

## Developments in Electron Beam Processing in Polymer and Petroleum Industries

Olgun Güven

Department of Chemistry  
Hacettepe University  
Beytepe, 06800, Ankara  
Turkey  
[guven@hacettepe.edu.tr](mailto:guven@hacettepe.edu.tr)  
[www.polymer.hacettepe.edu.tr](http://www.polymer.hacettepe.edu.tr)

**Abstract:** Recent estimates show that out of about 1400 electron accelerator units currently in use for industrial applications throughout the world, 1200 are being used for plastics and rubber processing. Commercial availability of new low, medium and high energy electron accelerators with varying powers and innovative formulations for better radiation processing of polymers have brought a synergy into electron beam processing in polymer industry. The objective of this paper is to highlight recent developments and emerging applications of radiation processing in polymer and petroleum processing industries. The emphasis will be made on the preparation of fuel cell membranes for low temperature fuel cells, specialty adsorbents for recovery of useful metals/removal of toxic chemical species from aqueous systems, nanostructuring of surfaces for tissue engineering, modification of fluorinated polymers as solid lubricants, advanced materials for biomedical applications, composites for automotive and aviation industries and upgrading of heavy oil.

### 1. Introduction

Radiation induced chemical changes brought about by the interaction of high-energy radiation with matter opened the way to a number of applications in health-care, agriculture, environmental protection and various industries. The early expectations in the use of ionizing radiation were very high and radiation chemistry was regarded as a tool for developing new and exotic materials and products. Over the years when all these applications were evaluated from technical and economic feasibility points of view only several areas have been identified to be of commercial viability. Among the early applications of radiation processing, radiation-induced crosslinking of polymers and radiation sterilization of single-use medical products have developed into large scale industries. The commonality of these two applications is the controlling of beneficial effect of ionizing radiation on macromolecules through free radical chemistry.

The irradiation of polymeric materials with ionizing radiation (gamma rays, X-rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates. These intermediates can follow several reaction paths which result in rearrangements and/or formation of new bonds. The ultimate effects of these reactions can be the formation of oxidized products, grafts, scissioning of main chain (degradation) or side chains or crosslinking. The degree of these transformations depends on the structure of polymer (presence or absence of radiation resistant groups such as aromatic groups, double substitution on a carbon atom on the main chain) and conditions of treatment before, during and after the

irradiation. Good control of all these processing factors facilitates the modification of polymers by radiation processing.

When the application of radiation processing in polymer and plastics industries is considered, the crosslinking effects are seen to dominate the field. In fact the first industrial use of electron accelerators started in late 1950s with the crosslinking of polyethylene wire insulation. Crosslinking is the formation of a three-dimensional network. Such networks are insoluble and infusible imparting superior mechanical and thermal properties to starting polymers. Radiation-induced crosslinking has already become a mature technology encompassing wide range of applications. Currently more than half of all of the industrial electron accelerators in the world are used in crosslinking of polyethylene. There are four major end-uses that are based on radiation-induced crosslinking of polyethylene:

- Wire and cable insulation
- Heat shrinkable tubing and sheets
- Polyethylene tubes for water supply and distribution
- Controlled density closed-cell foams

Radiation-induced polymerization/crosslinking is also widely accepted for the high speed curing of coatings and for the production of composite materials. It is therefore not surprising to see that currently out of about 1400 electron accelerator units in use worldwide, ~1200 are being used in polymer and plastics based industries. When the two major tools of radiation processing namely gamma irradiators and electron accelerators are compared, practical and economic considerations have initially favored the use of low-energy electron accelerators for applications requiring intense radiation with limited range whereas gamma-ray sources have been preferred where diffuse penetrating radiation is needed. The complementary nature of these technologies however, has become competitive as more powerful, high-energy accelerators are developed in response to increasing demand for the treatment of dense materials. Electron accelerators with low and high energies with very high powers are finding increasing new applications in material processing and for the conservation of environment. The limited penetration of even 10 MeV electron beams in polymeric materials prompted the development of X-ray generators. Industrially useful X-ray generation has the potential of becoming a major tool in radiation processing of dense and bulky materials. A significant difference exists between electron beam and gamma processing of polymers which is related to dose rate effect and ultimately to the oxidative degradation of the polymer at or near the surface.

