

Crosslinking of Partially Neutralized Carboxyl-Terminated Liquid Rubbers with Bisepoxide and Anhydride

HIDEAKI MATSUDA, *Research Laboratory, Okura Industrial Co., Ltd.,
1515 Nakatsu-cho, Marugame, Kagawa-ken 763, Japan*

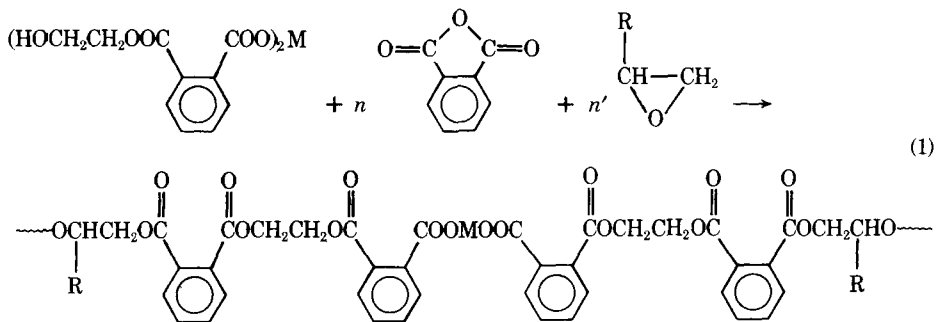
Synopsis

Crosslinking of partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) with bisepoxide and anhydride was investigated by the PNCTLR-bisepoxide-anhydride reactions. The PNCTLR were prepared, by the partial neutralization with MgO and CaO, from a polymer of butadiene (Hycar CTB 2000X162) and a copolymer of butadiene-acrylonitrile (Hycar CTBN 1300X8). As the bisepoxide, bisphenol-A diglycidyl ether was used, and hexahydrophthalic anhydride was the anhydride used. It was found that the metal carboxylate groups of PNCTLR catalyze the crosslinking reactions, and, further, the Mg carboxylate group showed higher catalytic activities than the Ca carboxylate group. As for the physical properties of the cured rubbers obtained, the rubbers containing Mg showed higher tensile strength and Shore A hardness than those containing Ca. In addition, the CTBN-series cured rubbers showed better physical properties than those of the CTB-series, because of a polarity effect of nitrile groups in the former rubbers. Resistances to water and chemical attack, thermal behavior, and stress relaxation are also discussed.

INTRODUCTION

Recently, liquid rubbers have attracted considerable interest from the scientific and industrial standpoints. It has been known for a long time that elastomers containing carboxyl groups can be crosslinked with metal ions and amine compounds.¹ However, ionic crosslinking of liquid rubbers having terminal carboxyl groups has not been studied to any great extent so far. Lately, an article² has reported ionic crosslinking of adduct polymers prepared by addition reaction of acid anhydrides to hydroxyl-terminated liquid polybutadiene. More recently, we have reported³ preparation of ionically crosslinked rubbers by neutralization of carboxyl-terminated liquid rubbers with metal oxides and metal carbonates, mainly with the former. The carboxyl-terminated liquid rubbers used were a polymer of butadiene (Hycar CTB 2000X162) and a copolymer of butadiene-acrylonitrile (Hycar CTBN 1300X8). The cured rubbers obtained were thermoplastic and showed poor strengths.

On the other hand, syntheses of ionic polymers using divalent metal salts of mono(hydroxyethyl)phthalate (HEP), that is, $(\text{HEP}-)_2\text{M}$ (where HEP- denotes the HEP residue and M is a divalent metal such as Mg or Ca) have been reported previously. It has been shown that metal-containing ionic polyesters are synthesized by the $(\text{HEP}-)_2\text{M}$ -anhydride-epoxide reaction,⁴ as shown by eq. (1). Interestingly, the metal carboxylate groups of the $(\text{HEP}-)_2\text{M}$ were found to catalyze the reaction. By applying the above synthetic route to the $(\text{HEP}-)_2\text{M}$ -anhydride-bisepoxide systems, metal-containing cured resins have been prepared⁵:



where M represents Mg or Ca.

