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GAMMA AND ELECTRON BEAM CURING OF POLYMERS AND COMPOSITES

**TRAITEMENT DES POLYMERES ET COMPLEXES AUX RAYONS GAMMA
ET FAISCEAUX D'ELECTRONS**

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**Whiteshell Nuclear Research
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GAMMA AND ELECTRON BEAM CURING OF POLYMERS AND COMPOSITES*

by

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RÉSUMÉ

La polymérisation nous a aidé à comprendre la chimie des polymères et joue un rôle de plus en plus grand dans le secteur des applications pratiques. Le traitement par irradiation représente actuellement environ 5% de tout le marché du traitement des polymères et complexes et le taux d'accroissement annuel du marché du traitement par irradiation est > 20% par an. Les avantages du traitement par irradiation sur le traitement thermique ou chimique sont les suivants: amélioration du réglage de la vitesse du traitement, réduction de la durée du traitement, traitement à des températures ambiantes, traitement sans le besoin d'excitants chimiques et traitement complet (100%) avec un minimum d'émissions chimiques toxiques. En outre, le traitement par irradiation peut servir à produire la réticulation et le greffage des polymères et complexes. Dans ces cas, le grand avantage est la capacité de traiter les produits en leur forme définitive. Les isolants de câbles, pièces de véhicules automobiles et d'avions et matériaux de construction perfectionnés sont certains des exemples d'applications industrielles du traitement et de la réticulation par irradiation, du présent et du proche avenir.

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ABSTRACT

Radiation polymerization has helped us understand polymer chemistry, and is also playing an increasing role in the field of practical applications. Radiation curing has a present market share of about 5% of the total market for curing of polymers and composites and the annual growth rate of the radiation curing market is $\geq 20\%$ per year. Advantages of radiation curing over thermal or chemical curing methods include: improved control of the curing rate, reduced curing times, curing at ambient temperatures, curing without the need for chemical initiators, and complete (100%) curing with minimal toxic chemical emissions. Radiation treatment may also be used to effect crosslinking and grafting of polymer and composite materials. The major advantage in these cases is the ability to process products in their final shape. Cable insulation, automotive and aircraft components, and improved construction materials are some of the current and near-future industrial applications of radiation curing and crosslinking.

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1. INTRODUCTION

Basic and applied research and development on radiation treatment of polymers and composites has continued since the first reported observation of radiation polymerization by Hopwood and Phillips in 1938 [1]. Several reviews of the radiation chemistry of monomers and polymers have been published [1-4] and there is continued wide interest in research and product development for new applications of radiation treatment of plastics [5,6]. Industrial uses of radiation polymerization began about 25 years ago. Although radiation curing represents only about 5% of the market today, market projections point to a growing share for radiation curing (>20% annual growth in the radiation curing market is expected for the next 5 years [7]), mainly due to the advantages it offers over other methods.

Atomic Energy of Canada Limited (AECL) has been involved in basic and applied research on radiation-induced polymerization since the 1960's [8]. The Radiation Applications Research Branch was formed recently to provide continued focus for research and development and to pursue industrial applications for ionizing radiation.

2. RADIATION INTERACTION MECHANISMS

One application of ionizing radiation is polymerization of selected polymer and composite systems. Mechanistic studies of radiation-induced polymerization have focused on monomers which undergo addition polymerization; very little work has been done on condensation polymerization [2,4]. Table 1 contains a list of selected monomers and the types of polymerization reactions they undergo [4,9].

The interaction of high-energy radiation with organic compounds produces a variety of potential initiators, including anions, cations and free radicals. The ensuing radiation-induced polymerization generally proceeds by the single mechanism that is most favored by the conditions of the system (monomer type, temperature, impurities present, etc.). Most vinyl-type monomers, except the α -olefins and nitroethylene, may be polymerized by free radical mechanisms [4,9] (Table 1) and thus are good candidates for radiation-induced polymerization. A free-radical polymerization process consists of chain initiation, propagation and termination reactions and proceeds by the following type of mechanism [2,4,9,10]:

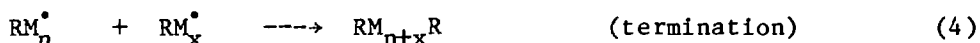
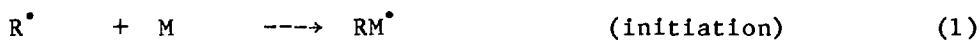


TABLE 1
POLYMERIZATION MECHANISMS FOR SELECTED MONOMERS [4,9]

