *aromatic ring association* in polystyrene and related systems may become a factor controlling their radiation stability

Another important feature of the proposed scheme is that the RH_2^+ ions resulted from ion-molecule reaction yield cyclohexadienyl-type radicals (products of H-addition to benzene ring) upon neutralization These radicals are clearly observed in the ESR spectra The overall scheme of the radical formation in the radiolysis of polystyrene may be presented as follows [1, 16]

$$\mathrm{RH} \rightsquigarrow \mathrm{RH}^{+\bullet},\ (\mathrm{RH})_2^{+\bullet},\ e^- \qquad (5)$$

$$e^- \longrightarrow e^-_{tr} \qquad (6)$$

$$\mathrm{RH}^{+\bullet} + \mathrm{RH} \longrightarrow \mathrm{RH}_2^+ + \mathrm{R}^\bullet_{\mathrm{benzyl}} \qquad (7)$$

$$\mathrm{RH}_2^+ + e^- \longrightarrow \mathrm{RH}_2{}^\bullet_{\mathrm{chd}} \qquad (8)$$

Here RH represents polystyrene unit, e^-_{tr} is the trapped electron, $\mathrm{R}^\bullet_{\mathrm{benzyl}}$ and $\mathrm{RH}_2{}^\bullet_{\mathrm{chd}}$ are benzyl-type and cyclohexadienyl-type radicals, respectively.

This scheme meets balance requirements and accounts for the observed dose dependence of the radical formation and effects of electron scavengers.

One more practical aspect of our studies of the radiolysis of polystyrene was concerned with the radiation stability of the polystyrene-based plastic scintillators. It was found that even small amounts of secondary luminophores added to polystyrene have considerable effect on the formation of macroradicals in irradiated polystyrene. One possible explanation is concerned with electron and hole scavenging by the additives. For this reason, degradation of luminophores may be significant even at small irradiation doses. On the other hand, accumulation of macroradicals is accompanied by degradation of the optical characteristics of scintillators. The presence of oxygen results in increase in the radiation stability of the scintillators. The ways of improvement of the characteristics of polystyrene-based scintillators may include both a search for more stable luminophore additives and modification of the matrix in order to enhance the oxygen permeability.

4.3. Other Hydrocarbon Polymers

Although other hydrocarbon polymers were not examined systematically in our studies, we have obtained some preliminary data, which indicate that the reactions of primary ionized molecules are basically significant for these systems too. In particular, addition of electron scavengers results in a noticeable increase in the radical yield in the radiolysis of polybutadiene. This also appears to be valid for other unsaturated polymers. The distribution of the radiation-induced events in these polymers may be controlled, at least partially, by formation of weak double bond associates, which affect the positive hole localization.

Generally speaking, we believe that the correlation between the properties of primary ionized molecules of prototype hydrocarbons and localization of primary radiation-induced events in corresponding polymers is obvious. From the fundamental point of view, this means that the knowledge about the features of chemical bonding in ionized hydrocarbon molecules may help us to predict the distribution of primary bond ruptures in real polymers. From the practical point of view, this implies that addition of *positive hole scavengers* (rather than quenchers of excited states) may represent the most efficient way to increase the radiation stability of hydrocarbon polymers. Another possibility is concerned with the variations in supramolecular organization, in particular, with changes in the degree of association.

4. 4. Polycarbonate

The polymers considered above show only negligible main chain scission. In contrast with these systems, bisphenol-A based polycarbonate (PC) is a typical destructible polymer, which exhibits favourable main chain scission. The radiation resistance of PC was studied in numerous works; however, the primary localization of the radiation damage cannot be deduced from these experiments. We have examined the radiation chemistry of PC irradiated at low temperature (77 K) using our combined spectroscopic approach [15, 16]. This method was found to be very suitable for PC because main paramagnetic (radical pairs) and diamagnetic (carbon monoxide and carbon dioxide) can be well characterized by the spectroscopic techniques used.

The IR spectrum of PC irradiated at 77 K shows rather intense new absorptions due to CO and CO_2 trapped in the polymer matrix [15, 30]. The maximum position and the shape of these bands exhibit clear dependence of their local environment (in particular, this allowed us to discriminate easily between atmospheric and radiolytically produced CO_2).

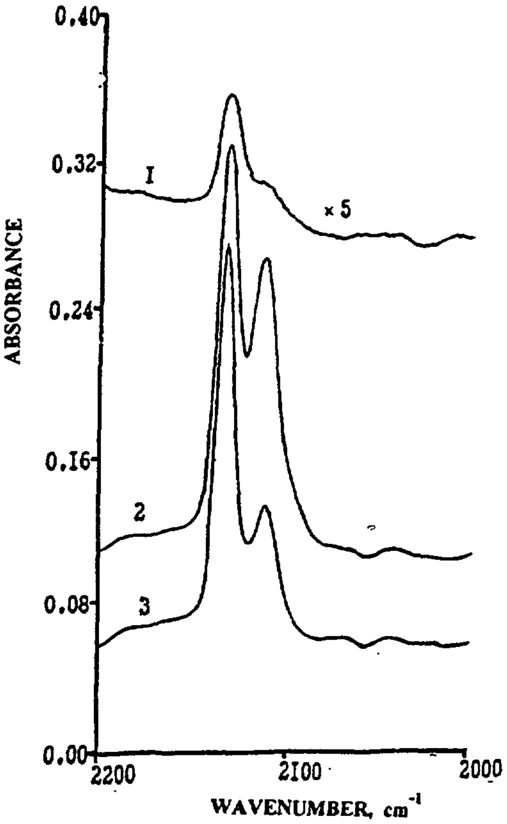

FIG. 4. The IR spectra of PC irradiated at 77 K up to the doses (1) 0.1 and (2) 2.0 MGy; the spectrum (3) was taken after annealing the sample at 200 K. All the spectra were measured at 77 K.

Fig. 4 demonstrates the fragment of the IR spectrum of irradiated PC corresponding to the CO absorption. A well-defined doublet structure of the absorption band was attributed to "non-perturbed" CO molecules (high-frequency component) and to CO molecules trapped in the vicinity of radiolytically produced negative ions [15, 30] The assignment is based on the analysis of dose dependence and annealing behaviour of this complex band, it is also supported by theoretical consideration of the effect of local ionic field on band position [30] The probability of electron trapping in the proximity of CO is sensitive to the polymer structure (it decreases with increasing the sample crystallinity)

The ESR spectra of PC irradiated under similar conditions exhibit signals from ionic species (most likely, trapped electrons) and neutral radicals of phenyl and phenoxyl types An important feature of primary radical formation in PC is that most radicals are trapped in the form of correlated radical pairs, which show doublet with a characteristic dipolar splitting that correspond to a specific interspin distance The radical pairs are separated by a CO molecule The interspin distance in the radical pairs was found to be quite sensitive to the polymer structure, in particular, it changes from 0 573 nm for the amorphous sample to 0 538 nm for the sample with 64% degree of crystallinity [30] This implies that measuring the dipolar splitting for radical pairs (which can be easily converted to the interspin distance) can be an informative test for the local environment of radiation damage in PC-based systems In addition to the dipolar splitting of the signal corresponding to allowed transition ($\Delta M_S = 1$), we also observed the ESR signal corresponding to forbidden transition ($\Delta M_S = 2$), which is characteristic of close radical pairs Measurement of relative intensity of these signals allowed us to estimate the fraction of the radical pairs, which was as large as ca 60% of the total amount of trapped radicals Thus, the formation of CO and corresponding radical pairs appears to be the most important primary process in the radiolysis of PC The formation of carbon dioxide and the corresponding radical pairs was also observed, however, the yield of this process was smaller [15] The shape of the IR band of carbon dioxide was found to be sensitive to the phase state of the polymer

More detailed analysis of the spectroscopic parameters of paramagnetic and diamagnetic products of the radiolysis of PC is given in Ref [30]

The results obtained can be rationalized in the form of the following scheme

$$[\text{-C(CH}_3)_2\text{-Ph-O-C(O)-O-Ph-}]^{*} \text{------->} [\text{-C(CH}_3)_2\text{-PhO}^{\bullet} + \text{CO} + {}^{\bullet}\text{O-Ph-}] \qquad (9)$$

$$[\text{-C(CH}_3)_2\text{-Ph-O-C(O)-O-Ph-}]^{**} \text{------->} [\text{-C(CH}_3)_2\text{-Ph}^{\bullet} + \text{CO}_2 + {}^{\bullet}\text{O-Ph-}] \qquad (10)$$

$$[\text{-C(CH}_3)_2\text{-PhO}^{\bullet} + \text{CO} + {}^{\bullet}\text{O-Ph-}] + e^{-} \text{-------->} [\text{-C(CH}_3)_2\text{-PhO}^{-} + \text{CO} + {}^{\bullet}\text{O-Ph-}] \qquad (11)$$

It should be noted that our studies revealed that CO and CO_2 resulted from different precursors, probably from two distinct excited states, which show different quenching behaviour Reaction (11) becomes more significant at higher doses

Therefore, the radiation-induced destruction of PC may be understood in terms of reactions of neutral excited states rather than those of ionic species The problem of stabilization of this polymer can be solved by the choice of appropriate quenchers (mainly aromatic carbonyl compounds with lower excitation levels)

4. 5. Poly(Alkylene Terephthalates)

The radiation chemistry of poly(ethylene terephthalate) (PETP) attracted considerable attention mainly for practical reasons The basic mechanisms of primary effects were not studied in detail Generally speaking, PETP shows rather high radiation stability Previous ESR studies [31] revealed formation of paramagnetic ions (disappearing completely at room temperature) and alkyl-type radicals In contrast with other aromatic polymers, no evidence for formation of the cyclohexadienyl-type radicals was reported The yields of destruction products measured at room temperature are typically low, the data concerning formation of stable products at low temperatures are unavailable The radiolysis of other poly(alkylene terephthalates) was not studied systematically In the frame of this work, we have investigated the radiolysis of PETP and poly(butylene terephthalate) (PBTP) at 77 K by ESR and IR spectroscopy IR spectroscopic studies show that the yield of CO_2 in both phthalates is relatively low (as compared to PC), and the formation of CO is negligible

The most important result of the ESR studies is the first detection of the cyclohexadienyl-type radicals in the radiolysis of PETP and PBTP [32] This result is illustrated by Fig 5 The cyclohexadienyl-type radicals represent a considerable fraction of the primary radicals in both polymers studied Thus, the earlier conclusion [31] that the cyclohexadienyl-type radicals are not formed in PETP because of peculiarities of its chemical structure appears to be wrong The structure of various types of radiolytically produced alkyl-type radicals was determined for PBTP [32] It was shown that the decay of both cyclohexadienyl and alkyl-type radicals at room temperature is described by the second-order kinetics This may be an evidence of radical combination reaction yielding crosslinks, which makes it possible to revise the radiolysis mechanism of this polymer Although the mechanism of formation of these radicals is not known, we may tentatively suggest significance of the ionic pathway similar to reaction (8) occurring in polystyrene

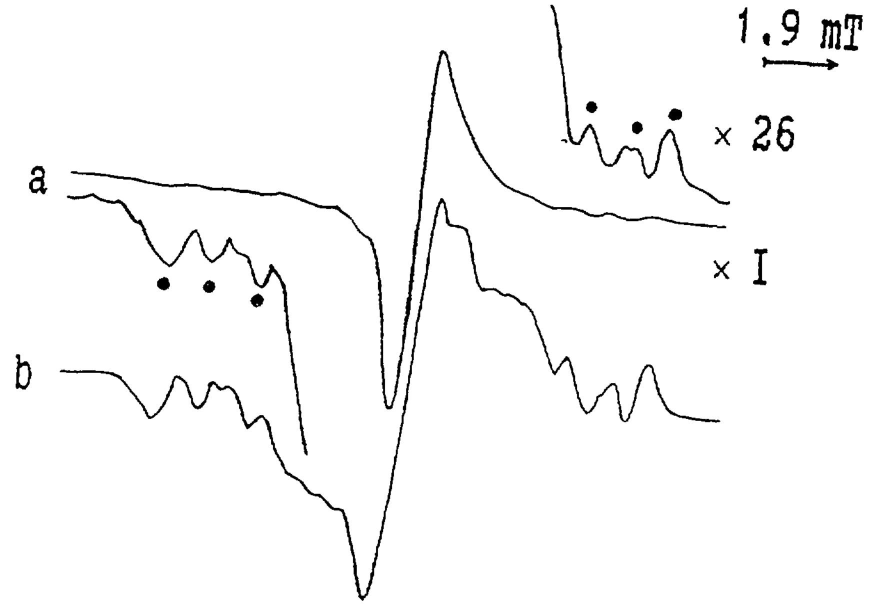

FIG 5 The ESR spectra of poly(ethylene terephthalate) irradiated up to 185 kGy at 77 K (1) immediately after irradiation, (b) after annealing the sample for 7 min at room temperature The signals from cyclohexadienyl-type radicals are marked

5. NON-ADDITIVE EFFECTS IN THE RADIOLYSIS OF MICROHETEROGENEOUS BICOMPONENT POLYMERIC SYSTEMS

Chemical and structural inhomogeneity is a typical feature of real polymeric systems. Meanwhile, a specific interest is concerned with the peculiarities of the distribution of radiation-induced events in bicomponent microheterogeneous systems (e. g., block copolymers and polymer blends). The systems of this kind are regarded as promising new polymeric materials. The radiation chemistry of these systems was virtually not investigated up to recently. The corresponding studies are of both fundamental and practical interest. In particular, if a microdomain size is comparable with the typical scale of primary radiation-induced processes (i. e., electron transfer, positive hole and excitation transfer), one may expect non-additive effects even at early stages of radiolysis. As a result, irradiation may cause *selective* modification of the microphases and specific changes in the material properties. We may define this problem as the ***microstructural aspect*** of the selectivity of radiation-induced events.

In the course of the present studies, we have examined the possibility of non-additive effects for several kinds of microheterogeneous systems irradiated at low temperatures.

5.1. Styrene-Butadiene Block Copolymers

Styrene-butadiene block copolymers are well-characterized microheterogeneous systems with microdomain size of ca. 10 nm and variable microdomain morphology. These copolymers attract considerable attention from the viewpoint of various applications. We have investigated the formation of paramagnetic species in styrene-butadiene block copolymers of various composition and morphology [13]. Fig. 6a shows the yields of paramagnetic species plotted versus electron fraction of polystyrene component. A negative deviation from the additive rule in the formation of paramagnetic species is clearly observed for the systems with a large content of polystyrene component. This deviation is not due to transfer of positive hole or excitation from polybutadiene to polystyrene via contact mechanism [33], because the fraction of contacted units of different components is not large for segregated microheterogeneous block copolymers. Detailed analysis of the ESR spectra [13] revealed that the effect was most likely due to interphase electron migration. The electrons generated in polystyrene microdomains migrate to polybutadiene microphases and react with allyl radicals to yield diamagnetic species. As a result, the concentration of paramagnetic species decreases in both microphases. This may be interpreted, at least formally, as *mutual protection*. We should note that the possibility of long-range electron migration in polystyrene was proved in the experiments with electron scavengers described in section 4.2 of this report.

5.2. Interpolymers Of Polystyrene And Polytrichlorobutadiene

It seems to be of special interest to test the significance of long-range electron transfer in the radiation chemistry of microheterogeneous polystyrene-based systems for a system containing electron-scavenging units. For this purpose, we have investigated the radiolysis of interpolymers of polystyrene with 1,1,2-polytrichlorobutadiene (PTCB) at 77 K [34]. Interpolymers are the products of irreversible reactions between two different macromolecules. In the case of incompatible components, solid interpolymers exhibit a characteristic microphase separation. The microstructure of such systems may vary significantly with the variations in the reaction conditions In general, such an approach may allow one to design the materials with specific valuable properties The radiation-chemical effects in interpolymers have not been studied

Fig 6b exhibits the yields of paramagnetic species in interpolymers of polystyrene and PTCB of various composition A specific feature of the systems under consideration results from high electron affinity of the PTCB units containing three chlorine atoms The electrons generated in polystyrene microdomains travel to PTCB microphases and react with the units of this component via dissociative electron capture to yield chloroallyl radicals [34] This process is very efficient even at rather small fractions of PTCB, so the cation-electron recombination in polystyrene is suppressed As a result, the yield of benzyl radicals formed in the reactions of primary radical cations in polystyrene microphases (reaction (7)) increases This leads to positive non-additivity in the total yields of paramagnetic species Such a behaviour can be described as *mutual sensitization*

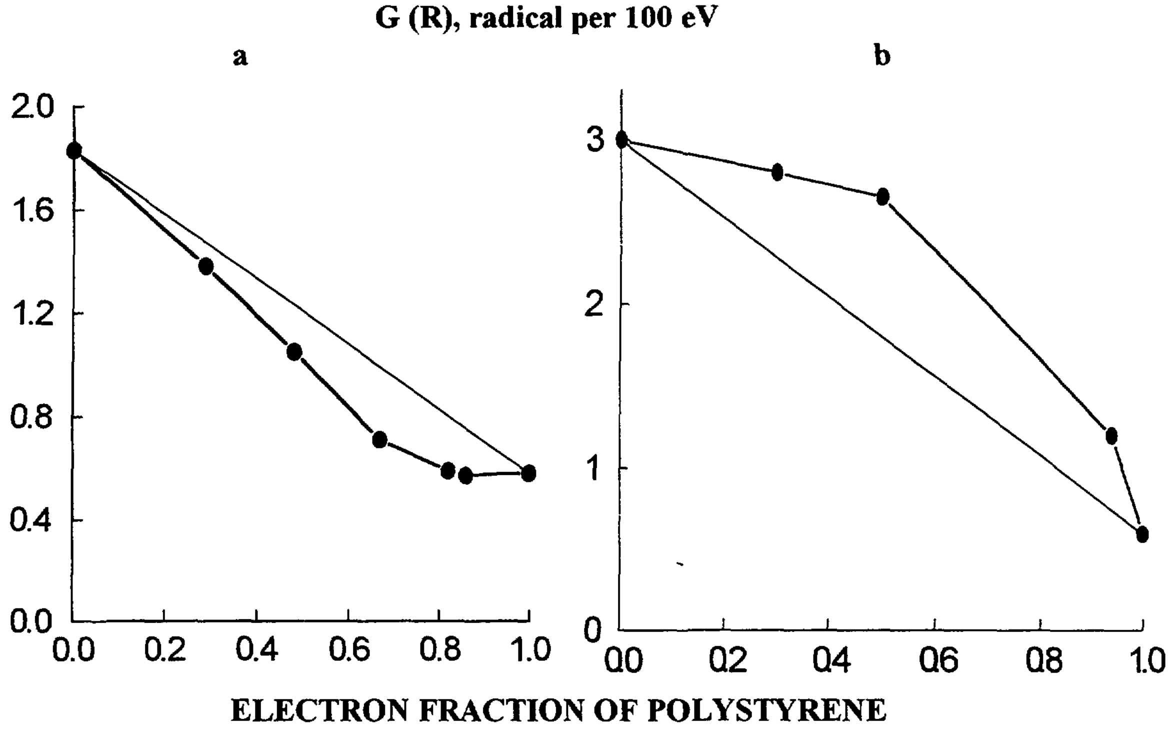

FIG 6 Non-additive effects in the yields of paramagnetic species in (a) styrene-butadiene block copolymers and (b) interpolymers of polystyrene and polytrichlorobutadiene irradiated at 77 K

Thus, the studies of the radiolysis of microheterogeneous polystyrene-based systems reveal both positive and negative non-additive effects due to interphase electron migration The sign of the effect is determined by electronic characteristics of the second component, which may result in either protective or sensitizing effects

5.3. Microheterogeneous Systems PC/Poly(Alkylene Terephthalate)

The materials based on PC/poly(alkylene terephthalate) blends are widely used in modern industry. The effects of irradiation on these systems were not examined up to recently. From a scientific point of view, an interesting feature of these compositions is a variability of their microstructure and chemical composition depending on the processing conditions. In particular, increasing the blending time or processing temperature results in two principal effects. On the one hand, partial homogenization of the blends occurs due to component interdiffusion. On the other hand, chemical reaction of transesterification leads to formation of block copolymers and, finally, statistic copolymers with essential destruction of the macromolecules. As a result, the properties of the materials change significantly. Varying the processing conditions (sample pretreatment) makes it possible to study the effects of chemical structure and degree of heterogeneity on the radiation-induced processes.

We have studied systematically the yields of the radiolysis products and localization of primary damage for the systems PC/PBTP irradiated at 77 K by means of low-temperature ESR and IR spectroscopy [15, 16, 30]. The blends used were prepared by processing PC/PBTP mixtures (50/50 by wt.) at 533 K for 5 min (sample 1), 1 h (sample 2) and 6 h (sample 3). The structure of the samples was characterized by DSC and IR spectroscopy. Sample 1 is a heterogeneous system with a comparatively low degree of component interdiffusion. Sample 2 can be described as a microheterogeneous system containing a rather large amount of block copolymer. Sample 3 is a completely soluble statistical copolymer with significant destruction.

The characteristics of the low-temperature radiation-induced damage of the components were described previously (sections 4.4 and 4.5 of this report). These results allowed us to make a quantitative analysis of the non-additive effects in the blends. Since PBTP is much more resistant to low-temperature radiation-induced destruction, formation of both CO and CO_2 is mainly due to main chain scission in the PC units. Addition of PBTP results in suppressing of the formation of these destruction products; the protective efficiency increases with increasing blending time as shown in the table. Formation of CO is more sensitive to the presence of PBTP; a similar trend is observed for CO-separated radical pairs. The results obtained were explained by excitation transfer from PC to PBTP units. Comparative analysis of these effects in various blends and model systems provides evidence for both intrachain and interchain transfer. The intrachain transfer is more efficient for suppressing the destruction process resulting in formation of CO and corresponding radical pairs.

Analysis of the spectroscopic parameters of radiolysis products shows significant changes in their localization with changing the system structure. In particular, the interspin distance in the CO-separated radical pairs (shown in the table) decreases with increasing blending time. The shape of the IR absorption band corresponding to CO_2 and the probability of localization of CO molecules in the vicinity of negative ions (see above) are also sensitive to the sample microstructure [30]. These features may be used for diagnostics of the localization of the primary radiation-induced damage.

RELATIVE CONCENTRATIONS AND MICROSCOPIC CHARACTERISTICS OF THE PRODUCTS OF THE RADIATION-INDUCED DESTRUCTION OF PC IN THE PC/PBTP BLENDS AT 77 K

Sample	[CO], rel.units[a]	[CO_2], rel. units[a]	[Radical pair], rel. units[b, c]	Interspin distance, nm
PC (amorph.)	1.0	1.0	1.0	0.573
Blend 1 (5min)	0.94	0.93	0.87	0.571
Blend 2 (1 h)	0.61	0.76	0.73	0.557
Blend 3 (6 h)	0.34	0.73	0.17	0.545

[a] Irradiation dose 1.0 MGy.
[b] Irradiation dose 150 kGy.
[c] Calculated from the integrated intensity of the signal corresponding to $\Delta M_S = 2$.

Generally speaking, the radiation stability of PC units in blends is higher than in pure polymer (this is also valid for the PC/PETP system). The most efficient way of stabilization of the primary radiation-induced destruction in PC is concerned with the introduction of quenching fragments (e.g., phthalates) into the polymeric chain. Although we cannot determine the distance of energy transfer for blend systems at this stage, crude estimation shows that this should be of the order of 1-5 nm (i. e., several elementary units). Some evidence for distant electron migration in the systems studied was also obtained [30].

6. THE EFFECT OF LOCAL MOLECULAR DYNAMICS ON THE SELECTIVITY OF RADIATION-INDUCED EVENTS IN SOLID POLYMERS

The localization of radiation-induced events can be changed essentially as a result of the reactions of primary species, which are determined by inhomogeneous molecular motion in solid polymers. Informally, this is an analogy with development of a photographic image. The "image" may remain sharp (the distribution of primary events reproduces the picture of primary localization) or become vague or even completely disappear (homogenization occurs). In general, this constitutes the ***dynamic aspect*** of the selectivity of the radiation-induced effects in polymers.

This problem was considered in detail in our recent review [3]. Here we shall present an outline. It is clear that large scale reactions will occur in amorphous polymers above the glass transition temperature because of large-scale molecular motion, which should induce homogenization of the radiation-induced events. Thus, the most interesting (and significant for many applications) situation is concerned with restricted molecular motion. Generally speaking, this is the case of *low matrix temperature* (if the temperature is considered as a measure of molecular motion). This situation was analysed in our studies.

First, we may consider the case of *low physical temperature* (10-100 K, well below T_g for all polymers). The molecular mobility is extremely frozen under these conditions. Nevertheless, we have shown [7-9] that some specific local reactions in polymers irradiated at 10-20 K occur due to *inhomogeneous spatial distribution of primary radiolysis products* (e.g., radical pair recombination) The reactions may proceed via a tunnel mechanism and are highly selective from a geometrical viewpoint The most interesting example is selective intrachain radical pair recombination via one-dimensional H-transfer (probably tunneling) occurring in highly-crystalline polyethylene at ca 65 K [8] This reaction was monitored by both radical decay (ESR) and formation of reaction products *trans*-vinylene double bonds (IR spectroscopy) To our knowledge, this is the first direct observation of one-dimensional selective radical site migration of this type Note that the character of reaction products (i e , formation of double bonds or crosslinks) may depend on the irradiation temperature because of the features of the local molecular dynamics Indeed, only crosslinking occurs in polyethylene irradiated at 77 K or higher temperatures as a result of random three-dimensional radical site migration [1]

The second case may be defined as the case of *low structural temperatures* This implies that the chain mobility is extremely restricted because of specific structural features of the polymer In particular, this is the case for highly-crystalline and highly-oriented polymers The mobility of taut macromolecules may be restricted even at rather high temperatures The reactions occur selectively in defect regions, and the radicals localized at the taut macromolecules may be very stable Probably, the most illustrative example is unusual temperature dependence of the radical decay in high-oriented high-modulus polyethylene (draw ratio = 200, E = 150 GPa) studied in our laboratory [12] Some radical decay associated tentatively with defect regions occurs at low temperatures, however, virtually no decay is observed in the temperature range of 200-300 K, i e , in the region of the glass transition This implies that cooperative molecular motions responsible for the glass transition are completely frozen in the sample under study (in contrast with other polyethylene samples) Furthermore, a rather large fraction of the radicals survives even after annealing this sample at high temperatures (373 K) This result should be taken into account regarding the long-term post-irradiation stability of high-strength materials based on high-modulus polyethylene

In addition, a specific situation may be realized for bicomponent microheterogeneous systems provided that the components exhibit large difference in relaxation behaviour (*different structural temperatures)* Upon annealing, the active species may survive in the microphase of a specific component, even more resistant to radiation from the point of view of primary events In particular, this is the case for polystyrene in interpolymers of PS and PTCB Thus, the post irradiation stability is determined essentially by the properties of these species, which can be modified to a certain extent by the effects of interphase boundary

7 CONCLUSIONS

Our studies reveal that the radiation-induced events in solid polymers, in general, are far more selective than one might expect from formal energetic reasons Using low-temperature experiments of specific design, we have obtained direct experimental evidences for the effects of macromolecule conformation and weak association on the selectivity of primary bond rupture upon radiolysis In the case of hydrocarbons and related polymers, it was shown that the selectivity of primary chemical events was determined by relative bond strength in *ionized molecules rather than in parent neutral molecules.* Thus, it is a strong appeal to both theoreticians and experimentalists to learn more about the effect of ionization on chemical bonding This may be the key issue of predicting the selectivity of primary bond rupture in the radiolysis of a wide class of polymers. It seems to be basically important for designing new principal approaches to the problem of the radiation stability of polymers.