Also, partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) are considered useful starting materials for the preparations of ionic cured rubbers into which metal is firmly incorporated. In addition, the metal carboxylate groups in PNCTLR were anticipated to have catalytic activities for the above type of curing reactions.

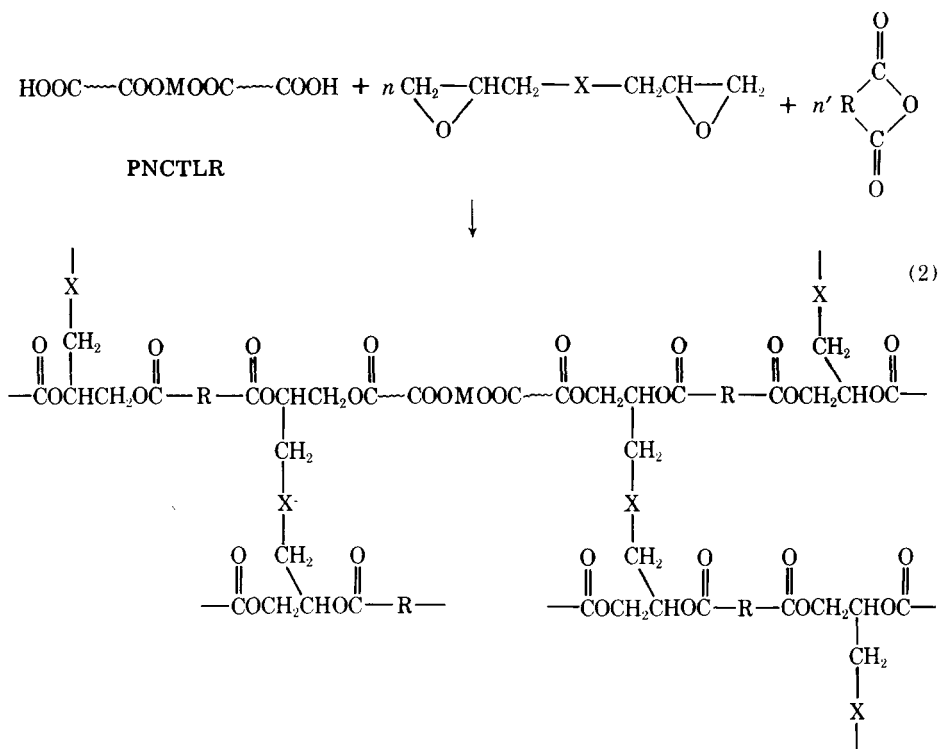
Therefore, it seemed of interest to investigate, by applying the above synthetic route, the preparation of cured rubbers by crosslinking (curing) of PNCTLR with bisepoxide and anhydride, as shown by eq. (2).

The cured rubbers obtained are considered to consist of the following two main blocks: a soft block based on PNCTLR, and a hard block from bisepoxide and anhydride. Bisphenol A diglycidyl ether (BADG) was used as the bisepoxide and hexahydrophthalic anhydride (HPA) was the anhydride used.

EXPERIMENTAL

Materials

The carboxyl-terminated liquid rubbers, Hycar CTB 2000X162 and Hycar CTBN 1300X8, were the same as those used in the previous study.³



where M = Mg or Ca. HPA was of extrapure grade and used as received. As the BADG, Epomik R 139, a product of Mitsui Petrochemical Epoxy Co., was used; the epoxide value was 5.387 equiv./kg (calcd. = 5.875 equiv./kg).

Preparation of Partially Neutralized Carboxyl-Terminated Liquid Rubbers (PNCTLR)

The degree of neutralization of PNCTLR was 50%. A coded system for the PNCTLR will be used in this discussion. For example, CTB(0.5 Mg) indicates that CTB 2000X162 was neutralized with MgO to the degree of neutralization = 50%.

