Liquid Rubber as a Reactive Softener for 1-Chlorobutadiene–Butadiene Rubber

KATSUMI SANDO,[1,2] SHINZO KOHJIYA,[3] YUKO IKEDA,[2,*] 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

Blending of hydroxyl-terminated liquid butadiene rubber (HT-BR) with 1-chlorobutadiene–butadiene rubber (CB–BR) was carried out in the presence of isopropylidenedicyclohexyl diisocianate (IPCI) or sulfur as a curing agent. It was found that the HT-BR/CB–BR blend displayed a good plasticity, i.e., its Mooney viscosity became lower than that of CB–BR, which brought about a good processability. The HT-BR fraction (E_S) from the HT-BR/CB–BR blend vulcanizates, which was prepared by the IPCI-cured system, was evaluated to be ca. 20% by the equilibrium swelling test in benzene. The E_S of the sulfur-cured blend was ca. 70%. This result shows that HT-BR acted as a reactive softener when it was compounded with CB–BR by curing with the diisocyanate. The tensile strength of the IPCI vulcanizate was exceedingly higher than that of sulfur-cured vulcanizate at all blend ratios of HT-BR to CB–BR. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Softeners such as naphtenic and aromatic mineral oils play an important role in preparing a rubber compound. A beneficial effect of softeners brings about an improvement in the processing of the rubber compound, i.e., it saves energy in the mixing process of rubber and makes it easier to disperse fillers in the rubber matrix. However, the addition of softeners often resulted in decrease of the mechanical properties, such as the lowering of the elastic modulus, tensile strength, and so on. Additionally, when the vulcanizates are in contact with a solvent, the softeners in them are extracted by the solvent to, consequently, change their physical properties. To overcome these problems, Eldred[1] studied the reactive softener for rubber compounds, in which the mixtures of a nitrile rubber and acrylate monomers were heated together in the presence of peroxide. The graft polymerization of acrylate monomer onto the rubber backbone improved the

extraction resistance of softener from the rubber. Takamatsu et al.[2] also reported a liquid hydrogenated polyisoprene as a reactive softener for polyethylene–propylene rubber or poly(isoprene-co-butylene) rubber using by the sulfur- or peroxide-cured method.

Generally, telechelic oligomers are expected to be one of the efficient reactive softeners for rubbers, when the end groups of oligomers are used for the crosslinking of rubber followed by the incorporation of oligomers into elastic networks. In this report, the improvement of the processability and physical properties of 1-chlorobutadiene–butadiene rubber (CB–BR) was studied by using hydroxyl-terminated liquid butadiene rubber (HT-BR) as a reactive softener. Originally, CB–BR was a copolymer of 1-chlorobutadiene and butadiene,[3,4] and it carries hydroxyl groups which were introduced by hydrolysis of reactive chlorines at a 1,4-addition unit of 1-chlorobutadiene.[5,7] In our previous study, CB–BR was crosslinked by a cocuring system of sulfur and diisocyanate which was allowed to react with the hydroxyl groups of CB–BR.[6,7] Therefore, HT-BR is expected to be suitable for a reactive softener of the CB–BR/diisocyanate system, because isocyanate

groups of the curing agent may be allowed to react with hydroxyl groups both of CB–BR and HT-BR. The properties of the CB–BR/HT-BR blend vulcanizates by the diisocianate-cured system are discussed in this study by comparing them to those prepared from the sulfur-cured system.

EXPERIMENTAL

Materials

1-Chlorobutadiene–butadiene rubber (CB–BR) was synthesized by the emulsion copolymerization at 5°C as reported previously.[4] The structure of CB–BR is shown in Figure 1 and its properties are summarized in Table I. The hydroxyl groups were introduced to CB–BR by hydrolysis of CB–BR latex by heating.[6] The hydroxyl group content was determined by UV spectroscopy.[5] The hydroxyl-terminated liquid polybutadiene (HT-BR) was a commercially available product from Idemitsu Petrochemical Co., whose degree of polymerization was 55 and hydroxyl content was 7.5×10^{-4} mol/g. Isopropylidenedicyclohexyl diisocyanate (IPCI) was used after purification by removing the urea parts, which did not dissolve in hot heptane. Other commercial ingredients were used without further purification other than drying.