From a more practical point of view, the results show that the positive hole scavengers (rather than excitation energy scavengers) should be considered as promising stabilizers for most hydrocarbon polymers. On the other hand, even trace amounts of electron scavengers may essentially reduce the radiation stability of such polymers (especially, for polystyrene).

The primary radiation-induced damage in polycarbonates (and probably in some other related polymers) is determined mainly by the properties of excited states. The degradation of PC depends essentially on the evolution of primary radical pairs, which is sensitive to the polymer microstructure. The best means of stabilizing such polymers may be with addition of carbonyl quenching fragments (e. g., phthalates) in the polymer chain.

The studies of microheterogeneous polymer systems show that interphase electron migration (and probably other transfer processes, such as excitation transfer between carbonyl groups) may result in essential non-additive effects (both positive and negative). This should be taken into consideration from the viewpoint of radiation stability and stabilization of such systems, which will be applied extensively in various fields in the near future. More work should be done to evaluate the role of the interphase boundary, which may be essential for determining the properties of irradiated material.

Local molecular dynamics plays an important part in the distribution of radiolysis products in irradiated polymers. This is especially important for low and super-low temperatures and for highly organized polymers with low defect concentration.

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RADIATION STABILIZATION EFFECTS IN AN ETHYLENE–PROPYLENE COPOLYMER AND IN EPOXY RESIN PARTICULATE COMPOSITES

S. BACCARO, B. BIANCHILLI, C. CASADIO[1]
Division Servizi Tecnologici,
ENEA,
Rome

G. RINALDI
Dipartimento Ingegneria Chimica dei Materiali, Materie Prime e Metallurgia,
Universita' La Sapienza,
Rome

Italy

Abstract

The aim of this work was to investigate the post-g-irradiation behavior of an ethylene-propylene copolymer loaded with an antioxidant containing the -NH functional group. The oxidative degradation of the polymer was studied using Infrared Absorption Spectroscopy. The shape of the oxidation profiles, and the dependence on thickness and on dose rate were in good agreement with the Gillen and Clough model. The interaction of polymeric free radicals with the antioxidant led to the formation of R-NO° stable radicals. These species are easily detectable using Electron Spin Resonance Spectroscopy. We used this technique to study the influence of the total absorbed dose, of dose rate and of oxygen and the time evolution of the oxidation products. High Performance Liquid Chromatography allowed us to determine the amount of antioxidant not involved in the oxidation reaction as a function of the total absorbed dose. The stabilization toward gamma radiation effects, of different types of curing agents for epoxide resins, and of fly ash as filler, were also investigated through monitoring the mechanical properties of such composite materials.

1. INTRODUCTION

The fundamental process of polymer degradation and stabilization has been extensively studied [1-3]. The most important effect on the irradiated polymers is the oxidative degradation initiated by the formation of peroxy radicals in the polymer, which led to the formation of carboxylic groups of different chemical nature, that are commonly evaluated using Infrared Absorption Spectroscopy (IR) [2-8]. Inhomogeneous oxidation effects in polymers exposed to ionizing radiation have been often found and extensively studied by different experimental methods [9-11]. The most used technique to obtain the oxidation profile is the measurement of the carboxylic content by IR absorption spectroscopy [8, 12, 13]. We used this technique to obtain the oxidation profile as the spatial distribution of carboxylic groups across the rubber plates [8]. The observed inhomogeneity is attributed to diffusion-limited oxidation, and in order to take into account such effects several theoretical models have been derived for pure polymers. Less attention has been devoted to crosslinked polymers loaded with antioxidant, in spite of their relevance for a wide variety of applications [3]. A preliminary study [7] performed on an ethylene

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[1] Current address: Chemistry Division, Argonne National Laboratory, Argonne, Illinois, United States of America

propylene co-polymer (EPR) loaded with antioxidant suggested that the observed inhomogeneity effects can be explained [16] with the Gillen and Clough model, even if this model does not take explicitly into account the presence of antioxidant. A more systematic study of the inhomogeneous oxidation of EPR rubber has been performed, and this hypothesis was confirmed. Oxidation profiles have been measured as a function of thickness, dose rate and antioxidant content.

Electron Spin Resonance (ESR) spectroscopy is of great importance in radiation damage studies in spite of its ability in the detection of radical species involved in the degradation process. The effects of gamma rays on an ethylene propylene loaded with antioxidant containing -NH functional groups have been previously investigated using ESR [17-19]. It was possible to ascertain that upon interaction with the antioxidant, the free radicals produced under irradiation of the polymer lead to the formation of R-NO° stable radicals. The R-NO° production starts during irradiation, and lasts for about 100 hours. A stable level was reached afterwards which depends on dose, antioxidant content and temperature [18-21]. The post-irradiation time evolution of the different radical species, and the influence of various parameters such as temperature and dose rate have been studied [22]. Once the ESR signal had reached a stable value after the irradiation and the storage in air at room temperature, an extraction procedure was applied and it was possible to determine the antioxidant extractable levels as a function of the total absorbed dose using HPLC, that for its high specificity and sensitivity is one of the most frequently employed analytical method for stabilizers in polymers [23].

In order to confirm the importance of the presence of stabilizing chemical functions in polymers, we also studied the effects of gamma radiation in an epoxy resin cured by means of two different curing agents, and the effect of fly ash as filler. We were able to evaluate the eventual changes of the mechanical properties of these composite materials, whose application in the confinement of low and medium waste radioactive material has recently been proposed [24, 25, 26].

2 EXPERIMENTAL METHODS

The material studied is an ethylene-propylene copolymer (30% propylene) and was supplied by Montedison. All the samples were manufactured by Pirelli Cavi S.p.A. Company adding an antioxidant with the -NH functional group, and crosslinked with dicumilperoxide in the final form of thin plates (10x10 cm^2).

The epoxy resin used was DGEBA type EPON 828 from Shell; the curing agents were tetraethylenepentamine (TEPA), Fluka Techn. Product and a polyaminophenolic oligomer (PAP) obtained from TEPA by reaction with phenol in the presence of formaldehyde [27]. Fly ash [28] was used as filler.

The irradiation of the samples has been performed in air at room temperature in the ^{60}Co irradiation plant Calliope at ENEA Casaccia Center (Rome). Fricke dosimetry was used to measure the absorbed dose.

2.1. EPR samples for infrared measurements

Samples have been irradiated in the dose range of 100-400 kGy at dose rates in the range of 0.21-1.31 Gy/s. In order to determine the oxidation profile we cut from the center of the plates a slice 0 25 mm thick orthogonal to the surface IR spectra of the slices were recorded using an FTIR 1720 Perkin Elmer equipped with a Spectra Tech mod Plan 11 microscope, the field of view was 300 x 300 mm

2.2. EPR samples for ESR measurements

The samples used to investigate the free radicals were irradiated in air at a dose rate of 1 6 Gy/s in the dose range of 10-375 kGy, and at 100 and 600 kGy with dose rates ranging from 0 009 up to 374 Gys^{-1} [22] Measurements were performed with a Bruker EMS104 EPR Analyzer

2.3. EPR samples for HPLC measurements

The samples used to measure the antioxidant extractable levels were irradiated in air at room temperature at a dose rate of 1 6 Gy/s in the dose range of 10-375 kGy The HPLC apparatus was a Bruker model LC 22, the column was a reversed phase analytical column All the solvents were RS Plus by Carlo Erba The extraction procedures and the set up apparatus have been described in a previous work [29]

2.4. Epoxy resin samples

The form and dimension of the samples were as prescribed by ASTM standards The infrared absorption spectra of samples (solid dispersion in KBr) were measured with a Perkin Elmer spectrometer mod.1213 The calorimetric curves of powdered specimens were obtained by using a DuPont (v4 1c-2100) Differential Scanning Calorimeter The IR absorption spectra of samples (solid dispertion in KBr) were recorded using a spectometer Perkin Elmer mod 1213 The samples were irradiated in the dose range 10 kGy-1 8 MGy at a dose rate of 350 Gy/s

3 RESULTS AND DISCUSSION

3.1. Infrared results and discussion

The infrared spectra have been analyzed using the procedure discussed in a previous work [7] in order to obtain the "differential spectra", i e the spectral changes due to the radiation The integrated absorption of the C=O band centered about 1720 cm^{-1} has been assumed to give a quantitative evaluation of the radiation induced oxidation The oxidation as a function of depth is obtained by integration of the spectra in the 1850-1650 cm^{-1} region A typical example of the results obtained is presented in Fig 1

The inhomogeneity of the oxidation is evident We have found that the oxidation depth is reduced and the profile becomes steeper with increasing dose rate For all the samples, the total oxidation increases linearly with absorbed dose in the dose range up to 400 kGy The dose rate dependence is evident and can be attributed to inhomogeneous oxidation effects The oxidation decreases linearly with the antioxidant content, and its effect seems to be independent from the dose rate, thus suggesting that the antioxidant content does not change the inhomogeneity of the oxidation The rate of oxidation under homogeneous conditions is related to the dose rate by the following equation [16]

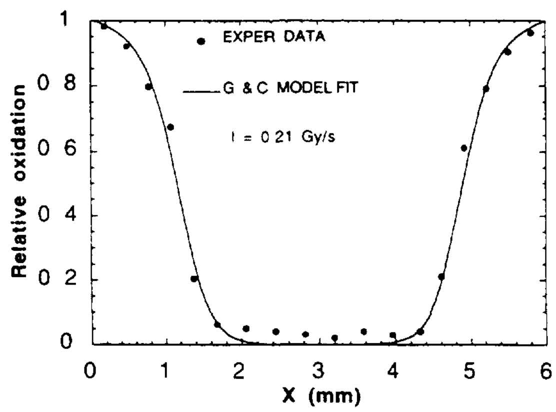

FIG 1 Oxidation profile for the sample irradiated at 150 kGy at the dose rate of 0 21 Gy/s

The inhomogeneity of the oxidation is evident We have found that the oxidation depth is reduced and the profile becomes steeper with increasing dose rate For all the samples, the total oxidation increases linearly with absorbed dose in the dose range up to 400 kGy The dose rate dependence is evident and can be attributed to inhomogeneous oxidation effects The oxidation decreases linearly with the antioxidant content, and its effect seems to be independent from the dose rate, thus suggesting that the antioxidant content does not change the inhomogeneity of the oxidation The rate of oxidation under homogeneous conditions is related to the dose rate by the following equation [16]

$$R \; \mu \; I^{g}$$

The total oxidation after the irradiation time t = D/I (where D is the absorbed dose) is given by

$$A \; \mu \; DI^{(g-1)}$$

At the dose rates used, our samples do not exhibit homogeneous oxidation, but we can assume surface oxidation as representative of the homogeneous oxidation process The pure unimolecular (g = 1) or bimolecular (g = 0 5) processes do not properly fit the experimental results, which are well-described assuming g = 0 7 in the equation This value agrees with the results found in the literature for similar materials [4] and indicates that the oxidation is due either to the superposition of unimolecular and bimolecular processes or to bimolecular processes involving products partially originating from a single spur In order to model the oxidation profile we have used the Gillen and Clough expression The obtained results confirm that the antioxidant content does not change the oxidation profile but only its absolute value [22]

3.2. ESR results and discussion

The ESR spectrum of samples recorded after irradiation in air (Fig. 2) can be interpreted as the superposition of two signals [19,20] The first is due to antioxidant R-NO° radical (g = 2 007) and the second to polymer free radicals P° (g = 2.003)

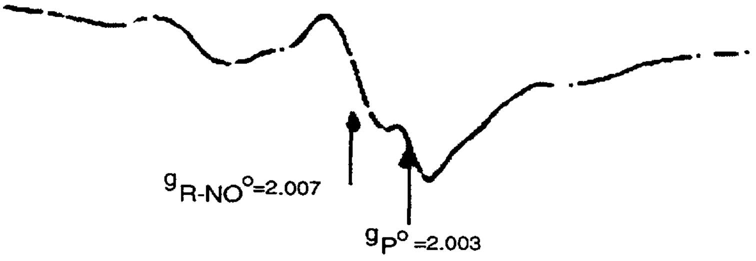

Fig. 2 - ESR spectrum of a sample measured soon after the irradiation in air at 100 kGy (dose rate 0 3 Gy/s).

During post-irradiation storage in air two different processes take place. i) the partial disappearance of the polymer radicals, and ii) the start of a bimolecular process leading to the formation of the R-NO° radical. For each dose rate, the sample reaches a stable condition about 150 hours after irradiation, and the ESR spectrum is dominated by the R-NO° component The R-NO° concentration, measured in the stable phase, decreases with dose rate [22]

To describe the radical behavior, a semiquantitative model has been proposed [22] ESR measurements obtained for a sample irradiated at a dose rate of 1.6 Gy/s in the dose range of 10-375 kGy confirm these results [31]. The relative R-NO° radical concentration after 1000 hours storage time, as a function of dose, is reported in Fig.3 for the sample irradiated at 0.3 Gy/s, and in Fig 4 for the sample irradiated at 1.6 Gy/s. The results suggest that the process involved in the R-NO° production is non linear with the dose.

Indeed at each dose value the ESR signal amplitude has been measured, and it increased linearly with the antioxidant content. Fig. 5 and Fig. 6 report an example of the time evolution of R-NO° radicals and of polymer P° radicals for the sample irradiated to 245 kGy at dose rate of 1 6 Gy/s The obtained results confirm previous evidence that in the presence of oxygen i) the recombination and production processes of the involved radicals are concomitant and ii) the R-NO° vs dose production is nonlinear with the involved radical concentrations It is well known that when antioxidant (A) is present in the material, the polymeric radicals react with each other and with the antioxidant producing radicals in the antioxidant itself and termination products [17, 33] Referring only to long-lived free radicals, the simplified reaction can be used to describe the process On the hypothesis that correlated nonlinear chemical reactions take place after gamma irradiation, it is possible to describe the processes of the three involved species with the following rate-equations

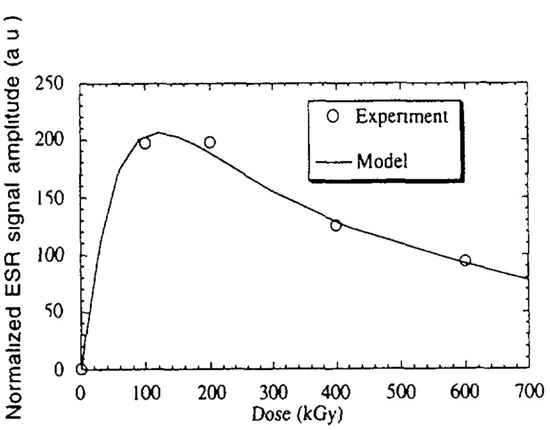

FIG 3 Normalized ESR signal amplitude for R-NO$^{\circ}$ vs dose (dose rate 0 3 Gy/s)

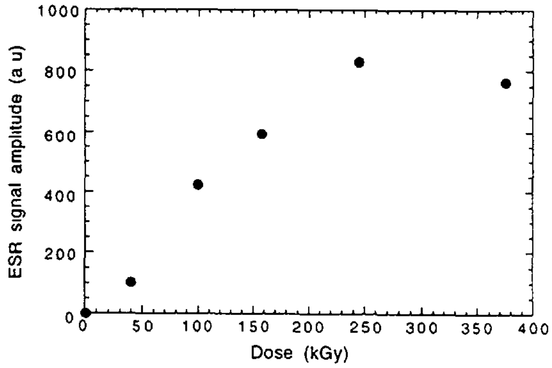

Fig 4- Normalized ESR signal amplitude for R-NO$^{\circ}$ vs dose (dose rate 1 6 Gy/s)

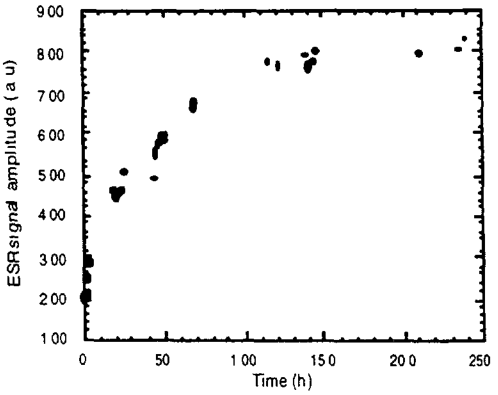

FIG 5 ESR signal amplitude for R-NO$^{\circ}$ radical irradiated at 245 kGy (dose rate 1 6 Gy/s)

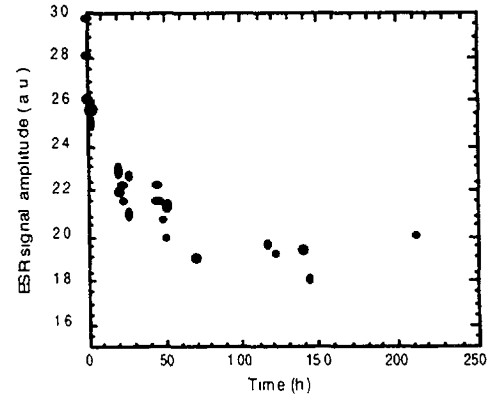

FIG 6 ESR signal amplitude for P$^{\circ}$radical irradiated at 245 kGy (dose rate 1 6 Gy/s)

The obtained results confirm previous evidence that in the presence of oxygen i) the recombination and production processes of the involved radicals are concomitant and ii) the R-NO$^{\circ}$ vs dose production is nonlinear with the involved radical concentrations It is well known that when antioxidant (A) is present in the material, the polymeric radicals react with each other and with the antioxidant producing radicals in the antioxidant itself and termination products [17, 33]. Referring only to long-lived free radicals, the simplified reaction can be used to describe the process. On the hypothesis that correlated nonlinear chemical reactions take place after gamma irradiation, it is possible to describe the processes of the three involved species with the following rate-equations:

$$\frac{dN_C}{dt} = -k_1 N_C N_B^{\alpha} - k_2 N_C$$

$$\frac{dN_B}{dt} = -k_1 N_C N_B^{\alpha}$$

$$\frac{dN_A}{dt} = -k_2 N_C$$

N_A, N_B and N_C are the concentrations of A, B and C species and a is different from 1 to take into account the nonlinear processes involved. In the studied material the antioxidant contains the -NH functional group, thus the NA radical concentration of the scheme can be related to the R-NO° radical concentration. Moreover, the ESR spectrum reported in Fig.2 suggests that the two components can be assigned to the N_B and N_C radical concentrations of the scheme. It is possible to give a theoretical prevision of the behavior of R-NO° ESR signal amplitude as a function of dose and the time evolution of the R-NO° and P° radicals by solving the equations with the initial condition; NC(0) and NB(0) proportional to the absorbed dose. The best agreement between experimental and theoretical data was obtained for a = 2. It is possible to hypothesize that B and C are species of type PO° and PO_2° that allow the following reactions [17]:

PO_2° + A => AO° + stable products

PO_2° + PO°=> stable products

In this hypothesis the number of radicals detectable on the polymer is always the sum of NB and NC. The proposed model well describes the R-NO° behavior with dose and the time evolution R-NO° and P° [22].

3.3. HPLC results and discussion

The set-up used allows a high selectivity since most by-products of reticulation and oxidation absorb at wavelengths between 250 and 280 nm. The use of m-nitophenol as internal standard was justified by the strong absorption of aromatic nitro compounds at the wavelength of our interest and by the sharp chromatographic peak obtained under our conditions. A typical chromatogram obtained is shown in Fig. 7. The measured quantity was the antioxidant versus internal standard peak area ratio; the data were obtained as the mean of six analyses belonging to a single extraction of each irradiated sample.

In Fig. 8 is reported the antioxidant extractable level as a function of the absorbed dose. The percentage value is referred to the total value (in weight) contained in the polymer. The experimental trend is in agreement with ESR results obtained for the same material, and is consistent with the reaction mechanism previously described.

The antioxidant extraction from the samples irradiated at the highest dose rate for HPLC analysis has been carried out when the ESR signal had reached the stable value. The analytical results show clearly that the extractable levels decrease as the dose increases. The observed behavior confirms that the antioxidant is consumed in consequence of oxidation reactions due to irradiation in air, according to the previously proposed reaction scheme. The low percentages are probably due to the fact that products derived from the degradation of the antioxidant occurring during initial processing and fabrication (zero dose value) and during post irradiation storage in air were becoming covalently bound to the polymer as a result of radical coupling processes.

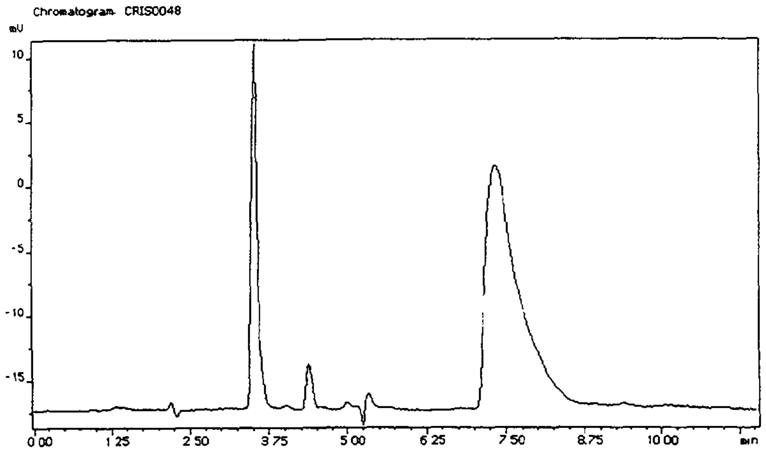

FIG. 7. *A typical chromatogram of an extract of the copolymer stabilized with 1 % of antioxidant. The two major peaks are due respectively to the internal standard (rt 3.55 min) and to the antioxidant (rt 7.7 min).*

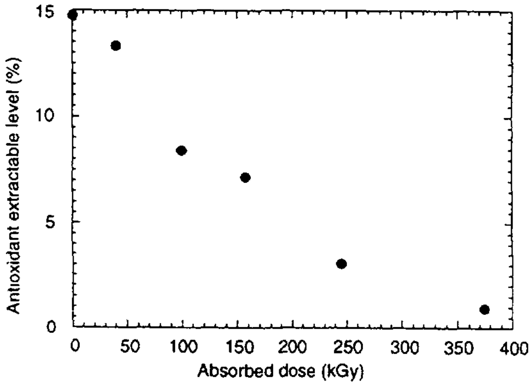

FIG. 8. Antioxidant exctractable level as a function of the total absorbed dose (dose rate 1.6 Gy/s).

3.4. Radiation effects on particulate composites

The high mechanical strength, the chemical, water and thermal resistance [27], the exceptionally high adhesion to every substrate and the good radiation resistance [28] of some epoxy-resins suggest their use in the confinement of low and medium activity radioactive wastes. Our interest in the study of radiation stabilization of polymers prompted us to evaluate this possibility of application by following the degradation of some mechanical properties, the changes in the IR spectra of different irradiated samples and the thermal resistance of such compounds after exposure to gamma radiation. The epoxy resin studied in this paper was dyglicidyl-ether of bisphenol A-type resin, cured at room temperature by means of a synthetic polyaminic product (P.A.P) containing some phenylic units linked to the nitrogen atoms of the main chain.

The aim of the research was to investigate the improvement of radiation resistance due to the PAP-curing agent and to the presence of fly ash from coal as filler (to obtain a particulate composite epoxy-fly ash). During exposure to gamma rays, typical damages that can take place in *thermosetting resins are the crosslink and cleavage reactions. Epoxy resins are generally resistant* up to a dose of 9.5×10^2 MGy without degradation [34], because of their aromatic units: benzene rings on the main chain and the use of aromatic curing agents can greatly enhance the radiation resistance of the cured resin through the protective effect of the aromatic arrangement of the p-electrons [27]. A series of tests were carried out on samples from the three experimental formulations: matrix cured with TEPA for reference, matrix cured with PAP, and composite of fly ash with epoxy-resin cured with PAP. The results of the mechanical tests are reported in Table I, while Fig. 9 refers to the results for the more interesting PAP-cured matrix alone.

From the obtained results, it can be stated that PAP-cured epoxy resin is a matrix that can safely withstand gamma irradiation, in comparison with the commercial polyaminic cured matrices, owing to the protective action of the phenolic group linked to the main chain of the "tailored" PAP curing agent. The decomposition in air of the non-irradiated TEPA-cured matrix starts at 145°C, while the irradiated one (1.8 MGy) decomposes at about 100°C; the PAP-cured matrix decomposes at 135°C after exposure at 1.8 MGy; that is quite similar to the decomposition temperature of the unirradiated TEPA-cured matrix. The infrared absorption spectra for the PAP-cured matrix remains unchanged, while the TEPA-cured product shows the increase of the effects at 725, 800, 1500, 1655, 1885 and 3040 cm^{-1}, interpreted as an increase of the non-aromatic unsaturations.

The raising of the content of unsatured groups can explain the lower thermal resistance of the matrix cured with the conventional aminic curing agent; on the contrary, PAP product protects the matrix that withstands unchanged. Similar considerations can explain the results obtained for the mechanical tests. Irradiation gradually enhances the static tensile and flexural strength of the formulations, the maximum being attained by the TEPA-cured matrix; the fly complex trend: PAP-matrix practically remains unchanged, while TEPA-matrix attains a maximum with "medium" dose, then gradually decreases. This trend can be explained as a result of an initial crosslinking action followed by a slow degradation. PAP-cured matrix shows higher stability both in static and dynamic strength. Shore D hardness increases for the TEPA-cured product (crosslinking effect), then decreases; PAP-cured matrix and composite above all remain practically unchanged.

In Fig. 10 the differential scanning calorimetric curves before and after irradiation for the matrix cured with PAP (a) and with TEPA (b) are reported.

Fig. 11 shows the changes occurring after irradiation in the infrared absorption region 1440 - 1550 cm^{-1} for the matrix cured with TEPA No changes in the infrared spectra have been observed for the matrix cured with PAP in this region

From the obtained results, it can be stated that PAP-cured epoxy resin is a matrix that ash composite and its matrix attain a minor static strength Impact strength shows a more complex trend PAP-matrix practically remains unchanged, while TEPA-matrix attains a maximum with "medium" dose, then gradually decreases This trend can be explained as a result of an initial crosslinking action followed by a slow degradation PAP-cured matrix shows higher stability both in static and dynamic strength Shore D hardness increases for the TEPA-cured product (crosslinking effect), then decreases; PAP-cured matrix and composite above all remain practically unchanged.