In the case of neutralization, a mixture of a fixed amount of liquid rubber and a sufficient quantity of MgO or CaO to give a degree of neutralization of 50% was heated with stirring under a stream of nitrogen at 100°C for 2 hr and at 140°C for 5 hr for MgO, and at 140°C for 2–3 hr for CaO. In MgO, a suitable amount of water was added to the mixture to allow the reaction to proceed smoothly. The systems were demosturized during the reaction. The acid values of the PNCTLR obtained were 0.2055 equiv./kg for CTB(0.5 Mg), 0.2726 equiv./kg for CTBN(0.5 Mg), 0.1906 equiv./kg for CTB(0.5 Ca), and 0.2656 equiv./kg for CTBN(0.5 Ca).

Curing Reactions

PNCTLR, HPA and BADG were placed in a 26 × 100-mm test tube, at a desired mole ratio, and the test tube was placed in a constant temperature bath

while stirring the mixture with a glass rod until gelation occurred. After a desired time, the mixture was subjected to acid and epoxide analyses. Moreover, the cure properties were determined for the curing systems of 5 g in a 18 × 180-mm test tube.

Rubber sheets for determining physical and other properties were prepared as follows: A mixture of PNCTLR, HPA, and BADG at a desired mole ratio was stirred at 160°C for 2–3 min, poured into molds, and cured at the same temperature for a fixed time.

Analytical Methods

Acidities of soluble samples were determined by titrating the solution of the sample in chloroform with 0.1*N* KOH–methanol using Thymol Blue–Cresol Red indicator. When the sample was insoluble, it was broken up into small pieces and swollen with chloroform overnight; the mixture was titrated in this form.

Epoxide values were determined, as in the previous articles,^{4,5} by the HBr method.^{6,7} In this case, chloroform was used for dissolving or swelling the samples.

Infrared spectra were determined with a Shimazu IR-400 instrument. Thermogravimetric analysis (TGA) were carried out in a Shimazu microthermobalance TGA-20 at a heating rate of 10°C/min in air. Differential thermal analyses (DTA) were carried out with a Shimazu thermal analyzer DT-20 B at a heating rate of 10°C/min in air.

Determination of Physical and Other Properties

Tensile strength and elongation were determined, by the same method as in the previous article,³ at 23°C [relative humidity (RH) = 50%] unless otherwise specified. The samples were aged before testing for one week at 23°C in a room of RH = 50%.

Shore A hardness was determined using UF Shore's durometer type A (Kamishima Seisakusho Co.) at 23°C (RH = 50%).

Effects of water on physical properties and on weight change of cured rubbers were determined as follows: Dumbbell-shaped specimens of JIS Z 1702 were immersed in water at 23°C. After a fixed time, the specimens were separated from water phase and, after rapid surface drying, subjected to the determinations.

Resistances to chemical attack were determined as follows: specimens of the cured rubbers (10 × 10 × 2 mm) were immersed in 100 g of solvent at 23°C. After 96 hr, the weight change and soluble part were determined.

Stress relaxation was determined as follows: Dumbbell-shaped specimens of JIS Z 1702 were strained to 50% of a elongation at break using the above autograph with a strain rate of 50 mm/min. The strained specimens were allowed to stand for 30 sec, followed by determining the initial stress. The stress was recorded at specific time intervals.

RESULTS AND DISCUSSION

Preparation of PNCTLR

While complete neutralization of terminal carboxyl groups of CTB 2000X162 and CTBN 1300X8 is difficult because of low reactivities of the carboxyl groups toward metal ions,³ partial neutralization is comparatively easy. In the present

study, the partial neutralization reaction was carried out, as described in the Experimental section, with MgO and CaO to a degree of neutralization of 50%. The partially neutralized products, that is, PNCTLR, were slightly brownish or yellowish viscous materials; the viscosity was higher in CTB(0.5 Mg) and CTBN(0.5 Mg) than in CTB(0.5 Ca) and CTBN(0.5 Ca).