Although crosslinking effect is still dominating in all industrially established applications of ionizing radiation, curing, chain scissioning and grafting are the other major effects that the polymer and more recently petroleum industries benefit. In the following some of the recent developments in electron beam processing of polymer and petroleum industries will be reviewed.

## **2. Polymer Processing**

### **2.1 Crosslinking of Synthetic Polymers**

Crosslinking is direct chemical bonding of one polymer chain to another which may occur at one or more points along the chain hence yielding different crosslink densities. The ultimate effect is the formation of three dimensional network which are insoluble and infusible. When polymers are irradiated they may undergo chain scissioning simultaneously with crosslinking. Predominance of either effect is determined by polymer chain structure,

irradiation atmosphere, presence or absence of some additives and dose rate. Extensive research work on the effect of ionizing radiation on polymers in either of these two forms, namely crosslinking and chain scission have shown that these processes take place exclusively in the amorphous phases of polymers. Since semi-crystalline polymers turn into fully amorphous structures above their melting points, during the last decade irradiation of certain polymers at relatively high temperatures had proven to show much improved efficiency in crosslinking [1]. Radiation-induced crosslinking of poly(tetrafluoroethylene) Teflon in inert atmospheres at high temperatures was such a surprising result [2]. At a crosslinking dose of ~100 kGy the wear and radiation resistance of Teflon has been improved by 3 orders of magnitude while maintaining its chemical and electrical properties [3]. Significant increase in the hardness of some engineering plastics such as polycarbonate and polysulfone has been shown to be achieved when they are irradiated at high temperatures. The efficiency of crosslinking has been shown to be much improved when polysulfone is irradiated in molten state as compared to irradiation carried out below its glass transition temperature [4]. An apparatus for continuous modification of polymers in the free-flowing state by means of electron irradiation has been developed and patented [5].

The use of some reactive compounds that would promote crosslinking has been shown to be very effective in room temperature crosslinking of poly(tetrafluoroethylene), polypropylene which would otherwise degrade upon irradiation and ultrahigh molecular weight polyethylene. PTFE with higher wear resistance and enhanced radiation stability has been shown to be obtained when it is EB crosslinked in the presence of acetylene at room temperature [6]. Electron beam crosslinking of atactic polypropylene in the presence of three or four functional crosslinking agents has been shown to yield 60% gelation at a dose of 200kGy which can be used as a new elastomer [7]. Acetabular cups initially machined into final dimensions were irradiated to 100kGy dose in the presence of acetylene yielded products with a crosslinked surface layer of 300 $\mu$ m [8].

The wear and tear resistance of prostheses made of ultrahigh molecular weight polyethylene used in hip and knee replacement surgeries were significantly improved by electron beam crosslinking. The problems associated with trapped radicals have been shown to be solved by incorporating minimal amounts of vitamin E,  $\alpha$ -tocopherol into the base material [9,10]. Ultrahigh molecular weight polymer blends with high wear resistance, high level of fatigue and crack propagation resistance have been claimed to be obtained by radiation induced crosslinking [11].

Heat resistance of connectors, relays, etc. used in automotive industry made of engineering plastics such as polyamides and poly(butylene terephthalate) have been improved to desired product properties by electron beam crosslinking [12].

## 2.2 Crosslinking of Natural Polymers

The desirable characteristics of natural polymers such as abundance, easy availability, biocompatibility, biodegradability have made them very attractive to explore their applications particularly polysaccharides in health care and agriculture. The functional properties of polysaccharides are directly linked to their structure. Therefore, a method to modify structure, without introducing new chemical groups, could prove of advantage, particularly if the process could be achieved in the solid state. Attempts to apply high energy ionizing radiation to polysaccharides has proved unsuccessful, since the main result of treatment with high energy ionizing radiation, either in the solid state or in solution is degradation due to the action of free radicals formed by the radiation. A method has been developed however, which allows the controlled modification of the structure of

