Vulcanization of 1-Chlorobutadiene–Butadiene Rubber with Diepoxy Compound

KATSUMI SANDO,[1,2,*] AZANAM SHAH HASHIM,[2] YUKO IKEDA,[2] SHINZO KOHJIYA,[3] SHINZO YAMASHITA,[2] and NARIYOSHI KAWABATA[2]

[1]Elastomers Development, Polymer Laboratories, TOSOH Corporation, Shin-nanyo-shi, Yamaguchi 746, Japan;
[2]Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan;
[3]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

SYNOPSIS

Diepoxy vulcanization system of 1-chlorobutadiene–butadiene rubber (CB–BR) having hydroxyl groups with diglycidyl ether of bisphenol A (DGEBA) was studied in the presence of acid anhydrides. Phthalic anhydride (PAn), hexahydrophthalic anhydride (HAn), maleic anhydride (MAn), and succinic anhydride (SAn) were investigated as cocuring agents. The results of this investigation indicated that the hydroxyl groups attached to the polybutadiene backbone react with DGEBA to afford a CB–BR vulcanizate. The vulcanization rate depended on the kinds of acid anhydrides in the following order: PAn > MAn > SAn > HAn. It is assumed that the reaction between the hydroxyl group in CB–BR and acid anhydride was the rate-determining step. The vulcanization of CB–BR with a higher amount of DGEBA afforded resinous rubber vulcanizates. Thus, DGEBA was concluded to act not only as a curing agent, but also as a reinforcing agent for CB–BR. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The addition of rubbers to plastics physically or chemically is usually carried out to improve the impact resistance of the materials. One example of these so-called rubber-toughened plastics is the acrylonitrile–butadiene–styrene (ABS) resin, which is obtained by copolymerizing acrylonitrile and styrene in the presence of polybutadiene latex.[1] Conversely, the properties of rubbers can be modified or improved by adding plastics. The dynamic vulcanization of polyethylene–propylene rubbers with polypropylene and the peroxide cure of tetraacrylate ester/natural rubber have been reported.[2-4] Epoxy reagents, which are normally cured with amines or anhydrides to yield thermoplastics with an excellent heat resistance,[5] seem to be suitable cross-linking agents for appropriately functionalized diene rubbers. These epoxy–rubber composites may exhibit some special or interesting properties. However, reports on the bulk reaction or cross-linking of diene rubbers with epoxies are not available. Therefore, we did an investigation on an epoxy–rubber system that involves the curing of 1-chlorobutadiene–butadiene rubber (CB–BR) with diglycidyl ether of bisphenol A (DGEBA) in the presence of acid anhydride as a cocuring agent.