Compounding and Vulcanization

CB–BR was blended with HT-BR and the other ingredients in a two-roll mill. The formulations are shown in Table II. Table II includes two curing systems: One is a popular sulfur/organic accelerator system. The other uses a diisocyanate, because both the rubber components, i.e., CB–BR and HT-BR, have hydroxyl groups. There are quite a few diisocyanate compounds, and we tried several for the present hydroxyl-containing butadiene rubber mixtures. However, all other than IPCI which are listed in Table II were not suitable: Several commercially available diisocyanates were examined, but both aromatic (e.g., toluene diisocyanate) and aliphatic diisocyanates (e.g., hexamethylene diisocyanate) were found to react too fast to control the curing reaction. In other words, when these compounds were mixed with the rubber in an open roll mill, the reaction with the hydroxyl groups started immediately, and
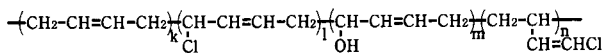

$$-\!\!\left(CH_2\text{-}CH\text{=}CH\text{-}CH_2\right)_{k}\!\!\underset{Cl}{\overset{|}{C}}H\text{-}CH\text{=}CH\text{-}CH_2\!\!\left)_{l}\!\!\underset{OH}{\overset{|}{C}}H\text{-}CH\text{=}CH\text{-}CH_2\!\!\right)_{m}\!\!\left(CH_2\text{-}CH\right)_{n}\!\!\underset{CH\text{=}CHCl}{\overset{|}{}}$$

Figure 1   Chemical structure of CB–BR.

Table I   Properties of CB–BR

Sample	$[\eta]^{a}$ (dL/mol)	M_n^{b} (g/mol)	$[Cl]^{c}$ (mol/kg)	$[OH]^{d}$ (mol/kg)
CB–BR	2.43	80,000	0.45	0.29

[a] At 25.9°C in toluene.
[b] By osmotic pressure method.
[c] By elemental analysis.
[d] By UV spectroscopy (see Ref. 6).

it became impossible to obtain the good mixing of the diisocyanate and the rubber. This is the trouble called "scorch" by rubber technologists.

On the other hand, IPCI was not so reactive, and it was possible to mix it in an open roll mill at room temperature (RT) followed by the curing at 100°C. The vulcanizates were obtained by heat-pressing the compound at a constant temperature for a prescribed time.

Measurements of Physical Properties

Mooney viscosity was measured on Mooney viscometer (Shimazdu Co.). A tensile test of the vulcanizates was carried out on an autographic tensile tester (Shinkoh Tushin Kogyo Co.) at RT. The test pieces were dumbbells prepared according to JIS Type 3. The equilibrium swelling method was employed to determine the network chain density of vulcanizates (ν_S). The equilibrium swelling of the vulcanizates in benzene was attained after 72 h at 25°C. ν_S is calculated by the Flory–Rehner equation,[8,9] where the interaction parameter (μ) between rubber and solvent was taken to be 0.395.[7] The sol fraction (S_F) was determined after swelling under the same conditions with the equilibrium swelling test.

RESULTS AND DISCUSSION

Plasticity of HT-BR/CB–BR Blends

HT-BR is expected to act as a softener for CB–BR because of its low viscosity. The influence of the HT-BR amount on the Mooney viscosity of the HT-BR/CB–BR blends without any other ingredients is shown in Figure 2. When the blend ratio of HT-BR to CB–BR was changed from 0/100 to 30/70, the Mooney viscosity decreased from 36 for HT-BR/CB–BR = 0/100 to 13 for HT-BR/CB–BR = 30/70. This remarkable decrease clearly suggested that HT-BR is an excellent softener for CB–BR.

Table II   Recipes for IPCI and Sulfur Vulcanizations of HT–BR/CB–BR Blends

Ingredient	Recipe			
	A	B	C	D
CB–BR	100	100	100	100
HT–BR	0–40	0–40	0–40	0–40
HAF carbon black	0	40	0	40
IPCI[a]	4.2–6.3	4.2–6.3	—	—
Stearic acid	—	—	0.5	0.5
ZnO	—	—	5	5
Sulfur	—	—	2	2
CZ[b]	—	—	1.5	1.5

[a] Isopropylidenedicyclohexyl diisocyanate, which was compounded as equivalent to hydroxyl groups of CB–BR.
[b] Cyclohexylbenzothiazyl sulfenamide.