polysaccharide hydrocolloids and other related materials in the solid state using ionizing radiation in the presence of a mediating alkyne gas [13]. The range of materials modified by this process includes non-substituted polysaccharides extending over both plant and animal derived polysaccharides, whether charged or uncharged. The process has also been applied to proteins either directly derived from animal connective tissue sources such as collagen, gelatine, and from human and animal products, such as casein, combinations of one or more such polysaccharides with proteins of plant origin, such as arabinogalactan proteins, biological tissues and materials derived therefrom used for tissue replacement and transplantation. A wide range of polysaccharides and proteins can be modified by the radiation mediated process such that their molecular dimensions can be increased in a controlled manner. If the process is continued beyond the limit of aqueous solubility, a hydrogel is formed. Blends of different polysaccharides or polysaccharides - proteins can also be joined using the process.

Another approach to radiation crosslink otherwise degradable polysaccharides has been to irradiate them in highly concentrated solutions. Radiation crosslinked carboxymethyl cellulose and similar derivatives were claimed to be suitable as health care products as surgical operation mats for the prevention of bedsores [14]. In aqueous solution at low concentration, gum arabic is known mainly to degrade however, in highly concentrated aqueous solutions, crosslinking occurred with minimal degradation. This novel crosslinking of gum arabic occurred without the need for any additives and only by using high solute concentrations. Such polymerized gum arabic could be useful as a component in food, cosmetic, agricultural, and hygienic materials [15].

## **2.3 Curing**

### **2.3.1 Polymeric Composites**

Radiation curing represents the second largest commercial application of radiation processing. Curing is three-dimensional polymerization of unsaturated oligomers or oligomer-monomer mixtures. Radiation curing is a faster process than thermal curing, consumes also much less Energy, it is a room temperature process, requiring less working space than thermal facilities and more environmental friendly. The extensive R & D works carried out during the last decades have shown that advanced composites can be easily radiation cured by electron beams and X-rays at very high throughput rates. The repair of fibre-reinforced composites by electron beam curing has seen a breakthrough with developments that allow conventional epoxies used by the aerospace industry to be cured by accelerated electrons. Composite components make up 20-25% of the structural weight of an Airbus 320 aircraft, it is therefore vital to use a repair technique for any components that get damaged. Satisfactory repair of aircraft parts has been demonstrated and a facility to repair aircraft parts by electron beams was built [16].

One of the most widespread applications of radiation curing is for the development of hard materials and surfaces. Radiation-curable nanocomposites in the form of functionalized alumina and silica particles have been successfully used for enhanced surface-mechanical properties [17]. Transparent, scratch and abrasion resistant coatings were obtained by radiation curing of acrylate formulations containing high amounts of nanofillers [18].

Since early 90s there has been a continuing interest in radiation curing of wood. Wood although obtained from renewable resource, decorative, cheap, so abundant, will suffer from microbial degradation and weathering in outdoor use if not protected. Natural wood

impregnated with monomeric materials such as hydroxy ethyl methacrylate that penetrate the walls of the lumens can be protected from microbial degradation and resist swelling when exposed to moisture. It has been shown that in-situ curing of monomers with high Energy X-rays is preferable to the use of high dose rate electron beams or thermo-chemical processes. Once incorporated into cellulose cell walls, these systems are not extractable as are historically used wood preservatives such as chromium, copper or arsenic salts that could leach out and contaminate the soil [19].

Radiation curing has also been considered as one of the most appropriate techniques for the fabrication of fibre-reinforced composites. Carbon fibre composites were cured in molds using X-rays derived from a high energy, high current electron beam. X-rays could penetrate the mold walls as well as the fibre reinforcements and simultaneously polymerize and crosslink the matrix system. Matrix materials made from modified epoxy acrylates were of low viscosity to ensure wetting and adhesion. Moderately low dose X-ray exposure was sufficient to attain functional properties such as resistance to heat distortions at temperatures as high as 180 °C. The matrix system contained an impact modifier which imparted toughness to the cured articles. Class A type high gloss surfaces were achieved. X-ray curing has proven to be a low temperature process that eliminates internal stresses which are imparted by conventional thermo-chemical processes. Two different X-ray cured carbon fibre vehicle fenders were produced in this way, one for a wide-wheeled motorcycle and the other for a sports car [20].

