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RADIATION CROSSLINKING OF CHLORINATED POLY(ISOBUTYLENE-*co*-ISOPRENE) WITH POLYFUNCTIONAL MONOMERS

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ABSTRACT

It is well known that poly(isobutylene-*co*-isoprene) (butyl rubber, IIR) is degraded by irradiation. However, we demonstrated that IIR, after chlorination (CIIR) crosslinks by electron beam (EB) irradiation. The gel dose for CIIR was 3.8 kGy. To avoid scission of the main chain, various polyfunctional monomers were added for crosslinking of CIIR at lower doses. It was found that trimethylolpropane trimethacrylate (TMPT) is the most effective accelerator for crosslinking of CIIR at a lower dose. The tensile strength of EB crosslinked by CIIR increases almost linearly with increasing TMPT content.

INTRODUCTION

Electron beam (EB) accelerators are very useful for modifying polymer materials by grafting, crosslinking, and degradation. These accelerators have been widely used to improve heat resistance by crosslinking of shrinkable tubes and insulating wires, and to pre-vulcanize car tires.

Poly(isobutylene-*co*-isoprene) (butyl rubber, IIR) has been widely used in industry because of its low permeability to moisture and gases, energy absorption over a wide temperature range, and resistance to chemicals including organic acids and detergents [1]. However, since IIR predominantly undergoes degradation rather than crosslinking by irradiation, this rubber is classified as a degradable polymer [2–4]. Recently, chlorinated poly(isobutylene-*co*-isoprene) (CIIR) rubber was developed. The valuable properties of CIIR are faster vulcanization by sulfur and heat resistance. It was confirmed by using ESR that the irradiating CIIR results in crosslinked products [5]. Polymeric materials often require large doses of radiation for crosslinking, so accelerators (sensitizers) are often used to reduce the required dose. Carbon tetrachloride, which produces radicals by degradation during irradiation [6], and polyfunctional monomers (PFM) with more than two double bonds per molecule [7, 8], are well known as sensitizers. In a previous paper [9] it was reported that poly(styrene-*co*-isoprene) (SBR) and *cis*-1,4-polyisoprene (IR) crosslink at lower doses in the presence of PFMs. The physical properties (tensile strength, elongation, and tear strength) of the crosslinked product was almost same as that of sulfur-vulcanized products obtained by the conventional method. In this article we report on the radiation crosslinking of CIIR in the presence of various PFMs.

EXPERIMENTAL

Materials

CIIR was supplied by Japan Synthetic Rubber Company. The chlorine content in CIIR is 1.2%. The PFMs used in this experiment are listed in Table 1.

Sample Preparation and Irradiation

CIIR was kneaded with a PFM for 8 minutes at 110°C at 40 rpm using a Labo Plastomill (Toyoseiki Co. Ltd.). Then, in order to make a sheet, the samples were hot-pressed at a pressure of 15 MPa for 3 minutes at 130°C using a spacer of 0.5 mm after preheating for 5 minutes at the same temperature.

Electron beam irradiation was carried out at a beam current of 1 mA and an acceleration energy of 1 MeV generated by a Cockroft-Walton type accelerator (maximum voltage and current of 2 MeV and 30 mA, respectively). The samples were irradiated by repeating 10 kGy/pass (1.43 kGy/s) to prevent thermal accumulation.

TABLE 1. Polyfunctional Monomers Used

Trade name	Chemical name	MW	F ^a	SU ^b
2G	Diethyleneglycol dimethacrylate	242	2	0.826
4G	Tetraethyleneglycol dimethacrylate	330	2	0.606
TMPT	Trimethylolpropane trimethacrylate	338	3	0.888
UA101H	Hexamethylene diisocyanate	624	4	0.641
UA306T	Tolyene diisocyanate	770	6	0.77

^aF: Functionality, number of double bonds in each monomer molecule.

^bSU: Specific unsaturation, mole double bonds per 100 g monomer.

Physical Properties of Irradiated CIIR

Tensile strength (Tb) and elongation at break (Eb) were estimated from stress-strain curves measured by using a tension meter (Storograph R-1, Toyoseiki Co. Ltd.). Tension speed was 500 mm/min.