CB–BR was synthesized by emulsion polymerization,[6,7] and it contains hydroxyl groups that were introduced by the hydrolysis of reactive chlorines that were attached to 1,4-addition unit of 1-chlorobutadiene.[8,9] In our previous study, CB–BR was cross-linked with diisocyanate by making use of the hydroxyl groups.[10] In this report, the curing reaction of CB–BR with DGEBA and acid anhydrides was studied. The reaction is considered to involve the initial and cross-linking steps as proposed in Figure 1. The OH groups of the rubber are first converted to COOH groups by an acid anhydride. Subsequently, the cross-linking reaction takes place between the COOH (of the rubber and excess anhydride) and the epoxies. Our investigation focused on the effect of each cocuring agent on the curing
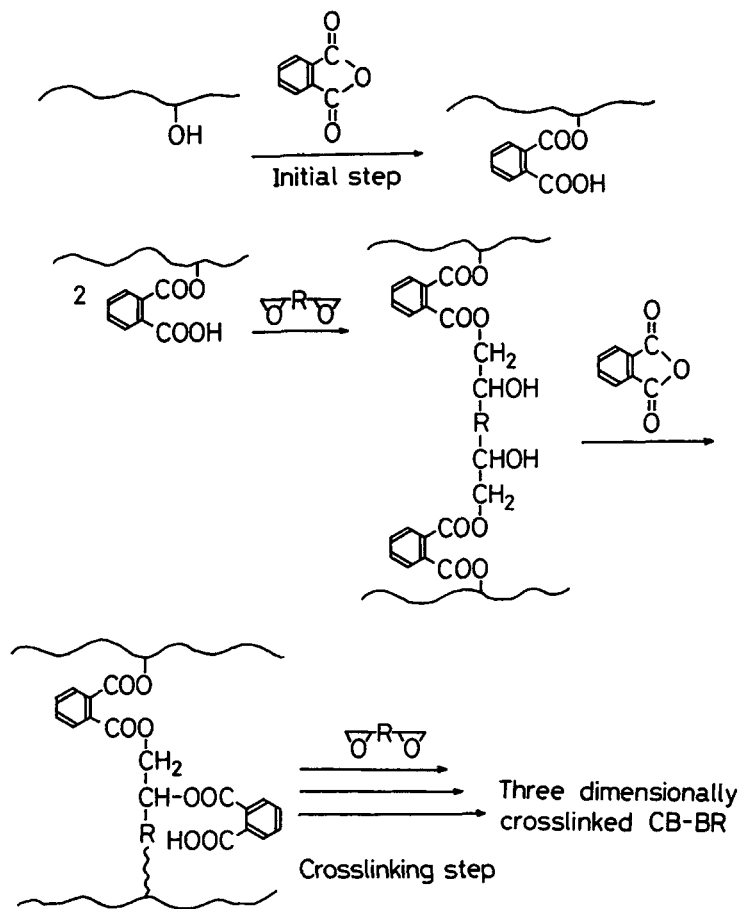
Figure 1   Cross-linking of CB–BR by DGEBA and acid anhydride.

behavior and the physical properties of the resultant vulcanizates.

EXPERIMENTAL

Materials

CB–BR was synthesized by low-temperature emulsion copolymerization according to the method reported by Yamashita and coworkers.[7] Two samples were prepared and their properties are shown in Table I. The hydroxyl group content of the samples were determined by the UV method reported previously.[8] Commercial DGEBA of molecular weight 340 and acid anhydrides were used in this experiment. The molecular structure and properties of each acid anhydride are shown in Table II with their abbreviations for simplicity.

Compounding and Vulcanization

DGEBA and acid anhydrides were blended with CB–BR on a two-roll mill to obtain mixes according to the appropriate recipes. The epoxy–rubber vulcanizates were obtained by heat-pressing the mixes at a constant temperature of 150°C for a prescribed time.

Table I   CB–BR Samples and Their Properties

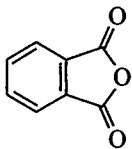| Sample	$(\eta)^a$	M_n^b $\times 10^{-4}$	$(Cl)^c$ (mol/kg)	$(OH)^d$ (mol/kg)
CB–BR(A)	2.19	—^{e}	0.23	0.18
CB–BR(B)	2.75	8.8	0.40	0.14

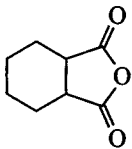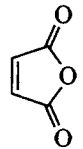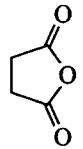^{a} At 25.9°C in toluene.
^{b} By osmotic pressure method.
^{c} By elemental analysis.
^{d} By UV spectroscopy.
^{e} Not determined.

Table II Acid Anhydrides and Their Properties

Acid Anhydrides	Abbreviation	MS[a]	MW[b]	mp[c] (°C)
Phthalic anhydride	PAn		148	134
Hexahydrophthalic anhydride	HAn		154	33
Maleic anhydride	MAn		98	55
Succinic anhydride	SAn		100	120

[a] Molecular structure.
[b] Molecular weight.
[c] Melting point.

IR Measurement

Infrared (IR) analysis was carried out by a Fourier-transform infrared spectrometer FTIR 4100 (Shimadzu Corp.) The attenuated total reflection (ATR) method was used for the vulcanizates. The prism was KRS-5, the incident angle was 45°, and the resolution was 4 cm⁻¹. Spectra were obtained after accumulation of 500 scans.

