Aspects of Electron Beam (EB) Processing of Polymers

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Of the many ways one can modify traditional polymers, electron beam irradiation (EBI) is one of the most attractive technique to the scientific and the industrial community, since it can profoundly affects the molecular structure providing polymeric materials with unique properties1-5.

The process has revolutionized the application of polymeric material in diverse areas including sterilization of medical devices, pollution control (treatment of sewage and sludge), food preservation, curing of cable insulations, manufacture of heat-shrinkable polymers, in orthopaedics, tire manufacturing and on1-4, 6,7. The process is carried out with electron accelerators (EA) that provide energies between 75 eV and 10 MeV2,8,9. The radiation interacts with the polymeric material, knocking-off labile atoms from the polymer to generate radicals1, 2 on the carbon backbone of the polymer. These radicals initiate reactions such as polymerization (e.g. curing of coatings), and cross-linking. Polymerization is possible with monomers having chemical unsaturations and proceeds through free-radical initiated addition reactions. Cross-linking results when two polymeric-radicals unite.

The target of the article is to summarize applications of the EB process to polymeric materials, describing the important benefits, how the process is quantified, how the best results can be achieved, current application trends and where the future lies.

Key Benefits Associated with EB Processing

In contrast to conventional thermo-chemical cross-linking, electron beams can trigger reactions at ambient temperature. Reactions are faster than those achieved by UV curing and also require no special compounding. Thus leads to modifications with higher dose rate than that achieved with gamma-irradiation technique. They are not only faster than the gamma-irradiation techniques, but also safer since there is no induced radioactivity that could pose health hazards. Finally, EB is more efficient than conventional polymerization techniques, since scrap material can be reused by treating it with additional doses of electrons to achieve the desired state of cure.

Can We Quantify the Effect of Radiation?

The amount of radiation absorbed by materials is usually measured in ‘rads’; the relevant SI unit is the Gray (Gy). The most common units are related by the following: 1 Gy = 100 rad. = 1 J/kg = 6.24 X 1015 eV/g = 104 erg/g.

The yield of an EB process is measured through determination of a G value, defined as the number of molecular changes of a given type per 100 ev of applied energy. This is widely used to express the yields of chemical functional groups, radicals, various gaseous products or cross-links1-2,10. The G value can be calculated with the help of concentration of different chemical species, determined with spectroscopic techniques like NMR (nuclear magnetic resonance), and IR (infra-red)10-12. Similarly ESR (electron spin resonance) measurements can provide the concentration of radicals present2.

Solvent swelling measurements provide a simple method to determine cross-linking/scission yield, G(X)/G(S). If cross-linking predominates, the cross-link density increases, leading to a decrease in swelling propensity. A plot of the extraction data, using the Charlesby-Pinner equation2, S + ?S versus 1/D (where S= sol fraction and D = absorbed radiation dose) generates a curve from which data on scission and cross-linking yields may be derived.

How the Polymer Structure Can Influence Cross-linking?

Polymer structure influences the cross-linking ability of polymer. Chain cross-linking and scission are the two reactions that occur during EB processing of polymers. Polymers typically undergo simultaneous scission and cross-linking, but in most-cases with one or the other clearly predominating.

Polymers irradiated in absence of oxygen can be grouped into two categories, in terms of predominance of scission and cross-linking2. A very useful rule of thumb for predicting whether cross-linking or scission prevails, holds for a large number of polyolefins: Polymers with a high concentration of quaternary carbon atoms along the chain (poly-isobutylene), poly(methyl methacrylate), poly(alpha-methyl styrene)) mainly undergo scission; while other polymers such as poly(ethylene), poly(styrene) and natural rubber mainly undergo cross-linking.

Presence of relatively bulky F in poly(tetrafluoroethylene), PTFE or –CH3 (methyl) group in poly(propylene), PP (as compared to H in PE) leads to chain-scission. Steric inhibition of radical-radical recombination following chain break, leading to increased yield of scission, is the most likely explanation of this phenomenon.