Figure 1 shows infrared spectra of CTBN(0.5 Mg) and CTBN(0.5 Ca), together with that of corresponding original rubber, that is, CTBN 1300X8. In the spectrum of CTBN 1300X8, absorption bands at 1710 cm^{-1} , owing to carboxyl group, and at 1640 cm^{-1} ($\text{C}=\text{C}$) are noteworthy. Meanwhile, in the spectra of the PNCTLR, the bands at 1600 cm^{-1} for CTBN(0.5 Mg) and at 1560 cm^{-1} for CTBN(0.5 Ca) owing to carboxylate group have newly appeared. This indicates that the neutralization reaction has proceeded, resulting in the formation of metal carboxylate groups. However, the band at 1710 cm^{-1} remained almost unchanged, indicating the presence of a considerable concentration of carboxyl groups. Moreover, the unsaturated groups in the rubbers are considered stable under the above reaction conditions, since the band at 1640 cm^{-1} has remained unchanged. Moreover, CTB(0.5 Mg) and CTB(0.5 Ca) showed similar spectra.

The PNCTLR obtained above might be considered to have the following average chemical formula:



Curing Reactions

Figures 2 and 3, as typical examples, show results of the curing reaction of the systems of CTB(0.5 Mg)-HPA-BADG, and CTBN(0.5 Mg)-HPA-BADG at a mole ratio of 1:10:6. The bath temperature was 160°C . The curing reactions proceeded smoothly at 160°C . Gelation of the systems occurred when conversions reached 20–40%. The acidities shown were determined by nonaqueous titration and are due to anhydride and carboxyl groups. The decrease in epoxide value is consistently a little greater than the decrease in acidity, with a tendency

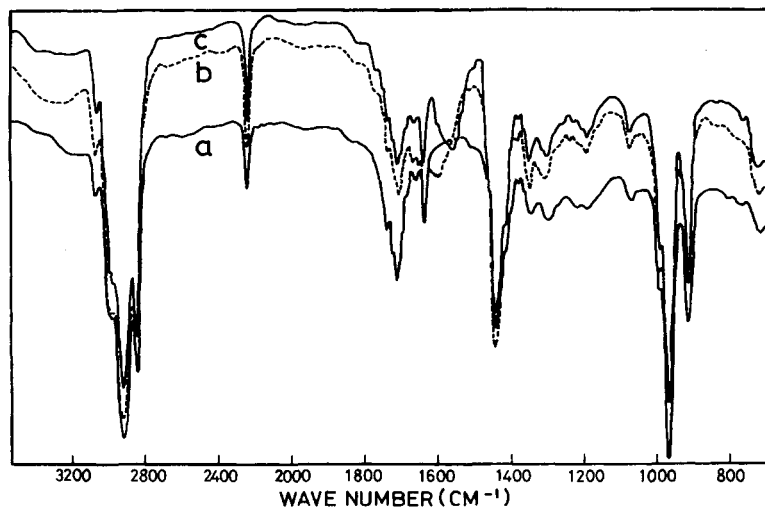


Fig. 1. Infrared spectra of (a) CTBN 1300X8; (b) CTBN(0.5 Mg); (c) CTBN(0.5 Ca).

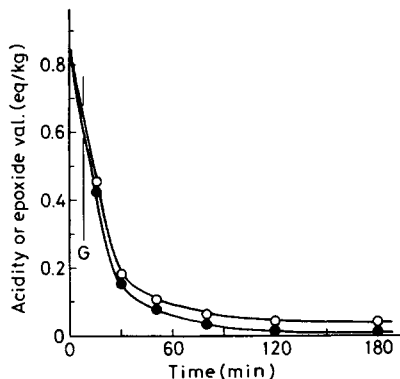


Fig. 2. Curing reaction of system of CTB(0.5 Mg)-HPA-BADG (1:10:6). Bath temperature, 160°C; G, gel point; (O) acidity; (●) epoxide value.

similar to that observed in the (HEP—)₂M-anhydride-bisepoxide systems of the previous study.⁵ This indicates that etherification of epoxide groups as side reactions occurred to a slight degree. In the above curing systems, about 96% of the epoxide groups reacted are considered to have reacted with carboxyl and anhydride groups rather than with each other. The conversions reached nearly maximum conversion attainable after 120–180 min.

In the above curing systems, the following main reactions are believed to occur: reaction of a carboxyl group with epoxide group to form an OH group, reaction of the OH group with an acid anhydride group to form a terminal carboxyl group, and reaction of an acid anhydride group with an epoxide group to form ester linkage. The tendency for the metal carboxylate groups in the liquid rubber to reequilibrate with any of the free carboxylic acids of the hexahydrophthalic group might also be possible.