To improve the fiber-matrix adhesion in composites and upgrading polymer network toughness, these two major challenges have been investigated from several points of view such as the reduction of the matrix shrinkage on curing, the wettability of carbon fibers, the design of fiber-matrix interface and the use of thermoplastic toughening agents. Significant improvements were achieved on transverse strain at break by applying original surface treatments on the fibers so as to induce covalent coupling with the matrix [21].

### **2.3.2 Advanced Ceramic Matrix Composites**

During the last decades research in fiber reinforced ceramic matrix composites (CMCs) has been of increasing interest. The opportunities of CMCs for high temperature applications in oxidizing and/or corrosive environments arise from the combination of the positive properties of ceramic matrix and fibers as well as the elimination of the negative matrix properties like brittleness. For an extensive adoption of the CMCs the properties and the price of the fibers play a decisive role. Until recently there has been no ceramic fiber commercially available at reasonable costs, which offers high strength and Young's modulus, good creep resistance and oxidation stability beyond 1200 °C. Though carbon fibers are available in various qualities with different properties and prices, they are all susceptible to oxidation already at temperatures of about 400 °C. In contrast, ceramic oxide fibers are stable in air but they are susceptible to creep at temperatures above 1100 °C. The determination of the gel fraction is a very good and useful method to characterize the state of cross-linking in a polymer material. In the case of the polycarbosilazane ABSE precursor the gel fraction after e-beam curing depends on both the molecular weight of the polymer and the e-beam dose. Knowing these two parameters it is possible to adjust the necessary gel fraction by a minimal e-beam dose for a successful subsequent pyrolysis. It has been found that an irradiation dose of only 300 kGy is enough to stabilize the shape of fibers melt-spun from an ABSE precursor with an average molecular weight of about 14000 g/mol [22]. In the case of a lower average molecular weight of about 3700 g/mol the necessary irradiation dose increases up to 1000 kGy. Compared to

the Hi-Nicalon or other SiC fibers which are cured with e-beam doses from 7.5 up to 20 MGy [23], it is possible to save more than 95% of the irradiation costs by using a high molecular ABSE precursor.

A novel process for producing SiOC ceramic foams has been proposed. Methylsilicone resin was foamed in a single step manufacturing process by EB irradiation. The polymer precursor was expanded by the gaseous products that evolved from the condensation crosslinking reactions during irradiation. The required irradiation dose for methylsilicone resin, at dose rate of 2.8 kGy/s, was found to be between 1.0 and 3.5 MGy. The foams obtained with radiation dose of 3.5 MGy exhibited a high degree of crosslinking (95.2%) and a high ceramic yield (89% in N<sub>2</sub> atmosphere). The compression strength of foams pyrolyzed at 1200 °C was about 6.8 MPa. The results of this investigation indicated that the proposed novel processing method is suitable for manufacturing porous SiOC ceramics from irradiated methylsilicone and suggests a new trend to study polymer derived ceramics by EB radiation curing [24].

Silicon carbide (SiC) films seem to be excellent for scratch resistant coatings on metals, glass, and ceramics applied to improve the surface toughness. SiC thin-layer ceramics are expected to surpass the performance of polymeric silica and carbon membranes. A very convenient way for SiC production is employment of silicon containing polymer precursor. Deposition from solution or melt spinning followed by pyrolysis are techniques easy to perform and do not require sophisticated instruments. Polycarbosilane (PCS) is known as a good precursor for SiC ceramic products, from which melt spun PCS-originated SiC fibers are the most common. Thermal curing of preceramic polymers is the most general method to preserve the object shape before pyrolysis, utilization of ionizing radiation however in the form of electron beam (EB) or  $\gamma$ -rays has a significant advantage over conventional heat treatment since it can proceed at ambient temperature [25]. Silicon carbide (SiC) ceramic coating was developed from precursor polymer blend of polycarbosilane and polyvinylsilane on porous alumina substrate by radiation curing. The polymers were crosslinked in air atmosphere during irradiation and pyrolyzed at 850°C in order to convert the polymer into SiC ceramics. Fabricated SiC film was used as a membrane for gas separation, achieving high separation ratios of 206 for H<sub>2</sub> and 241 for He over the nitrogen at 250°C [26].