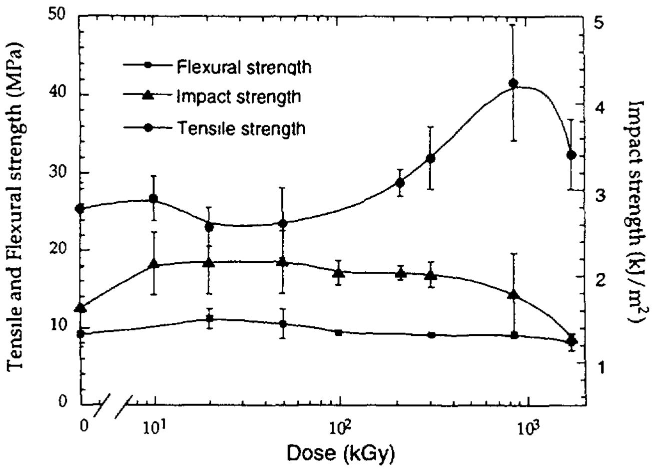

FIG. 9 - *Mechanical strength of PAP-cured matrices during irradiation tests.*

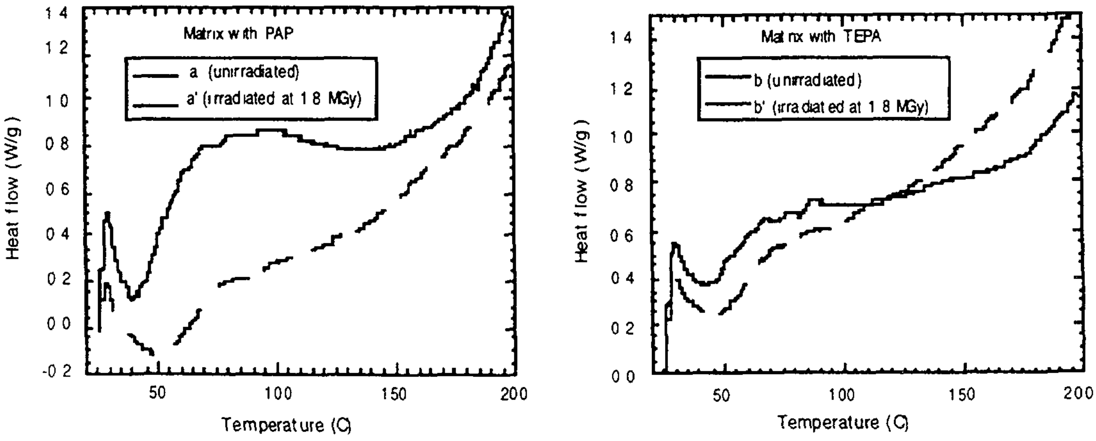

FIG 10 DSC curves of the matrices before and after irradiation (1800 kGy) PAP (a, a') and TEPA (b, b') curing agents

TABLE I. MECHANICAL STRENGTH OF THE IRRADIATED FORMULATIONS (DOSE RATE 350 Gy/s).

	Impact Strength [kJ/m^2]			Tensile Strength [Mpa]			Flexural Strength [MPa]		
Dose [kGy]	TEPA	PAP	Fly Ash-PAP	TEPA	PAP	Fly Ash-PAP	TEPA	PAP	Fly Ash-PAP
0	3.19±0.44	1.64±0.46	3.80±0.29	36.65±2.6	25.38±3.4	37.14±4.5	9.11±0.3	9.19±0.4	5.39±0.6
10	-	2.15±0.37	-	-	26.74±2.8	-	-	-	-
20	2.82±0.41	2.16±0.37	3.02±0.39	44.50±4.8	23.10±2.5	37.34±4.8	12.15±0.9	11.19±1.3	6.47±0.6
50	2.68±0.50	2.17±0.37	2.96±0.26	36.06±3.3	23.58±4.5	38.61±3.5	12.25±0.6	10.56±1.9	5.68±0.5
100	-	2.04±0.14	-	-	-	28.81±5.6	-	9.41±0.3	-
212	-	2.04±0.08	-	-	28.80±1.7	-	-	-	-
340	3.26±0.40	2.02±0.15	3.90±0.14	32.24±6.0	31.99±4.0	31.46±4.2	12.05±0.6	9.11±0.1	5.78±0.7
850	-	1.80±0.47	-	-	41.62±7.4	-	-	9.11±0.4	-
1800	2.51±0.36	1.28±0.06	2.95±0.35	53.21±3.7	32.40±4.5	37.53±5.8	11.37±0.8	8.10±1	5.59±0.1

In conclusion epoxy matrices and their particulate composites are globally more resistant to gamma radiation by means of a "tailored" curing agent containing aromatic units. The Polyalkylenepolyaminophenolic product, formerly synthesized to obtain an epoxy matrix more resistant to the leaching action of water, is also advantageous from the gamma ray resistance point of view. It can be finally noted that during irradiation the particulate composite always shows the best mechanical properties (hardness, impact and tensile strength) except for flexural strength.

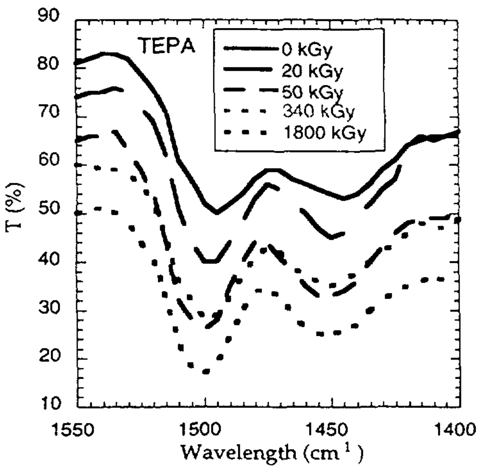

FIG.11. IR spectra after irradiation (0 - 1800 kGy) of the matrice cured with TEPA

ACKNOWLEDGEMENTS

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IMPROVEMENT OF POLYMER STABILITY BY RADIATION GRAFTING

F. RANOGAJEC
Ruder Boskoviç Institute

M. MLINAC-MISAK
Organic Chemical Industry

Zagreb, Croatia

Abstract

Losses of the stabilizer due to extractability or volatility immediately affect ultimate performance of polymer product. A new approach to increase the persistence of the stabilizer in the final product is to chemically bind it to the polymer backbone. Radiation grafting or crosslinking could be an efficient method for this, when the stabilizer is polymerizable. By a mutual gamma irradiation method, photoprotector 2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone (HMB) has been readily grafted to low density polyethylene (LDPE) in benzene, tetrahydrofuran and methanol solution, respectively. Surface grafting occurs in a methanol solution of stabilizer, while in benzene and tetrahydrofuran solutions of stabilizer, grafting proceeds more or less in the inner parts of the polymeric film as well. The grafted LDPE film in methanol and tetrahydrofuran (containing 1 w/w % of grafted HMB), 1 w/w % blended HMB with LDPE and nongrafted LDPE film, were all exposed to accelerated aging and natural weathering and their spectral changes, expressed by the carbonyl index, were then compared. The change of elongation at break and tensile strength were measured in the course of aging. UV stability tests on aged films and change in mechanical properties indicate a pronounced protective effect achieved by grafted stabilizer. Grafting in methanol solution appears to be an efficient photostabilization treatment and the most economical with respect to the consumption of monomer, the grafting yield being less than 0.5%. Surface grafting is an efficient photostabilization method since grafted stabilizer is chemically bound to a polymeric surface and in this way the problem of evaporation of blended stabilizers during the prolonged use of polymeric materials is eliminated.

1. INTRODUCTION

The improvement of polymer stability continues to be an area of active industrial concern and intensive research effort [1-5]. Most organic polymers require protection against the effects of heat, oxygen, light, high energy radiation and so on. Demands for more efficient stabilizers and antioxidants increase. Stabilizer performance is affected essentially by three factors. The first is its ability to function as an energy deactivator and/or radical scavenger. The second is compatibility or solubility of the stabilizer in the polymer matrix. The third factor is the volatility or fugative nature of the stabilizer. Widely used low molecular weight organic stabilizer molecules which are simply incorporated into the polymer matrix can be lost during use time by migration to the polymer surface, followed by evaporation. Therefore the third factor is probably the most important. Evaporative loss may be particularly problematic for uses involving high temperatures or vacuum environment (as in space vehicle applications). By covalently binding stabilizer to the polymer backbone this problem can be eliminated. Radiation grafting or crosslinking could be an efficient method to realize it when the stabilizer is polymerizable. That new approach is applied in this work. Grafting of 2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone onto polyethylene was performed and the photostability of grafted polyethylene was studied.

2 EXPERIMENTAL

Low density polyethylene films (LDPE) commercial blown, free of additives (d = 0 919 g/cm^3, melt flow index 2 g/10 mm) were supplied by INA-Organic Chemical Industry, Zagreb

High density polyethylene films (HDPE) (d = 0 95 g/cm^3, and 0 96 g/cm^3) were supplied by BASF

2-hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone (HMB) was chosen as UV protector for polyethylene

Monomer used was commercial grade as supplied by National Starch Chemical Co , USA Solvents benzene, tetrahydrofuran, methanol and hexane were analytical grade supplied by Merck-Shuchardt, Darmstadt

The monomer was dissolved in tetrahydrofuran, methanol and benzene respectively and used for grafting as 20 wt % solution

Polymer films were extracted in boiling tetrahydrofuran or benzene and dried at 50 °C to constant weight

Weighed polymer films were immersed in the monomer solution in reaction tubes and connected to a vacuum line Oxygen was removed by freezing the polymer-monomer solution mixture and evacuation to 10^{-5} mm Hg followed by thawing Freezing-thawing cycles were repeated three times before reaction tubes were sealed off under vacuum

Reaction tubes were then subjected to gamma radiation from a ^{60}Co source at a dose rate of 0 15 kGy h^{-1} and temperature of 50 °C The grafted polymer films were removed from the monomer solution after the irradiation, extracted with boiling tetrahydrofuran and dried to constant weight The weight increase of polymer films after the grafting reaction was taken as the grafting yield

Polyethylene grafted with HBM in tetrahydrofuran and methanol (grafting yield being 1% of HMB or less), nongrafted polyethylene containing 1% HBM (obtained by mixing polyethylene pellets with HBM in a Brabender Plasti-Corder at 150 °C and pressing), and polyethylene without HMB, were exposed to artificial accelerated aging by using a high pressure mercury lamp, Type Q 1200 W Hanau at room temperature

In the same time an identical set of polyethylene samples was exposed to natural weathering in free atmospheric conditions

In the course of aging the change of photostability was tested by IR spectroscopy using a Perkin Elmer spectrometer, type 599B

Changes in mechanical properties were followed by determination of elongation at break and tensile strength using an Instron Testing Machine

3 RESULTS AND DISCUSSION

The grafting (%) vs irradiation time curves are shown in Fig 1 for direct grafting of HMB onto low density polyethylene in benzene, tetrahydrofuran and methanol solution respectively Film thickness was 0.05 mm and reaction temperature was 50 °C

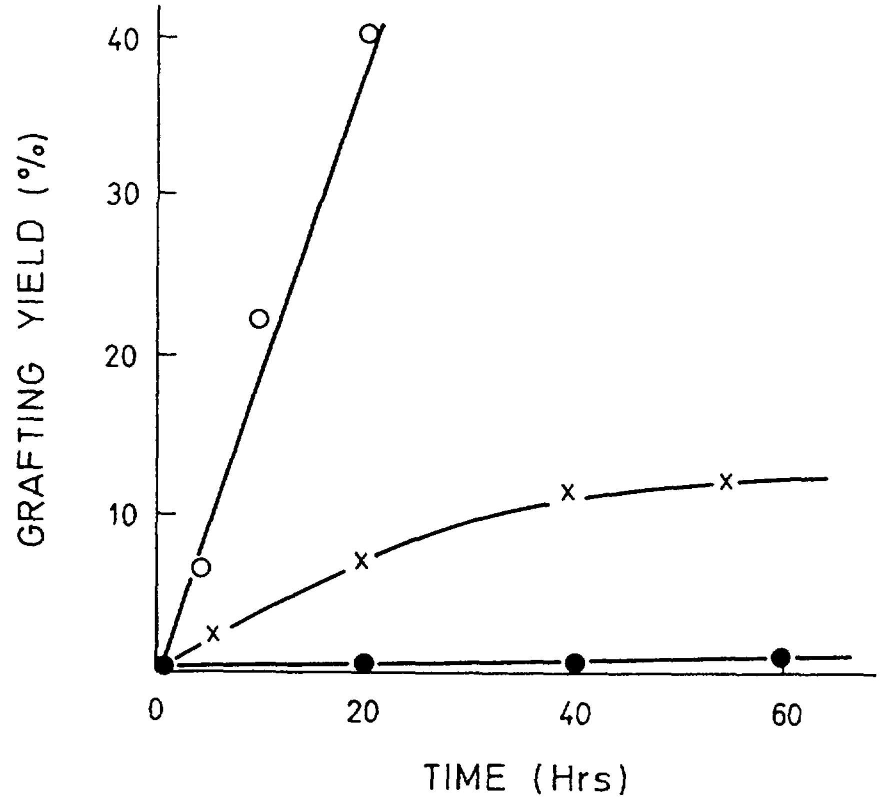

FIG 1. Changes in the grafting yield of poly-HMB in LDPE during gamma irradiation (0.15 kGy h^{-1}) at 50 °C in benzene O, tetrahydrofuran X and methanol O solution of HMB (20 % wt)

It is obvious that the nature of the solvent strongly influences the rate and yield of grafting and location of grafted HMB onto LDPE.

In the benzene solution the yield of grafting increases linearly with time up to high yields as was found in many grafting systems. The yield of grafting increases as the dose rate increases, and a linear dependence of the grafting rate on the square root of dose rate was obtained, which suggests bimolecular termination reaction of growing poly-HMB-chains and nondiffusion controlled propagation reaction in the grafting reaction on LDPE in that case

On the other hand when LDPE under the same experimental conditions was grafted with HMB in tetrahydrofuran solution, a limiting value of grafting yield was obtained after an initial increase of yield, the limiting value of grafting yield being about 10% A dose rate effect was observed only during the initial increase of grafting yield [6] The percent of grafting decreases if the foil thickness and polyethylene density increase

When LDPE films were immersed in methanol solution of HMB and gamma irradiated under the same conditions as in the case of benzene and tetrahydrofuran, very low weight increase of film was observed but grafted poly-HMB was readily detected by IR-spectroscopy

On basis of the obtained results it may be concluded that surface grafting of HMB onto LDPE occurs in methanol solution of monomer The grafting of HMB from tetrahydrofuran occurs primarily close to the surface layer of LDPE, whereas the grafting in benzene occurs more or less homogeneously throughout the film of LDPE

Direct evidence of surface grafting in tetrahydrofuran was obtained by ATR IR spectroscopic measurement [7] Tetrahydrofuran swells polyethylene similarly as benzene The main difference between the two solvents is that tetrahydrofuran dissolves poly-HMB and benzene does not, and it could be the reason for different grafting behavior The grafting reaction begins in polyethylene swollen with tetrahydrofuran containing dissolved HMB in a similar way as in benzene However, while poly-HMB is well dissolved in tetrahydrofuran it is barely dissolved in benzene During the grafting reaction in tetrahydrofuran the quantity of grafted poly-HMB within the film increases and when the reaction slows down its concentration is several times higher than that of the monomer A stronger interaction of grafted poly-HMB with tetrahydrofuran as compared to that with benzene means less free solvent for monomer within the film in tetrahydrofuran Thus the driving force for monomer diffusion into the film decreases as the concentration of grafted poly-HMB increases and reaction slows down

To test the improvement of photostability by grafting of stabilizer, grafted and nongrafted polyethylene samples were exposed to artificial accelerated aging using a high pressure mercury lamp at room temperature, and to natural weathering which means exposure to long-term direct action of sun light and all climatic factors Photooxidative changes were determined by IR spectroscopy

It is well-known that in photochemical oxidation of polymeric materials some oxidized groups are generated, and it is a common practice to determine the change of these groups during the oxidation of polymeric materials Carbonyl groups are an indication of chemical changes occurring in polyolefin during oxidative degradation The absorption band in the carbonyl region increase in the course of UV irradiation

Although the grafted monomer HMB has two different absorption values for carbonyl groups (1620, 1720 cm^{-1}), the photoinduced carbonyl groups in LDPE could nevertheless still be detected due to their much broader absorption band, a fact that can be seen after aging

Experimental results in Fig 2 show that during ultraviolet radiation of grafted LDPE films, the 2-hydroxy-benzophenone absorption band at 1620 cm^{-1} slowly disappears, while a new absorption band belonging to carbonyl group appears at 1720 cm^{-1}

The grafted LDPE film in methanol and tetrahydrofuran (containing 1 w/w % of grafted HMB), 1 w/w % blended HMB with LDPE and nongrafted LDPE film were all exposed to accelerated aging and their spectral changes expressed by the carbonyl index, which represents the ratio of absorbance at 1720 cm to that at 1890 cm^{-1}, were then compared These data are shown in

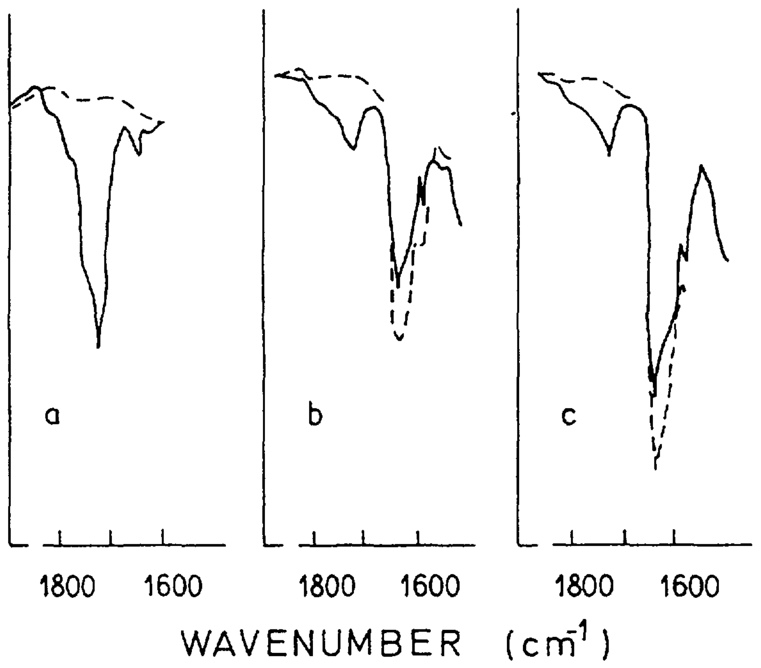

FIG. 2. IR absorption band of carbonyl groups in:
a - LDPE; b - LDPE + HMB mixture; c - LDPE + HMB grafted, before .... and after ________ UV irradiation.

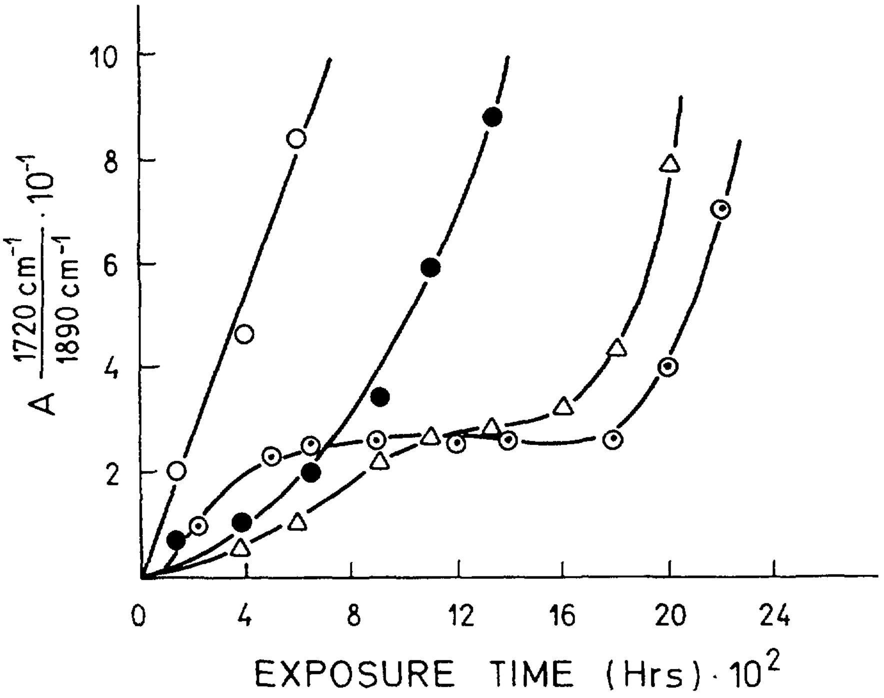

FIG. 3. Changes in the carbonyl index during UV irradiation at room temperature: O LDPE; O LDPE + 1% HMB added; O LDPE + 1% Poly-HMB grafted in tetrahydrofuran; Δ LDPE + less than 0.5 % Poly-HMB grafted in methanol.

Fig 3 In each curve the original values are subtracted to show the change in the quantity of oxidized groups

The growth of carbonyl in the unprotected film and in film containing added HMB is much higher than in grafted films, and indicates that a pronounced protective effect is achieved by monomer grafting From the photochemistry of polyolefins it is well-known that photooxidation begins at the polymer surface, and the excited chromophores are concentrated close to the film surface Therefore surface grafting should be the most efficient for photoprotection.

As expected the highest increase of carbonyl index was observed in the case of non protected LDPE Carbonyl index increased linearly with the time of accelerated aging and after about 600 hours polyethylene was almost completely destroyed In the case of LDPE with incorporated HMB, during the first 800 hours of aging the increase of carbonyl index was much slower than in LDPE without HMB, but a similar increase of carbonyl index was observed after 800 hours of aging Different behavior was observed in the case of accelerated aging of LDPE grafted with HMB in THF and methanol solution After an initial moderate increase, the carbonyl index remains approximately constant until about 1600 hours of aging and than again increases like in the case of nongrafted LDPE

In order to get evidence about the role of HMB as UV stabilizer in the course of photooxidation, the change in the 2-hydroxybenzophenone absorption band at 1620 cm^{-1} was followed by IR spectroscopy in the course of accelerated aging of LDPE The results are presented in Fig. 4. Two experimental facts should be noted First, in LDPE grafted with HMB, a slow, almost linear decrease of 2-hydroxy benzophenone absorption band at 1620 cm^{-1} does not indicate dramatic increase of carbonyl index after 2000 hours of aging as observed in Fig 3 Second, in LDPE mixed with HMB, the initial quantity of HMB being the same as in LDPE grafted with HMB in tetrahydrofuran 1 w/w %, the 2-hydroxy benzophenone absorption band at 1620 cm^{-1} is much lower and completely disappears after 1200 hours of aging

It is well known that polyolefins may degrade if they are irradiated with UV radiation for a long time In the course of photodegradation, physical properties of the polymers are changed In practice, it has been found that the elongation at break is one of the most sensitive properties Therefore we investigated the change of elongation at break in the course of accelerated aging of LDPE to describe photodegradation of nongrafted and grafted LDPE with HMB by the comparing it with the change of carbonyl index and HMB concentration in the polymer The results are presented in Fig 5

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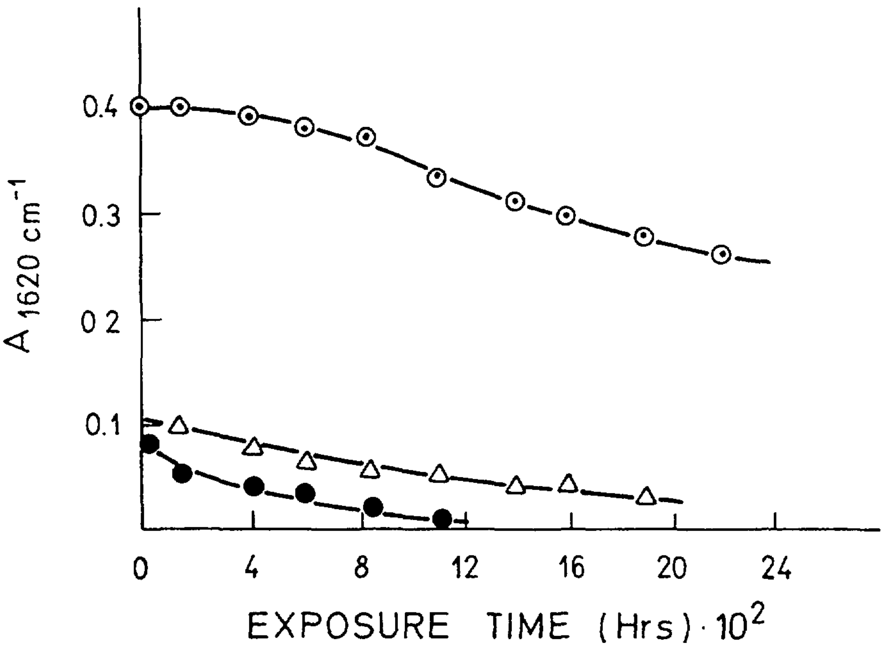


FIG 4 *Changes in 2-hydroxy-benzophenone carbonyl absorption during UV aging of LDPE at room temperature O LDPE; O LDPE + 1% HMB added, O LDPE + 1% Poly-HMB grafted in tetrahydrofuran, Δ LDPE + less than 0.5 % Poly-HMB grafted in methanol.*

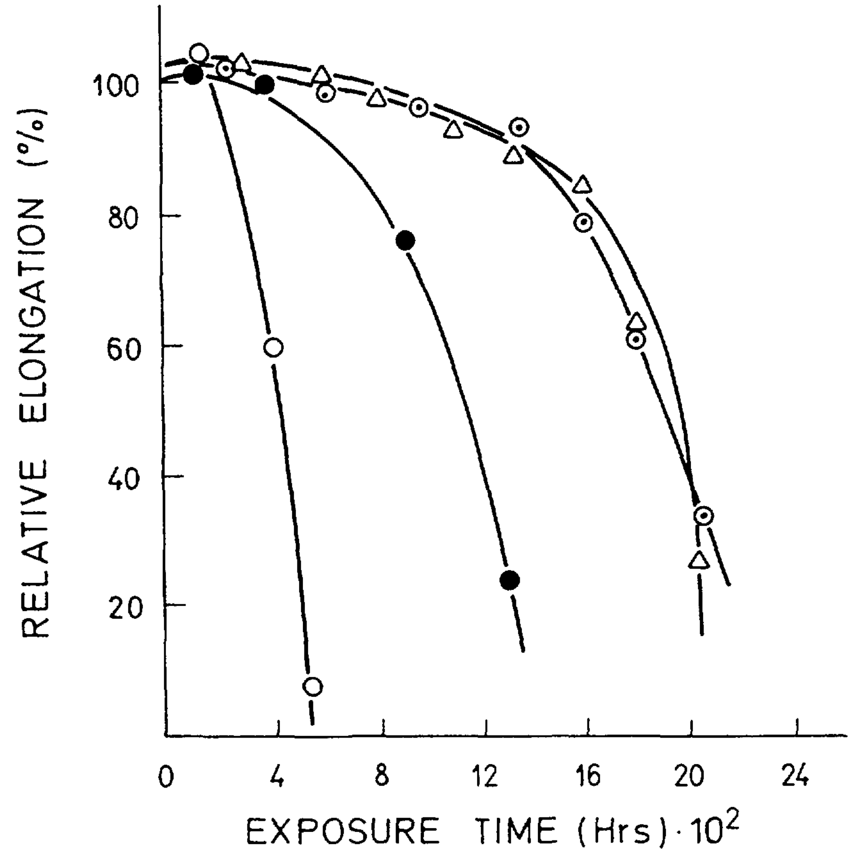


FIG 5 *Changes in elongation at break of LDPE during UV aging at room temperature O LDPE, O LDPE + 1% HMB added, O LDPE + 1% Poly-HMB grafted in tetrahydrofuran, Δ LDPE + less than 0 5 % Poly-HMB grafted in methanol*

In an initial period of UV irradiation the elongation at break slightly increased due to crosslinking, than returned to its original value and after decayed more or less rapidly depending on the LDPE sample. To describe the UV radiation induced degradation of LDPE the times of UV irradiation at which the elongation at break reaches half of its original value were compared. These times can represent the life time of the polymer in practical use In investigated conditions the life time of unstabilized LDPE was about 400 hours. The life time of LDPE with incorporated 1 % of HMB was about three times longer, and the life time of LDPE grafted with about 1 % of HMB was about five times longer than of LDPE without HMB.

