IAEA-CN-115-68

New Opportunities for the Utilization of Electron Accelerators in Polymer Processing Industries

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Abstract. A review on the current and emerging applications for electron beam processing shows that polymers dominate the industry. Electron beam treatment of polymers has been extensively researched to understand how to exploit and control the effects of ionizing radiation to design and manufacture commercially viable new products. Some examples of recently established and newly emerging applications with high potential for commercialization is reviewed in this paper under the subtitles of crosslinking, curing, grafting and chain scissioning.

1. Introduction

Industrial uses of electron accelerators started in late 1950s with the crosslinking of polyethylene wire insulation. Since then with the development of energy, power and cost efficient and reliable accelerators, various industries benefited from the unique advantages of using ionizing radiation generated by electron accelerators. The new developments hence opportunities appearing in electron beam processing of polymers are continously arising as a result of the synergy achieved through the developments on design and manufacturing of new low, medium and high energy accelerators with relatively high powers and innovative approaches in material formulation better responding to radiation processing.

Irradiation of polymeric materials with ionizing radiation (gamma rays, X-rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates, free radicals, radical ions and excited states. These intermediates can follow several reaction pathways which result in disproportionation, hydrogen abstraction arrangements or formation of new bonds. The ultimate effects of these reactions are the formation of oxidized products, unsaturation, grafts, scission of main chains which is also called degradation 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 the conditions of treatment before, during and after irradiation. Good control of these factors makes the modification of polymers possible by radiation processing.

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. 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.

New innovations in the application of ionizing radiation to polymeric materials have reached sustainability through the efforts of radiation and polymer researchers all over the world. The growing interest in radiation processing of polymers has been substantiated by the organization of biennial conferences devoted solely to this subject under the title of "Ioinizing Radiation and Polymers" IRaP. The proceedings of these meetings covering the entire spectrum of electromagnetic and corpuscular radiations and their interactions with polymers are published as special issues of the Journal "Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms" [1-3].

2. Mature Electron Beam Applications in Polymer Processing

The polymer, plastics and rubber industries have benefited from the unique advantages of ionizing radiation since its inception as an industrial tool to modify their properties thus adding value to the end products. Radiation-induced crosslinking has already been considered as a very well established technology in wire and cable industry where crosslinking of insulators and sheaths imparts resistance to solvents, ageing and high temperatures. Thin wires are crosslinked at very high speeds (>300 m/min) by medium energy high power accelerators. Radiation crosslinked polyethylene tubings are being currently used as hot water pipes especially in floor heating systems. 80 million meters of polyethylene pipe are radiation crosslinked per year only in Germany [4]. The production of heat-shrinkable packaging films, tubings and other more complicated shapes have been one of the greatest commercial successes of radiation technology in polymer-packaging industry. Radiation technology is also used for the production of polyethylene based foamed products. Crosslinked polyethylene foam can be obtained in a continuous process contrary to batch process. Articles made from PE foams are used in civil engineering, automobile industry and in the manufacture of sports goods. Radiation pre-crosslinked rubber strips are used in the manufacturing of automobile tyres. The combination of radiation and conventional sulfur vulcanization favors an increase in the mechanical properties of rubber, while reducing the amount of polyisoprene to be used in the final formulation. Radiation curing is commercially used on a large scale in surface finishing of coatings, lacquers and inks. For very large production volumes and when the curing formulations are opaque, heavily loaded with pigments and magnetic particles, electron beam curing is of particular advantage over UV curing. Radiation-induced degradation which is the opposite effect of crosslinking, has found its greatest application in the irradiation of Teflon which reduces the molecular weight and particle size hence allowing its use as a filler for various applications. Due to very large throughput volumes involved in all of the above applications which necessitate high dose rates, the electron accelerators has become the major industrial tool for radiation processing of polymers.

3. Emerging Electron Beam Applications in Polymer Processing

The emerging applications of electron beam processing of polymers are still based on the already known major effects of ionizing radiation on polymers, namely crosslinking, curing, grafting and chain scissioning. The new developments hence market opportunities appearing in electron beam processing of polymers are arising as a result of the synergy achieved through the developments on design and manufacture of new low, medium and high energy accelerators with relatively high powers, availability of more sophisticated under beam handling systems and innovative approaches in material formulation better responding to radiation processing.

Some examples of recently established and newly emerging applications of electron beam processing of polymers with commercial potential will be reviewed in this paper under the subtitles of crosslinking, curing, grafting and chain scission with short descriptives notes on some selected applications.