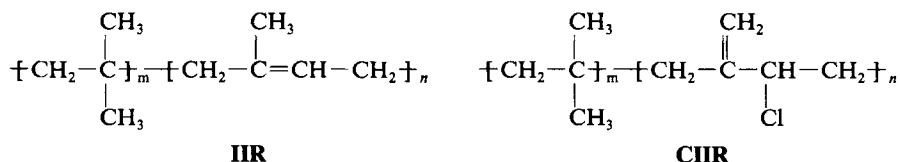
Gel Content and Volume Swelling Ratio

Solvent extraction and swelling methods were adopted to analyze the gel content (gel %) and volume swelling ratio (Q_v) [5, 14].

RESULTS AND DISCUSSION

Irradiation Effect of CIIR

It was reported [3, 10, 11] that irradiation by gamma-rays or an electron beam leads to the reduction of molecular weight and a decrease of physical properties of IIR. An acceptable explanation [1, 3] for this in IIR cannot be radiation-induced crosslinking because the double bond is very difficult to access due to overcrowding of the methyl groups attached to and surrounding the polymer chain backbone as shown below.



This overcrowding effect also prevents chain flexibility of CIIR, which was found in our experiment. Figure 1 shows the gel content, solubility fraction (S), and volume swelling ratio of EB-irradiated CIIR. Irradiated CIIR without a PFM gave a gel fraction of 80% at 50 kGy. By plotting $\log S$ against $\log D$, the value of the gelling dose (D_g), 3.8 kGy, was obtained. At a higher dose (> 100 kGy) the gel % decreased slightly as the dose increased as shown in Fig. 1. It is deduced that this reduction of gel % is due to degradation with a higher dose. This was verified by the decrease of $Q_v^{-5/3}$ as illustrated in Fig. 1. Since crosslink density is linearly

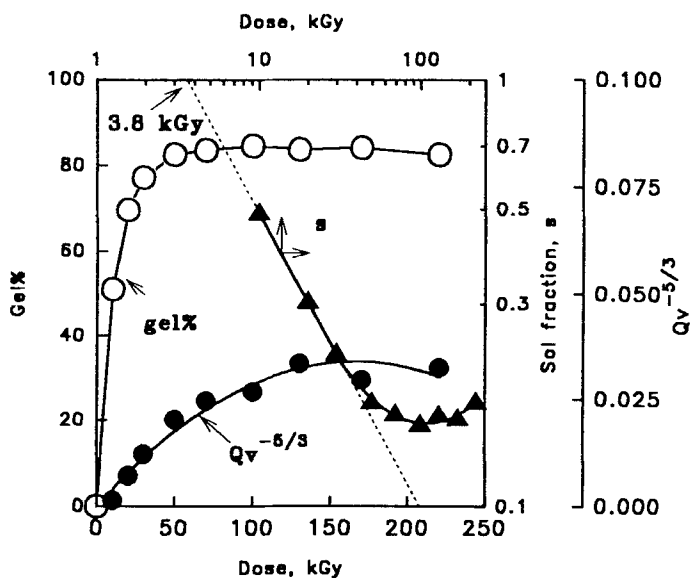


FIG. 1. Gel fraction and volume swelling ratio of EB crosslinked CIIR.

proportional to $Q_v^{-5/3}$ according to Flory's swelling theory [10], the decrease of $Q_v^{-5/3}$ means the reduction of crosslink density is caused by degradation of the crosslinked networks.

From the chemical repeat unit of CIIR [1, 4, 11] and IIR, as shown above, it is obvious that the double bonds of the IIR polymer chain lead to pendant groups after chlorination. These pendant unsaturated bonds are easily activated by irradiation and are more readily accessible so that active sites lead to a crosslinked network. However, the degradation reaction still occurs on the isobutylene chain units. It is predictable that gradual depletion of the reactive sites by crosslinking will lead to a predominance of chain scission and cause a decrease of the gel content as shown in Fig. 1. For the radiation crosslinking of CIIR, it is especially important to find effective means to reach the optimum degree of crosslinking at a low dose in order to avoid serious degradation which would cause a quick reduction in the physical properties.

Sensitizing Efficiency of Various PFMs

In recent years it was found that PFMs are effective for modification of polymer materials by crosslinking [2]. It was suggested that the mechanism by which this improvement occurs is crosslinking of the PFM grafted on the polymer backbone chain. In general, there are two factors which enhance efficiency of crosslinking by PFM [12]. One is the degree of unsaturation in PFM, and the other is the solubility of PFM in the polymer. If solubility is low, the monomer molecules cannot be well dispersed within the polymer. The PFM was added during kneading with CIIR using a Labo Plastomill. The solubility of monomers in polymers was evaluated by measuring the kneading force in the mixer. A lower kneading force is

required when slipping occurs between the polymer and the blades of the mixer, which indicates lower solubility of the PFM in the polymer.