Similar results are obtained by measurements of tensile strength in the course of accelerated aging of LDPE samples prepared in the same way. These results are shown in Fig. 6 The tensile strength decreases in the course of UV irradiation in a similar way to elongation at break, but it reaches half of its original value at somewhat longer time of irradiation, which shows that the half value for elongation is a more sensitive measure of the degradation than the half value for tensile strength

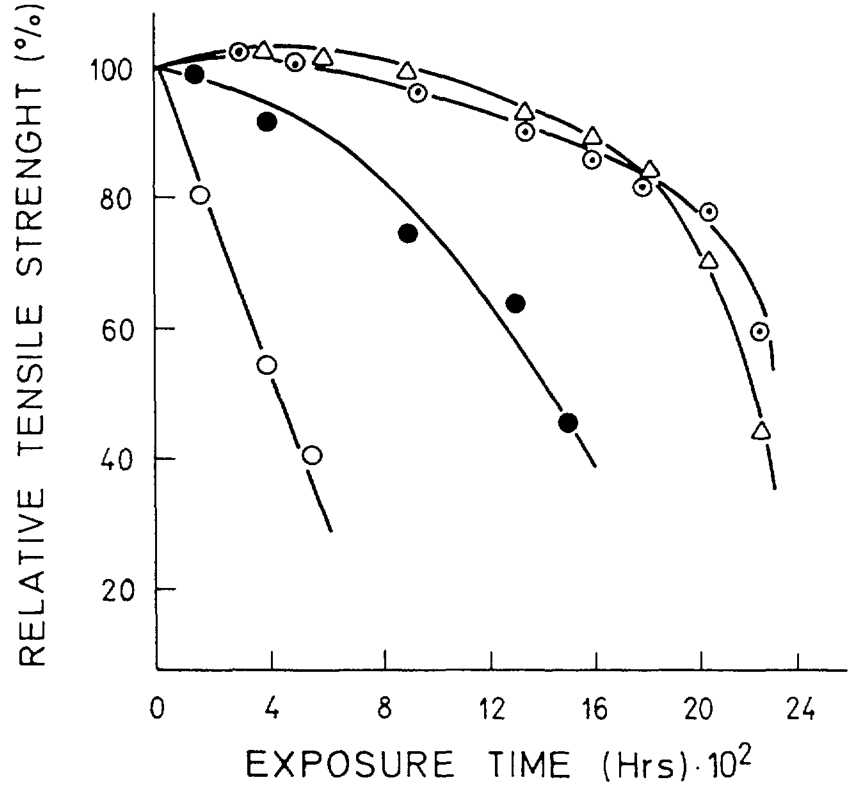


FIG 6 *Changes in tensile strength of LDPE during UV aging at room temperature O LDPE, O LDPE + 1% HMB added; O LDPE + 1% Poly-HMB grafted in tetrahydrofuran, Δ LDPE + less than 0.5 % Poly-HMB grafted in methanol.*

Many polymers and especially polyolefins do not strongly absorb the shorter wavelengths of the sun spectrum However, light-absorbing impurities may be introduced during synthesis or during processing of a polymer (traces of unreacted initiator, breakdown products from initiator, traces of transition metal ions) and they are responsible for photooxidative degradation of commercial polymers such as PE and PP. After some controversies during the past two decades in polymer photochemistry, the general consensus is now that hydroperoxides are the most important photoinitiators during the early stages of UV irradiation

Photo-oxidation is a chain process involving a large number of chemical reactions which are subsequent to the primary event - absorption of a photon, which induces free radical generation. A simplified scheme may be written as follows:

Initiation $\text{Polymer} \xrightarrow{hy} R^{\cdot}$ (1)

In the presence of air, addition of oxygen to a free radical is generally a rapid process producing a relatively stable peroxy radical so that the second step in the cycle (3) is the rate determining step

Propagation

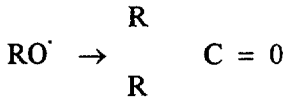
$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (2)

$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$ (3)

With a long chain length a single primary initiation reaction will produce a large number of hydroperoxide species, each one capable of initiating further photo-oxidation. A consequence of this fact is that in this stage of photo-oxidation the initiation by photolysis of hydroperoxides is the predominant process. Every molecule of hydroperoxide produced subsequently undergoes photolysis to generate an alkoxy radical which both provides new initiating radicals and at the same time produces carbonyl compounds (predominately ketones):

$ROOH \xrightarrow{hy} RO^{\cdot} + {}^{\cdot}OH$ (4)

$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$ (5)



$$RO^{\cdot} \rightarrow \begin{matrix} R \\ \\ R \end{matrix} C = 0$$ (6)

At a later stage these carbonyl-containing products assume a main role in chain session reactions according to Norrish I and II type processes. Although both of the Norrish photocleavage processes can cause backbone session, only the Norrish I type reaction generates free radicals which can initiate the oxidative process:

$RCOR \xrightarrow[\text{Norrish I}]{hy} RCO^{\cdot} + R^{\cdot}$ (7)

$\begin{matrix} RCO^{\cdot} \\ R^{\cdot} \end{matrix} + RH \rightarrow R^{\cdot} + \text{peroxides}$ (8)

Termination reaction may be as follows:

Termination $RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROOR + O_2$ (9)

$RO_2^{\cdot} + R^{\cdot} \rightarrow ROOR$ (10)

$R^{\cdot} + R^{\cdot} \rightarrow R - R$ (11)

The scheme outlined above is an oversimplification of the real process of photo-oxidation but it gives a good representation of which reactions must be slowed down or stopped for the purposes of stabilization of polymers

Outdoor performance of polymers can be markedly improved by a choice of suitable stabilizers A basic requirement for an efficient photostabilizer is that the stabilizer itself, its transformation products derived from it during the processing, and photoproducts of the parent and the derived products, should be stable during the period of exposure to UV light without being destroyed or transformed into sensitizing products In general, a good UV stabilizer is capable of absorbing UV light and dissipating it harmlessly as heat HMB belongs to the class of substituted 2-hydroxy benzophenone UV stabilizers which are extremely stable to UV radiation in solution in the absence of oxygen, because they can harmlessly dissipate UV light via keto-enol tantomerism in excited states

The limitation of this class of stabilizers is therefore not their intristic instability to photolysis but their instability to hydroperoxides and carbonyl compounds under photooxidation conditions

Comparing the results of carbonyl index change with 2-hydroxy benzophenone absorption band change and with mechanical properties change in the course of accelerated aging, it could be concluded that photooxidation of LDPE occurs in at least two distinct stages

In the initial period, the photoinitiator is hydroperoxide and the rate of carbonyl formation is proportional to concentration of hydroperoxide If the change of carbonyl index indicates the rate of photooxidation then it is the highest in unprotected LDPE, and in LDPE with grafted and nongrafted HMB depends on unprotected surface areas accessible for photolysis The best initial photoprotection is achieved in LDPE grafted with HMB from methanol, where the grafted HMB is located mainly at the surface of the PE film In unprotected LDPE the rate of carbonyl formation is approximately constant to the failure of PE In LDPE with ungrafted HMB, during the second stage of photooxidation the rate of carbonyl formation becomes auto-autoaccelerating

In the LDPE grafted with HMB, at the end of first stage the rate of carbonyl formation auto-retards to give a plateau The duration of the plateau depends on HMB concentration It lasts longer if the concentration of HMB is higher In the range of the plateau, elongation at break and tensile strength decrease very slowly indicating effective photoprotection of LDPE by grafted HMB At the same time 2-hydroxy benzophenone absorption decreases The above results suggest that HMB does not act by a single mechanism but by a combination of mechanisms HMB acts primary by absorbing UV light and dissipating it harmlessly as thermal energy, but also acts in part as radical scavenger The main advantage of radiation grafted LDPE with HMB is that HMB is located mainly at the PE surface and is more homogeneously distributed HMB can not be lost during UV exposure because it is chemically bound to the PE Grafted HMB can be consumed only in reactions occurring during photooxidation

On the other hand HMB incorporated in LDPE is more inhomogeneously distributed throughout the PE More unprotected surface area of PE may be available for photooxidation from the beginning of UV exposure, and unprotected area may increase during exposure due to losses of stabilizer at the polymer surface This is the reason that several times higher initial

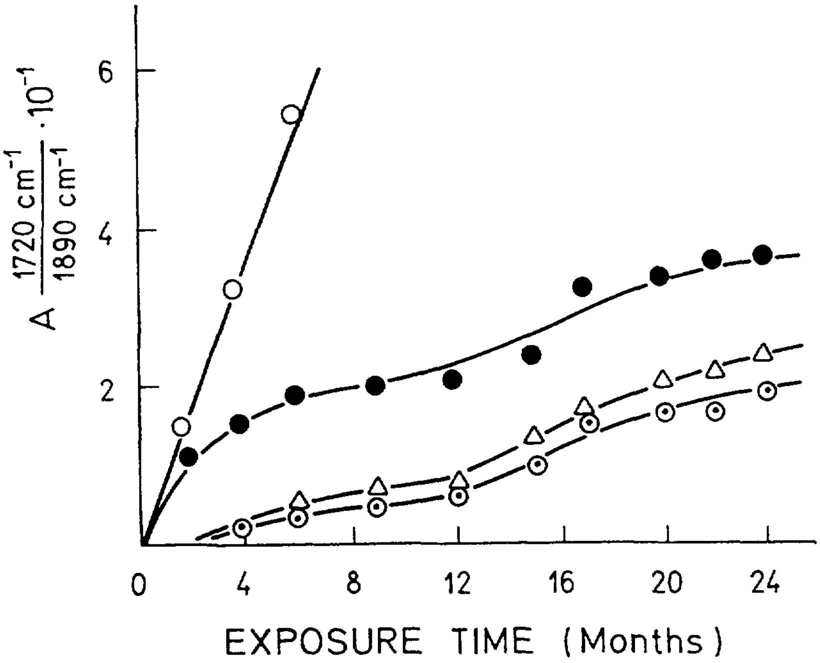


FIG 7 *Changes in the carbonyl index during natural weathering aging of LDPE at free atmosphere conditions*
O LDPE, O LDPE + 1% HMB added,
O LDPE + 1% Poly-HMB grafted in tetrahydrofuran,
Δ LDPE + less than 0.5 % Poly-HMB grafted in methanol

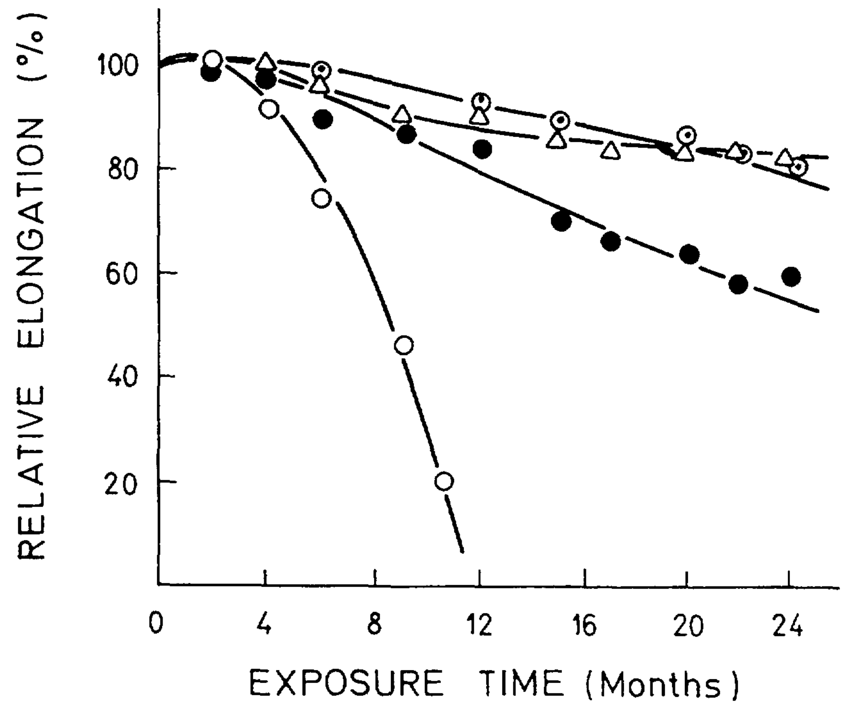


FIG 8 *Changes in elongation at break of LDPE during natural weathering aging at free atmospheric conditions*
O LDPE, O LDPE + 1% HMB added,
O LDPE + 1% Poly-HMB grafted in tetrahydrofuran,
Δ LDPE + less than 0.5 % Poly-HMB grafted in methanol

quantity of incorporated HMB in LDPE is much less effective in photoprotection of PE than a much lower quantity grafted from methanol

At the end it is interesting to compare the results of accelerated aging of grafted and nongrafted LDPE with HMB, with the results of natural weathering aging Natural weathering means long-term combined action of solar radiation, temperature, oxygen, water, ozone and atmospheric impurities like sulfur dioxide and nitrogen oxides The most important of all climatic factors is the UV component of solar radiation It is capable of breaking chemical bonds in a polymer molecule and initiating degradation processes, the most important being oxidative degradation

The test specimens where prepared in the same way as for accelerated aging, and were exposed to natural weathering in free atmospheric conditions The angle of the specimens to the horizon was 45° and the exposed surface faced the south The change of carbonyl index and change of elongation at break were measured in the course of weathering over a period of 24 months The results are presented in Figures 7 and 8 Similar behavior could be observed as in the case of accelerated aging The best photostability was obtained when photo-stabilizer was grafted onto LDPE Although 24 months is a short period of natural weathering aging, it may be concluded that results obtained in accelerated short time aging provide a good basis for prediction of long-term behavior of LDPE under UV irradiation

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RESULTS OF RADIATION TESTS AT CRYOGENIC TEMPERATURE ON SOME SELECTED ORGANIC MATERIALS FOR THE LHC

M. TAVLET, H. SCHÖNBACHER
European Organization for Particle Physics Research,
Geneva

Abstract

In the near future, particle accelerators and detectors as well as fusion reactors will operate at cryogenic temperatures. At temperatures as low as 2 K, the organic materials used for the insulation of the *superconducting magnets and cables will be exposed to high radiation levels. In this work, a representative* selection of organic materials comprising insulating films, cable insulations and epoxy-type-impregnated resins were exposed to neutron and gamma radiation of nuclear reactors, both at ambient and cryogenic temperatures, and were subsequently mechanically tested. The results show that the radiation degradation is never worse in a cryogenic fluid than it is in usual ambient conditions.

1. INTRODUCTION

Future multi-TeV particle accelerators like the CERN Large Hadron Collider (LHC) will use superconducting magnets where organic materials will be exposed to high radiation levels at temperatures as low as 2 K. A representative selection of organic materials comprising insulating films, cable insulations and epoxy-type impregnated resins were exposed to neutron and gamma radiation of a nuclear reactor. Depending on the type of materials, the integrated radiation doses varied between 180 kGy and 155 MGy. During irradiation, the samples were kept close to the boiling temperature of liquid nitrogen, i.e. 80 K, and thereafter stored in liquid nitrogen and transferred at the same temperature into the testing device for measurement of tensile and flexural strength. Tests were carried out on the same materials at similar dose rates at room temperature, and the results were compared with those obtained at cryogenic temperature.

2. SELECTED MATERIALS

The materials selected for this programme are being considered for the LHC machine and/or experimental detectors; they are listed in Table 1. They range from the most common materials such as PETP films, polyolefin cable insulations and standard epoxy resins up to high performance materials such as Kapton films and carbon fibre reinforced composites. All of them are halogen-free and comply with the safety regulations of CERN.

3. IRRADIATION CONDITIONS

The irradiations at room temperature RT were carried out either in a nuclear reactor in Austria, at a dose rate of the order of 200 kGy/h, and where the neutron dose is less than 5% of the total dose, or with a cobalt 60 source, at a dose rate of the order of 4 kGy/h.

The irradiations at liquid-nitrogen temperature (77 K) were carried out in a nuclear reactor in the Russian Confederation, at a dose rate of the order of 20 MGy/h, depending on the material composition; the neutron dose is of the order of 50% to 70% of the total dose.

It has also been checked that the dosimeters currently in use for absorbed dose measurements in the CERN accelerators are suitable for measurements at cryogenic temperatures. The results have shown that calibration curves can be drawn at each temperature for the alanine-based dosimeters, and a temperature coefficient has been calculated [2]; the radio-photoluminescent dosimeters (RPL) can be used up to 1 kGy without any correction, but cannot be used above that level [3].

TABLE I. LIST OF SELECTED MATERIALS

Ref. No.	Material	Type
M 701	Polyethylene terephtalate	*Mylar* sheet (250 µm)
M 702	Polymide, pure, amorphous	*Kapton* H film (125 µm)
M 702'	Polyimide + $Al_2(OH)_3$	*Kapton* AH film (125 µm)
M 703	Polyether-etherketone	*Litrex* a film(amorphous) (125 µm)
C 763	Cable insulation	EPR + acetate copolymer 85-2/179
C 764	Cable sheath	Vinyl Acetate Copolymer thermoplastic 85-4/20
C 1011	Wire insulation	Olisafe (= Siltem) (PEI + silicone)
C 1027	Cable insulation	Polyethylene DFDM 6005
C 1028	Cable sheath	Polyolefin EVA BPD 537
C 1047	Cable sheath	EPR = ethylene-propylene rubber
C 1048	Cable sheath	EVA = ethylene-vinyl acetate
R 422	Epoxy resin	*Araldite* EPN1138/MY745/CY221/HY905/DY73
R 423	Epoxy resin	*Araldite* MY 745/HY 906/DY 073 (100/90/1.5)
R 453	Epoxy moulding compound	XB 3183
R 455	Epoxy moulding compound	XB 3192
R 533	Thermoplastic resin	PEI = polyether-imide
R 534	Thermoplastic resin	PES = polyether-sulfone
R 535	Thermoplastic resin	PSU = polysulfone
R 538	Epoxy laminate (prepreg)	*Vetronite* epoxy G 11 (epoxy + glass)
R 545	Epoxy laminate (prepreg)	Epoxy + glass fibres
R 546	Epoxy laminate (prepreg)	*Vetronite* (epoxy + glass)
R 547	Epoxy laminate (prepreg)	Epoxy + E glass fibres
R 548	Epoxy laminate (prepreg)	Epoxy + E glass fibres + *Kevlar*
R 549	Composite	Epoxy + carbon fibres
R 550	Composite	Epoxy + carbon fibres

4. MECHANICAL TESTS

After irradiation, the samples were kept close to the boiling temperature of liquid nitrogen, i.e. 80 K, and thereafter stored in liquid nitrogen and transferred at the same temperature into the testing device for the measurement of their mechanical properties. The mechanical tests were performed according to the recommendations of the International Electrotechnical Commission publication 544 [4]. The rigid materials were submitted to three-point flexural tests carried out in accordance with the ISO 178 standard. The flexible materials were submitted to tensile tests carried out in accordance with the ISO R527 standard. The speed at which these tests have been performed ranged between 2 mm/min for the flexural tests at 77 K to 50 mm/min for the tensile tests at RT.

5. RESULTS AND DISCUSSION

The results are discussed separately for each type of materials.

5.1. Films

The initial values of the ultimate tensile strength is higher at 77 K than at RT. When the samples are irradiated in air at RT, they degrade by radiation and oxidation. The degradation is less pronounced in the liquid nitrogen. Figure 1 compares the degradation at 77 K and at RT for the PEEK film.

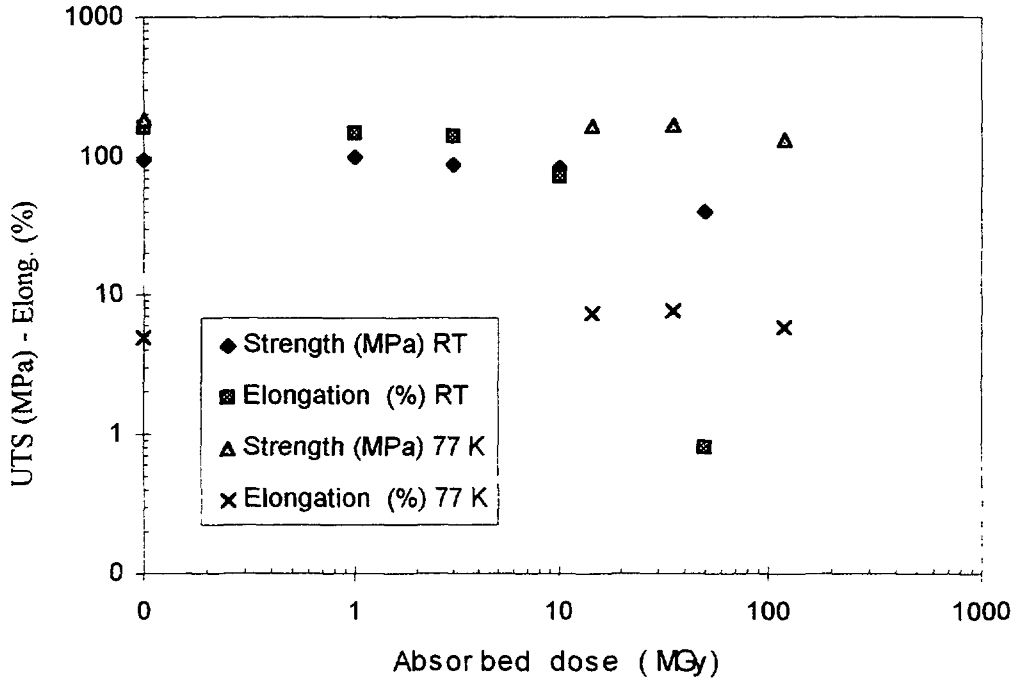

Fig. 1. Radiation effects on polyether-ether-ketone film M 703.

5.2. Cable insulations

The elongation at break of these types of materials is dramatically reduced at 77 K. The most common cable insulations such as polyolefins and rubbers cannot be used at cryogenic temperature because they become too brittle.

Only the copolymer of silicone and polyether-imide (C 1011) is a possible candidate for use in cryogenic application; its degradation is also less severe in the liquid nitrogen than in air.

5.3. High-performance thermoplastics

The change of the initial mechanical properties with the testing temperature of these selected materials (PEI, PES and PSU) stays within a factor of two. This makes them suitable for cryogenic applications. Again, the radiation degradation is less pronounced in a cryogenic fluid than in air Figure 2 compares the degradation at 77 K and at RT for the polyether-sulfone (PES) thermoplastic resin

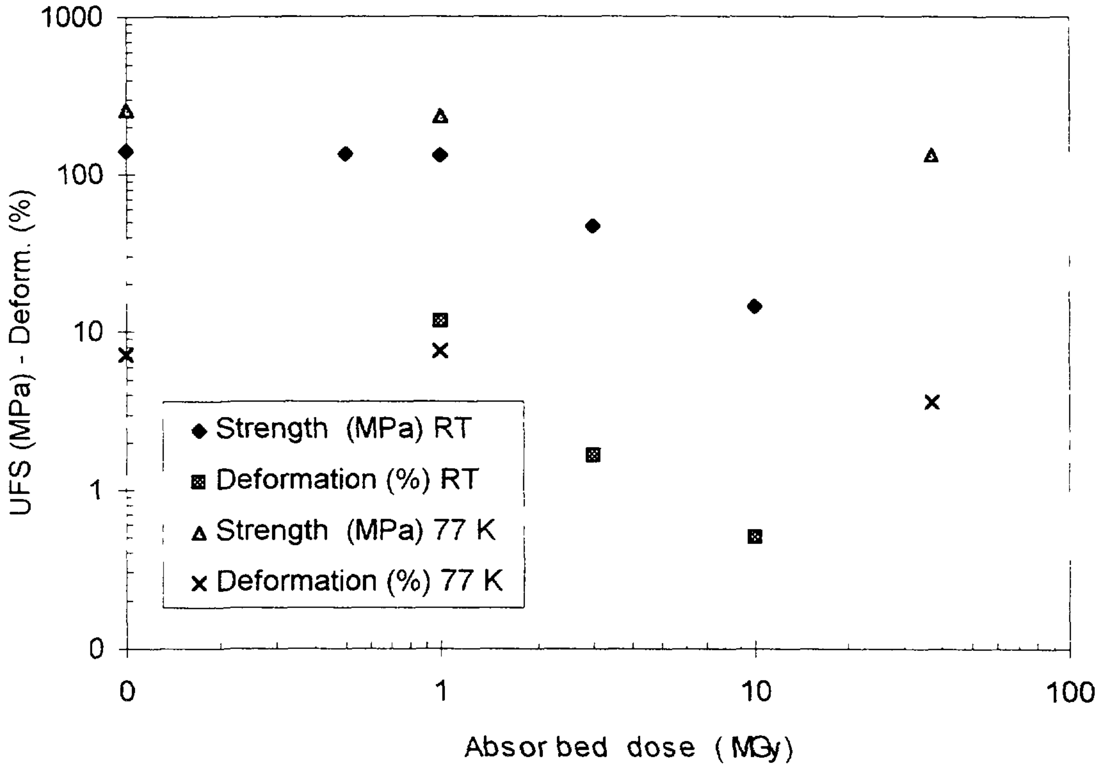

FIG 2 Radiation effect on Erta-PES R-534

5.4. Thermosets

The influence of the testing temperature is almost insignificant for these materials The results show that the most recent epoxy moulding compounds are usable beyond 100 MGy, both at room temperature and at cryogenic temperature

5.5. Laminates and carbon-epoxy composites

The more recently developed composites, with glass-fibre or carbon-fibre reinforcements, have excellent radiation resistance, both at RT and at 77 K, up to the highest dose obtained in this experiment, i.e. 156 MGy. Figure 3 compares the degradation at 77 K and at RT for a prepreg based on epoxy resin reinforced with Kevlar and glass fibres.