The presence of an aromatic ring in a polymer exerts a strong influence on yield of radiation induced cross-linking or scission. Polymers with aromatic functionality are particularly useful in applications where radiation resistance is required. The reason is assigned to transfer of radiation energy through resonance along the aromatic ring structure, which acts as energy scavengers. For this reason, cross-linking yield of poly(ethylene), PE is higher that of poly(styrene), PS, under the same irradiation conditions. Again, scission yield of poly(?-methyl styrene) is lower that of poly(isobutylene), the methyl group of the latter being substituted by a radiation-resistant aromatic ring in the former.

How Can One Increase the EB Efficiency and Get the Best Properties?

The EB process can be controlled through an appropriate choice of the irradiation conditions, as well as by the polymer structure. Processing in air promotes radiation induced degradation owing to incorporation of oxygenated groups on polymer backbone leading to chain scission. Scission reduces cross-linking efficiency and degrades the properties of polymers (chemical resistance, mechanical and dielectric strength). However oxidative degradation can be eliminated by carrying out EB irradiation in an inert atmosphere such as nitrogen3. For instance PTFE degrades when irradiated under ambient conditions, but when irradiation is done on the melted polymer in inert atmosphere, PTFE undergoes cross-linking12. Increased thermal energy is understood to enhance the mobility of the radical intermediates, which favors the cross-linking process through radical recombination.

Irradiation under mechanical stress can degrade the mechanical properties of a polymer due to weakening of some of the chemical bonds.

Lower dose-rates (e.g. 0.25 - 4 Gy/h) in air result in more extensive degradation3 per equivalent absorbed dose, as oxygen has more time to diffuse in bulk of polymer. Hence, increasing the dose rate could partially suppress the degradation process and enhance the performance of a polymer. Cross-linking reduces the crystallinity of a semi-crystalline polymer due to reduction in molecular packing of polymer chains.

How Compounding Can Affect the Polymer Properties?

As stated earlier, EB processing requires no special compounding to modify a polymer. However additives can be used to modify the efficiency of cross-linking. For instance, scission-yield of polymers undergoing EB irradiation can be reduced through blending with polyfunctional monomers such as trimethylol propane triacrylate and other multifunctional unsaturated acrylates13. Such compounds promote the cross-linking reaction through radiation induced rapid free radical induced propagation reactions and aid in formation of a three-dimensional network structure via grafting through their double bonds. They also act as plasticizers providing efficient contact between chains. This result in the enhancement of such properties as the mechanical strength of the EB treated polymer.

Polycyclic aromatic compounds such as naphthalene and anthracene are known as ‘antirads’ because they offer radiation protection, since they scavenge energy by easily forming excited states. Antirads can be used to control the radiation-induced chain scission in polymers.

In some cases radiation protection can be achieved by substituting aromatic species for certain additives used in the formulation. For instance, poly(vinyl chloride) materials containing aromatic plasticizers have better radiation resistance than formulations containing the usual aliphatic plasticizers. Phenolic antioxidant stabilizers can be used to reduce radiation-induced color formation, arising from the formation of conjugated, unsaturated chromophores or trapped radicals.

Current Multitude of Applications

The EB process is being commercially exploited in the cross-linking of polymers for wire and cable insulations as well as for seals and gaskets. EB cross-linking of gasket material is promising as the resultant products have a lower compression set over a broad range of temperature. This is because of the formation of heat stable carbon-carbon linkages.

Use of heat-shrinkable PE and EVA materials in cable-jointing is another important application. Here, EB treated materials is heated above its melting point, stretched and cooled down while still stretched. When the resultant material is heated, the cross-links pull the material back to original shape.

In automobile tire fabrication, Firestone implemented the EB technique to increase the green strength of rubber compounds used to process tire components.

Frequently, EB is used in sterilization of medical devices. Cured hydrogels (three-dimensional network of EB cross-linked hydrophilic polymers such as poly(N-vinyl pyrolidone) swollen with water) are finding important applications in wound-dressing. Biodegradable hydrogels from polysaccharides are also being investigated14. Researchers at Baxter Corporations have demonstrated the superiority of EB sterilization of PP/PE based medical devices over ?-irradiation (GIR) where more oxidative degradation is encountered for the latter15. Owing to lower dose rates in GIR process, oxygen has more time to diffuse into the bulk of the polymer thus causing relatively increased molecular degradation.