Measurements of Physical Properties

The tensile test of the vulcanizates was carried out on an autographic tensile tester (Shinkoh Tushin Kogyo Co.) at room temperature. The extension speed was 500 mm/min. The test pieces were dumbbells prepared according to JIS Type 3. The equilibrium swelling method was employed to determine ν_s, the network chain density of the vulcanizates. The equilibrium degree of swelling of the vulcanizates in benzene was attained after 72 h at 25°C. ν_s is calculated using the Flory–Rehner equation,[11,12] where the rubber–solvent interaction parameter (μ)

is taken to be 0.395.[10] The sol fraction (S_F) was determined after swelling under the same conditions as those of the equilibrium swelling test.

RESULTS AND DISCUSSION

Diepoxy Vulcanization of CB–BR

Diepoxy vulcanization of CB–BR rubber was carried out with DGEBA in the presence of an acid anhydride as a cocuring agent. CB–BR(A) was compounded with DGEBA and phthalic anhydride (PAn) according to the recipes in Table III, followed by pressing the resultant mixes at 150°C for 1, 2, and 4 h. IR spectra of these compounds showed the absorbances of the carbonyl stretching vibration at ca. 1700 and 1850 cm⁻¹ and the C=C stretching vibration of phenyl group at ca. 1600 cm⁻¹ together with absorbance peaks derived from CB–BR. However, the characteristic absorbance of the reverse symmetry ring stretching vibration of epoxy groups in DGEBA, which was expected to be observed at

Table III Compound Recipes in phr for Diepoxy Vulcanization of CB–BR with PAn as a Cocuring Agent

Ingredient	Recipe			
	A	B	C	D
CB–BR(A)	100	100	100	100
DGEBA[a]	1.7	3.4	5.1	6.8
PAn[b]	2.7	4.0	5.3	6.7

[a] Molar ratio of epoxide in DGEBA to hydroxyl group in CB–BR was 0.5, 1.0, 1.5, and 2.0, respectively.

[b] Molar ratio of PAn to hydroxyl group in CB–BR was 1.0, 1.5, 2.0, and 2.5, respectively.

ca. 910 cm^{-1}, was not confirmed because of overlapping with that of CB–BR at ca. 910 cm^{-1}. The carbonyl stretching vibration absorbance became weak with increasing cure time and a new absorbance of ester group at ca. 1730 cm^{-1} was observed. The larger the amount of DGEBA and PAn, the stronger the intensity of the carbonyl stretching vibration. ν_s vulues of these vulcanizates as a function of DGEBA concentration are shown in Figure 2. For each cure time, ν_s of each vulcanizate approaches some constant value at about 5 phr of DGEBA. It can be inferred from the figure that the cross-linking reaction continues beyond 4 h at 150°C for each recipe. However, for a particular cure time, an optimum cure seems to be attainable at a particular concentration ratio of PAn to DGEBA, beyond which one of the two is already in excess. When the cure time
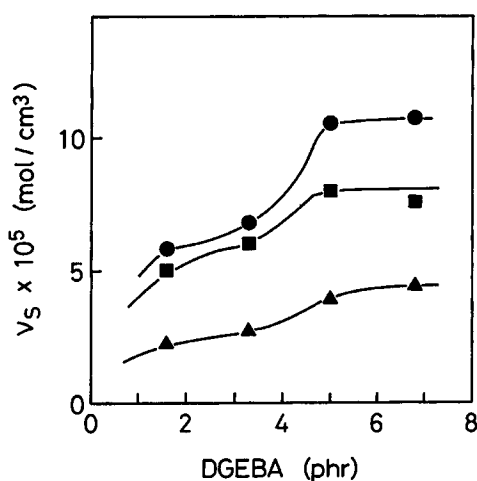
is sufficiently long, there is an apparent critical ratio of PAn and DGEBA for optimum cure. It is therefore of interest to determine what this particular ratio is and also the effect of the concentration of each curing agent on the curing behavior of this system.