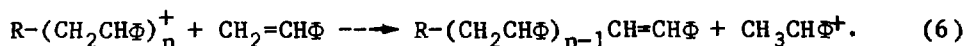
Monomer Type	Polymerization Mechanism ^{a)}			
	Radical	Cationic	Anionic	Coordination ^{b)}
Ethylene	+	+	-	+
Propylene and α-olefins	-	-	-	+
Isobutylene	-	+	-	-
Dienes	+	-	+	+
Styrene	+	+	+	+
Vinyl chloride	+	-	-	+
Vinylidene chloride	+	-	+	-
Nitroethylene	-	-	+	-
Acrylic and methacrylic esters	+	-	+	+

a) + = high polymer formed; - = no reaction or oligomers only.

b) polymerization by reaction with coordination catalysts, usually solids.

where R[•] is an initiating free radical, M is a monomer, RM[•] is the chain propagating intermediate, S is a free-radical scavenger and RMnS[•] is a non-propagating radical. The initiation and propagation reactions are straightforward sequential additions of monomer units to a free-radical initiator. Chain termination may occur by reaction of the propagating intermediate with a free radical initiator, another intermediate or a free-radical scavenger, e.g. molecular oxygen. Due to the inhibiting effect of oxygen on free radical polymerizations, many monomers must be polymerized in an inert atmosphere, e.g. nitrogen or vacuum. The dose range required for most polymerization processes, as well as for crosslinking and grafting applications, is 40 to 160 kGy, depending on the process objective and the material to be irradiated [11].

Cationic and anionic polymerization reactions occur by a similar mechanism, except that the initiator and chain-propagating intermediates are ions and the non-scavenged termination step is an ion-pair recombination reaction. Chain transfer reactions appear to be more common in ionic polymerization. Chain transfer is the process by which the reactivity of the propagating intermediate is transferred to the monomer or to an oligomer. For example, in the cationic polymerization of styrene, a proton may be transferred from the propagating intermediate to the monomer producing an oligomer with a terminal unsaturation and a 1-phenylethyl cation capable of chain propagation:



The rates of ionic polymerization reactions are about 100 times faster than those of free radical processes since the activation energies of the propagation step tend to be significantly lower for the ionic mechanisms [2,4]. Low temperatures favour ionic polymerization mechanisms because of the higher activation barriers for the free radical reactions and because of the reduced rates of the ionic chain termination reactions. Ionic polymerization reactions may be terminated by reaction of the propagating intermediate with water. Cyclic compounds (epoxides, ethers, imines and sulphides) must be dried carefully prior to radiation-induced, ring-opening polymerization, and they almost invariably proceed by an ionic mechanism.

High-energy irradiation of polymers can cause crosslinking or scission. Crosslinking is the process by which chemical bonds are formed between neighboring polymer chains and scission is the process of breaking the polymer chains [1,3,4,11]. Controlled crosslinking may lead to an improvement of the mechanical properties of the irradiated polymer but scission usually leads to a deterioration of mechanical properties. Crosslinking and scission occur simultaneously when polymeric materials are irradiated but one process usually dominates, e.g., polyethylene, polyamides and polyesters crosslink but polybutylene, polymethylmethacrylate and cellulose undergo scission. The irradiation conditions may also favour crosslinking over scission, e.g., crosslinking is favoured during irradiation under vacuum, in nitrogen atmospheres and at high dose rates.

High-energy radiation may also be used to form chemical bonds between polymers and other materials; this process is termed grafting [1,4,11]. Grafting may be effected either by the simultaneous irradiation of a monomer and the substrate or by postirradiation grafting which involves prior irradiation of a substrate known to retain the ability to induce polymerization of a monomer long after irradiation. The postirradiation grafting of monomers onto organic polymers is due to the formation of long-lived peroxides during irradiation of the polymer in an oxygen-containing atmosphere. These peroxides decompose by reaction with monomer molecules thereby initiating polymerization of the monomer and creating chemical bonds between the two materials.

3. RADIATION SOURCES

Industrial radiation processing is conducted using gamma emitting isotopes or electron-beam accelerators. A typical gamma-irradiation facility consists of the radiation source, usually ^{60}Co , the radiation shield and source containment system, and the material conveying mechanism [12]. Electron beam (EB) accelerators for industrial processing consist of four major subsystems: a power supply, a control system, an electron accelerator and a beam scanner [13,14]. The electrons are generated from the cathode and accelerated by an electric field, in a vacuum, to the desired energy. Shielding and conveying systems are also required for an EB facility.