Crosslinking

Polymeric materials are normally exposed to radiation in air at ambient temperature due to convenience of operational conditions. During the last decade however, irradiation of certain polymers at high temperatures has been shown to improve their mechanical properties significantly reaching results not obtainable by room temperature irradiation. One surprising result came out with the radiation-induced crosslinking of Teflon at high temperatures which under normal circumstances is a typical chain scissioning polymer. Crosslinking of Teflon can be achieved at a narrow temperature range just above its melting temperature in inert atmosphere. At a crosslinking dose of 100 kGy the wear and radiation resistance of Teflon has been improved by 3 and 2 orders of magnitude respectively while maintaining the chemical and electric resistance properties of the original material. The process was initially developed almost simultaneously in China and Japan [5,6] and commercial application has recently been launched in Japan.

Ultrahigh molecular weight polyethylene prostheses have been used for quite some time in knee and hip replacement surgery. The wear and tear of these replacements however, have resulted in health problems for many of the recipients. It has now been established that the use of electron beam crosslinked UHMWPE prostheses improves this situation. Gradient crosslinking of UHMWPE in molten state has been exploited by a group from MIT, USA [7,8]. The acetabular liners were irradiated at 140 ^{o}C in the molten state of the polymer using a 2 MeV electron beam with limited penetration of the effects of radiation into polyethylene. The gravimetric wear rate was 27+/-5 mg/million cycles using the Boston hip Simulator with the conventional liners, while the melt-irradiated acetabular liners did not show any weight loss.

High temperature irradiation of engineering plastics seems to open a new application pathway especially by improving the hardness of these materials. Electron beam irradiation of polycarbonate and polysulfone near their glass temperatures at relatively small doses of 3-5 kGy, has been shown to increase their hardness and wear resistance by 30% [9,10].

Crosslinking of PE tubes for water and gas supply with lengths of up to 12 m, crosslinking of devices made of polyamide, poly(butylene terephtalate) have already been commercial applications yielding products of improved heat resistance for automotive and electrical and electronic industries. In glass fibre reinforced polyamide a radiation dose of 50 kGy has been found to be sufficient to achieve a degre of crosslinking of 70% which in practice is perfectly adequate to reach desired product properties. Radiation crosslinked poly (butylene terephtalate) withstands soldering iron temperatures of 350 ^{o}C which imparts thermal stability required in actual soldering processes [11].

Electron irradiation of aqueous hydrophilic polymer solutions for preparing hydrogels as wound and burn dressings was the first commercial application in the field of biomaterials. Due to their tissue-like properties hydrogels provide many desirable properties. They form an efficient barrier against contamination of wound from outside, show good adherence to wound without sticking thus enabling painless replacement, provide good access to oxygen, absorb exudates, prevent loss of body fluids, reduce the possibility of scar formation, remain transparent for easy monitoring of healing. The polymeric network within the hydrogels imparts high flexibility and softness yet retaining good mechanical strength. Poly(vinyl alcohol) based hydrogels [12] and incorporation of healing aids such as radiolytically generated silver [13] constitute some of the developments in this area.

The results of a comprehensive program launched by the IAEA in South East Asia have shown the advantages of using ionizing radiation for the crosslinking of natural rubber latex to be used in the preparation of dipped products such as examination gloves, catheters, baloons, etc. The advantages of replacing sulfur vulcanization by radiation induced vulcanization are the elimination of protein allergy and environment friendly handling of rubber waste. The relatively higher cost of gamma processing has been shown to be reduced by using low energy electron (250 keV) irradiation [14].

Curing

Curing is the process of simultaneous polymerization and crosslinking of oligomeric resins. Electron beam curing has the inherent advantages of using solvent-free systems, energy savings, high extent of cure and high throughput rates. Electron beam curing and electron beam repair of fibre-reinforced composites has seen a breakthrough with developments that allow the conventional epoxies used by the aerospace industry to be cured by electron beam irradiation. These developments have removed most of the technical barriers in large scale use of this technology in aerospace, marine and other industries that use fibre-reinforced composites. Satisfactory repair of aircraft parts has been demonstrated and a facility to repair aircraft parts by electron beam is being built [15].