Subsequently, a few recipes containing a high and constant amount of DGEBA were investigated. Recipe E in Table IV shows a DGEBA concentration of 20 phr, whereas that of PAn varies. The lower hydroxyl content CB–BR and the higher amount of DGEBA were chosen in order to increase the probability that all the OH groups will be converted to COOH groups in the initial step of Figure 1, followed by their reaction with epoxy groups. The effect of PAn concentration on the tensile properties, i.e., modulus at 100% (M_{100}) and 200% elongation (M_{200}), the S_F, tensile strength (T_B), and elongation at break (E_B), was observed and are shown in Figures 3 and 4. The tensile properties and S_F approach some constant values at approximately 12 phr of PAn. These results suggest that the optimum cure or the cross-link density could be obtained at this concentration of PAn under the present experimental conditions. Beyond this concentration, assuming that all the functional groups can fully react, there seems to be more than enough COOH for the epoxy groups to react with.

The molar quantities of reactive functional groups contained in recipes A, B, C, D, and E are calculated. By analyzing the data, the critical molar ratio for optimum cure seems to be roughly at ($M_{PAn} - M_{OH}$): M_{DGEBA} of 1 : 1, where the former is the difference in moles between PAn and OH, where M_{OH}, M_{PAn}, and M_{DGEBA} are the respective moles of OH, PAn,

Figure 2 Effect of DGEBA concentration on ν_s for diepoxy vulcanizates of CB–BR with PAn as a cocuring agent (recipes A, B, C, and D in Table III). Cure temperature, 150°C. Cure time: (▲) 1 h; (■) 2 h; (●) 4 h.

Table IV Compound Recipes for Diepoxide and Sulfur Vulcanization of CB–BR

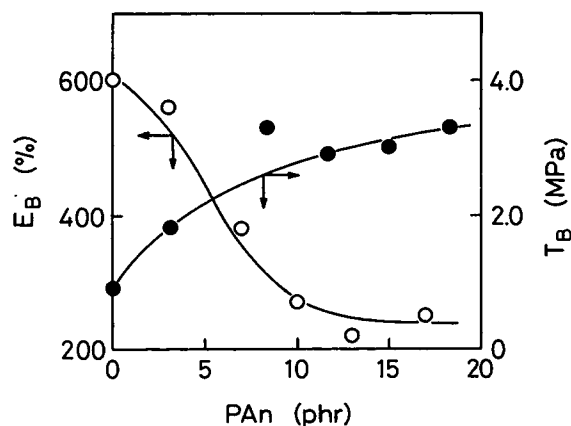| Ingredient	Recipe		
	E	F	G
CB–BR(A)	—	100	100
CB–BR(B)	100	—	—
DGEBA	20	5–30	—
PAn	0–30	5.1–15.7[a]	—
HAF black	—	40	40
Process oil	—	—	0–22
Stearic acid	—	—	1.0
ZnO	—	—	5
Sulfur	—	—	2
CZ[b]	—	—	1.5

[a] [PAn] = [OH]$_{CB-BR}$ + [DGEBA].

[b] Cyclohexyl benzothiazyl sulfenamide.
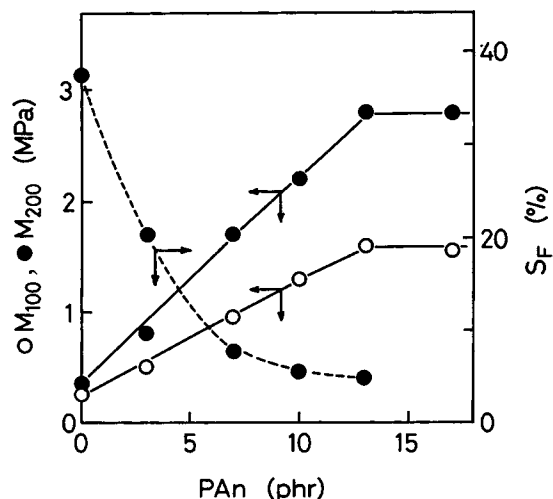
Figure 3 Effect of PAn concentration on M_{100}, M_{200}, and S_F of diepoxide vulcanizates of CB–BR (recipe E in Table IV). Cure conditions: 150°C, 80 min. (○) M_{100}; (●) M_{200}; (●) S_F.