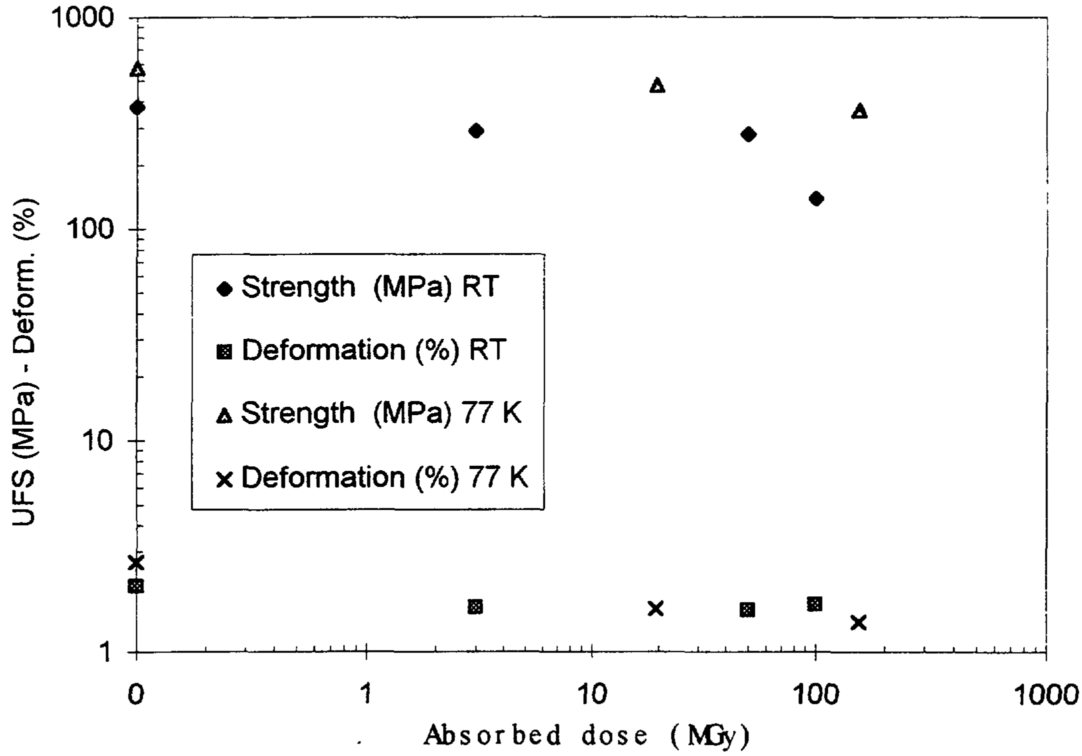

FIG. 3. Radiation effect on epoxy-glass-kevlar laminate R 548.

6 CONCLUSIONS

A representative selection of organic materials have been irradiated both at room temperature and at 77 K, at similar dose rates. Mechanical tests were carried out at the same temperature, without any warm-up between the irradiation and the test, and the mechanical properties were compared.

The results show that, the radiation degradation of thermoplastic materials is less pronounced in a cryogenic fluid than in air. This could be related to the absence of oxygen during irradiation The effect is very pronounced with thin films.

No significant influence of the irradiation temperature is observed on the radiation degradation of thermosets and composites. Within the selected dose range, a number of organic materials are suitable for use in the radiation field of the LHC at cryogenic temperature.

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EVALUATION OF STABILITY OF POLYMERIC INSULATION MATERIALS IN RADIATION FIELDS AND DEVELOPMENT OF RADIATION STABLE PVC AND POLYPROPYLENE FOR MEDICAL DEVICES

M.E. GONZÁLEZ, A.S. DOCTERS
Ezeiza Atomic Center,
National Atomic Energy Commission,
Buenos Aires, Argentina

Abstract

Radiation stability of polypropylene and polyvinylchloride medical products of local origin was evaluated, establishing their functionality by appropriate methods. A device for a mechanical test of syringes and another device for puncture testing of plastic films were constructed and tested. Shelf-life anticipation of irradiated products was examined by treating to high doses and in other cases by storing irradiated products at high temperatures. In both cases negative results would anticipate no functionality for real time aged products. Radiation stability improvement was tried by incorporating light protectors and antioxidants into polypropylene homopolymer. A composition with added light protector was obtained that did not discolor and that kept mechanical stability during aging. Polyvinylchloride tubing was examined and found stable in comparison with imported materials. A non-discoloring product could not be obtained. Evaluation of local commercial polyvinylchloride insulations of wires similar to the wires used in the conveyor system of the Irradiation Facility of Ezeiza Atomic Center suggested that the limit of 50 % reduction in elongation to break in relation to control samples as an indication of failure is too conservative, because this limit was reached much earlier than the actual period of use of installed wires.

1. INTRODUCTION

In the Co-60 Irradiation Facility of Ezeiza Atomic Center, different products for medical care, cosmetic, or laboratory use are currently sterilized. About 25 % of these products are made from Polypropylene or PVC, which are materials sensitive to ionizing radiation [1-7]. According to legal requirements the expiring date shall be stated on the package, so the manufacturer shall assess that the product will be functional up to that date. To be able to make such assessment it must be established that the product does not suffer alterations affecting its functionality after irradiation and during the shelf life period. It is necessary then to have some way of evaluating functionality of products. This is a complex matter considering that the properties that govern the functionality depend not only on the characteristics of the product such as shape and components but also on its intended use. In some cases the properties determining functionality are mechanical, in other cases chemical and in other cases just the color may determine the functionality of a product. Materials components of the products must be evaluated by using standard methods, but for stability assessment it is necessary to evaluate the final products [8]. In addition, manufacturers wish to be able to make an anticipated evaluation of long term post-irradiation functionality of their products. In this respect, methods to accelerate aging refer mainly to materials [4,6] and are not usually used on final products.

Local production of PP and PVC amounts to about 85 % and 68 % respectively of total consumption [9] but there are no commercial compositions especially stabilized for radiation sterilization.. Importation of medical products is currently done but the market for medical products that will undergo radiation sterilization is not large enough to justify the importation of special polymers.

In relation to the Irradiation Facility, it would be interesting to anticipate the durability of parts permanently exposed to radiation. We are therefore conducting an evaluation of the durability of PVC insulations of wires that are used in the conveyor system.

In relation to radiation sterilization we intend to evaluate the radiation stability of devices of different shapes and final uses, manufactured from PP and PVC of local origin. In each case, it is necessary to define one or more properties essential to the product functionality, that allow the assessment of functionality after the irradiation and the aging time. In the cases of syringes and film for packaging, we constructed special devices to perform in each case a test representative of functionality.

In addition, we intend to evaluate two ways of anticipating the durability of the irradiated products: irradiation to a higher dose, and the storing of irradiated products at a temperature higher than room temperature.

Finally, we intend the improvement of radiation stability by using some additives known as effective antioxidants or light stabilizers.[5,6,10,11,12], by the preparation of samples through different processing methods

2. EXPERIMENTAL

2.1. Materials

- Products for medical care or cosmetics, or for laboratory use, or their packages, manufactured locally with PP or PVC of local origin. In the cases of PP syringes and PVC tubing, imported products or materials were also used for comparison purposes.
- PP homopolymer (Petroken);
- PP random copolymer, with 2.2 % ethylene (Petroquímica.Cuyo)
- additives were obtained from Ciba:
- Tinuvin 622 LD (butanedioic acid, polymer with 4-hydroxy 2,2,6,6-tetramethyl-1-piperidineetanol)
- Irganox1010 (pentaerytrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate])
- Irganox PS 800 (dilauryl ester of β,β'-thiodipropionic acid)
- Irganox B900 (Irganox 1010/Irgafos168 1:4)
  {Irgafos 168: tris-(2,4-di-tert-butylphenyl)-phosphite}
- wire insulation of PVC of local commercial origin, similar to the wires employed in the conveyor system of the Irradiation Facility.

2.2. Irradiation

Irradiation was carried out in the Co-60 Irradiation Facility of Ezeiza Atomic Center, or in the privately owned Co-60 facility of Ionics, in Buenos Aires Province. For irradiation of medical products and samples of PP and PVC compositions, a site in the plant with dose rate of 5 kGy/h was used.

PVC insulated wire was cut in 20 cm long pieces, the conductor separated, and located for irradiation in bundles of 5 to 10 pieces. A site in the irradiation plant was selected where cables are most exposed. Average dose rate was determined to be about 0.15 kGy/h by previous dosimetric calibration. Dose rate varied according to the source position (storage-operation), and the carts circulation. The samples were left at the position during 100 days, and some of them were taken at intervals in order to have in total 6 groups of samples with different applied doses. Samples of the same material, prepared in the same way, were irradiated at different dose-rate and temperature, using an electrical heated device previously calibrated at three temperatures. The samples were accomodated in this device and it was positioned in three sites of the irradiation room where the dose-rate had been determined. Dose-rates were: 1.4 kGy/h; 3.8 kGy/h; 5.4 kGy/h. Temperatures were: 65 °C; 80 °C; 100 °C. At different times some of the samples were removed. Total applied doses ranged from 50 to 300 kGy.

2.3. Mechanical testing

Tensile, compression, and flexure measurements were performed with an Instron 1122 machine with 500 kg load cell. For a mechanical test on syringes a device adapted to the Instron machine was constructed: The device consists of a tubular mainpiece, 3 cm longer than the syringes, on top of which different adaptors of appropriate diameter can be placed in order to test syringes of different sizes. The syringes were put inside, where they hung supported only by their flanges. On the other hand a moving piece (penetrometer-like) slides inside the syringe applying a load to it [Fig.1].

For a test of puncture on plastic films, a device was constructed also as an adaptor to the Instron machine. The device consists of two concentric iron rings (approx. $\Phi e = 15$ cm, $\Phi i = 5$ cm each) embedded one on top of the other, grasping the film between them. A vertical movement punch is pressed against the film perpendicularly until the film is broken.[Fig 2] When it was not possible to perform an instrumental test because of the shape of the dimensions of the product or sample, manual tests were done, taking care to reproduce the actual use of the product.

2.4. Discoloration

Visual tests were performed making use of a scale prepared with tones of yellow. PP products were observed against a white sheet of paper. PVC tubing was cut in rings 2 mm thick and placed on a white sheet of paper. Observation was done under the white light of a chromatoviewer.

2.5. Chemical test

Evolution of HCl from PVC was tested through the assay for acidity of aqueous extracts Aqueous extracts were obtained according to the ISO standard for blood transfusion sets [13] The assay was performed according to the same standard

2.6. Preparation of samples containing additives

Compression moulding was performed by means of an electrically heated press, at a pressure of 20 ton and temperature of 195-215°C The samples prepared by extrusion or injection moulding were prepared by manufacturers of medical devices or by polymer and masterbatch producers

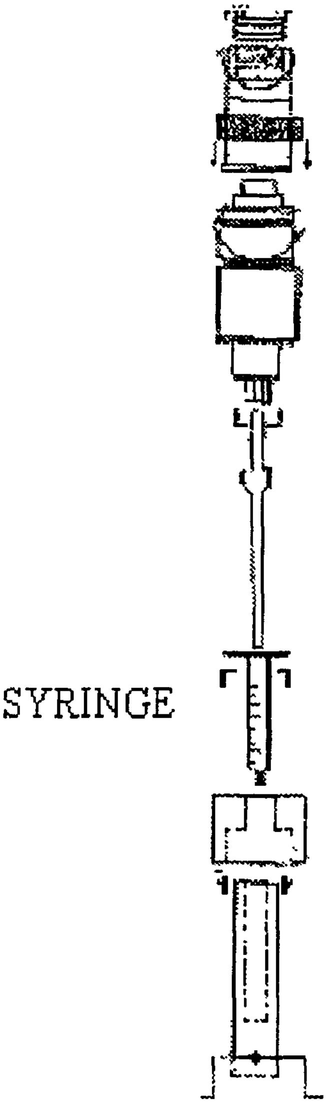

FIG 1 Device employed for mechanical testing of syringes

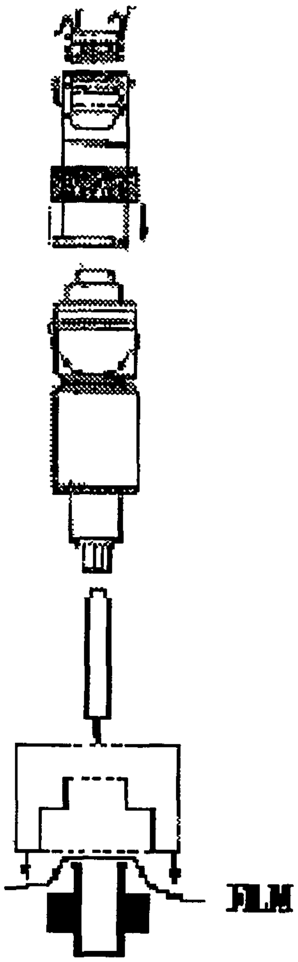

FIG 2 Device employed for testing of puncture on films

3. RESULTS AND DISCUSSION

3.1. Radiation stability of medical devices

Sheets of PP were processed by injection moulding, for a medical device intended to stand flexion and torsion. As an assay for functionality, pieces of the product were subjected to manual bending. We considered that a reduction of 40% was the limit for this product functionality, according to its purported use. Comparison was done with non irradiated control pieces and with pieces irradiated to 60 kGy at the different times of testing. Dose applied was 30 and 40 kGy. Time of testing was up to 2 years. A strong reduction in bending ability occurred during the period up to 200 days following irradiation but the product was still functional. The product was functional up to almost 2 years after irradiation, when observation was stopped. In all times of testing the samples of 60 kGy recently irradiated were much more fragile (not functional) than the irradiated, aged samples. On the other hand, 40 kGy irradiated samples reached the limit for functionality at about 2 years. This fact could be considered as indicative that the product treated with sterilizing dose will be stable for longer time (Fig.3).

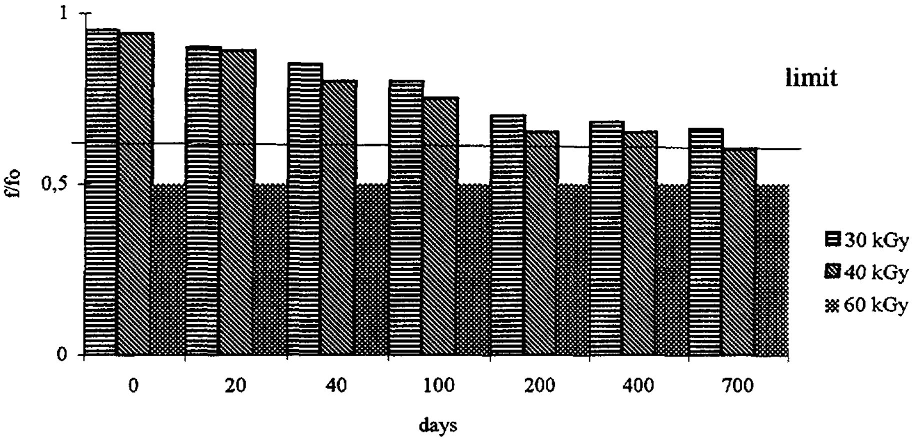

FIG. 3. Stability of injection moulded sheets of PP irradiated to 30 and 40 kGy.

Handles of brushes for cosmetic use and of dental mirrors and instruments were made of PP filled with carbon black and with talc. In this case according to the use of these products of lineal geometry the bending by means of the Instron machine was tested, by fastening one end and applying load to the other end. The angle of bending at break was measured, in relation with that corresponding to non-irradiated control samples. An angle of 90° was taken as the limit of functionality. The dose applied was 32 and 64 kGy for carbon black filled PP and 28 kGy for talc filled PP. The 32 kGy irradiated samples were functional 3 years after irradiation. The 64 kGy irradiated samples were functional 6 months after irradiation. The stability of 64 kGy irradiated samples could be an indication of stability at longer time of the product irradiated to sterilizing dose. 28 kGy irradiated samples were functional 3 years after irradiation. The irradiated samples stored at 60°C for 15 days were functional also. In this case storing at high temperature was also indicative of long term functionality of the irradiated product (Fig. 4).

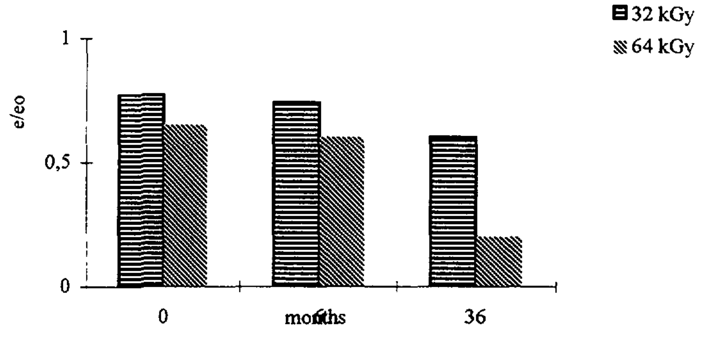

FIG. 4 (a). Stability of handles of carbon black filled PP irradiated to 32 and 64 kGy.

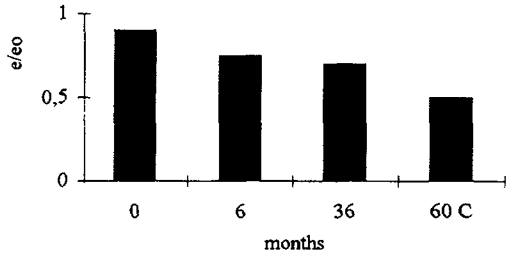

FIG. 4 (b). Stability of talc filled PP irradiated to 28 kGy.

PPBO film, 40 μm, used as package for medical devices, was irradiated to 25 kGy. The irradiated product was kept at room temperature and at 60°C for 40 days. Elongation to break was measured on strips of film. The product was still functional two years after irradiation. The higher temperature test could be used to anticipate the duration of functionality (Fig.5).

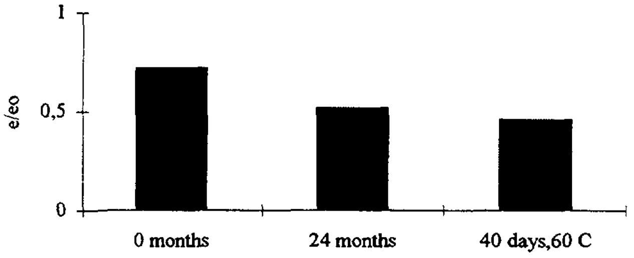

FIG. 5. Stability of PPBO film irradiated to 25 kGy.

PPBO film (40 μm) was irradiated to 26 and 35 kGy was tested by elongation to break and also by making use of the device constructed to measure puncture on films There was good concordance between both methods of testing (Fig.6). The radiation stability of the film was good.

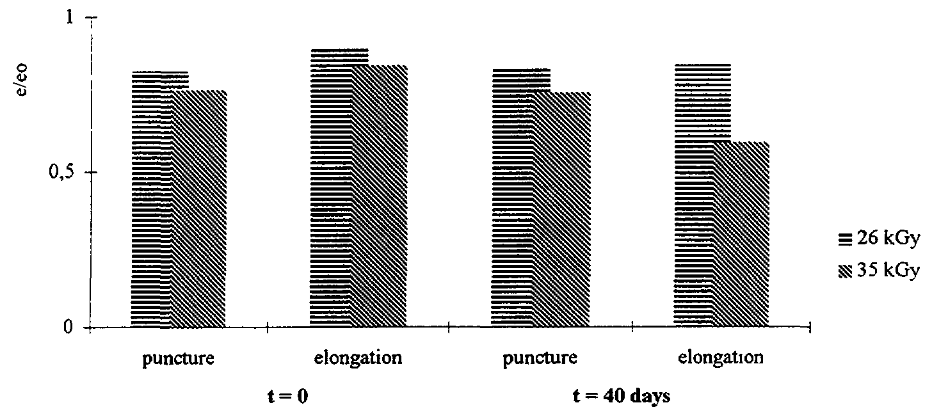

FIG. 6. Stability of PPBO film, as measured by elongation to break and by puncture test.

PPMO film (40 μm) was irradiated to 28 kGy and stored at room temperature and at 60°C for 15 days. Elongation to break was measured on strips of the film, According to this test the product was functional for two years after irradiation. The test on samples stored at high temperature could be used as indicaton of the long term duration (Fig 7).

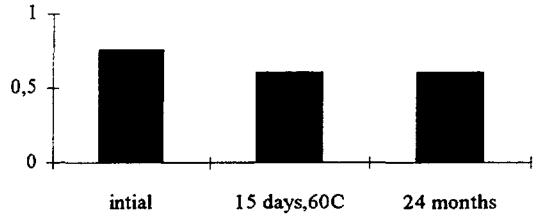

FIG. 7. Stability of PPMO film irradiated to 28 kGy.

Syringes irradiated to 26 and 44 kGy were evaluated with the device constructed for that purpose. For comparison a set of syringes of German origin were irradiated and tested by the same method. A strong fall in the property measured was noticed during the period of two months after irradiation. The syringes kept their functionality during the observation period of 14 months. In this case the irradiation to higher dose allowed anticipation of the long term duration (Fig. 8). German syringes were found to be more stable, particularly during the first aging period.

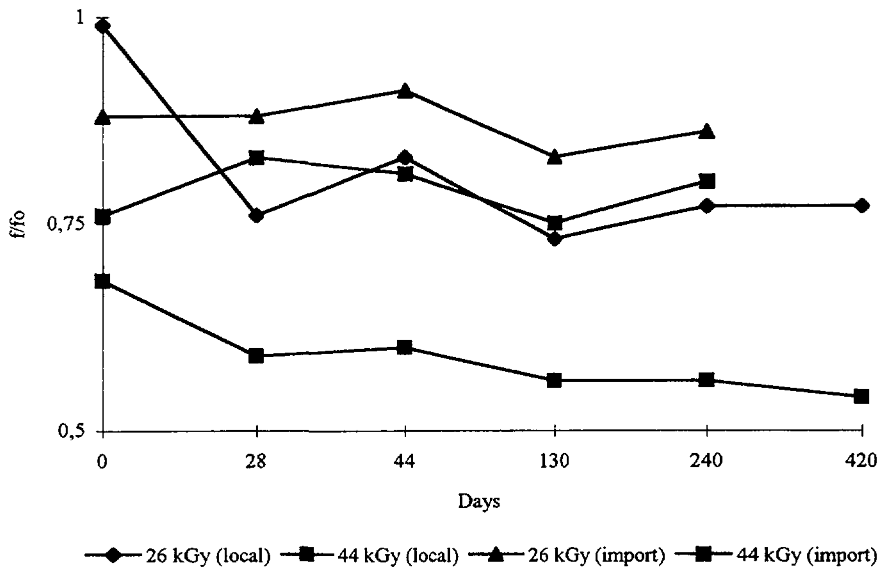

FIG. 8. Stability of syringes measured with the device shown in Fig.1.

3.2. Stability improvement

Samples of PP homopolymer with different additives prepared by compression moulding were irradiated to 25 kGy (Table I). Elongation to break was measured after irradiation and at 12 months of aging at room temperature. Previous experiments with samples prepared in the same way without additives had shown a strong effect of post irradiation degradation and this effect could be anticipated by the effect of a higher applied dose (Fig 9). The effect of additives was significant as all of additivated samples could be considered functional after aging (Fig 10).

TABLE I. ADDITIVES INCORPORATED INTO PP

		ADDITIVE (% w/w)		
Composition	Tinuvin 622LD	Irganox B225	Irganox PS800	Irganox 1010
a	0,3	0,2	0,6	
b	0,3	0,4		
c	0,3		0,3	0,2
d		0,4	0,3	

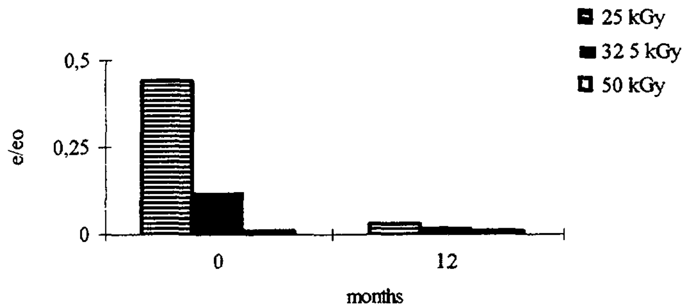

FIG 9 Samples of compression moulded PP irradiated to 25, 32 and 50 kGy

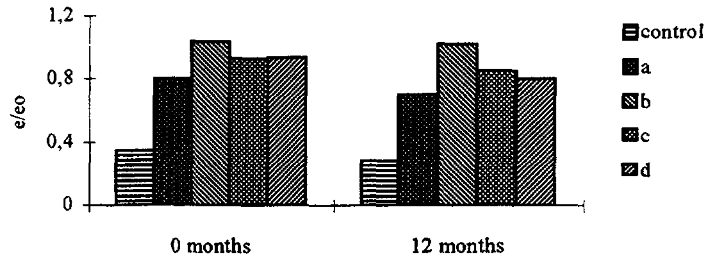

FIG 10 Samples of compression moulded additivated PP irradiated to 25 kGy

Eppendorff tubes prepared by extrusion with the addition of Tinuvin 622 were irradiated to 28, 44 and 70 kGy Two ways of testing functionality were tried traction of the union between the tube and the cap, that appears as the weakest part of the device, and compression to breakage of the tube Both tests were done by means of adaptors to the Instron machine Comparison of results show the equivalence of both tests Higher dose (44 kGy) anticipated the long term duration the 28 kGy irradiated tubes were functional during the time of observation (32 months) after irradiation (Fig 11)

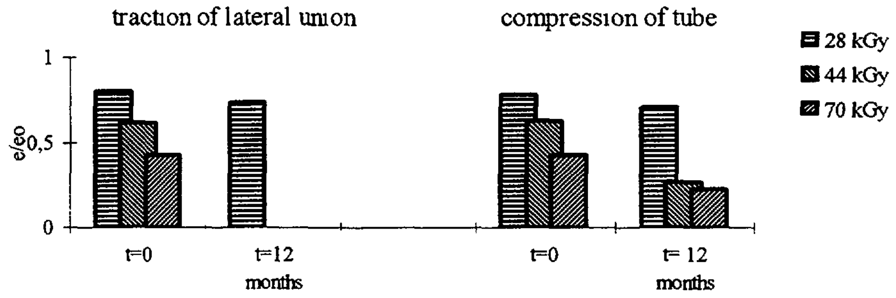

FIG 11 Eppendorf tubes made of PP with Tinuvin 622 LD, irradiated to 28, 44 and 70 kGy

Samples of PP homopolymer with the addition of 0.3% Tinuvin 622 LD for flexion measurements prepared by injection moulding were irradiated to 21 and 32 kGy. Other samples containing the same proportion of Tinuvin 622 and 0.1% Irganox B900 were irradiated to 25 kGy. Both samples showed good resistance to radiation in flexion tests. According to these tests the samples were functional 12 months after irradiation (Fig.12) but there was an important difference regarding discoloration, between both samples, as the former did not show discoloration at all.

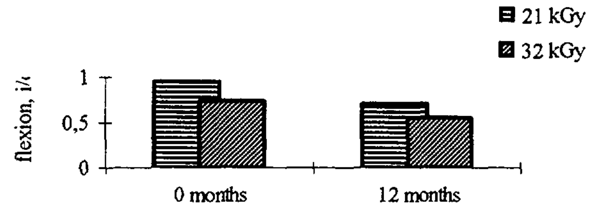

FIG. 12. Injection moulded bars of PP with Tinuvin 622LD irradiated to 21 and 32 kGy.

Samples for flexion of PP random copolymer prepared by injection moulding were irradiated to 25 kGy. Test methods for flexure properties [14] were not applicable because they passed the strain limit, so tensile tests were performed. Considering a reduction of 50% in elongation to break related to control samples as a limit for functionality, these samples were functional and no fall was observed during the first 100 days after irradiation (Fig.13).

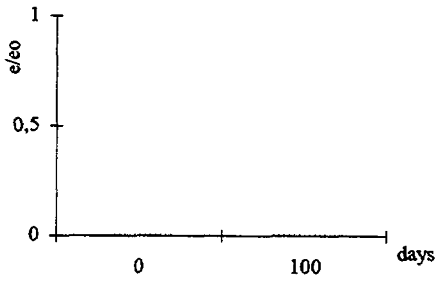

FIG. 13. Bars of PP random copolymer (0,2 % ethylene monomer) irradiated to 25 kGy.