Most of our polymer work to date has used gamma rays as the radiation source. Future research at WNRE will be conducted in the new Accelerator Applications Research Facility. This facility is designed to accommodate electron accelerators with a maximum beam energy of 10 MeV and average beam powers of up to 10 kW [15]. A 1 kW, 10 MeV electron-beam machine will be installed in the facility in mid-1987.

4. ADVANTAGES OF RADIATION CURING AND CROSSLINKING

Some of the key features of radiation curing and crosslinking [11,16] are:

- (1) Increased rates of polymerization. The rate of a radiation-induced polymerization reaction is usually an increasing function of the dose rate and, hence, the rate of polymerization can be controlled by changing the radiation dose rate. Polymerization reaction times of the order of a second can be obtained with high-power electron accelerators.
- (2) Uniform and efficient polymerization. Radiation can be used to create a uniform distribution of initiating species in a mixture to be polymerized and the subsequent polymerization reaction will proceed uniformly (no "hot-spots"). Appropriate radiation doses give almost 100% curing; the residual monomer concentrations are very low.
- (3) Ambient processing temperature. Radiation-induced polymerizations proceed at adequate rates at room temperature. It is not usually necessary to heat the monomer to effect polymerization. Ambient-temperature curing also leads to better control of product dimensions and reduces residual stress.
- (4) The depth of cure can be controlled. The depth of penetration of electron-beam radiation into a material is determined by the electron-beam energy and the electron density of the material [17]. Proper selection and control of the electron energy leads to efficient use of radiation energy and minimizes damage to the substrate.
- (5) Chemical initiators and waste solvents are eliminated. Chemical initiator residuals in plastic products reduce their resistance to chemical attack. Organic solvent vapor emissions are reduced in radiation curing because the material is not heated significantly during radiation treatment. Reactive diluents may be used in radiation-curing processes where it is desirable to reduce the initial viscosity of the resin.

- (6) A major disadvantage of using radiation is the requirement for an inert gas blanket, such as nitrogen, in most cases. This blanket eliminates oxygen, which is a scavenger of the free radical reaction intermediates. However, resin formulations are being designed to reduce this oxygen effect and eliminate the need for an inert gas blanket.

5. POTENTIAL APPLICATIONS AND MARKET TRENDS

Current markets for EB curable systems exist in coatings, inks, adhesives, electronics, fiber optics and electrical insulation, along with a number of smaller applications. As the market for industrial applications of radiation increases, a wide spectrum of radiation sources from low-energy (0.3 MeV) to high-energy (10 MeV) electron accelerators, as well as isotopic gamma ray sources, are expected to be used. Some of the current and near-future industrial applications [11] are:

- (1) Wire and cable insulation. Research and development in extrusion technology and radiation chemistry is increasing the gauge limit of the produced cables, opening a market for higher energy EB systems. Currently, electron accelerators with up to 5 MeV energy are being used for this application.
- (2) Rubber vulcanization. Radiation processing has been used with limited success in tire manufacturing primarily because of material limitations (butyl degradation) and the cost of equipment downtime. As the process reliability improves, radiation should become a more useful tool in the manufacturing of tires and other rubber products (hoses, belts).
- (3) Plastics and advanced composites in the automotive and aircraft industry. The increased use of these materials can reduce weight, manufacturing costs and improve the product quality (18). Radiation processing of large molded parts is a potential application of gamma rays or high-energy EB and this is a focus of ongoing research at many laboratories. Any resin formulation that is currently cured in thin films with low-energy electron beams can be cured in thicker products with higher energy electron beams.
- (4) Wood-plastic and concrete-plastic composites. Monomers can be impregnated in wood or mixed with concrete. Radiation can cure the monomer to produce construction materials with improved mechanical properties. In Europe and in the United States, plywood is being manufactured using 1-2 MeV electron accelerators (19).
- (5) Property modification (crosslinking, scission). Examples of this application include irradiating polyethylene pipe to improve stress-cracking resistance, polyethylene foam to improve creep and cell-size control, and Teflon degradation for spray lubricants.

6. CONCLUSIONS

The Radiation Applications Research Branch of AECL is investigating potential applications for gamma rays and electron beams to 10 MeV in the field of polymers and composites. Radiation polymerization technology has some unique advantages over other techniques. Successful commercial exploitation of radiation will depend on continuing research on polymer formulations, process design and reliability to reduce costs, and the willingness of potential users to accept this emerging technology.

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