and DGEBA. This implies that all the OH groups of the rubber were converted to COOH according to the initial step in Figure 1 and that the epoxy was reacting with the anhydride stoichiometrically as a normal epoxy–anhydride curing system. In this case, the curing reaction occurs in a rubber matrix and the cured epoxy is expected to be chemically linked to the rubber chains as an integral part of the network.
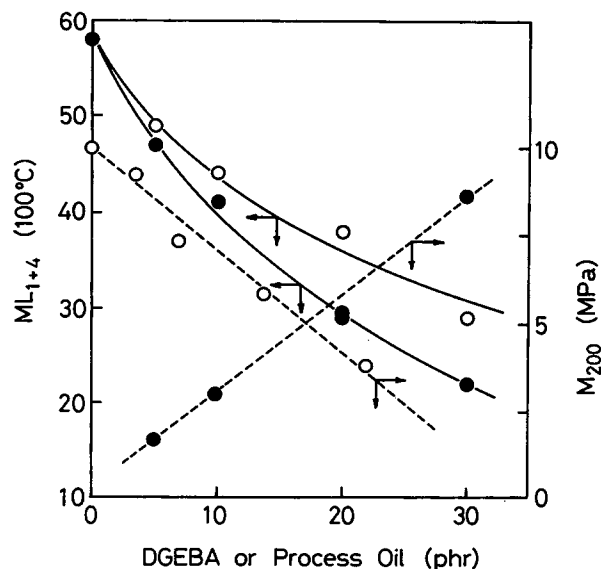
The optimum S_F can also be taken to represent the optimum cure, which seems to occur when the S_F stabilizes at about 5% as shown in Figure 3. By comparing Figure 2 to Figure 3, the effect of DGEBA

and PAn concentrations on the optimum cure time is apparent. The optimum cure time could be reduced from more than 3 h for recipes A, B, C, and D to about 80 min for recipe E with 10 phr PAn by increasing the ratio of ($M_{PAn} - M_{OH}$) and M_{DGEBA}. It is interesting to note that the sol fraction for the recipe with 0 phr of PAn is not so high against our prediction as shown in Figure 3, which indicates the presence of cross-linking in compounds without PAn. The most probable cross-linking reaction in this case is believed to be between OH of the rubber and DGEBA. However, the tensile properties observed under these conditions are relatively low and very much comparable to the typical green strength of uncross-linked rubbers. Thus, the contribution of these cross-links to the physical properties is insignificant and can be ignored.

The effect of increasing DGEBA on the Mooney viscosity (ML_{1+4} at 100°C) of the mixes and M_{200} of the vulcanizate at equivalent moles of PAn to OH groups on CB–BR plus DGEBA is demonstrated by Figure 5 (recipe F in Table IV). Carbon black was added to the compounds so that the handling of the viscous one is made easy. Thus, a typical sulfur-cured vulcanizate with an increasing amount of process oil (recipe G) is included for comparison. It is obvious that DGEBA is not a plasticizer but rather a reinforcer unlike the process oil. The observed reinforcing effect could only be explained by assum-

Figure 4 Effect of PAn concentration on T_B and E_B of diepoxide vulcanizates of CB–BR (recipe E in Table IV). Cure conditions: 150°C, 80 min. (○) E_B; (●) T_B.

Figure 5 Effect of process oil and DGEBA concentration on ML_{1+4} at 100°C and M_{200} of diepoxide and sulfur vulcanizates of CB–BR (recipes F and G in Table IV). Cure conditions: 150°C, 80 min. (○) DGEBA; (●) process oil.

Table V Compound Recipes for Diepoxy Vulcanization of CB–BR with Different Acid Anhydrides as Cocuring Agent

| Ingredient	Recipe		
	H	I	J
CB–BR(A)	100	100	100
DGBEA[a]	5.1	5.1	5.1
HAn[b]	5.6	—	—
MAn[b]	—	3.5	—
SAn[b]	—	—	3.6

[a] Molar ratio of epoxide in DGBEA to hydroxyl group in CB–BR was 1.5.

[b] Equivalent mole of acid anhydride to epoxide in DGEBA plus hydroxyl group in CB–BR was used.

ing that the DGEBA is chemically bonded and forms an integral part of the network structure.