In all cases where discoloration was noticed this factor was no determinant to functionality. Discoloration did not intensify with time, but was a function of the applied dose. Discoloration was observed in samples prepared by compression moulding with additives and in the samples of random copolymer. The samples prepared by injection moulding with only the light protector added showed no discoloration at all, but when an antioxidant was added discoloration was again noticeable.

PVC tubing for medical use was studied. Considering that mechanical properties are not affected by radiation in the range of dose applied in sterilization [1,3,7], and that discoloration is not significant for the purported use of these products, the possibility of evolving HCl that could be dissolved by the circulating or contacting liquids was taken as the property determining functionality of these products. This would be also valid for containers of flexible PVC for fluids of biologic origin.

Samples were irradiated to 38 and 59 kGy. The results of aqueous extract acidity tests were always below the limit imposed by the ISO standard, which was taken as a limit for functionality [11] (Fig 14)

Comparison of local origin PVC tubing with the one made from imported radiation stable PVC and with imported PVC tubing, showed that the performance was similar Discoloration increased during the first 8 months of aging, but remained approximately constant afterwards It was comparable between tubings made from local PVC and from imported radiation stable PVC The color of these tubings irradiated to 38 kGy and aged for 2 years was considered acceptable when shown to users of PVC medical devices Previous experiments with PVC tubing for medical use had shown that storing irradiated samples at high temperature (40-60°C) produced much stronger discoloration than that of aged irradiated samples For this reason we did not try this way of anticipating aging The tests of acidity of aqueous extracts on samples irradiated to higher dose gave results comparable to the results corresponding to aged irradiated samples. This could be used as a way of anticipating functionality of irradiated products Because of inaccesibility of processing means of PVC we could not go beyond this stage to improve discoloration effect on this material

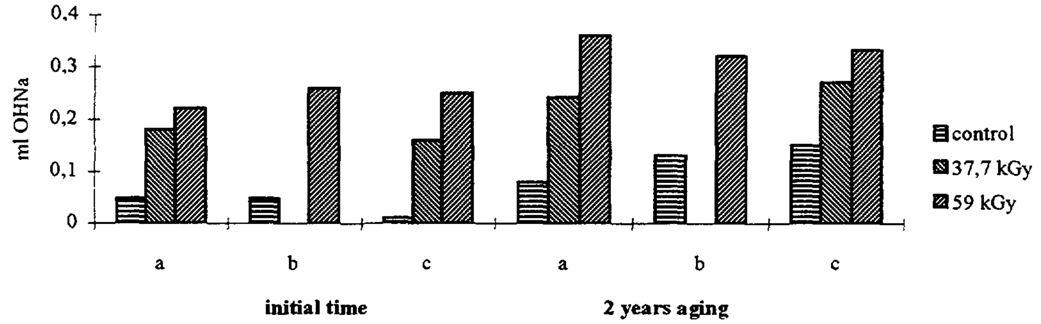

FIG 14 Acidity tests on aqeuous extracts of PVC tubing for medical use, irradiated to 38 and 59 kGy (a) local tubing, (b) imported radiation stable PVC, (c) imported tubing

3.4. Wire insulation

Tests performed over real time showed that elongation decreased smoothly, reaching the proposed ratio of e/eo = 0 5 at about two months (137 kGy) of exposition to radiation (Fig 15) However, wires used in the plant are not replaced with that frequency, the normal operation involves replacement at about one year frequency It could be established that the wires were safe in spite of the mechanical degradation

The results obtained in the experiment with different dose rates and temperatures of irradiation did not allow an estimation of longer term degradation comparable to the real-time experiment described above However we found that these conditions allowed us to obtain degraded samples in short times The doses in kGy required to decrease the elongation to break to 50% of original value (e/eo = 0 5) were calculated from the results for the different conditions of irradiation (Table II) Approximately 5 days of irradiation at 65°C and 1 4 kGy/h produced the same mechanical degradation as the real time irradiated samples.

TABLE II. IRRADIATION DOSE FOR 50 % DECREASE IN ELONGATION OF PVC WIRE INSULATION

kGy/h	65 °C	80 °C	100 °C
1.4	181	165	133
3 8	243	210	201
5 4	240	237	192

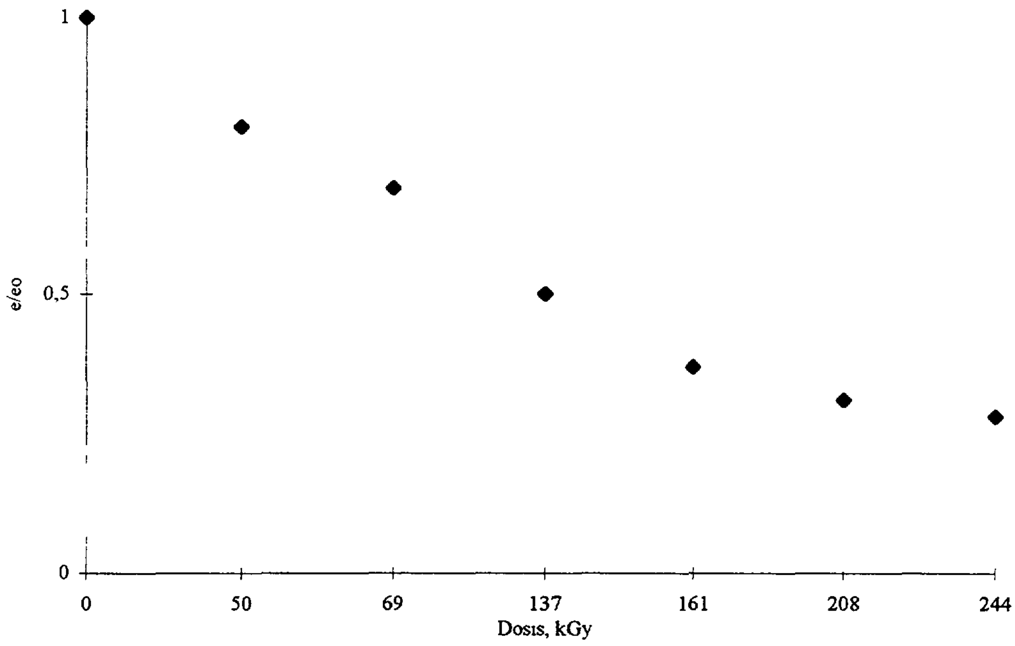

FIG 15 Elongation to break related to control samples for PVC wire insulation irradiated in a site at the irradiation facility with average dose-rate aprox 0 4 Gy/s

4 CONCLUSIONS

Measurement of puncture in films for packages was much easier to perform and at least as effective as elongation to break For syringes, the device built that reproduces the actual use of the syringe measuring the force necessary for bending the flanges gave results representative of functionality and was of simple operation.

Medical products of PP from local origin were stable regarding their post-irradiation functionality. Injection moulded and filled PP products were the most stable. Discoloration was noticeable in all cases, except for films or filled PP products. It did not increase with aging, thus making it possible to evaluate the effect inmediately after irradiation.

Regarding the possibility of anticipating the durability, both irradiation to higher dose and storage at higher temperature gave indication of stability. However, the conclusion should better be taken in the negative sense: a non-functionality result anticipates that the product will not be functional in the long term.

In relation to radiation stability improvement, discoloration of PP homopolymer was eliminated by the incorporation of the light protector in the samples prepared by injection moulding. Addition of antioxidants improved mechanical stability in samples prepared by compression moulding and by injection moulding, but they had a negative effect in discoloration. The introduction of a comonomer in the polymer (random PP copolymer) resulted in an appreciable effect in mechanical stability but did not have an effect on discoloration.

In the case of flexible PVC the local product was indicated to be stable when measured by the acidity of the extract. Its stability was comparable with that of imported product and the product manufactured with imported radiation stable PVC. Regarding discoloration the effect in the local product was considerably slighter than that of the product manufactured with imported radiation stable PVC. The lifetime could be anticipated by means of irradiation to a higher dose.

In the case of PVC wire insulation of local origin, the actual duration of wires in the Irradiation Plant is much longer than would be expected according to the results of elongation to break with a limit of e/eo = 0.5. Normal permanence of wires in use in the plant is superior in about 1000 %, suggesting the limit is too conservative. Samples have been obtained by irradiating at different conditions of temperature and dose-rates with the same degree of mechanical degradation as the ones irradiated in actual conditions. This may be a method of probable utilization to obtain aged samples in shorter times.

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CHANGES IN MOLECULAR STRUCTURE AND PROPERTIES OF IRRADIATED POLYMERS OF DIFFERENT COMPOSITIONS — ESR AND NMR STUDY

T. CARSWELL-POMERANTZ, A. BABANALBANDI,
L. DONG, D.J.T. HILL, M.C.S. PERERA, P.J. POMERY,
G. SAADAT, A.K. WHITTAKER
Polymer Materials and Radiation Group,
Department of Chemistry,
University of Queensland,
St Lucia, Australia

Abstract

Investigations of molecular structural changes in polymers during exposure to high energy radiation is the long term interest of the Polymer Materials and Radiation Group at the University of Queensland. Recently, the group had looked at a range of polymers including natural and synthetic rubbers, methacrylates and polyesters. The objective of the work has been to investigate the relationships between polymer structure and sensitivity towards high energy radiation, including gamma radiation. This report will focus on the Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR) studies of the effects of gamma irradiation on these polymers. Other methods such as Gas Chromatography (GC), Gel Permeation Chromatography (GPC), Fourier Transformed Infra Red (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) have also been used as these methods combine with ESR and NMR, to provide a more complete picture of the mechanism of the structural changes.

1. INTRODUCTION

The primary event which occurs when a molecule interacts with ionising radiation involves the ejection of an electron to form a cation radical. This ejected electron may become trapped on a site in the matrix of the material to form an anion radical or alternatively, the electron may be captured by a cation radical to produce an excited molecule. The cation radicals, anion radicals and excited state species are very reactive and generally undergo further chemistry to form neutral radicals. These neutral radicals may undergo further reactions, and in polymers, these reactions may result in crosslinks, depropagation, chain scission, change in stereochemistry, formation of grafts etc.

The effects of radiation on polymer materials is an area of increasing interest. Several high technology industries require speciality polymers that exhibit a specific response upon exposure to radiation. For instance, the electronic industry requires materials that undergo radiation induced scission and crosslinking for resist applications, while aerospace and medical applications require highly radiation stable materials. Further, there is an increasing interest in industrial use of radiation processing. The design and development of appropriate chemistry for these applications requires full understanding of the effect of radiation on polymer materials. It is through fundamental understanding of the radiation chemical processes occurring in polymers that the technological advances required by today's industries can be realised.

In the work reported in this paper all irradiations were carried out in vacuum as our group was interested in understanding the primary pathways of radiation chemistry. ESR provides information of the primary radicals that are formed during irradiation, radical intermediates and their yields. NMR (both solution and solid state) provides information on the final structural changes. For polymers where $G(S) > 4G(X)$, the polymer will not form a crosslinked gel during irradiation, and therefore remains soluble. Since there is no increase in the viscosity on irradiation, the solution state ^1H and ^{13}C NMR spectra of these polymers are of comparable or superior quality to the original material. To observe structures formed on irradiation of polymers which undergo mainly crosslinking, that is where $G(S) < 4G(X)$, solid state NMR methods are necessary. Combination of techniques such as high-power ^1H dipolar decoupling (DD), rapid magic angle spinning (MAS), and cross polarisation (CP) of ^1H and ^{13}C nuclear spins permits the observation of high-resolution ^{13}C NMR spectra for solid samples. A certain amount of information could be derived from the spectra so obtained, though peaks were less well resolved than solution state spectra. However, much care is required to obtain quantitative peak intensities. We will demonstrate in this report, how the information obtained from ESR and NMR techniques, is used to propose reaction pathways of radiation degradation of polymers.

2. RUBBER

2.1. Polyisobutylene (PIB)

Polyisobutylene undergoes [1] main chain scission on irradiation, by virtue of the presence of tertiary carbon atoms in the polymer main chain which form relatively stable free radical intermediates. Several possible mechanisms for the chain scission have been postulated. We have used variety of methods, including ESR, GPC and solution state NMR to determine which of the mechanisms are most likely to occur. ^{13}C NMR spectra of unirradiated and irradiated PIB are shown in the Figure 1.

The spectrum of the unirradiated polymer consists of three main resonances at around 59, 38 and 31 ppm due to the three types of carbons in the repeat unit. A large number of new resonances appear in the spectrum of the irradiated PIB. These peaks were assigned on the basis of well known additivity rules, of Linderman and Adams, Grant and Paul, Beebe, and Pretche et al.. The major products were vinylidene end group (S1), $-CH_2-C(CH_3)=CH_2$, t-butyl end group (S2), $-C(CH_3)_3$, formed by β-scission of a methylene radical, and a disubstituted unsaturated end group, (S3), $-CH=C(CH_3)_2$ and secondary butyl end group, (S4), $-C(CH_3)_2H$ formed by β-scission of a methine radical. Peak areas were then used to calculate the radiation chemical yields and are compared with the values obtained from GPC results shown in Table I. On the basis of these results, we have critically evaluated the mechanisms proposed by several authors.

2.2. Butyl Rubber [2]

Butyl rubber is a copolymer of isobutylene and a small percentage (1%) of isoprene units. Polyisobutylene undergoes predominantly, if not exclusively, chain scission during high energy irradiation [3]. In butyl rubber, crosslinking would be expected through the isolated isoprene units, but scission of the isobutylene sequences predominates. The decrease in molecular weight, due to chain scission, results in well resolved solution state NMR spectra offering the possibility of observing the ^{13}C NMR resonances due to crosslink structures of both the H and Y links. The majority of these crosslinks are Y-link structures. GPC results were analysed using equations derived for H-link and Y-link situations and are compared with the values calculated from NMR in Table II. The results further confirm the Y-linking mechanisms.

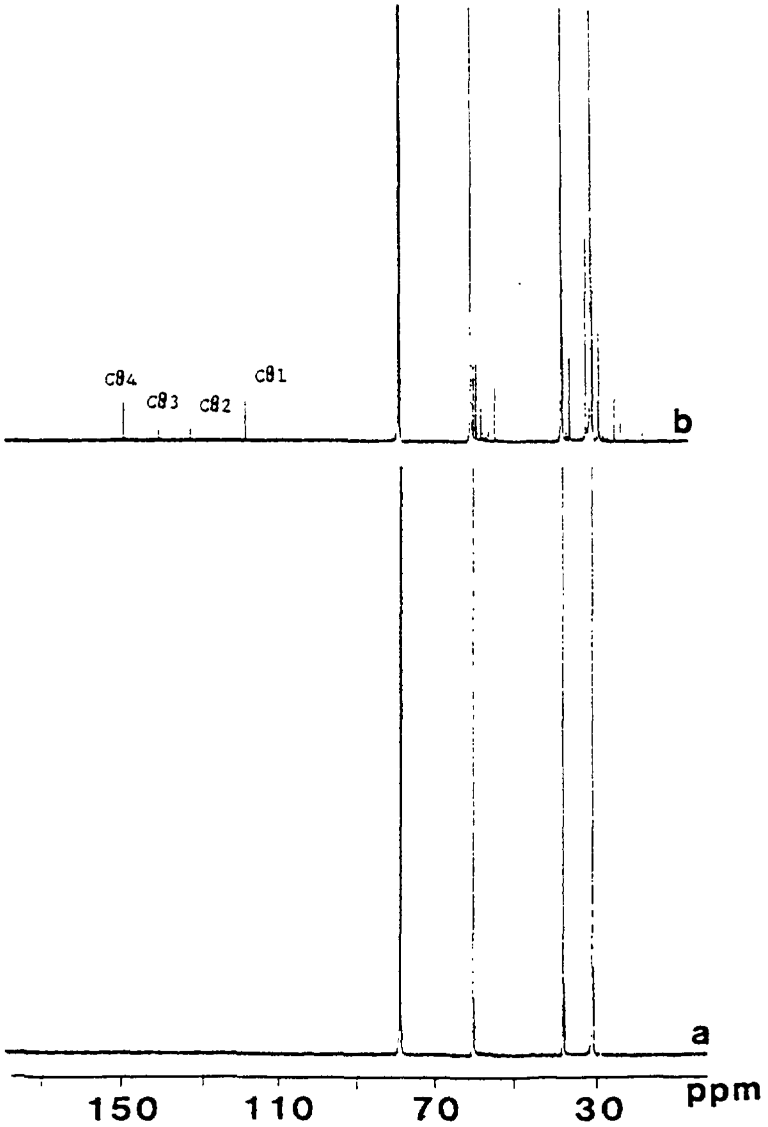

FIG. 1. ^{13}C NMR spectra of Polyisobutylene in CDCl$_3$ (a) unirradiated (b) irradiated to 9MGy in vacuum at 303K.

TABLE I. RADIATION YIELDS OF DIFFERENT STRUCTURAL UNITS AND SCISSION FOR POLYISOBUTYLENE

Radiation Yields-G	NMR Results	GPC Results
S1	2.4	
S2	3.6	
S3	0.5	
S4	0.7	
Total	7.2	
All unsaturated ends	2.9	
Scission	3.6	3.6
Scission/unsaturated ends	1.2	

2.2. Butyl Rubber [2]

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2.3. Halogenated Butyl Rubber [4]

Chlorinated and brominated butyl rubber is obtained by halogenating the isoprene units in butyl rubber. ESR was used to study the radical intermediates obtained when these rubbers are irradiated with high energy radiation. Most of the radicals were found to be generated on the halogenated isoprene units, due to the labile C-X bond as shown in Table III. Radiation yields for radicals at 77 K were 4.3 and 3.7 for chloro butyl and bromo butyl rubbers respectively, compared with 2.3 for butyl rubber.

A higher radiation yield for scission was observed in chlorinated butyl rubber than in brominated butyl rubbers as shown in Table IV. This is due to the ready abstraction of hydrogen from the main chain by the chlorine radicals to give main chain radicals, which are known to contribute to scission in butyl rubber. These main chain radicals could be observed in the ESR spectra during warming up of the sample in the ESR cavity as shown in Fig. 2. They are the methine radical produced by hydrogen abstraction from the methylene group of the backbone giving a two line spectrum, and methylene radical produced by the hydrogen abstraction from the

TABLE II. RADIATION YIELDS OF SCISSION AND CROSSLINKING IN IRRADIATED BUTYL RUBBER CALCULATED USING GPC AND NMR DATA

GPC Data assuming Scission only		
	G(S)	2.8
GPC data assuming H-linking		
	G(S)	3.15
	G(H)	0.35
GPC data assuming Y-linking		
	G(S)	3.63
	G(Y)	0.75
NMR Data		
	G(S)	3.9
	G(X)	0.4

TABLE III. RADICALS GENERATED DURING HIGH ENERGY IRRADIATION OF CHLOROBUTYL RUBBER

Structure	Percentage	G(R)
Radical anion	66	2.8
Methylene	16	0.7
Methyne	20	0.9
Allyl	10	0.4

TABLE IV. RADIATION YIELDS FOR HALOGENATED BUTYL RUBBER

	G(X)	G(S)
Polyisobutylene	0.0	3.7
Chlorobutyl rubber	3.62	1.71
Bromobutyl rubber	3.7	0.44

methyl groups giving a three line spectrum. In addition to that, there is evidence for the formation of the allylic radicals by hydrogen abstraction from the methylene groups of the halogenated isoprene units. In both polymers, crosslinking predominates over scission up to a limiting dose of about 50-100 kGy as shown in Figure 3. The gel dose for both polymers is about 30-40 kGy.

2.4. Ethylene Propylene Rubber (EPR)

Radiation effects on EPR (without any unsaturated ter monomer) was investigated [5,6] for comparison with studies of the radiation chemistry of polyethylene and polypropylene.

EPR undergoes both crosslinking and scission, with G(S) =0.38 and G(X)=0.82. After relatively low irradiation doses the polymers could be swollen with organic solvents, thus permitting high resolution ^{13}C NMR spectra. Well resolved peaks due to three types of new chain ends were observed. A G(S) =0.37 was obtained from the area of the peaks produced on irradiation. Further analysis of the relative proportions of the new chain ends demonstrated that the scission of the main chain was 1.6 times more likely to occur adjacent to a methine branch than at an isolated methylene group.

After higher irradiation doses the yield of crosslinks could be estimated from the solid state ^{13}C NMR spectra. A broad range of environments were observed, consistent with the large number of possible H-link structures that could be formed on recombination of the radicals observed by ESR. Y-links were not observed. The yield of crosslinks, G(X) =0.84 obtained from the area of the NMR peak was in excellent agreement with that obtained from soluble fraction analysis (G(X)=0.82).

2.5. Polybutadiene

The effect of irradiation on diene elastomers including polybutadiene (PBD) was studied [7] by techniques including solid state ^{13}C NMR. In addition to the crosslinking reaction, we also obtained information on the rate of radiation induced isomerisation of the double bonds from cis to trans conformations. Since the polymers remain highly heterogeneous after irradiation, great care is required to interpret the data and obtain any quantitative results.

After irradiation a broad peak due to new crosslinked structures could be identified and quantified.

The G value for crosslinking of 1,4 PBD was equal to G(X)=33 at low doses, and decreased to G(X)=10 at up to 10 MGy dose. These G values were in good agreement with the G values for the loss of double bonds. The rate of cis-trans isomerisation (G(cis->trans)=16.2) was consistent with previous studies. The large G values suggested a chain reaction mechanism, and the discrepancy between G(X) determined by NMR and that determined by soluble fraction analysis (G(X)=3-5) arises from a nonrandom spatial distribution of crosslinks resulting from the chain reaction. As a further example of the importance of chain reactions, the G-values for loss of double bonds in 1,2 PBD was determined to be G(-d,b.)=237.

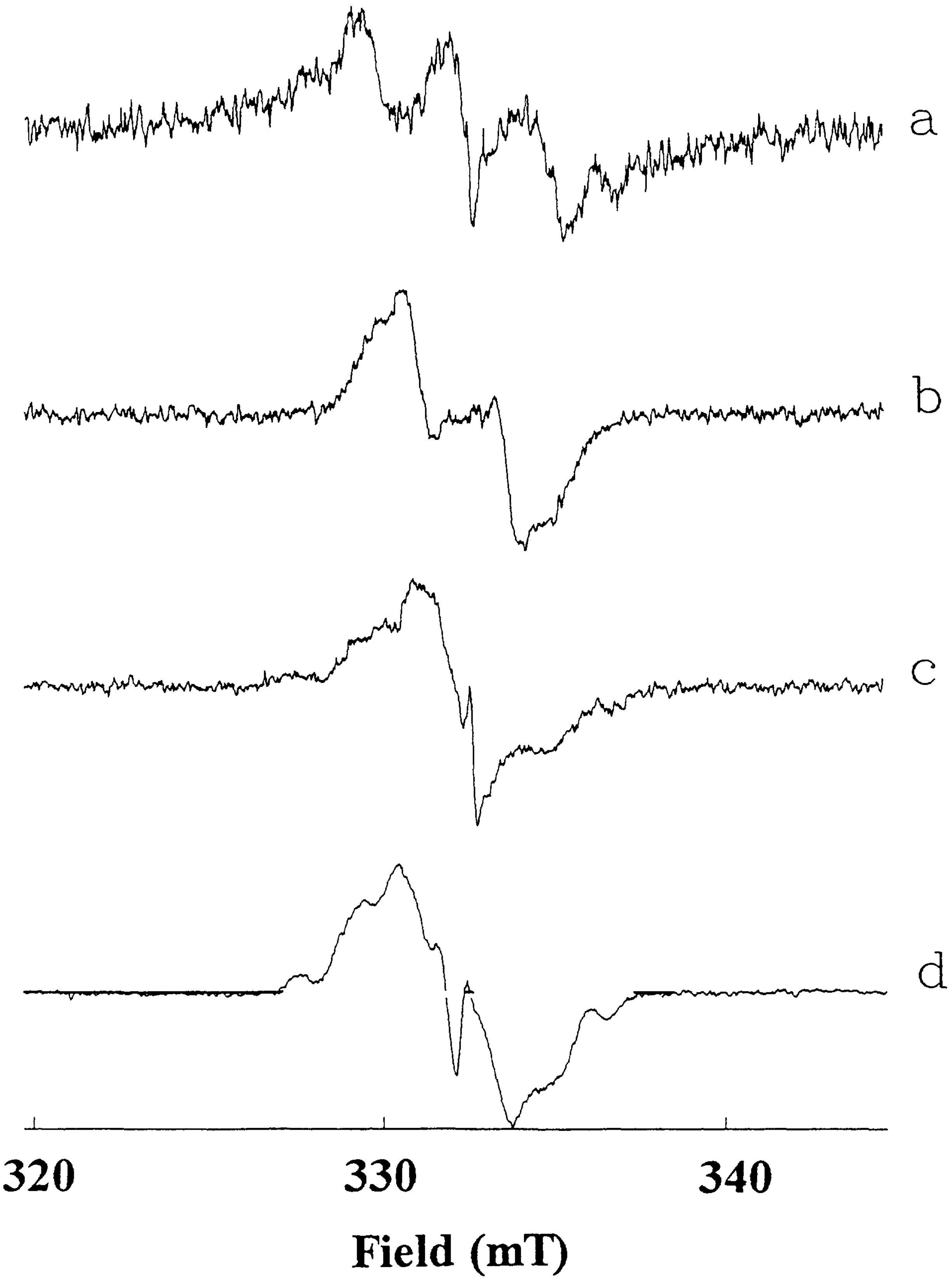

Figure 2. ESR spectra of Chlorinated butyl rubber (a) between 110 and 215 K, (b) between 215 and 240 K and (c) at 245 K. (d) ESR spectral difference between chlorobutyl and polyisobutylene measured at 77K

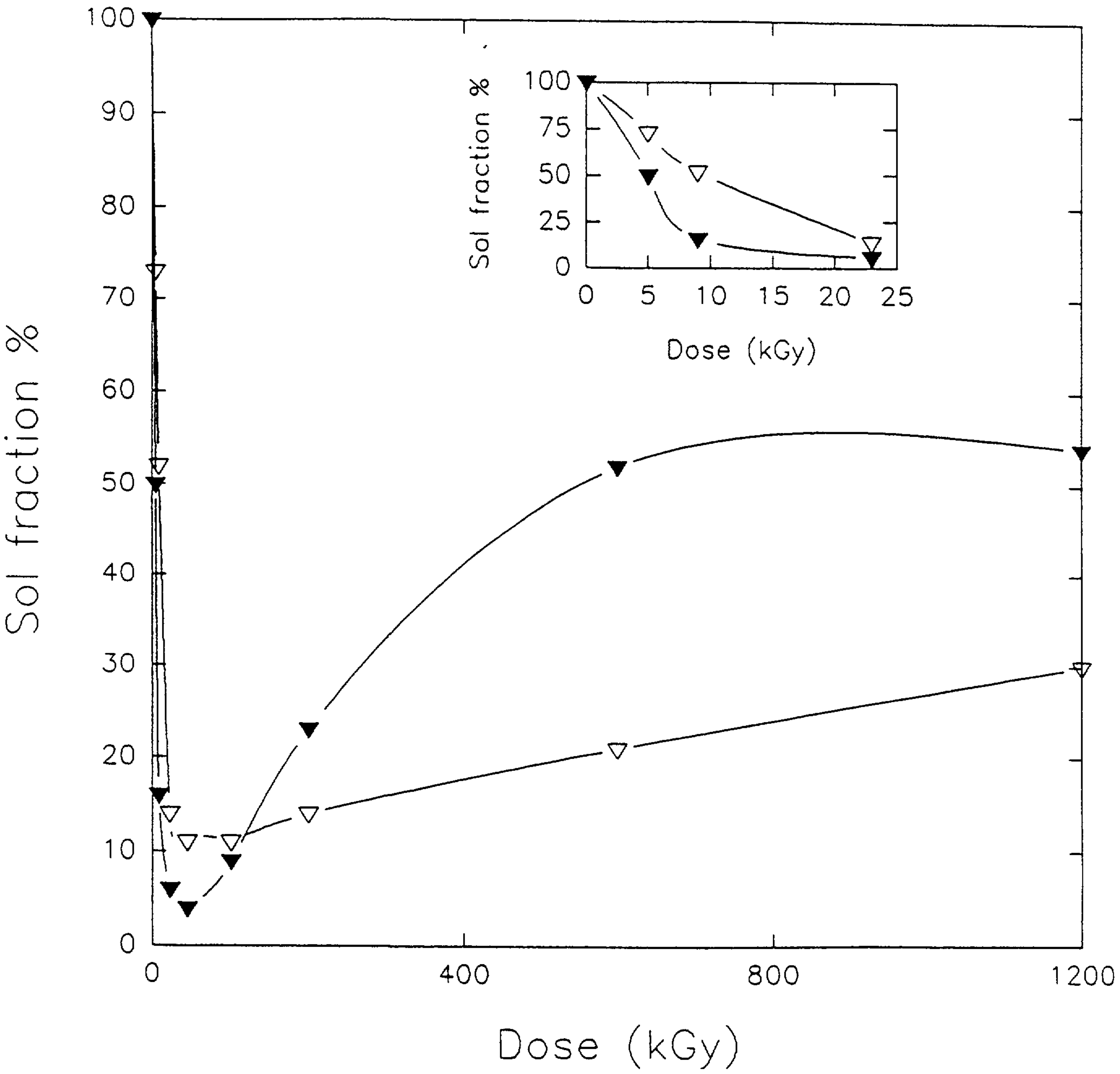

FIG. 3. Sol fraction vs dose for chlorobutyl (∇) and bromobutyl (▼) rubbers.