SiC fiber has been used as a reinforcement material in advanced ceramic matrix composites used in aerospace, nuclear, and high-temperature material applications. For many applications, the required anisotropic properties can be achieved in fiber-reinforced composites in the form of woven structures such as mats. These mats are used as filters, composite reinforcement sensor, in biomedical fields, template for the preparation of functional nanotubes and electrochemical photovoltaic electrodes. Electrospinning is a simple and inexpensive technique for producing continuous submicron- to nano-sized polymeric fibers, and it provides high specific surface areas. This technique can be used with a variety of polymers to produce nanoscale fibers. Curing is an essential step in the preparation of SiC mat which is to prevent the mat melting during the carbonization phase. Polycarbosilane (PCS) was used as a precursor for SiC and PCS mat was fabricated using electrospinning method. The electrospun PCS mat was cured by e-beam irradiation and then pyrolyzed in a tube furnace at atmospheric pressure under an argon atmosphere at a temperature of 1300 °C for 1h [27].

## 2.4 Grafting

For most applications modification of polymer surfaces with certain functional groups is required. A promising approach for the control over the surface layer structure and chemistry

is based on treatment of surfaces with accelerated electrons. The radicals generated by impinging electrons on the polymer surfaces will provide the active sites for further attachment of monomers to grow into graft chains. Radiation-induced graft polymerization has been one of the underutilized aspects of radiation processing of polymers until recently. It has now gained much more acceptance for the manufacturing of advanced polymeric materials by modifying the surfaces of commercially available commodity polymers. Currently radiation-induced grafting is developing in the following directions: polymeric membranes, polymeric adsorbents and polymers for medicine and biotechnology [28].

Fuel cells are considered to be the clean energy sources of the future. A polymeric membrane showing high proton conductivity and capability to operate in aggressive conditions for sufficiently long operational times is the key component of a fuel cell. One of the best alternatives to the commercially available Nafion membranes for use in fuel cells is the synthesis of membranes based on fluorine containing polymers through radiation-induced graft polymerization. The substrate materials used for these membranes have been poly(tetrafluoro ethylene) PTFE, poly(vinylidene fluoride) PVDF, a copolymer of tetrafluoro ethylene and hexafluoropropylene FEP, or a copolymer of ethylene and tetrafluoroethylene, ETFE. Due to its radiation sensitivity PTFE has been used in already radiation crosslinked form [29]. In a typical grafting procedure the substrate films were first irradiated with low energy electrons in nitrogen atmosphere then dipped into a solution of styrene to induce grafting. Grafted chains were later sulfonated to acquire proton conductivity. The resulting membranes show a large ion exchange capacity reaching 2.6 meq/g which exceeds the performance of commercially available films such as Nafion. It has been claimed that the manufacturing cost of membranes produced by the use of radiation-induced grafting by the pre-irradiation method with inexpensive low energy accelerators is lower than the manufacture of commercial fluorine containing Nafion membranes by a factor of 8-10 [28]. The most recent developments in Fuel Cell technologies and particularly membranes prepared by radiation induced grafting can be found in the recent compilation by G. Scherer [30].

Considerable amount of research has been done on developing specialty adsorbents by using radiation-induced grafting technique. The sorbents are generally prepared for the recovery of valuable metal ions present in trace amounts in sea water or for the removal of toxic anions or cations from aqueous streams. Non-woven fabrics made of PE or PP are preferred as the base polymer on which acrylonitrile is grafted. The nitrile groups of graft polymers are converted into amidoxime groups which are known to show selectivity towards uranyl ions in sea water. Monomers with enriched amidoxime groups have been developed to increase the efficiency of uranyl uptake [31,32]. The same approach has been used in preparing other graft polymers showing selectivity for other metal ions. The amidoximated non-woven fabric have already been used in pilot scale applications in southern part of Japan. By proper selection of grafting monomer and its further functionalization it would be possible to prepare a variety of specialty adsorbents showing maximum selectivity towards a target metal ion or anion [33]. A manufacturing process line for radiation induced graft polymerization has been recently put into operation in Japan [34].