Of the PFMs used for EB crosslinking of SBR and IR, TMPT, A-TMPT, and 2G were the most effective for improvement of physical properties [9, 14]. In this study the solubility of monomers in the rubber was estimated by measuring monomer absorption after immersion of rubber in monomers at 60°C for various time periods. High monomer absorption into the rubber gave a high crosslinking efficiency. For CIIR the relationship between kneading force and modulus (strength) at 500% elongation was investigated. Figure 2 shows the kneading force of CIIR in the mixer before irradiation and the modulus (E) of CIIR containing PFMs of 5 phr by irradiation at 30 kGy. The kneading forces of CIIR containing TMPT, 2G, and 4G are nearly the same as that of pure CIIR. This means that these monomers are well dispersed in CIIR. UA101H and UA306T showed a lower kneading force, suggesting that these PFMs are not well dispersed in the polymer. The modulus at 500% elongation (estimated from the stress-strain curve in the tension test) increased linearly with the crosslinking density, indicating that the modulus corresponds to the crosslinking density [10, 13]. The modulus increased in the following order: UA101H < UA306T < 4G < 2G < TMPT. As shown in Table 1, although UA101H and UA306T have SU values of 0.641 and 0.77, respectively, their crosslinking density is lower than that of 4G (SU 0.606), which has the minimum SU. TMPT has the highest SU and is well dispersed in CIIR according to the kneading force number. Hence, it is concluded that among the five PFMs, TMPT is the most effective for enhancing the crosslinking efficiency of CIIR due to better dispersion in CIIR and higher reactivity (SU 0.888).

Effect of Monomer Concentration on the Properties of CIIR

Figure 3 shows the change in the volume swelling ratio (Q_v) of EB-crosslinked CIIR with different TMPT contents. Q_v apparently decreased quickly in the presence of TMPT, especially at lower doses. The volume of Q_v at 10 kGy decreased

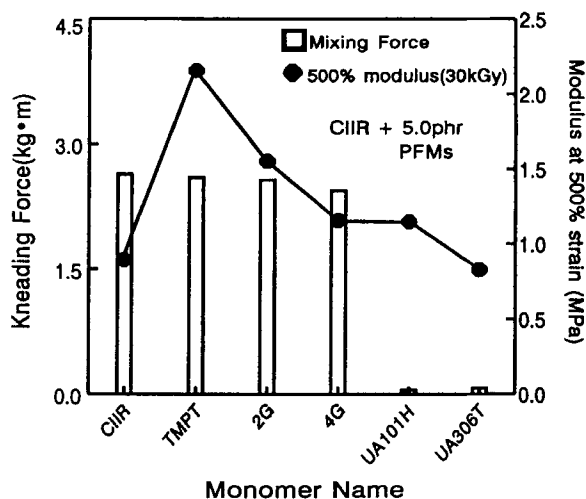


FIG. 2. Kneading forces and modulus of CIIR with 5.0 phr PFMs.

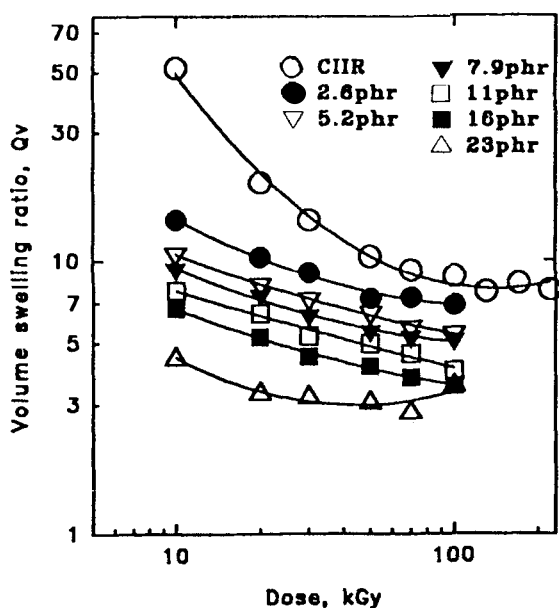


FIG. 3. Effect of TMPT content on the volume swelling ratio of CIIR.

from 52 to 14 by the addition of 2.6 phr TMPT. According to Flory's swelling theory of elastic polymers [10], a decrease of Q_v means an increase of crosslinking density. As shown in Fig. 3, the crosslinking density of CIIR increased with increasing TMPT concentration at the same dose. The gel fractions of CIIR irradiated by using TMPT are shown in Fig. 4. It can be seen that TMPT gave a higher gel

