Crosslinking of *Cis*-1,4-Polyisoprene Rubber By Electron Beam Irradiation

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ABSTRACT: Various unsaturated polyfunctional monomers were kneaded into *cis*-1,4-polyisoprene containing fillers under 80°C and then irradiated using an electron beam accelerator to prepare vulcanized rubber with good quality. Results showed that 2G (diethyleneglycol dimethacrylate) is the best sensitizer. The optimal tensile strength of vulcanized IR was obtained by using 14 phr 2G and irradiated to 180 kGy. Compared with the sulfur vulcanizate, greater values of tensile strength, elongation at break, and 100% stress were found with the radiation-cured IR. Their Young's modulus and tan δ were similar. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 113–116, 1997

Key words: *cis*-1,4-polyisoprene; radiation crosslinking; electron beam; polyfunctional monomer; physical properties

INTRODUCTION

As early as in the 1950s,[1] rubbery polymers were found be crosslinkable by exposing to high energy radiation. Radiation crosslinking has many advantages[2] such as being fast, energy saving, and without pollution. But the necessary curing dose for rubbers was very high,[3] and deterioration of properties was caused by main-chain degradation. For these reasons radiation vulcanization has not yet been widely adopted in the rubber industry except in precuring of some types of tyres. But recently, the development of radiation vulcanization was accelerated by advances in radiation processing technology and the stimulating appeal of environment protection.

In previous articles the radiation crosslinking of styrene–butadiene rubber (SBR),[4] chlorinated IIR (CIIR),[5] and ethylene–propylene rubber (EPM)[6] have been investigated. The present article discusses the electron beam irradiation curing of *cis*-1,4-polyisoprene rubber containing fillers by using polyfunctional monomers to lower the curing dose and to optimize the properties of cured rubber.

EXPERIMENTAL

Materials

Cis-1,4-Polyisoprene rubber (Kuraprene IR-10) was supplied by Kuraray Co. Ltd. The unsaturated polyfunctional monomers listed in Table I were directly used in our experiment without further purification. Other reagents including fillers were all market source.

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Table I Polyfunctional Monomers Used in Experiments

Trade Name	Chemical Name	Molecular Weight	F[a]	SU[b]
2G	Diethyleneglycol dimethacrylate	242	2	0.83
TMPT	Trimethylolpropane trimethylacrylate	338	3	0.89
A-TMMT	Tetramethylolmethane tetraacryate	352	4	1.14

[a] F: Functionality, number of double bonds in each monomer molecule.
[b] SU: Specific unsaturation, mol double bonds per 100 g of monomer.

Sample Preparation

Raw rubber samples were prepared by kneading fillers into IR according to ASTM D3184 (IR 100phr, ZnO 5 phr, C 35 phr, Stearic acid 2 phr, kneading at 80°C for 8 min), and then divided into two master batches: one was for radiation curing and the other for sulfur curing, as shown in Figure 1.

Radiation Curing

Polyfunctional monomers were kneaded into the above raw rubber samples on a Laboplastomill at 80°C, and then sandwiched between two 0.1-mm thick polyester film, hot pressed into 0.5-mm thick sheet samples under 15 MPa and 100°C. The sheet sample was irradiated using a Cockroft-Walton-type accelerator (EPS type, Nishin High Voltage) with working beam current of 1.00 mA and electron beam energy of 1.00 MeV. Absorbed dose determination has been described before.[4]

Sulfur Curing

This was according to the ASTM D3184 method to prepare a sulfur-cured IR sample.

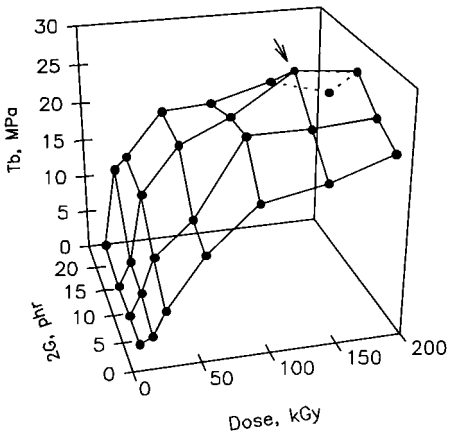

Figure 1 The tensile strength of radiation-cured IR.

Physical Properties Analysis

Tensile strength and elongation at break were measured on a Toyoseiki Storograph R-1 type tension meter conforming to the Japanese Industrial Standard (JIS) K6301. Dynamic mechanical thermal analysis (DMTA) was carried out on a Rheometrics RSA-II-type viscodynamic analyser.

RESULTS AND DISCUSSION

Sensitizer Selection and Radiation Curing Condition

When exposed to high-energy radiation, IR crosslinked, as described previously,[7] the accompanying degradation reaction becomes very serious under the required high curing dose. Consequently, it has been very difficult to obtain radiation-cured rubber with satisfactory properties. Various ways have been tried to sensitize the curing reaction to lower the necessary curing dose. Previous reports[4–6] showed that polyfunctional unsaturated monomers are effective radiation curing or crosslinking sensitizers for rubbers and other polymers.