Another interesting application of radiation-induced grafting is radiation-initiated nano-surface modification for regenerative medicine. By optimizing electron beam grafted responsive polymer thickness, cells grown on a polystyrene substrate grafted with nanometer thick poly(N-isopropyl acrylamide) were harvested by controlling the external stimuli such as temperature. Electron beams are uniquely useful to prepare large amount of stimuli-responsive culture surfaces required for tissue engineering in a very simple way. The cell

sheets thus obtained have already been clinically applied in plastic constructive surgery and ophthalmology, periodontology and as cardiac cell patches [35].

### 3. Petroleum Processing

Radiation methods for petroleum processing have been attracting attention of researchers since early 1960s when the discovery of the phenomenon of radiation-thermal cracking (RTC) had demonstrated an opportunity of using ionizing irradiation for the high-rate deep oil processing.

In the beginning of this decade new technologies were ready for scale-up for industrial use. Radiation-thermal cracking of oil feedstock represented an advancement in overcoming many acute problems of oil industry. However, all the processes based on radiation-thermal cracking still require heightened temperatures (350-450<sup>0</sup>C) in the case of heavy oil feedstock. The development of an economically competitive technology for heavy oil radiation processing required significant reduction in the process temperature. As distinct to RTC, the PetroBeam process proceeds at lowered temperatures in conditions favorable for radiation-induced chain propagation.

#### 3.1. Processing of fuel oil

Fuel oil (oil #6) was processed in the pilot line of PetroBeam facility. Conversion of 35% for the heavy residue boiling out above 450<sup>0</sup>C was reached at the electron irradiation dose of 24 kGy. The changes in the fractional contents of the feedstock were accompanied by the drop in the product viscosity by 86% [36].

#### 3.2. Processing of bitumen

The feedstock was characterized by the density of 0.9781 g/cm<sup>3</sup> (API gravity 13.2<sup>0</sup>) and the kinematic viscosity of 2912 cSt. Bitumen is the heaviest type of hydrocarbon feedstock with the highest concentrations of pitches and asphaltenes. In view of the depletion of the world resources of light crude oils, bitumen rocks are the most perspective source of hydrocarbons spread all over the world but most difficult for processing by conventional methods. Changes of bitumen fractional contents after PetroBeam processing resulted with reduced viscosity. The tests of the technology at the PetroBeam pilot line have demonstrated its high efficiency for upgrading the heaviest types of petroleum feedstock. It has been demonstrated that it provides high-rate processing of heavy oil and bitumen at temperatures lower than 150<sup>0</sup>C and at nearly atmospheric pressure without application of any catalysts.

### 4. References

- [1] T.Seguchi, T. Yagi, S. Ishikawa, Y. Sano, Rad. Phys. Chem., **63**, 35 (2002)
- [2] J.Sun, Y.Zhang, X.Zhong, X.Zhu, Rad. Phys. Chem., **44**, 655 (1994)
- [3] A. Oshima, Y. Tabata, H. Kudoh, T. Seguchi, Rad. Phys. Chem., **45**, 269 (1995)
- [4] M. Stephan, D. Pospiech, R. Heidel, T. Hoffmann, D. Voigt, H. Dorschner, Polym. Deg. Stab., **90**, 379 (2005)
- [5] M.Stephan, G. Heinrich, H. Dorschner, PCT Int. App. WO 2007039380 (2007)
- [6] N. M. Bolbit et al., High Energy Chemistry, **42**, 354 (2008)
- [7] U. Schulze, P.S. Majumder, G. Heinrich, M. Stephan, U. Gohs, Macromol. Mat. Eng., **293**, 692 (2008)