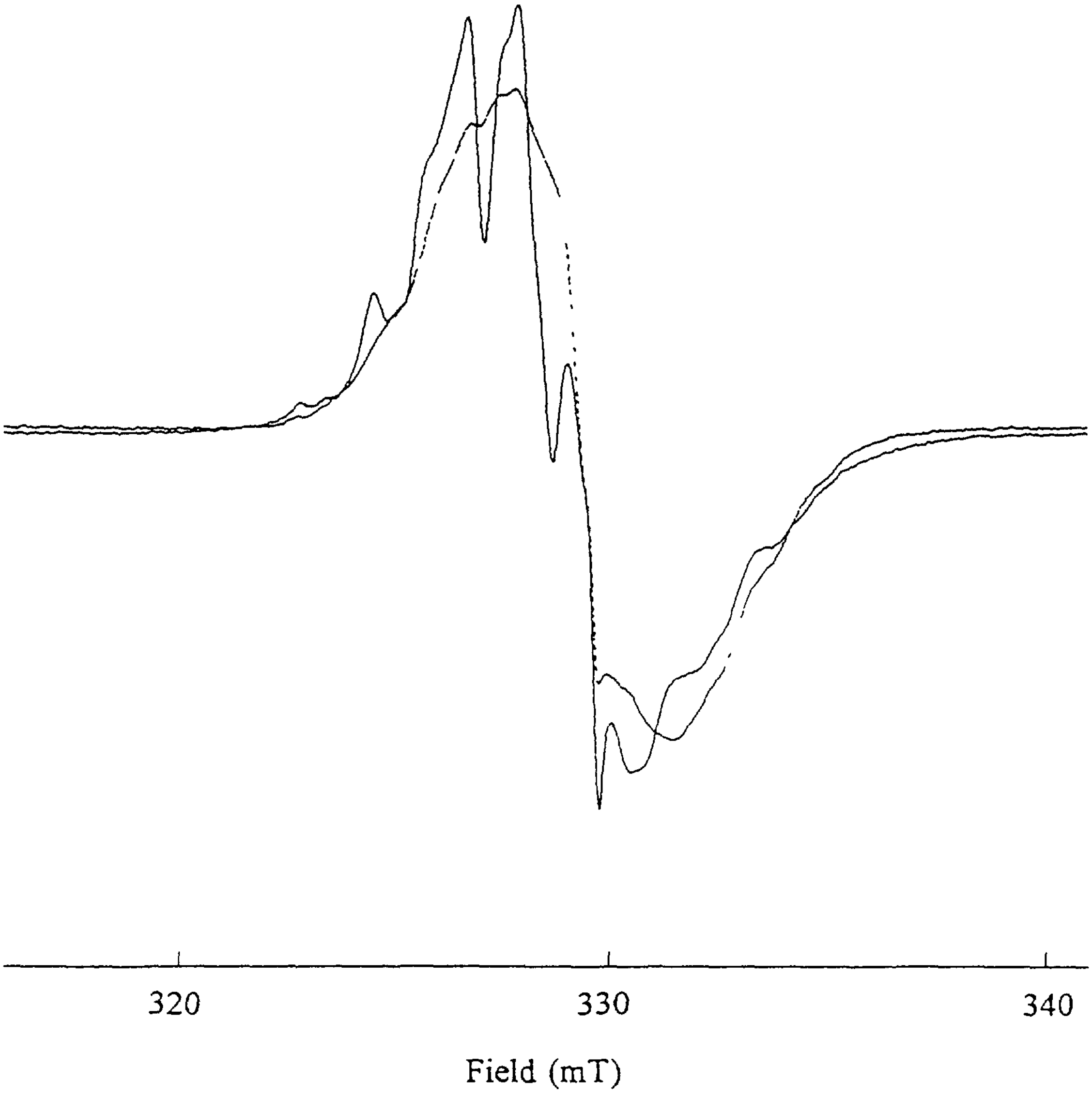

FIG 4 ESR spectral shape of NBR at (—) 110 K and (– –) 190 K

2.6. Nitrile Rubber [8]

Nitrile rubbers are copolymers of butadiene and acrylonitril. ESR spectroscopy indicates that during high energy irradiation, most of the primary radicals are generated on the acrylonitrile units. These radicals then abstract hydrogen from butadiene units resulting in the formation of allylic radicals. This could be observed in the Figure 4 where change in the ESR spectral shape during sample warm up is shown. The allylic radicals are known to react to form inter and intra molecular crosslinks. Radiation yields of radicals increase with increasing acrylonitrile content from 1.42, 1.58 to 2.42 for 18, 30 and 45% acrylonitrile rubbers respectively.

Due to net crosslinking in these polymers during high energy radiation, solid state NMR techniques need to be used to investigate the new structures. High probe temperatures were used to obtain better resolution. Radiation yields of crosslinking (inter and intra molecular) were evaluated from these spectra. The radiation yields for intermolecular crosslinking were higher in rubbers with higher acrylonitrile contents, giving G values of 17.8, 21.3 and 24.5 for 18, 30 and 45% acrylonitrile rubbers respectively. FTIR studies shown in Figure 5 confirm that the reaction of butadiene sites is more favoured over acrylonitrile sites. The peaks at 2995 and 2840 cm^{-1} were assigned to C-H stretching of the CH_2 group of butadiene and acrylonitrile units respectively. Spectra after irradiation indicate the drop in intensity of the peak at 2990 compared to the peak of 2840 cm^{-1}. Further, DD/MAS NMR spectra of the olefinic region of the unirradiated and irradiated rubber shown in Figure 6 suggest that the reactions occur at butadiene units in acrylonitrile-rich triads rather than in butadiene-rich triads. In this group of peaks, the peaks at the centre are assigned to BBB triads and the outer peaks are assigned to ABA triad. This confirms intramolecular radical transfer from acrylonitrile units to butadiene units. Radiation chemical yields for NBR are given in Table V. As in PBD the higher G(X) values observed by NMR compared to other techniques indicate chain reaction and crosslink clustering, but an increase in the acrylonitrile content reduces this effect.

Cyclisation (intra molecular crosslinking) occurs in the initial stages of the irradiation but ceases with loss of butadiene dyads. There is no evidence for chain scission.

Cyanide groups take part in the reaction at higher doses forming -C=N-H and conjugated -C=N- structures as indicated by the development of peaks at about 1600 cm^{-1} and the drop in the peak at 2250 cm^{-1} in the FTIR.

TABLE V. RADIATION CHEMICAL YIELDS FOR NBR

G-value	Method	NBR18	NBR33	NBR48
G(cyclic)	NMR	26.3	20.1	14.5
G(X)	NMR	17.8	21.3	24.5
	Swelling	9.9	5.1	16.2

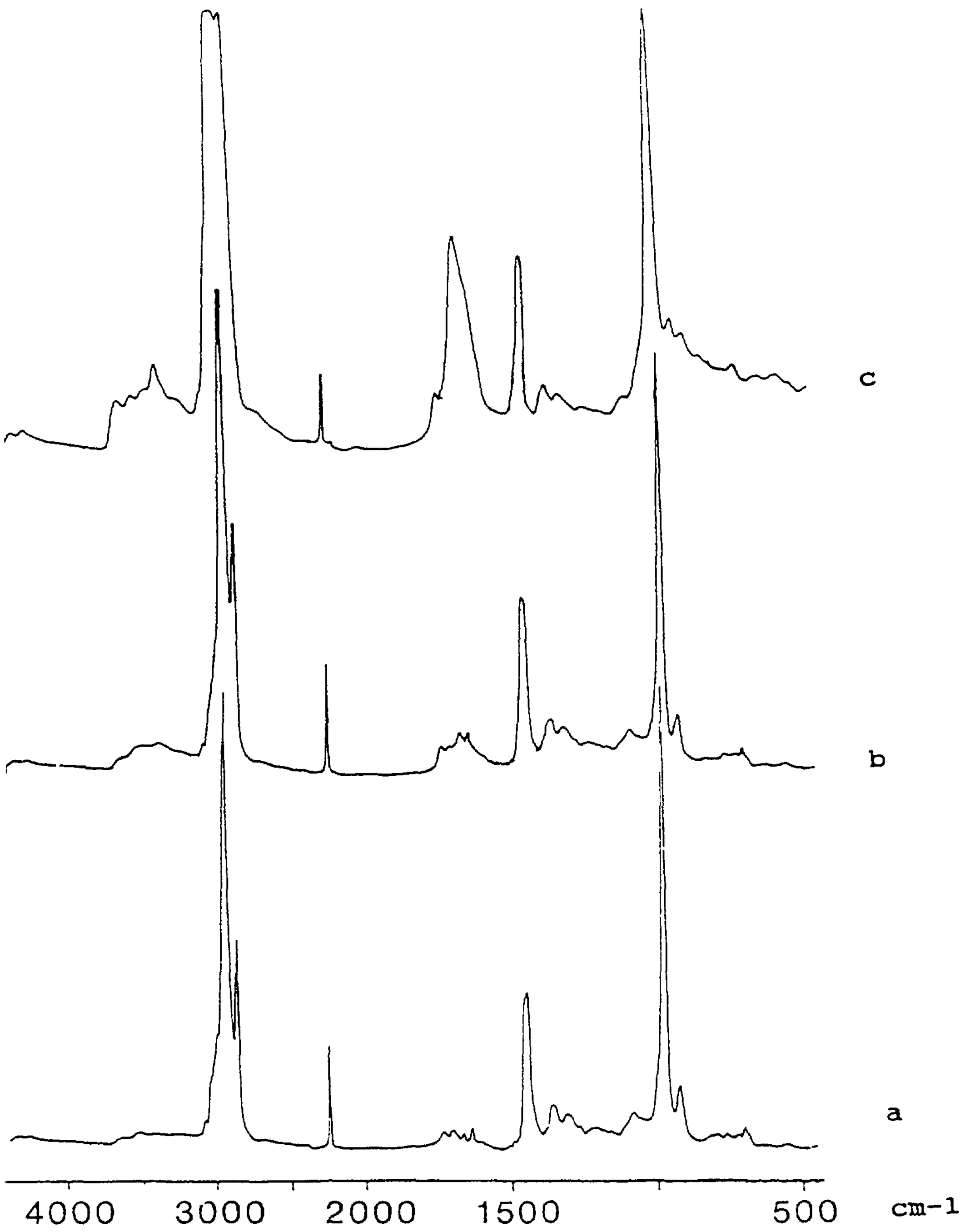

FIG 5 FTIR spectra of (a) unirradiated and (b) 1 5 MGy and (c) 4 6 MGy irradiated NBR

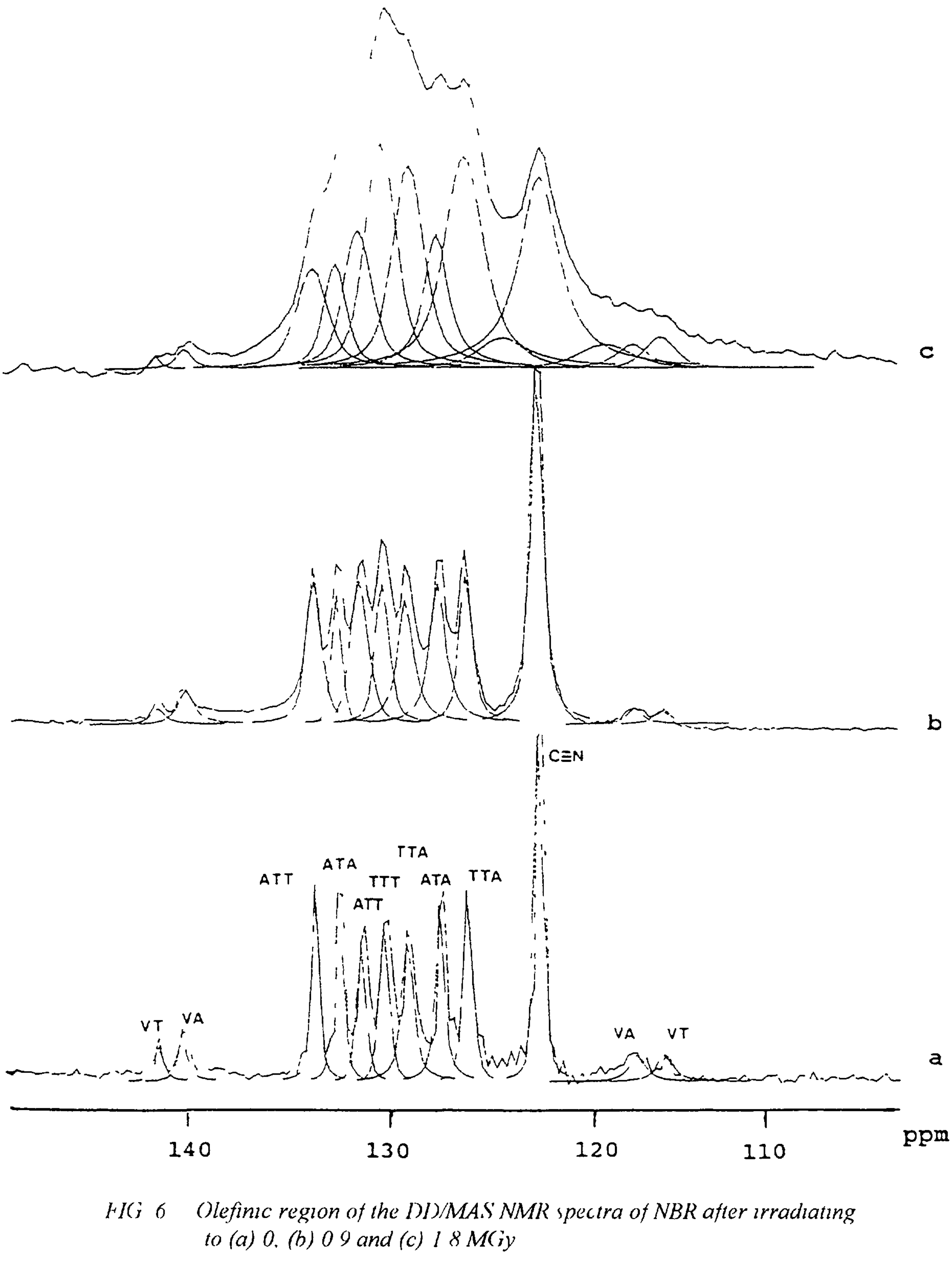

FIG 6 Olefinic region of the DD/MAS NMR spectra of NBR after irradiating to (a) 0, (b) 0 9 and (c) 1 8 MGy

2.7. Chloroprene rubber

ESR spectroscopy shows[9] the presence of radical anions and a variety of chlorinated allyl and polyenyl radicals when polychloroprene is exposed to high energy radiation, with G(R)=3.0. Solid state NMR was used to observe the crosslinking. In contrast to other diene rubbers (polybutadiene, polyisoprene, nitrile rubber) NMR spectra did not give higher G(X) values than other methods. For example, G(X) values calculated are 3.8(NMR), 4.8(Swelling Index) and 3.2(Soluble fraction). This suggests that crosslinking does not proceed through a kinetic chain reaction producing clusters. New chlorinated end group and main chain structures were identified.

3. POLYMETHACRYLATES

3.1. Polymethylmethacrylate [10]

The changes in the stereo regularity in isotactic polymethylmethacrylate (i-PMMA0 and syndiotactic polymethylmethacrylate (s-PMMA) were followed by changes in the tacticity of the α-methyl group observed by ^{13}C NMR. For i-PMMA, when the polymer is below Tg, there is no observable change in the tacticity during irradiation. However, when the polymer is irradiated above Tg, the increased chain mobility allows for the rotation of the main chain after the initial cleavage and rehealing of the main chain bond. A model for the reaction has been proposed in which the probability of recombination of the broken bond in to the meso or racemic configuration is equal to that observed during the free radical polymerisation of the polymer at the irradiated temperature. No other parameters are required. Similar results were obtained for s-PMMA.

3.1. Syndiotactic polymethacrylates

The gamma irradiation of syndiotactic polymethacrylates with various ester groups was investigated [11] by solution state NMR. Formate esters were observed among the small molecular products from the analysis of the NMR spectra of the polymers with aliphatic ester chains, but toluene and 1,2 diphenyl ethane were observed as the major products of the side chain scission in poly(benzyl methacrylate). The radiation chemical yields for scission and crosslinking calculated from GPC are given in Table VI. For poly(2-methyl heptyl methacrylate), G(S) was less than 4G(X), indicating gel formation.

TABLE VI. RADIATION CHEMICAL YIELDS FOR SCISSION AND CROSSLINKING IN POLYMETHACRYLATES

Ester Group	G(S)	G(X)
Methyl	1.1	0
Ethyl	1.7	0
Isopropyl	1.8	0
Isobutyl	0.8	0.1
n-Butyl	1.3	0.4
2-Methyl heptyl	0.3	0.5
Benzyl	0	0

3.3. Poly(2-hydroxyethyl methacrylate)

ESR spectroscopy was utilised [12] to examine the effect of high energy radiation on poly(2-hydroxyethyl methacrylate). The ESR spectrum at 77 K is a combination of six types of radicals, $\cdot CH_3$, $\cdot CH_2CH_2OH$, $\cdot COOCHCH_2OH$, $\cdot COO-$, methine and $\cdot CHO$. However, after room temperature irradiation, the spectrum is a combination of methacrylate main chain scission radical and a methine radical. The high stability of the methine radical at room temperature suggests the system is rigid as a result of hydrogen bonding from the inherent side chain structure and radiation induced crosslinking due to labile hydrogen atoms in the side chain.

4. POLYESTERS

4.1. Polyhydroxy butyrate [13]

The biodegradable polymer poly(hydroxy butyrate) PHB has attracted a wide amount of interest for applications which may require radiation sterilisation. Accordingly it is important to understand the radiation chemistry of these materials. PHB also undergoes chain scission on irradiation, due to the presence of radiation sensitive ester linkages in the polymer main chain. The primary yield of radicals determined by ESR is approximately G(R)=1.9 and 1.6 at 77 and 300 K respectively. The main gaseous products formed on irradiation were CO and CO_2, indicating that the cleavage of the ester group is indeed responsible for the degradation. The total G value for CO and CO_2 is 1.7 at 300 K. On warming, primary free radicals that are formed undergo further reaction leading to main chain scission. The GPC results indicate G(S)=1.3. The new structures formed on irradiation have been identified by solution state NMR, and the principle of these are the propyl and iso-propyl end groups formed by loss of the ester linkage. The yield of chain ends determined by NMR gives a G value of 1.4.

4.2. PolyLactic and Glycolic acids [14,15,16]

The effects of gamma irradiation on poly-L-lactic acid (L-PLA), poly-D,L-lactic acid (D,L-PLA), polyglycolic acid (PGA) and copolymers of PLA and PGA were examined using ESR and NMR spectroscopy. The G-values of radical formation at 77 K and 300 K are given in Table VII. The ESR spectrum at 300 K for the PLA is assigned to one radical, that resulting from hydrogen atom abstraction from the quaternary carbon atom. At 77 K three radicals were observed, the second and third due to main chain scission.

$-O-C(CH_3)-CO-$ $\qquad$ $-CH(CH_3)$ $\qquad$ $-CO$

Two radicals were observed in the ESR spectra of PGA. They were formed by main chain scission and elimination of ester group. The ESR spectrum at 300 K is due to one radical, that formed by hydrogen abstraction from methylene group.

The ^{13}C NMR spectrum of the irradiated PLA is shown in Figure 7. The three major peaks are due to CH3, CH and CO of the monomer unit lactic acid. The new peaks observed after irradiation were assigned with the help of HETCOR and COSY 2D NMR techniques and the results are given in Table VIII. The major new saturated chain ends formed on irradiation of PLA

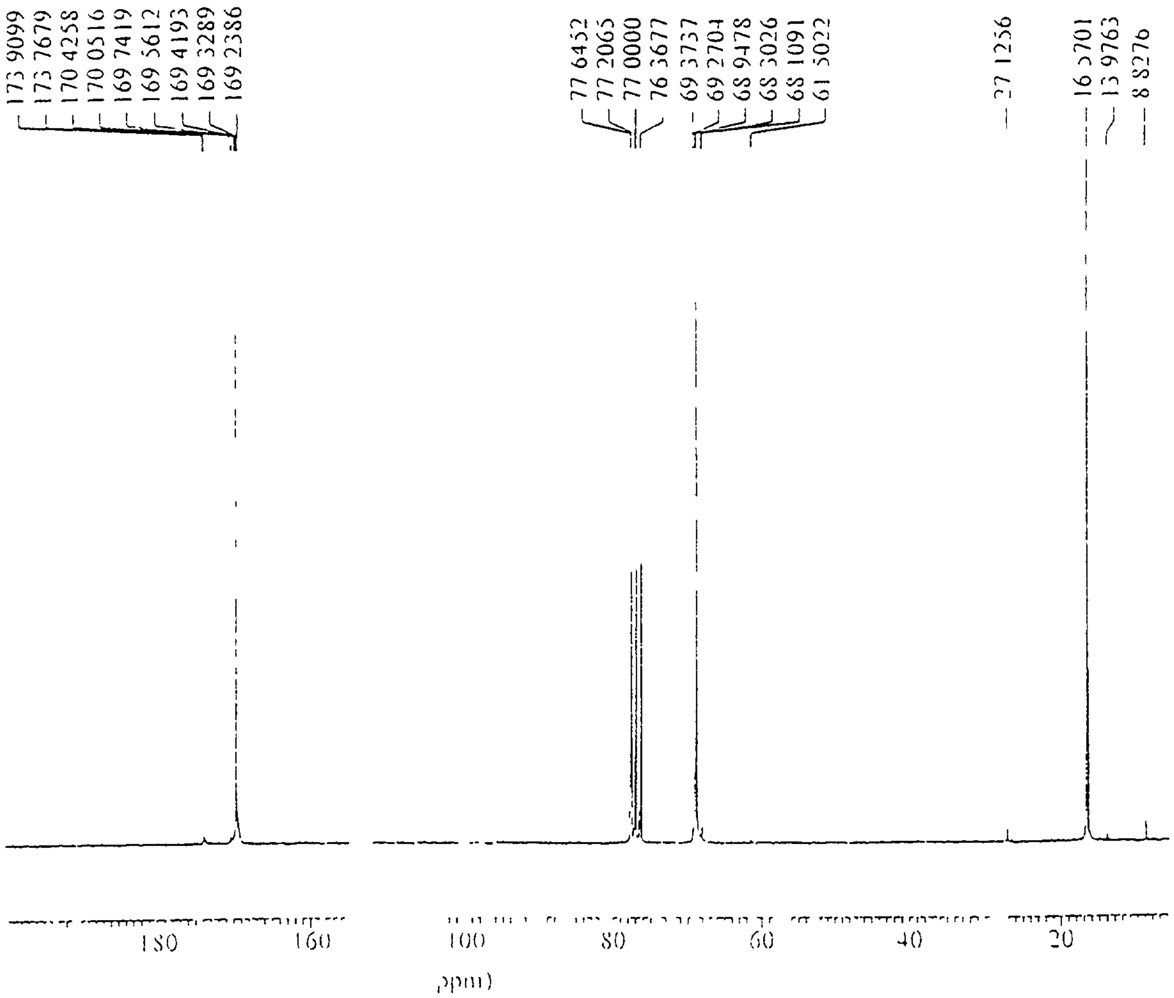

FIG 7 ^{13}C NMR spectrum of irradiated L-PLA

TABLE VII. RADIATION YIELDS OF RADICALS FOR POLY PLA, PGA

	77	300
L-PLA	2.0	1.5
D,L-PLA	2.4	1.2
PGA	1.7	1.5

have been found to be CH_3-CH_2-COO- and CH_3-CH_2-O-CO-. There is also evidence for the formation of esters of formic acid, HCOO-CH(CH_3)-COO- in low yields. Unsaturated chain ends such as CH_2=CH-COO- and CH_2=C(CH_3)-COO- were also identified. The yields of the major new structural changes were calculated from NMR and the G(CH_3-CH_2-COO-) was found to be similar to the value of G(S) obtained by molecular weight analysis.