Cross-linking Rate of Diepoxy Vulcanization of CB–BR

The effect of various acid anhydrides as cocuring agents on the cross-linking rate was investigated. HAn, MAn, and SAn were compared with PAn. The recipes, in which the moles of acid anhydrides and epoxides are kept the same as those of recipe C, are
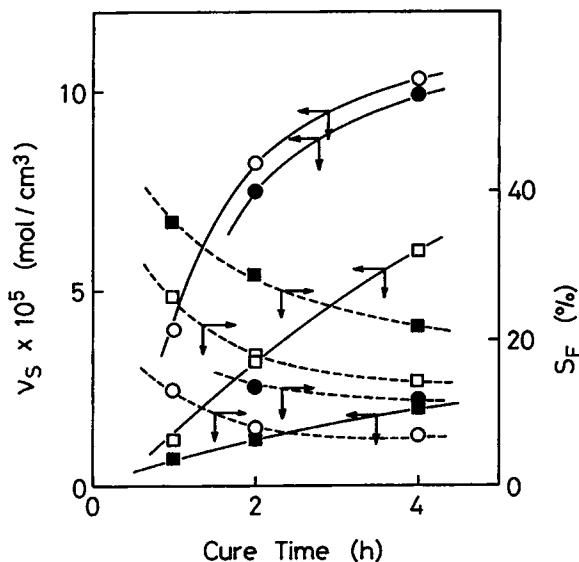
Figure 6 Effect of cure time on ν_s and S_F for diepoxy vulcanizates of CB–BR with various acid anhydrides (recipes C, H, I, and J in Tables III and V). Cure temperature: 150°C. Acid anhydrides: (O) PAn; (●) MAn; (□) SAn; (■) HAn.

shown in Table V. Figure 6 shows the effect of cure time on the ν_s and S_F, for each acid anhydride. It is observed that the cross-linking rate varies with the kinds of acid anhydrides and decreases in the following order of the acids:

$$PAn > MAn > SAn > HAn$$

Consistently, the S_F of the vulcanizates was found to decrease in the same order as that of the acids. These results indicate that the cross-linking rate of CB–BR with DGEBA depends very much on the kinds of acid anhydrides used. Assuming first-order kinetics, the apparent cross-linking rate constant (k) can be calculated from eq. (1):

$$d\nu/dt = k\nu_\infty - k\nu \qquad (1)$$

where ν is the cross-link density at cure time t, and ν_∞, the asymptotic value of ν. Both $d\nu/dt$ and ν are available from the ν_s vs. the t curve in Figure 6 at each time t. The plot of $d\nu/dt$ against ν gives a straight line with a slope k; the intercept, which was obtained by extrapolating the slope to $d\nu/dt = 0$, gives ν_∞. The calculated k and ν_∞ for each recipe are shown in Table VI. The values indicate that k and ν_∞ of the epoxy-curing system by using PAn became the same order and magnitude as those of the sulfur-curing system. By analyzing Tables II and VI, the molecular weight and melting temperature of the anhydrides would not be the probable causes for the differences in k and ν_∞. The differences may be due to the solubility differences of each anhydride

Table VI Rate Constant and Limiting Cross-link Density of Diepoxy and Sulfur Vulcanizates

Ingredient	k^a (L/min)	$\nu_\infty{}^b$ (10^4 mol/cm^3)
Diepoxy vulcanizate[c] with		
PAn	0.025	1.10
MAn	0.009	1.10
SAn	0.007	0.76
HAn	0.004	0.37
Sulfur vulcanizate[d] with		
S-CZ	0.041	1.76

[a] Rate constant of cross-linking reaction.

[b] Limiting cross-linking density.

[c] PAn vulcanizate was prepared by recipe D in Table III. MAn, SAn, and HAn vulcanizates were prepared by recipe H, I, and J in Table V, respectively.

[d] Sulfur vulcanizates by recipe G without process oil was cured at 150°C as shown in Table IV.

in the rubber, which is much related to its chemical nature in the same way that cyclic alkene is a better solvent for rubber than is cyclic alkane. It seems that SAn and HAn are so limited in their solubility that not all the hydroxyls of CB–BR are probably converted to COOH groups. This would be one of the reasons why recipes with SAn and HAn had lower k values and could not attain ν_∞'s comparable to those recipes with PAn.

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