Effect of Cure System on Swelling Properties of HT-BR/CB-BR Blends

The gum stock vulcanization of HT-BR/CB–BR blends was carried out by using IPCI (the molar ratio of [NCO] to [OH] was 1.0) or sulfur according to recipe A or C, respectively, as shown in Table II. Figures 3 and 4 show the effect of the HT-BR/CB–BR blend ratio on ν_S and S_F of the vulcanizates, which were obtained from the swelling experiments in benzene. The ν_S decreased and S_F increased with increase of the blend ratio. Comparing their sol fractions of vulcanizates which were blended with 33% of HT-BR, the S_F of the IPCI-cured system was only 7%, while that of the sulfur-cured system was 23%. It was noticeable that the IPCI-cured sys-

tem showed a much lower S_F than that of the sulfur-cured system.

To evaluate the amount of HT-BR incorporated into the elastic networks, the fraction (E_S) of the extracted HT-BR in benzene to the total amount of HT-BR was calculated as follows:

$$E_S(\%) = (S_{F,\text{blend}} - S_{F,\text{CB-BR}} \times P_{\text{CB-BR}})/P_{\text{HT-BR}} \quad (1)$$

where $S_{F,\text{blend}}$ is the percent of the sol fraction of the HT-BR/CB–BR blend vulcanizates, $S_{F,\text{CB-BR}}$ is that of the CB–BR vulcanizate, and $P_{\text{CB-BR}}$ and $P_{\text{HT-BR}}$ are the fraction of CB–BR and HT-BR in the HT-
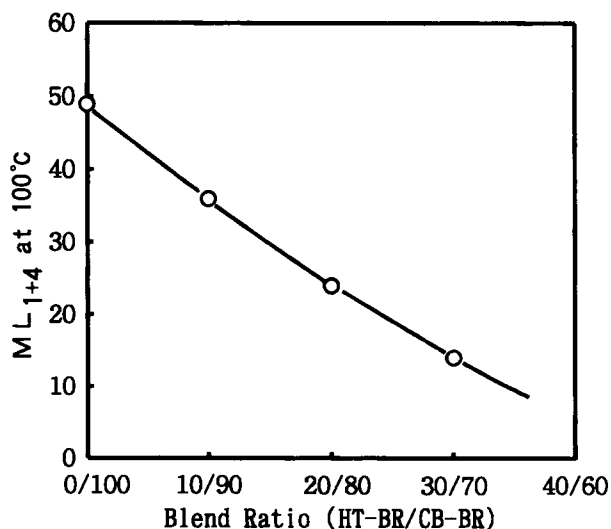
Figure 2   Effect of HT-BR ratio on the Mooney viscosity of HT-BR/CB–BR blends.
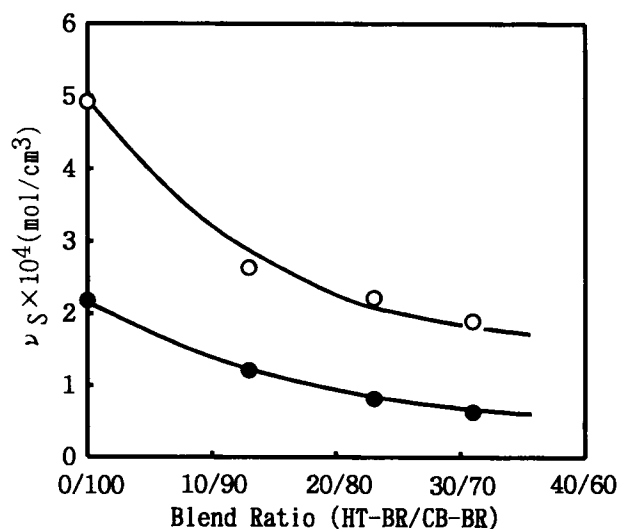
Figure 3   Effect of HT-BR content on ν_S of HT-BR/CB–BR blend vulcanizates by IPCI- and sulfur-cured systems without carbon black. Cure conditions: (○) by IPCI at 100°C for 80 min; (●) by sulfur at 150°C for 20 min.
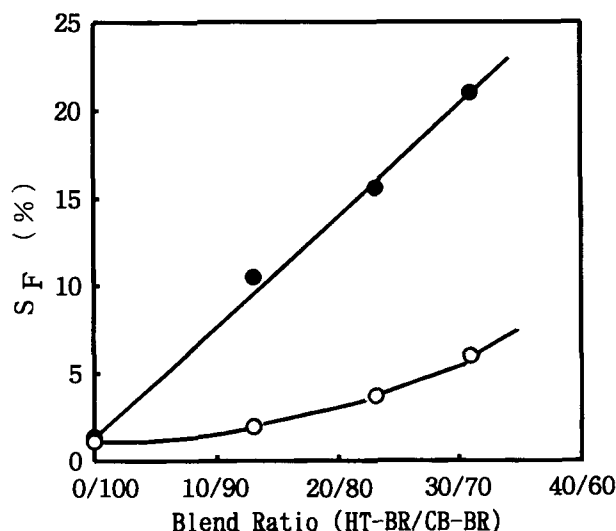
Figure 4   Effect of HT-BR content on S_F of HT-BR/CB-BR blend vulcanizates by IPCI- and sulfur-cured systems without carbon black. Cure conditions: (O) by IPCI at 100°C for 80 min; (●) by sulfur at 150°C for 20 min.