TABLE VIII. ASSIGNMENT OF ^{13}C NMR SPECTRUM OF IRRADIATED PLA

Peak (ppm)	Assignment
8.83	Methyl of CH_3-CH_2-CO-O-
13.98	Methyl of CH_3-CH_2-O-CO-
27.13	Methylene of CH_3-CH_2-CO-O
61.5	Methylene of CH_3-CH_2-O-CO-
170.42	Carbonyl of CH_3-CH_2-O-CO-
173.90	Carbonyl of CH_3-CH_2-CO-O-

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DEVELOPMENT OF FORMULATIONS OF POLYETHYLENE-BASED FLAME RETARDANT, RADIATION RESISTANT WIRES AND RADIATION-COMPATIBLE POLYPROPYLENE

S. AHMED,
Pakistan Institute of Nuclear Science & Technology,
Islamabad, Pakistan

ZHOU RUIMIN
Shanghai University of Science & Technology,
Jiading, Shanghai, China

Abstract

Formulations of fire retardant and heat resistant insulations have been developed using low density polyethylene (LDPE) as the base polymer and a cobalt facility as the irradiation source. Addition of suitable antioxidants, processing stabilisers, flame-retardant materials, lubricants and agents for catalysing the crosslinking process has been made to impart the desired properties to the insulation. Optimum radiation dose and ideal conditions for irradiation of batches of wires have been explored. TGA and DTA studies have been carried out to assess thermal stability imparted by the addition of the antioxidants to the formulation. As part of endeavours to develop radiation compatible formulations of (*i*) polypropylene, the influence of the nucleating agent p(t-butyl) benzoic aluminium on various crystallisation parameters, e.g. Tp, Tonset Δ H (heat of crystallisation) and Tm has been investigated. Clarity is adversely influenced on addition of the nucleating agents. Gains in thermal stability were found as determined by TGA and DTA of the blends of the nucleating agent with (*i*) polypropylene.

SECTION-A: DEVELOPMENT OF FORMULATIONS OF FLAME RETARDANT AND RADIATION RESISTANT WIRES USING COBALT-60 AS IRRADIATION SOURCE

1. INTRODUCTION

High specialty fire retardant and heat resistant thin wires find use in the field of electronics, automobiles, large commercial buildings and aeronautics. Radiation resistant wires are used worldwide in electron beam (EB) installations, γ-ray facilities and nuclear power stations. One of the problems encountered in developing new applications is that of relating experimental results to an industrial production situation. Because of the high cost of evaluating experimental materials on electron beam production lines, studies are needed for assessing the suitability of gamma radiation sources by a batch process. Another major impediment in the way of transfer of radiation technology in developing countries is the proprietary nature of formulation. Work in developing countries remains confined to a study and production of chemically crosslinkable materials. The need for indigenous development of these formulations prompted us to carry out this work.

2. EXPERIMENTAL

2.1. Materials

LDPE used was of commercial grade. Antioxidant, Irganox-1010 (Ciba-Geigy) and DLTP (Monsanto Corp. USA) lubricant and decabromodiphenylether oxide were used as such without further purification. Antimony trioxide (Sb_2O_3, BDH) was of analytical grade.

2.1.1. Mixing of materials

The materials were mixed together thoroughly and then hot-blended using a Haake type mixer at 145°C and at fixed RPM of 45 for 10 minutes, followed by granulation of the product. Sheets for testing for tensile strength and elongation % at rupture were prepared by heat pressing the product under a pressure of 150 kg cm^{-2} for 5 minutes at 200°C using a spacer of 0.5 mm after preheating of the product for 10 minutes at the same temperature. The product was immediately cooled between the plates of a cold press at 25°C. The test pieces (dumbbell-shaped specimens of 0.5 mm thickness) for the tensile tests were cut from the pressed sheet.

2.2. Extrusion of wires

The granulated material was extruded on to a copper conductor (diameter 0.90 mm) using the industrial extrusion facility at Prime Cables Ltd. Lahore. The diameter of the finished wire in case of all the wires was 4.1 mm.

2.3. Irradiation and post irradiation measurements

The wires were irradiated using γ-rays from a Co-60 source at ~1 kGy per hour rate at PARAS (Pakistan Radiation Services), an irradiation facility at Lahore. To avoid oxidation due to long residence times required for irradiation up to a level of 15 Mrads, two modes of packing were specially adopted:

i). The wires in spool form were vacuum packed.
ii). The wire spools were packed using heat shrinkable film.

For comparison the irradiation of wire spools was also carried out in tightly packed PE bags.

2.4. Thermogravimetric analysis (TGA)

TGA was carried out using simultaneous thermal analyses by Netzsch Germany, with Pt:10% Rd thermocouple at a heating rate of 15°C min^{-1} in the temperature range of 25-800°C at a flow rate of 200 cm^3 min^{-1}.

3. TESTS AND PROCEDURES

3.1. Gel fraction determination

The gel-fraction was determined by boiling the test samples (300 mg) in commercial grade xylene for 24 hours, followed by weighing the remaining insoluble fraction after drying to a constant weight using a Soxhlet apparatus.

3.2. Hot set test

The irradiated finished wire insulation samples were put in the oven preheated for 15 minutes at 200°C and with some standard weight (area in mm^2 x 20 N) at the end of the sample. The test corresponds to the IEC 502/540 standard. The samples should not elongate more than 175 % at the end of the test.

4. RESULTS AND DISCUSSION

4.1.Formulation and testing of radiation crosslinked PE insulation

The flame retardant PE formulation was as shown below:

Polymer	LDPE
Antioxidants	Primary: Irganox 1010 Secondary: DLTP
Fire retardants	Antimony trioxide (Sb_2O_3) and Decabromodiphenylether oxide
Lubricant,	Dibasic lead sulphate
Crosslinking catalyst	TMPTA

4.1.1. Tests

The wire drawn was smooth and its appearance was very good. The results of various tests carried out are as shown below:

Oxygen index (01)	29%
Tensile strength, Tb	5.6 N/mm^2
Elongation at break, Eb	242%
Electric volume resistance	20 M Ω
High voltage test (AC)	5 kV, no breakdown.

The gel fraction of insulation, packed under vacuum and irradiated at doses of 120 kGy, 150 kGy and 170 kGy were as shown below:

Dose (kGy)	Gel fraction %
120	48.30
150	53.00
170	60.00

In the formulation the lubricant was added at 1 phr level; its quantity should be kept lower to get insulation with better tensile strength properties. An alternate for decabromodiphenylether oxide is a mixture of magnesium hydroxide and aluminum hydroxide. The use of decabromodiphenyloxide (halogen containing additives) because of its implicated nature as an ozone depleting substance is not permitted.(1) For the improvement of tensile strength addition of 1% carbon black is desirable. The wire vacuum packed and irradiated at 180 kGy dose was found to pass a hot-set test. Other wires irradiated at 120 kGy, 150 kGy failed the test.

4.2. Formulation and testing of heat resistant radiation crosslinked PE insulation

Heat resistance is a desirable property when wire is used in a hot environment or in the tropical countries. In this formulation, addition of MB (mercaptobenzoimidozole) was made to impart the desired properties. Rest of the formulation remained unchanged.

4.2.1. Tests

Tensile strength, Tb	10.2 N/mm^2
Elongation % at break, Eb	>300
High voltage test (AC)	5 kV, no breakdown
Electric volume resistance	20 MΩ

A heat ageing test carried out by keeping the sample at 158°C for 168 hours in a Gear type oven demonstrated retention of at least 75% properties of tensile strength and elongation % at rupture, Eb.

The wire irradiated at 180 kGy, packed under vacuum conditions, passed the hot set test showing that the desired crosslinking had been achieved. Wires irradiated to doses of 100 and 150 kGy failed the test.

4.3. Formulation and testing of radiation resistant, radiation crosslinked PE insulation

PE is a preferred olefin compared to polypropylene and PVC because it has a better radiation resistance. This property alone, however, will not suffice for use in nuclear power stations and in the environment of high radiation activity. To achieve this, a radiation resistance imparting agent, UV-531, was added. The formulation was as shown below:

i). LDPE
ii). DLTP and Irganox-1010
iii). UV-531
iv). TMPTA
v). Lubricant

4.3.1. Tests

Tensile tests demonstrated quite low values so another formulation containing less quantity of lubricant was prepared.

The test results were as under:-

Tensile strength, Tb	10 N/mm^2
Elongation % at break, Eb	>200
High voltage test (AC)	5 kV, no breakdown

All the wires irradiated at 120, 150 or 180 kGy did not pass the hot-set test. A test of radiation resistance of a wire (to be used in nuclear power station) necessitates the exposure of wire to 70 Mrad (in USA) or 50 Mrad (in Japan) [2] and is meant to represent an exposure of wires in a power station for 40 years. The test is to be completed.

4.3.2. Optimum radiation dose for all wires

An assessment of the changes in properties, in general, suggested that a radiation dose of 180 kGy produces an optimum level of properties. A larger dose such as 200 kGy gave a minimal improvement whereas smaller doses such as 150 kGy and 120 kGy did not produce wire which could pass a hot-set test, showing thereby the inadequate crosslinking.

4.3.3. Wire insulation stability tests

Thermogravimetric analysis of flame retardant formulation irradiated to a dose of 175 kGy and of the same formulation prepared under identical conditions, but without antioxidants Irganox 1010 and DLTP, showed that the formulation without antioxidant and the one containing the antioxidant started to decompose at around 340°C and the losses in weight at 20%, 40%, 60% and 80% also occurred at around same temperatures (Table I). In DTA of the samples, however, changes corresponding to oxidation and degradation of the molecular chain appear to occur at slightly elevated temperatures as shown in Figure 1. The thermogravimetric analysis was carried out under static condition as well as with flow of air. TGA of both the samples, when carried out under air-flow conditions, was identical.

TABLE I. THERMOGRAVIMETRIC ANALYSIS OF FLAME RETARDANT FORMULATIONS

Nature of sample	Losses % at Temperature (°C)				
	10	20	40	60	80
FR Formulation containing antioxidants	355	370	460	480	500
FR Formulation without antioxidants	350	370	460	480	500

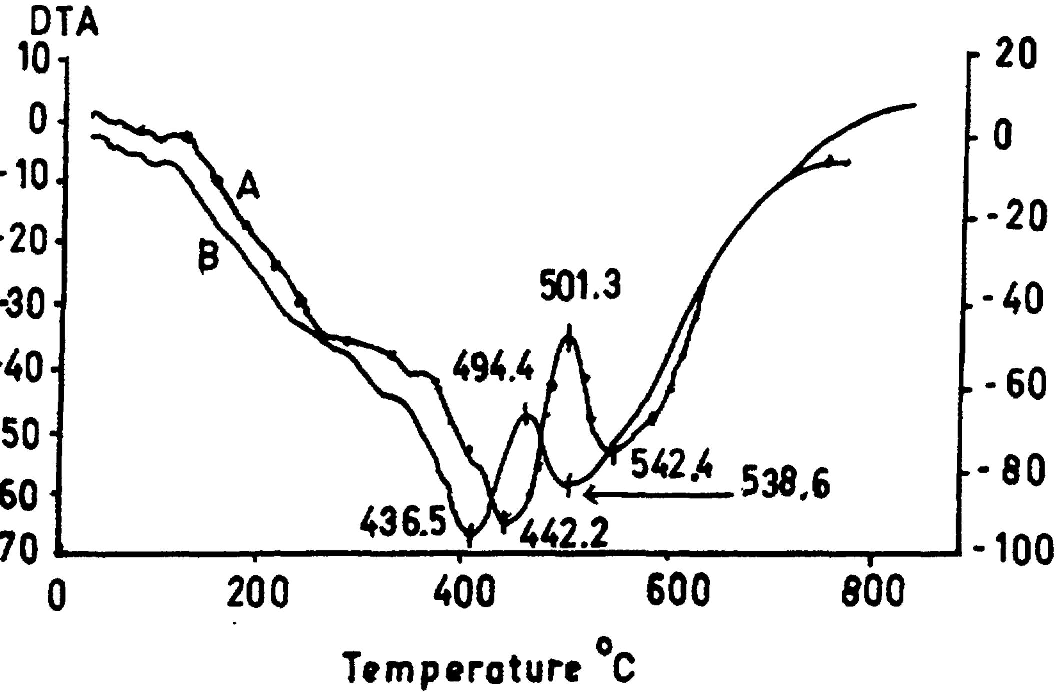

FIG. 1. DTA Curves of Flame - Retardant formulation FR 105 (Irradiation dose 175 kGy) (A).Complete formulations (B).Formulation without antioxidants.

5. CONCLUSION

Formulations developed for fire retardant, heat resistant and radiation resistant insulations can be irradiated to achieve the desired properties using a Cobalt-60 source using special procedures. Vacuum packaging of wires, their packaging by heat shrinkable film or packing tightly in minimum air condition were techniques applied to achieve the desired results. All wires (except the radiation resistant wire formulation which failed in the hot-set test) pass the electrical and mechanical tests expected from such wires. The presence of antioxidants plays an important role in protection and retention of mechanical properties of wires during ageing.

SECTION-B: DEVELOPMENT OF RADIATION RESISTANT POLYPROPYLENE: A DSC/TGA STUDY OF THE HETEROGENEOUS NUCLEATION OF CRYSTALLIZATION IN POLYPROPYLENE COPOLYMER

1. INTRODUCTION

Nucleating agents are added to PP in order to obtain optimum physical properties. It has been reported that the addition of nucleating agent changes the polymer's crystallization temperature, spherulite size, density, clarity, impact and tensile properties considerably [2]. In this paper we report crystallization of a random copolymer of PP with 6% ethylene with a nucleating agent, *p*-(t-butyl) benzoic aluminium, with the nucleating agent content varying from 0.1% to 2%. The random copolymer of PP with 6% ethylene has been particularly selected in view of its reported improved radiation stability compared to pure polypropylene due to lower crystallinity of the former [3].Various crystallization parameters were estimated from differential scanning calorimetry. TGA has been carried out to assess thermal stability conferred upon propylene copolymer by the addition of nucleating agent.

2. EXPERIMENTAL

2.1. Materials

Polypropylene copolymer containing 6% ethylene was from Chisso Corporation Japan. The nucleating agent (NA) used was (t-butyl) benzoic aluminum and was used as such without further purification.

2.2. Mixing of materials

The mixing of copolymer with nucleating agent was carried out using a "Haake" mixer (Germany) at 40 r.p.m and 140°C. The product was compressed into sheets by molding under a pressure of 150 kg/mm^2 for 3 minutes at 170°C using a spaces of 0.5 mm after preheating for 5-7 minutes at the same temperature. The hot sheets were then immediately cooled between the plates of a cold press at room temperature. For comparison of clarity, thin films were prepared by heat pressing the aforementioned sheet between aluminum foil at 170-180°C and under a pressure of 150 kg/mm^2.

2.3. Measurements

For TGA/DSC studies, a Simultaneous Thermal Analyzer by Netzsch, Germany was used. The measurements were carried out at a heating rate of 5°C min^{-1} for DSC studies. The cell was heated from room temperature to 185°C, and held for 15 minutes in order to eliminate any crystallization memory. Thermograms were acquired during the heating cycle and during the cooling cycle under static conditions. As all the experiments were carried out under identical setting, the data generated could be used to directly compare crystallization parameters. To ensure reproducibility of results, the measurements were done on at least 3 samples of each composite composition.

Thermal gravimetric analysis and DTA of the copolymer and the blends were carried out by taking the sample in the crucible of the Netzsch (Simultaneous Thermal Analyzer) STA 509 with S:Pt thermocouple at a heating rate of 5°C min^{-1} in the temperature range 25-600°C and at a flow rate of 200 cm^3 min^{-1}.

3. RESULTS AND DISCUSSION

3.1. DSC Thermograms of crystallization of propylene copolymer and blends

As mentioned earlier, a factor of considerable importance is the influence exerted by varying amounts of the nucleating agent on the degree of supercooling of propylene copolymer denoted by T_p-T_m. T_p is the peak temperature and occurs at the intercept of the tangents to the sides of the exothermic curve and is a measure of the temperature when the bulk of the polymer has crystallized. Figure 2 shows a “closed loop” thermogram of the melting and crystallization of pure copolymer; the degree of supercooling exhibited is around 36.5°C.

Figure 2 shows two peaks belonging to pure copolymer and blend containing 2% NA. Prominent crystallization exotherm peaks were observed for the copolymer as well as blends with nucleating agent. A steady increase of about 5°C up to 2% volume of the nucleating agent was observed (Table II) resulting in the decrease in super cooling. In the mass production of medical supplies, it means that the molding cycle will be shorter and hence more economical.

Various crystallization parameters estimated from the DSC thermograms included (Table III) T_{onset}, T_c-T_p, Si, ΔH, and ΔW and the significance of these parameters are described here and illustrated for clarity in Figure III.

1. T_{onset} is the temperature of onset of crystallization which is the temperature when the thermogam initially vertically deviates from the baseline on the high temperature side of exotherm.

2. Another temperature described as the “constructed temperature” and referred to as T_c is obtained at the intercept of tangents to the base line and high temperature side of the exothermic peak.

3. The rate of nucleation is also indicated by the parameter Si.

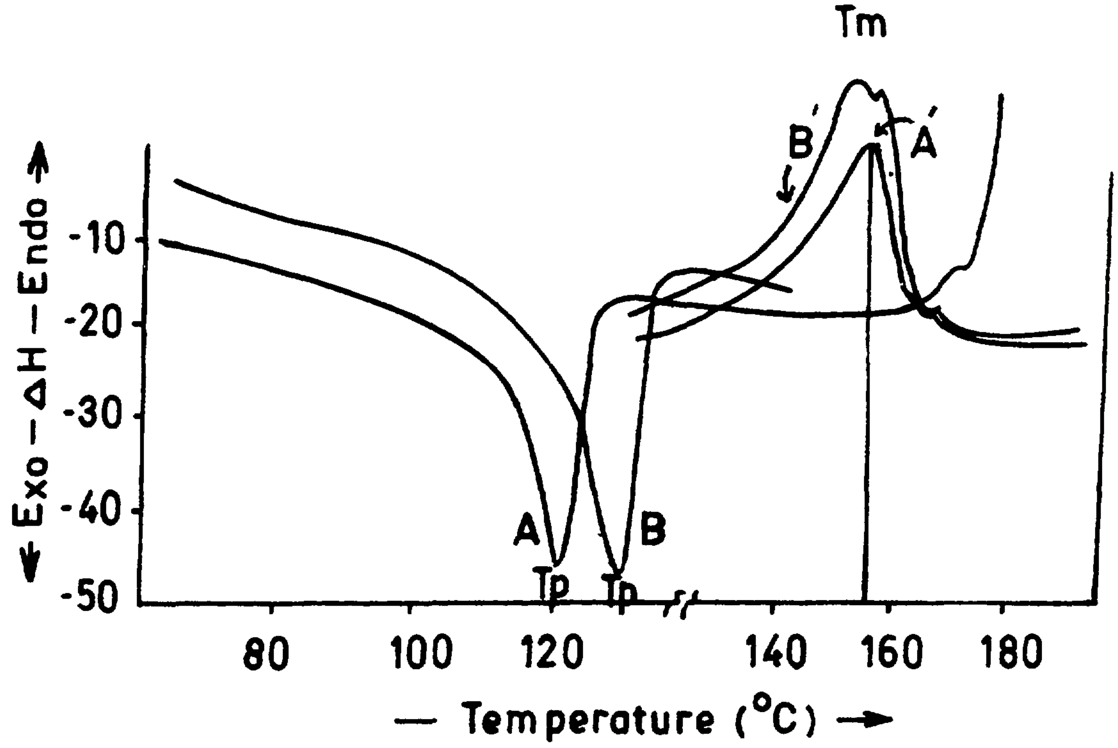

FIG. 2. DSC Exotherms
(A) Crystallisation curve of PP (Co), *('A) Its melting curve*
(B) Crystallisation curve of PP (Co) +2% NA, *('B) Its melting curve.*

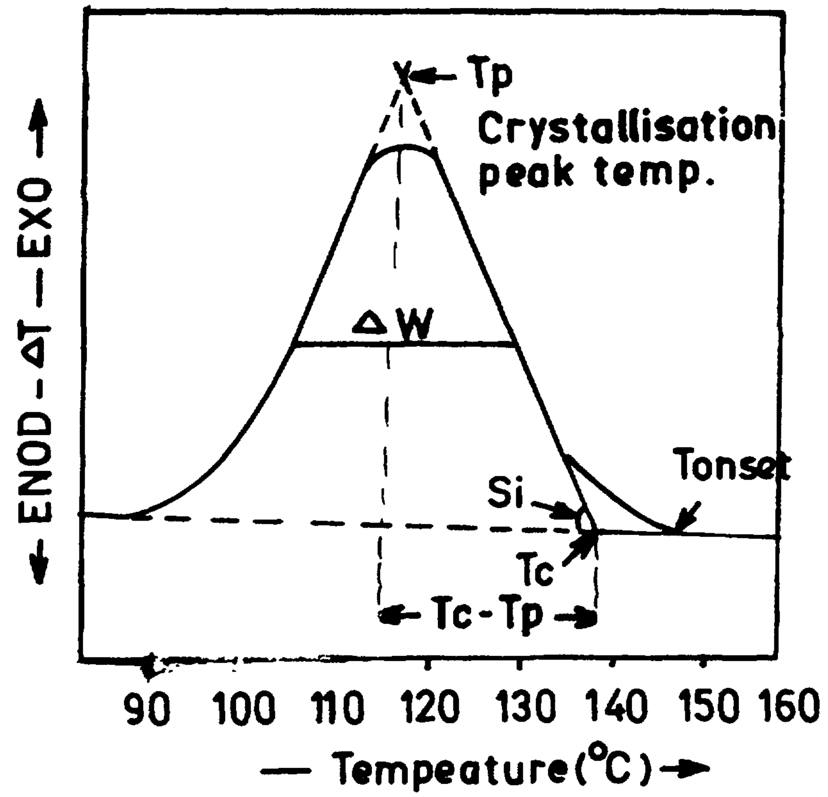

FIG. 3. Schematic of the method of estimation of various crystallisation parameters from the DSC crystallisation exotherm peak.

TABLE II. VALUES OF VARIOUS CRYSTALLIZATION PARAMETERS OF PP (Co) IN PP (Co)/NA BLENDS FROM DSC AND T_m VALUES.

T_m (°C)	Sample Composition	$T_{(P)}$ (°C)	$T_{(on\ set)}$ (°C)	T_cTp (°C)	ΔW arbitrary units	ΔH J/G
156.5	PP(co)	120	129	7.5	10 mm	95.01
156.4	PP(co)+0.1% NA	122.4	129.25	6.85	10 mm	86.65
155.1	PP(co)+0.25% NA	122.8	128	5.2	10 mm	63.71
154.7	PP(co)+0.5% NA	123.4	129.8	6.4	11 mm	81.09
150.6	PP(co)+1.0% NA	124.3	130	5.9	9 mm	78.03
150.0	PP(co)+2.0% NA	126	132	6.0	8 mm	91.25

TABLE III. THERMOGRAVIMETRIC ANALYSIS OF PP COPOLYMER AND PP (COPOLYMER + NUCLEATING AGENT BLENDS).

Nature of sample	Losses % at Temperature (C°)				
	10	20	40	60	80
Pure PP(Co)	290	320	350		400
PP(co)+0.1% NA	280	320	350	370	410
PP(co)+0.25% NA	280	320	350	370	410
PP(co)+0.5% NA	290	340	370	390	410
PP(co)+1.0% NA	320	350	400	415	430
PP(co)+2.0% NA	300	350	400	410	430

4. The quantity T_c-T_p indicates the overall rate of crystallisation. The smaller the value the greater the rate of crystallisation.

5. The width at half-height of the exothermic peak is denoted by ΔW which is a measure of crystallite size distribution; the smaller the ΔW, the narrower the distribution and vice versa.

6. The quantity ΔH is the measure of the heat of crystallisation.

T_c-T_p value was found to decline generally from pure copolymer to blends containing higher amounts of nucleating agent. It demonstrates an increase in the overall rate of nucleation. With increase in T_p, the corresponding increase in T_{onset} would be expected which is indeed the case as exhibited by higher values of T_{onset}. Si was found to increase progressively with the increase in quantity of additive. An increase in Si upon addition of nucleating agent was observed in polypropylene by Beck etal. [4].

ΔW values were unchanged at lower volumes of the nucleating agent. However a decline in value was observed in blends containing 1% or 2% as well as a narrower distribution. This presumably could be due to a faster rate of crystallization culminating in similar size of spherulites and thus narrower distribution.

The ΔH values were found to be low for the blends, demonstrating a low trend for 0.1, 0.25, 0.5% of nucleating agent, but the sample containing 2% of NA registered an increase. Although a higher rate of crystallization is achieved, the nucleating agent appears to depress the heat of crystallization, presumably due to suppression of the activation energy barrier thus facilitating the formation of crystallites requiring less thermal input.

Prominent melting endothermic peaks of PP copolymer and its blends with NA were observed. T_m is found to decrease steadily, and a lowering of 5°C in the blend containing 2%NA is observed (Table II). The decrease could be attributed to the depressing of melting point induced by impurities, as generally observed in the melting behavior of organic compounds.

3.2. TGA of copolymer and blends

In the blend range containing 0.1% to 0.5% of NA, the thermograms show no improvement in thermal degradation rate, as shown in Table III. In the blend range 1% and 2%, considerable increase in temperature for losses of weight at 10%, 20%, 40%, 60% and 80% of the polymer was observed, indicating imparting of thermal stability to the blends by the nucleating agent

3.3. Clarity of PP copolymer blends

The visual examination of thin films of copolymer, and those belonging to blends with NA, showed progressive increase in haze (lack of clarity) with the increase in amount of NA from 0.1 to 2 volume percentage. Our results agree with the observations of Zarah et al [5] who have concluded that the addition of the nucleating agent t-butyl (benzoic aluminium) did not improve the transparency, but a higher value of Tp was observed. This study however was confined to only addition of 0.1 % NA and recording of only one of the crystallization parameters, T_p.

4. CONCLUSION

Three desirable properties needed to be improved in polypropylene comprise clarity, an increase in crystallization temperature and radiation resistance. Somewhat moderate improvement in T_p (or degree of supercooling) has been observed on addition of NA. The clarity seems to be affected adversely on addition of higher amounts of NA. As regards radiation resistance, one may expect that with the decreasing amorphous fraction of PP in the copolymer, the radiation resistance will be also not favourably influenced due to morphology. The dependence of radical termination rates on percent crystallinity in gamma irradiated isostactic polypropylene has been reported by Dunn et al [6]. Gains in thermal stability associated with the addition of NA can be exploited in applications where clarity and radiation resistance may not be important considerations.

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LIST OF PARTICIPANTS

Ahmed, S.	Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, Nilor-Islamabad, Pakistan
Baccaro, S.	ENEA-Dipartimento Innovazione, Divisione Servizi Tecnologici, INN/TEC/IRR Centro Ricerche Casaccia, Via Anguillarese 301-00060, Rome, Italy
Clough, R.L.	Materials Aging and Reliability Department, SANDIA National Laboratories, P.O. Box 5800, MS 1407, Albuquerque, New Mexico 87185, United States of America
Feldman, V.I.	Karpov Institute of Physical Chemistry, Vorontsovo Pole Str. 10, Moscow 103064, Russian Federation
González, M.E.	Unit of Industrial and Technological Applications, Centro Atomico Ezeiza, Comision Nacional de Energia Atomica, Av. Libertador 8250, 1429 Buenos Aires, Argentina
Güven, O. *(Scientific Secretary)*	International Atomic Energy Agency, Wagramerstrasse 5, P.O. Box 100, A-1400 Vienna, Austria
Perera, S.	School of Science, Griffith University, Nathan, Australia
Ranogajec, F.	Department of Materials Chemistry Ruder Boskovic Institute, Bijenicka cesta 54, 10000 Zagreb, Croatia
Sun, J.	Department of Radiation Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, People St. 159, Changcun, China
Tavlet, M.	European Organization for Nuclear Research, CH-1211 Geneva 23, Switzerland