Table I shows the results of curing reactions carried out on various combinations of components. Generally, temperature exotherm is small (below about

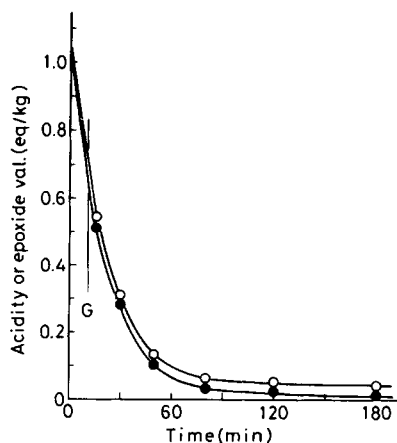


Fig. 3. Curing reaction of system of CTBN(0.5 Mg)-HPA-BADG (1:10:6). Bath temperature, 160°C; G, gel point; symbols as in Fig. 2.

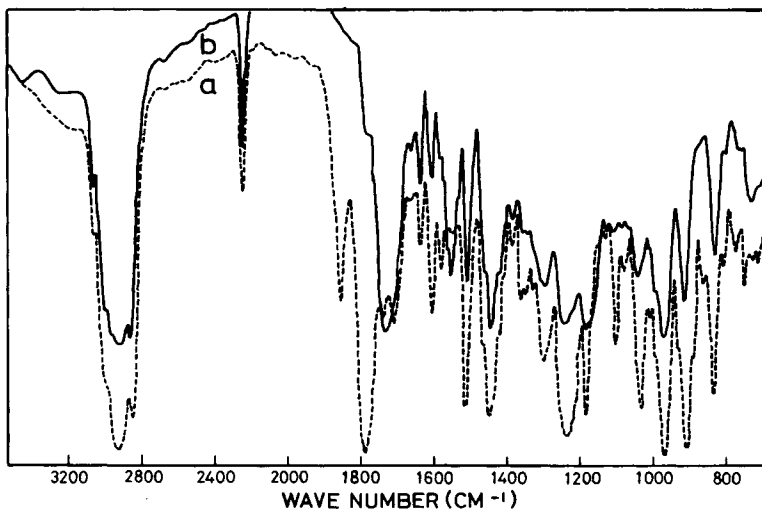


Fig. 4. Infrared spectra of system of CTBN(0.5 Ca)-HPA-BADG (1:10:6). (a) Initial curable mixture; (b) cured at 160°C for 4 hr.

12°C). With increase in the metal content, gel time becomes shorter, indicating the catalytic effect of the metal carboxylate groups. Moreover, increase in temperature reduces gel time and increases exotherm peak temperature a little; thus, the effect of temperature is also clearly demonstrated.

Generally, at the same temperature, the systems containing Mg showed shorter gel times and higher exotherm peak temperatures than those containing Ca. This fact indicates that Mg has higher catalytic activities than Ca has toward the curing reaction. It is advantageous for the metal carboxylate groups in PNCTLR to catalyze this type of reaction. On the other hand, the species of rubber has little effect on the cure properties.

In most systems, the final conversions were 93–99% and conversion differences between acidity and epoxide values were generally very small. However, curing at 140°C of the system containing CTB(0.5 Ca) resulted in lower final conversions because of the lower curing temperature.

Figure 4 shows, as a typical example, the infrared spectra of the system of CTBN(0.5 Ca)-HPA-BADG (1:10:6). In spectrum (a), of the initial curable mixture, absorption bands at 1850 and 1780 cm^{-1} , characteristic of the anhydride, and at 860 cm^{-1} , characteristic of the epoxy ring, are noteworthy. On the other hand, in spectrum (b), of the cured rubber, these bands have disappeared, indicating that the polyesterification has proceeded. Moreover, the cured rubber showed the band at 1550 cm^{-1} owing to carboxylate group.

Based on these results, curing reactions to obtain samples for determining physical and other properties were carried out further under the following conditions: for systems containing Mg, 160°C for 3 hr; for systems containing Ca, 160°C for 4–5 hr.