- [8] G.O. Phillips, A.T. du Plessis, S. Al-Assaf, P.A. Williams, PCT Int. App. WO 2002072862 (2002)
- [9] E. Oral, O.K. Muratoglu, Nuclear Inst. Meth. Phys. Res. B, **265**, 18 (2007)
- [10] O.K. Muratoglu, S.H. Spielberg, US Patent Appl. 20080215142 (2008)
- [11] A. Bellare, T.S. Thornhill, Int. Pat. WO 2008/101073 A2 (2008)
- [12] J. Gehring, IRaP2006, 7th Int. Symp. "Ionizing Radiation and Polymers", Antalya, Turkey, 23-28 Sept. 2006
- [13] S. Al-Assaf, G.O. Phillips, P.A. Williams, Food Hydrocolloids, **20**, 369 (2006)
- [14] M. Tamada, N. Seko, F. Yoshii, Rad. Phys. Chem., **71**, 221 (2004)
- [15] T. Katayama, M. Nakaura, S. Todoriki, G.O. Phillips, M. Tada, Food Hydrocolloids, **20**, 983 (2006)
- [16] V.J. Lopata, J.W. Barnard, C.B. Saunders, T.M. Stepanik, Nuclear Inst. Met. Phys. Res. B, **208**, 102 (2003)
- [17] F. Bauer, H.-J. Glasel, E. Hartmann, E. Bilz, R. Mehnert, Nuclear Inst. Met. Phys. Res. B, **208**, 267 (2003)
- [18] H.-J. Glasel, F. Bauer, E. Hartmann, R. Mehnert, H. Möbus, V. Ptatscek, Nuclear Inst. Met. Phys. Res. B, **208**, 303 (2003)
- [19] M. Cleland, R.A. Galloway, A.J. Berejka, D. Montenev, M. Driscoll, L. Smith, L.S. Larsen, Rad. Phys. Chem., **xx**, xxx (2009)
- [20] A. Herrer, R.A. Galloway, M. Cleland, A.J. Berejka, D. Montenev, D. Dispenza, M. Driscoll, Rad. Phys. Chem., **xx**, xxx (2009)
- [21] X. Coqueret, M. Krezeminski, P. Ponsaud, B. Defoort, Rad. Phys. Chem., **xx**, xxx (2009)
- [22] T. Yamaki, M. Asano, Y. Maekawa, Y. Morita, T. Suwa, J. Chen, N. Tsobokawa, K. Kobayashi, H. Kubota, M. Yoshida, Rad. Phys. Chem., **67**, 403 (2003)
- [23] S. Kokott, G. Motz, Soft Materials, **4**, 165 (2007)
- [24] S. Kamimura, T. Seguchi, K. Okamura, Rad Phys. Chem., **54**, 575 (1999)
- [25] R.M. Rocha, E.A.B. Moura, A.H.A. Bressiani, J.C. Bressiani, J. Mater. Scien. **43**, 4466 (2008)
- [26] K. Okamura, T. Seguchi, J. Inorg. Organomet. Polym., **2**, 171 (1992)
- [27] R.A. wach, M. Sugimoto, M. Yoshikawa, J. Am. Ceram. Soc., **90**, 275 (2007)
- [28] P.-H. Kang, J.-P. Jeun, D.-K. Seo, Y.-C. Nho, Rad. Phys. Chem., **xx**, xxx (2009)
- [29] V. Ya. Kabanov, High Energy Chemistry, **38**, 83 (2004)
- [30] S. Sawada, T. Yamaki, S. Kawahito, M. Arano, A. Suzuki, T. Terai, Y. Maekawa, Polym. Deg. Stab., **94**, 344 (2009)
- [31] G. Scherer, Editor, Fuel Cells I & II, in Advances in Polymer Science, Vol. 215 and 216 (2008)
- [32] P.A. Kavaklı, N. Seko, M. Tamada, O. Güven, Adsorption, **10**, 309 (2004)
- [33] P.A. Kavaklı, N. Seko, M. Tamada, O. Güven, Sep. Sci. Tech, **39**, 1631 (2004)
- [34] P.A. Kavaklı, C. Kavaklı, N. Seko, M. Tamada, O. Güven, Nuclear Inst. Meth. Phys. Res. B, **265**, 204 (2007)
- [35] K. Fujiwara, Nuclear Inst. Meth. Phys. Res. B, **265**, 150 (2007)
- [36] M. Yamato, T. Okano, MaterialsToday, pp.42, May 2004
- [37] Y.A. Zaikin and R.F. Zaikina, paper 2008-461, World Haevy Oil Congress, Edmonton, 10-12 March 2008