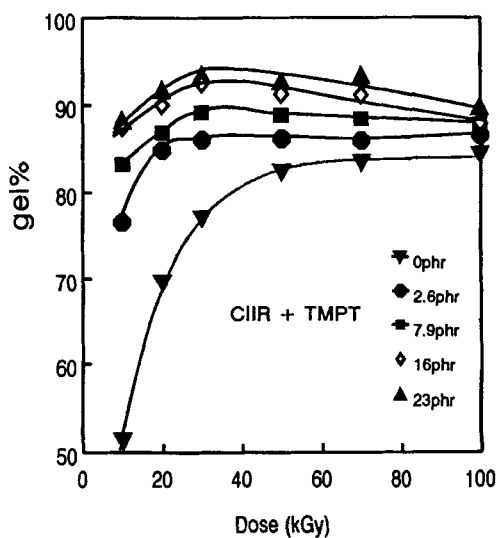


FIG. 4. Gel fraction of CIIR containing various amounts of TMPT.

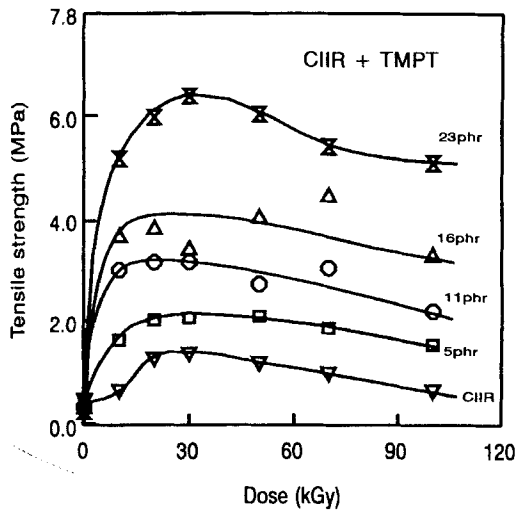


FIG. 5. Tensile strength of EB crosslinked CIIR with TMPT.

fraction at lower doses, and that the increase of gel fraction ceases at 20 kGy. TMPT is effective for radiation crosslinking of SBR (styrene-butadiene rubber) and IR (isoprene rubber) [12, 14]. The gel fraction of CIIR was higher than that of SBR and IR even at a lower dose with 2G as the sensitizer. For example, the gel fraction in SBR with 6 phr and in IR with 5 phr with 54 and 62%, respectively. CIIR with TMPT at 2.6 phr had a gel content of 85% even at 20 kGy irradiation. Figure 5 shows the change of tensile strength (Tb) against dose of EB-crosslinked

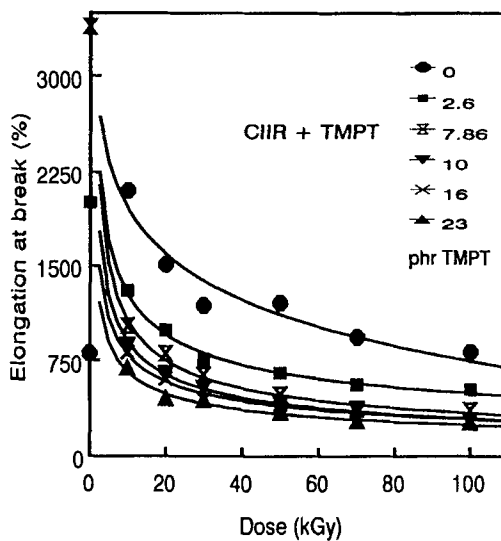


FIG. 6. Elongation at break of EB crosslinked CIIR with TMPT.

CIIR at different TMPT concentrations. The tensile strength increased with increasing TMPT concentration, and the maximum value was observed versus a dose of 30 kGy. A maximum tensile strength is often observed in radiation crosslinking of polymer materials; this is due to a reduction of elongation (Fig. 6) with increasing crosslinking density.

CONCLUSION

IIR radiation crosslinking is aided by chlorination. The resulting CIIR formed gels at a lower dose, 20 kGy. Among of 5 PFMs, TMPT is the most effective for enhancing the physical properties of CIIR because of its good solubility. The tensile strength of CIIR crosslinked using 23 phr TMPT was 7 MPa at 30 kGy. It is suggested that this is a practical technique for crosslinking CIIR containing fillers.

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