BR/CB-BR blend vulcanizates, respectively. To simplify the calculation of E_S, it was assumed that the extracted CB-BR is proportional to the content of CB-BR in the HT-BR/CB-BR blend vulcanizates. The E_S of the HT-BR blended vulcanizates which were cured with sulfur was about 70%, while the E_S of the system cured with IPCI was less than 20%, as shown in Figure 5. These results suggested that the IPCI-cured system is much more effective than is the sulfur-cured system in order to combine HT-BR to the network structure, i.e., HT-BR acted as a reactive softener of CB-BR compounds when the IPCI system was used as a curing method for CB-BR.

Difference of HT-BR Reactivity on the Isocyanate- and the Sulfur-cured Systems

The results described in the previous section may suggest the probability of the crosslink of HT-BR and CB-BR in each cure system. In the sulfur-cured system, functional groups for cross-linking are double bonds of butadiene units. The average numbers of the butadiene unit (D_P) in HT-BR and in CB-BR were 55 and 1480, respectively. The CB-BR vulcanizate by the sulfur-cured system was crosslinked in every 70 butadiene units (U_C), i.e., the concentration of crosslinking was 2.4×10^{-4} mol cm^{-3}, which was calculated from the ν_S of CB-BR sulfur vulcanizate. The average number of crosslinks (N_C)

in an HT-BR chain was 0.79, which was obtained from dividing D_p (=55) by U_C (=70). The N_C of HT-BR is smaller than unity, which means that some portion of HT-BR was not incorporated into the network structure. The N_C of CB-BR was 21, which suggested that every CB-BR was connected to the network structure. Therefore, the low crosslink efficiency of the blending of CB-BR with HT-BR by the sulfur-cured system could support the high S_F of the sulfur vulcanizates. Table III shows the resulting ν_S of HT-BR/CB-BR blend vulcanizates with their retention percent (R_ν) to ν_S of CB-BR vulcanizates, which was calculated by the following equation:

$$R_\nu = (\nu_S \times 100)/(\nu_{S0} \times r) \tag{2}$$

where ν_{S0} is the crosslink density of CB-BR vulcanizate without HT-BR and r is the blend ratio of HT-BR. The R_ν of the sulfur-cured system were lower than those of IPCI-cured system.