Physical Properties

Figure 5 shows stress-strain curves of representative cured rubbers. The cured rubbers with higher PNCTLR content and lower crosslinking densities were soft and showed higher elongation but lower tensile strength. With a decrease in

TABLE I
Curing Reactions of Systems of PNC/TLR-HPA-BADG

Components	Mole ratio of components	Cure conditions, ^a		Cure properties			Final conversions	
		Temperature, (°C)	Time (min)	Gel time (min)	Exotherm peak temperature (°C)	Exotherm time ^b (min)	Epoxide value (%)	Acidity (%)
CTB(0.5 Mg)-HPA-BADG	1:10:6	140	240	17.5	143.0	16	97	95
	1:10:6	160	180	8.5	170.0	9.5	99	96
	1:20:11	160	180	11	171.6	8	98	97
CTB(0.5 Ca)-HPA-BADG	1:10:6	140	300	60	142.7	25	88	85
	1:10:6	160	300	26	162.4	15	97	93
	1:20:11	160	300	32	161.2	21.5	97	97
CTBN(0.5 Mg)-HPA-BADG	1:10:6	140	240	19	145.8	17.5	96	95
	1:10:6	160	180	9.5	170.5	9.5	99	97
	1:20:11	160	180	14	170.7	10	99	96
CTBN(0.5 Ca)-HPA-BADG	1:10:6	140	300	46	142.5	49	98	96
	1:10:6	160	240	17.5	165.8	20.5	99	98
	1:20:11	160	240	21	167.8	17.5	98	96

^a Bath temperature.

^b Time required to reach peak exotherm temperature.

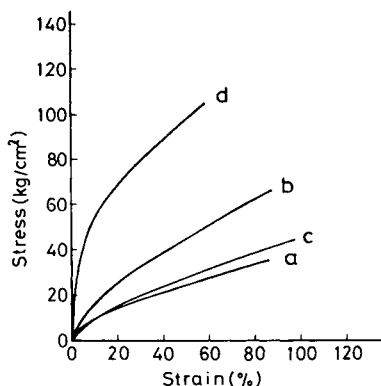


Fig. 5. Stress-strain curves of cured rubbers of (a) CTB(0.5 Mg)-HPA-BADG (1:10:6); (b) CTBN(0.5 Mg)-HPA-BADG (1:10:6); (c) CTBN(0.5 Ca)-HPA-BADG (1:10:6); (d) CTBN(0.5 Mg)-HPA-BADG (1:16:9).

PNCTLR content and an increase in the crosslinking densities, elongation decreased and tensile strength increased (sample b vs. sample d).

In Table II physical properties of the cured rubbers of various combinations of components are summarized. Reference cured rubbers were also prepared from original liquid rubber, HPA, and BADG, using *N,N*-dimethylbenzylamine (DMBA) as a catalyst. The variation in the mole ratio of components does not change the metal content in the cured rubber significantly; however, the concentration of the PNCTLR part suffers considerably large changes by the variation in the mole ratio. The concentration of the PNCTLR part might be regarded as that of the soft blocks, and, the concentration of the liquid rubber part in the reference cured rubber might be regarded similarly.

The cured rubbers in which the mole ratio of PNCTLR:HPA:BADG is 1:20:11 showed much higher tensile strength and Shore A hardness than those in which the ratio is 1:10:6. This is considered to be probably a result of lower concentration of the soft blocks and also higher crosslinking densities of the hard blocks in the former rubbers. The steady remarkable increase in these properties can be seen in the CTBN-series cured rubbers. Meanwhile, an almost reverse trend was observed for elongation.

It is obvious on comparing the cured rubbers with corresponding reference ones that the cured rubbers of PNCTLR-HPA-BADG at a 1:20:11 mole ratio contain about the same concentration of the soft blocks as do the reference ones of liquid rubber-HPA-BADG at the ratio of 1:10:6. However, the metal-containing cured rubbers show considerably higher tensile strengths and Shore A hardnesses than the reference ones do. This is especially true for the CTB-series cured rubbers, probably because of ionic crosslinking and higher crosslinking density of the hard blocks in the former rubbers. Thus, the effect of introducing metal is clearly apparent.