The sensitizing efficiency of polyfunctional monomers is affected by two factors[4]: (1) the reactive degree or the specific unsaturation (SU value) of the PFM; and (2) the solubility of PFM in the target polymer. However, the PFM's molecular weight is usually beyond 10^2, and is very difficulty to determine by common methods. When a Laboplastomill was used to mix PFMs into the polymer, we found that the kneading torque could be used to characterize the PFM's solubility semiquantitatively.[4,5] When its solubility is not high enough, the PFM wraps around the polymer particles just like a lubricant, and the kneading torque cannot rise high enough to disperse the PFM well.

Table II Tensile Strength of IR Cured with 5 phr PFM and 200 k Gy

	IR	2G	TMPT	A-TMMT
Kneading torque/kg · m	3.14	3.11	2.95	2.11
Tensile strength/MPa	14.3	20.6	21.9	20.2

Data in Table II show that the tensile strength of electron beam cured IR with 2G, TMPT, and A-TMMT all are very high, but the kneading torques for TMPT and A-TMMT are smaller; therefore, 2G was selected as the sensitizer to cure IR.

Figure 1 shows the tensile strengths of electron beam-cured IR samples filled as referred in ASTM D3184 described above. When 2G content was 14 phr and curing dose was 150 kGy, maximum tensile strength was achieved via electron beam irradiation of the samples. Increasing 2G to a larger content or elevating the curing dose will both decrease the tensile strength.

Properties of Cured Rubber

Results in Table III and Figure 2 show the the tensile strength, elongation at break, and 100% modulus of electron beam-cured IR are all higher than those of the sulfur cured IR. Figure 3 shows the cured IR samples have similar modulus and tan δ. Thus, this further verified that better elastomers can be achieved through radiation curing by using suitable composition and curing condition. The tear strength of electron beam-cured IR was smaller than for the sulfur vulcanizate. This might be caused by the different crosslinking bonds formed in the cured rubber.

The dynamic moduli and tan δ of the crosslinked samples are shown in Figure 3. Energy loss or damping is one of the basic properties of rubbery polymers. Elastomers with higher damping coefficient (tan δ) have better vibration-dampening and noise-elimination properties, but this is accompanied by a loss of dimensional stability. Tan δ is an important factor for engineering materials. Figure 3 show the electron beam-cured IR has similar damping properties as sulfur vulcanizate; their tan δ change in a similar way with temperature. The dynamic modulus or Young's modulus (E') directly reflects the strength of the cured rubber. Electron beam-cured IR has similar modulus–temperature properties to sulfur-cured IR, as shown in Figure 3.

Table III Physical Properties of IR Cured by Radiation and Sulfur[a]

	Radiation	Sulfur
Hardness, Hs(JIS A)	55	50
Tensile strength, MPa	29.6	28
Elongation at break, %	690	620
100% modulus, MPa	1.8	1.6
Tear strength, kN · m^{-1}	36	49

[a] 14 phr 2 G was used and absorbed dose was 150 kGy.

CONCLUSION

The important results found in the present work are summarized as follows: (1) the overall physical properties of electron beam-cured IR with proper polyfunctional monomers are similar to sulfur crosslinked rubber; and (2) the best polyfunctional monomer for electron beam curing of IR is 2G among the monomers tested in this article.

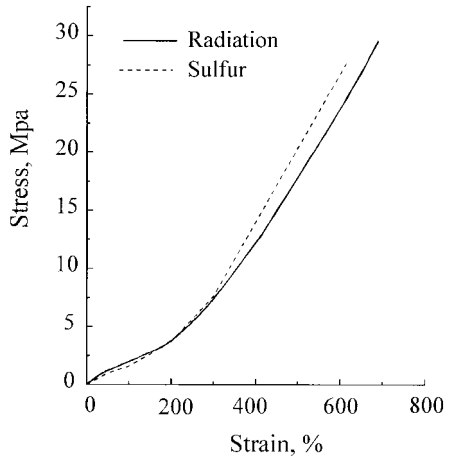

Figure 2 Stress–strain curve of radiation and sulfur-cured IR.

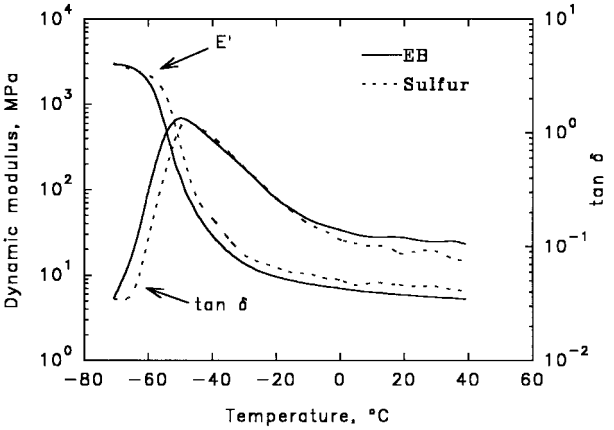

Figure 3 DMTA curve of radiation and sulfur-cured IR at 10 Hz.

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