On the other hand, in the IPCI-cured system, the functional group which was allowed to react with diisocyanate is the hydroxyl group, which is present both in HT-BR and CB-BR. The average content of hydroxyl groups of HT-BR and CB-BR is 2.2 and 10, respectively. They were larger than unity. When the equimolar diisocyanate to the total hydroxyl group was compounded in the HT-BR/CB-BR blends according to recipe A, most of the polymer chains might be incorporated into the vulcanizate
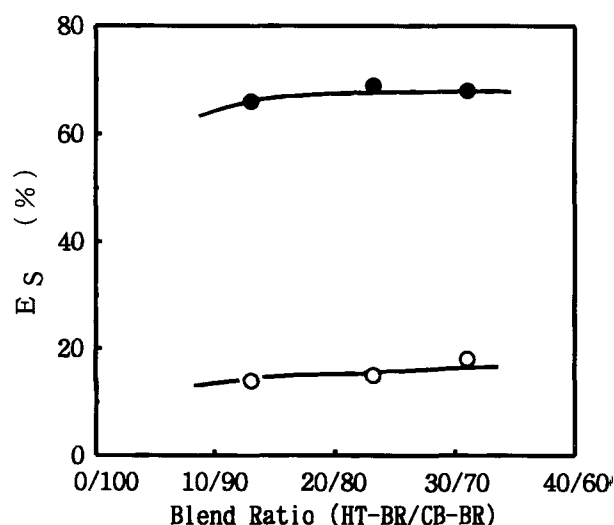
Figure 5   Effect of HT-BR content on E_S of HT-BR/CB-BR blend vulcanizates by IPCI- and sulfur-cured systems without carbon black. Cure conditions: (O) by IPCI at 100°C for 80 min; (●) by sulfur at 150°C for 20 min.

Table III Effect of HT–BR/CB–BR Blends on Retention of Crosslink of CB–BR Gum Stock Vulcanizates

| Blend Ratio of HT–BR and CB–BR (%)	IPCI		Sulfur	
	ν_S[a] $(10^{-4}$ mol/cm^3)	R_ν[b] (%)	ν_S[a] $(10^{-4}$ mol/cm^3)	R_ν[b] (%)
0	4.9	100	2.4	100
13	3.0	70	1.3	62
23	2.5	66	1.0	56
31	1.9	56	0.7	41

[a] Crosslink density.
[b] Retention percent calculated by eq. (2).

networks. Figure 6 shows the influence of the IPCI amount on the S_F of the HT-BR/CB–BR blend vulcanizate (HT-BR/CB–BR = 30/70), where the fraction of [OH] of HT-BR to that of the blend system was set at 0.53. The S_F increased with decrease of the amount of diisocyanate. It is noticeable that there was an apparent critical [NCO]/[OH] ratio, which was about 0.5, i.e., the S_F seemed to increase remarkably when [NCO] in the blends was less than equimolar of the [OH] of HT-BR. This result is suggestive of the difference between the reactivities of hydroxyl groups of HT-BR and CB–BR with diisocyanate. The reaction of NCO group of IPCI with the OH group in HT-BR was considered to be more favorable than that with the OH group in CB–BR, because the primary hydroxyl groups of HT-BR are more reactive than are the hydroxyl groups of CB–

BR.[6] HT-BR is liable to be linked to the network chains. Thus, the IPCI vulcanization is concluded to be more useful than is the sulfur-cured system for HT-BR/CB–BR blends.