Comparing the cured rubbers containing the same series of PNCTLR, at the same mole ratio, the rubbers containing Mg showed better physical properties than the rubbers containing Ca, probably because of higher interionic attraction of Mg^{2+} . In addition, the CTBN-series cured rubbers showed better physical properties than the CTB-series ones. This is considered to result from a polarity effect of nitrile groups in the former rubbers. Similar tendencies were also ob-

TABLE II
Physical Properties of Cured Rubbers from PNCTLR, HPA and BADG

Components	Mole ratio of components	Metal in cured rubber (%)	PNCTLR in cured rubber (%)	Tensile strength (kg/cm ²)	Elongation (%)	Shore A hardness
CTB(0.5 Mg)-HPA-BADG	1:10:6	0.17	73.2	34	87	73
	1:20:11	0.14	58.9	98	59	95
CTB(0.5 Ca)-HPA-BADG	1:10:6	0.28	73.2	26	107	59
	1:20:11	0.23	59.0	48	83	80
CTB 2000X162-HPA-BADG ^a	1:10:6	—	57.6 ^b	17	53	67
	1:10:6	0.21	67.0	66	88	84
CTBN(0.5 Mg)-HPA-BADG	1:16:9	0.18	56.8	106	58	100<
	1:20:11	0.16	51.6	166	48	100<
CTBN(0.5 Ca)-HPA-BADG	1:10:6	0.35	67.0	44	97	75
	1:16:9	0.30	56.9	94	56	95
CTBN 1300X8-HPA-BADG ^a	1:20:11	0.27	51.7	120	63	100<
	1:8:5	—	55.2 ^b	104	83	94
	1:10:6	—	50.3 ^b	115	58	90

^a Reference cured rubber cured at 160°C for 4–5 hr. Catalyst: DMBA (0.15 wt % based on BADG).

^b Concentration of CTB 2000X162 or CTBN 1300X8 part in the cured rubber.

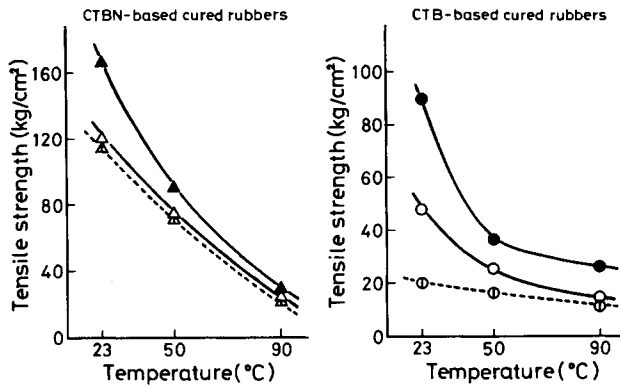


Fig. 6. Temperature dependence of tensile strength of (a) CTBN-based and (b) CTB-based cured rubbers. (●) CTB(0.5 Mg)-HPA-BADG (1:20:11); (○) CTB(0.5 Ca)-HPA-BADG (1:20:11); (◐) CTB 2000X162-HPA-BADG (1:10:6); (▲) CTBN(0.5 Mg)-HPA-BADG (1:20:11); (△) CTBN(0.5 Ca)-HPA-BADG (1:20:11); (◄) CTBN 1300X8-HPA-BADG (1:10:6).

served in the previous study.³ It is noteworthy that the CTBN(0.5 Mg)-HPA-BADG (1:20:11) rubbers showed high tensile strengths of 166 kg/cm² for Mg and 120 kg/cm² for Ca.

Figure 6 shows the temperature dependence of tensile strength for the representative cured rubbers. The tensile strength decreases markedly with increase in temperature. In addition, with temperature increase, the effect of the metal species on the strength decreases and at 90°C the strength approaches that of the reference rubber, especially for the CTBN-based cured rubbers. However, the CTB(0.5 Mg)-HPA-BADG (1:20:11) rubber still retains the effect of introducing Mg on the strength at 90°C.