Radiation-curable polymeric nanocomposites with enhanced surface-mechanical properties have been developed [16]. Adequate electron beam curing activity was imparted on inorganic nanoparticles, e.g. silica and alumina, by grafting onto them functionalized trialkoxysilanes, yielding covalent-bonded hydrolsis-stable surface compounds. Transparent, scratch and abrasion resistant coatings were obtained by radiation curing of acrylate formulations containing high amount of nanosized modified silica and alumina fillers [17]. Radiation curing has shown its great potential particularly in fabricating protective polymeric composite coatings.

Electron beam curable adhesives for commercial applications that can bond composite to composite, aluminum to composite and aluminum to aluminum have been developed with the objective of producing adhesives with glass transition temperatures around 200 ^{o}C and lap shear strengths greater than 35 MPa for aluminum and 11 MPa for graphite composite [18].

Grafting

Radiation-induced graft polymerization was 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. Grafting is based on the generation of active ionic or radicalic sites on various polymers by the action of ionizing radiation followed by graft polymerization of a selected monomer. Currently radiation-induced grafting is developing in the following directions: polymeric membranes, polymeric adsorbents and polymers for medicine and biotechnology.

Proton exchange membranes for fuel cell applications were prepared by radiation-induced grafting of styrene into radiation crosslinked poly(tetrafluoro ethylene) films with subsequent sulfonation of phenyl rings [19]. 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 [20].

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 precious metal ions present in trace amounts in sea water. 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 [21]. Monomers with enriched amidoxime groups have recently been tested to increase the efficiency of uranyl uptake [22, 23]. 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.

Another interesting application of radiation-induced grafting is radiation-initiated nano-surface modification for tissue enginering. By optimizing electron beam grafted responsive polymer thickness, cells grown 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 [24].

In the case of biomaterials used in direct blood contact applications, numerous attempts have been made to modify the material surfaces by radiation treatment. The specific polymers for grafting are selected to induce biocompatibility, to enhance cell adhesion, to control blood coagulation response of the surfaces. The albumin grafting onto polycarbonate, polypropylene, and poly(vinyl chloride) resulted in substantial improvement in the blood compatibility of oxygenators [25].

The sensitivity of cotton which is a universally accepted material for clothing to bacterial and fungal attack especially in moist environments has been remedied by radiation-induced grafting of germicidic monomers. The grafting of vinyl benzylammonium chloride onto cotton imparted excellent anti-bacterial activity against strains like E. Coli, S. Aureus [26]. The anti-bacterial activity of the grafted cotton samples was shown to be retained after several cycles of washing and drying in a commercial detergent.

Chain Scissioning

Poly(methyl methacrylate) PMMA, is typical polymer that undergoes chain scissioning when exposed to ionizing radiations. Due to its high sensitivity to radiation it has been the material of choice as the positive resist in lithography. Electron beams and X-rays are the major tools used in radiation-based microlithography. Feature sizes as small as 25 nm have been reported to be obtained by 50 keV e-beam writer with a 15 nm beam size [27]. Structures of lines down to 50 nm and dots with a diameter of sub 20 nm have been presented by a lift-off process for nanoimprint technology [28]. The need for pattern definition on a nanometric scale is spreading beyond electronics and diffractive optics. Biological cells respond to topographic features as small as 30 nm in their environment. A method was described which uses an electron beam lithographic tool to fabricate features as small as 20 nm in diameter on 100 nm pitch which provide arrays of nano-dots for cellular engineering [29].

It is very well known that when polysaccharides are irradiated with ionizing radiations in solid form or in aqueous solutions they immediately degrade to smaller molecular weight species. This effect has been utilized for the controlled degradation of a number of polysaccharides of marine origin namely, chitosan, alginates and carrageenans [30]. The degraded forms of these carbohydrates show various kinds of biological activities such as anti-microbial activity, promotion of plant growth, suppression of heavy metal stress in plant growth, phytoalexins induction etc.

Irradiation of polymeric wastes seems to offer new solutions to this problem. Due to the ability of ionizing radiation to alter the structure and properties of bulk polymeric materials and the fact that it is essentially applicable to all polymer types, radiation processing holds promise for mitigating the polymer and rubber waste problem. Recycling of irradiated butyl rubber from bicycle inner tubes is a commercial process now in China [31].

The above cited list of developments is by no means exhaustive and there are a number of new results and applications emerging in using ionizing radiation generated by electron accelerators to modify, upgrade and shape polymeric materials. Developments in source technologies, material handling systems, formulation of new polymeric compositions and innovative approaches will continue to bring new radiation treated products into the market.

3. References

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