Tensile Properties of HT-BR/CB–BR Blends

The tensile strength at break (T_B) and the elongation at break (E_B) of the carbon black-loaded CB–BR/HT-BR blend vulcanizates are shown in Figures 7 and 8, respectively. The T_B of the IPCI vulcanizates linearly increased with increase of HT-BR, while the relationship of T_B and the HT-BR/CB–BR ratio displayed a maximum in the sulfur-cured system and every T_B value was lower than those of the IPCI-
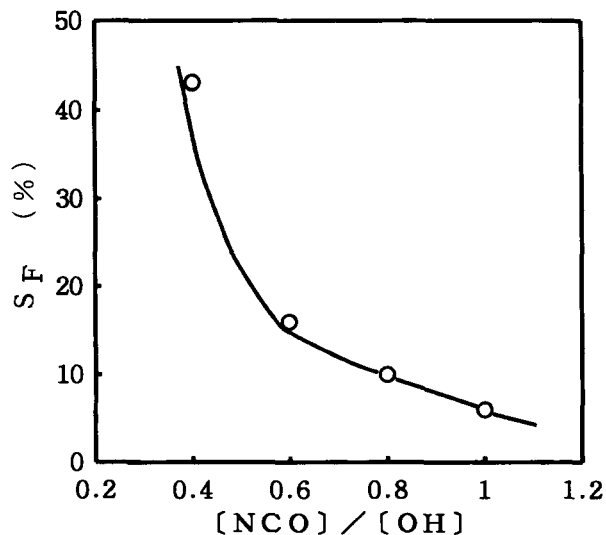
Figure 6 Effect of [NCO]/[OH] on S_F of HT-BR/CB–BR blend vulcanizates by IPCI-cured systems at 100°C for 80 min without carbon black.
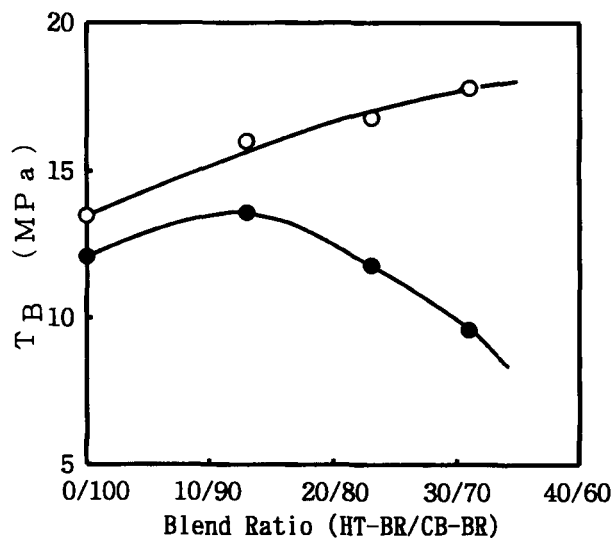
Figure 7 Effect of HT-BR content on T_B of HT-BR/CB–BR blend vulcanizates by IPCI- and sulfur-cured systems with carbon black. Cure conditions: (○) by IPCI at 100°C for 80 min; (●) by sulfur at 150°C for 20 min.
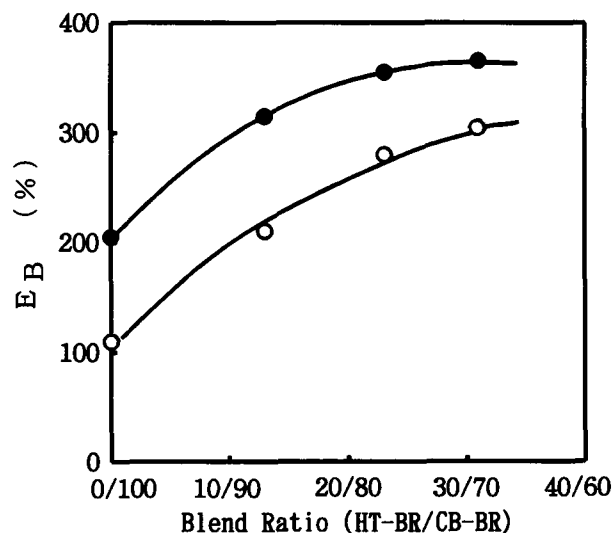
Figure 8 Effect of HT-BR content on E_B of HT-BR/ CB-BR blend vulcanizates by IPCI- and sulfur-cured systems with carbon black. Cure conditions: (O) by IPCI at 100°C for 80 min; (●) by sulfur at 150°C for 20 min.

cured system. The E_B of the both vulcanizates increased with increase of HT-BR in the blends.

The large T_B of the IPCI vulcanizates may be attributed to the uniformity of the crosslinking chain length. The chemical structure of the crosslink site of the IPCI-cured system may also contribute to the large T_B, because the urethane group of the crosslink site is expected to interact with each other by their hydrogen bonding and to reinforce the rubber.[10] On the other hand, the low T_B of the sulfur vulcanizates is due to the small crosslink density and the heterogeneity of the crosslinking molecular length. These results concluded that HT-BR not only acts as a reactive softener of CB-BR but also enhances elasticity of the vulcanizates by the IPCI-cured system.

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