One recent breakthrough in EB processing of polymers is the successful use of cross-linked polyethylene for surgical implants. Ultra high moleculear weight polyethylene (UHMWPE) is well known for its use as the bearing material in hip and knee joint replacements. Here, the major problem associated with the use of UHMWPE is the wear of the polymer used in acetabular liners in knee-joints6,7 often leading to component loosening, bone loss and fractures, and revision surgery. Researchers at Harvard Medical School and Massachussets General Hospital have discovered that the wear resistance of UHMWPE could be significantly improved through EB cross-linking. However, EB irradiation leads to generation of residual free radical causing long-term oxidative degradation involving polymer embrittlement that counteracts the benefits of the enhanced wear resistance. This problem has been eliminated through irradiation followed by melting. Melting enhances the mobility of residual radicals on polymer chain favoring recombination. This avoids in vivo molecular oxidation of the polymer that causes product failure.

Among others, due to low surface energy of PTFE, EB degraded poly(tetrafluoroethylene) micropowders find use as slip additives in inks and coatings.

Researchers at Acsion Industries Canada and Oak Ridge National Laboratory have pioneered commercially successful manufacture of EB cured carbon fiber reinforced composites widely used in aircraft, aerospace, sporting goods and transportation industries. Diaryliodonium salts of weak bases and other cationic initiators have been used to obtain composites with higher glass-transition temperatures, lower moisture absorption and less shrinkage than conventional auto-clave cured counterparts16.

The EB process has enabled scientists at Japan’s Atomic Energy Research Establishment to develop a novel biodegradable poly(lactide), PLA17 with improved thermal and mechanical properties. The EB process has also allowed German researchers to promote the long chain branching of linear poly(propylene)18. This modifies the rheology and enhances the melt strength of PP, facilitating its use in processing operations such as film extrusion and foaming.

Another useful application of the EB irradiation technique is the electron beam lithography2, 20-24 (EBL) in which a beam of electrons is focused and scanned over a polymer surface at a controlled rate to create the very fine patterns required by the modern electronics industry for integrated circuits. The dimension of the patterns generated could range from few tens to hundred of nanometers2, 20, 21. EBL offers higher resolution patterns than optical lithography due to the shorter wavelength of electrons. Lithography functions by using radiation to change the solubility of polymer molecules in exposed regions. Chain scission, cross-linking or side group modification of a polymer changes the polarity. This in turn changes the solubility of the polymer, so that a patterned polymer surface is formed during a subsequent solvent development step. EBL research is led by Bell Labs working with Texas Instruments, Motorola and Samsung2. Their approach makes uses a 100 keV electron beam with a magnetic lens and an electron scattering mask to produce the pattern.

IBM and Nikon scientists are developing a competitive process, using some differences in mask design2. Researchers in Germany21, have patterned film of a biocompatible polymer poly (N-vinyl pyrrolidone) cast on a silicone substrate using scanning electron microscopy.

Conjugated polymers are relevant materials for use in optoelectronics22,23. Recently, scientists in Italy have improved the emission performance of conjugated polymer by patterning the polymer surface with EBL. The modified polymer has the potential of being used as feedback laser.

Future Trends

The EB irradiation technique is of growing importance because of its flexibility, its environmental efficiency and its impact on bioactivity3, 4.

Also, the process is raising interest as a way to blend polymers for polymer recycling operations from municipal waste3, 4. EB process improves the blend compatibility of polymers with interfacial cross-linking. EB processing of polymers is expected to lead to commercially significant applications in nanotechnology (nanopatterning of biomacromolecular surfaces such as proteins and peptides24, in biosensors, biomaterials, and in tissue engineering. Immobilizing proteins on a nanoscale could lead to the development of diagnostic protein nanoarrays, while patterning peptides could lead to a greater control over cell/biomaterial interface.

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