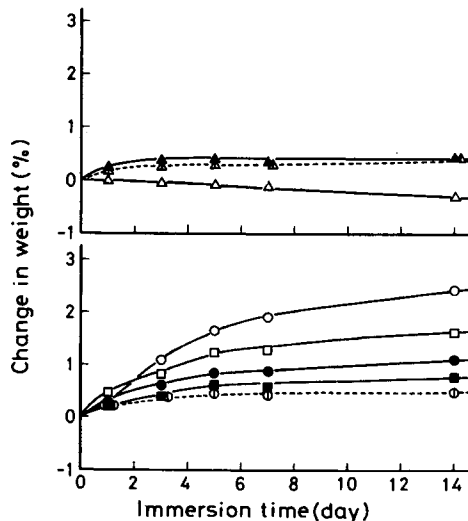


Fig. 7. Effect of water on weight change of cured rubbers. (▲) CTB(0.5 Mg)-HPA-BADG (1:20:11); (△) CTB(0.5 Ca)-HPA-BADG (1:20:11); (◄) CTB 2000X162-HPA-BADG (1:10:6); (○) CTBN(0.5 Mg)-HPA-BADG (1:10:6); (●) CTBN(0.5 Mg)-HPA-BADG (1:20:11); (◐) CTBN(0.5 Ca)-HPA-BADG (1:10:6); (■) CTBN(0.5 Ca)-HPA-BADG (1:20:11); (◑) CTBN 1300X8-HPA-BADG (1:10:6).

Water Resistance of Cured Rubbers

Figure 7 shows the effect of water on weight change of representative cured rubbers. Increasing the metal content in the cured rubber resulted in the increase in water absorption; in addition, it is of interest to note that Mg imparted higher water absorption than Ca, tendencies observed also in the previous study.³ Further, the CTBN-series cured rubbers showed higher water absorption than the CTB-series ones. As shown in Figure 8, tensile strength decreased with the water absorption, and the decrease became remarkable nearly in the order of the water absorption. Even the reference cured rubbers showed the water absorption and the strength decrease, owing to the plasticizing effect of water. The plasticizing effect of water on the metal-containing cured rubbers might also be explained on the basis that hydration of the metal ion occurs and reduces the tendency for coordination with the carboxylate groups.

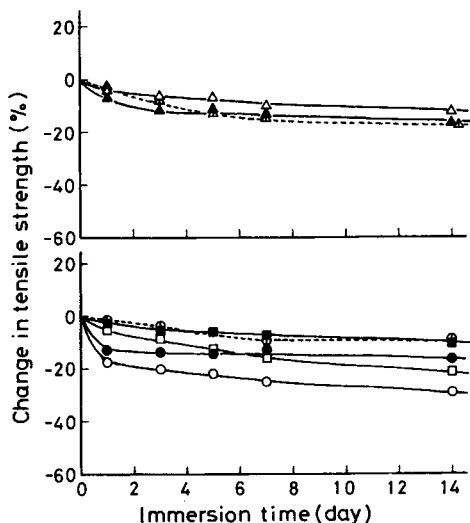


Fig. 8. Effect of water on tensile strength of cured rubbers. (\blacktriangle) CTB(0.5 Mg)-HPA-BADG (1:20:11); (\triangle) CTB(0.5 Ca)-HPA-BADG (1:20:11); (\blacktriangle) CTB 2000X162-HPA-BADG (1:10:6); (\circ) CTBN(0.5 Mg)-HPA-BADG (1:10:6); (\bullet) CTBN(0.5 Mg)-HPA-BADG (1:20:11); (\square) CTBN(0.5 Ca)-HPA-BADG (1:10:6); (\blacksquare) CTBN(0.5 Ca)-HPA-BADG (1:20:11); (\odot) CTBN 1300X8-HPA-BADG (1:10:6).

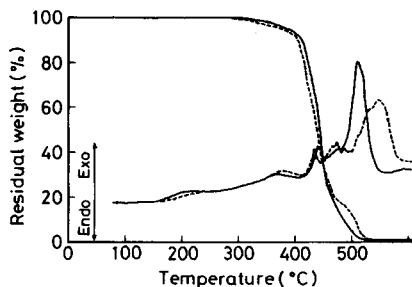


Fig. 9. TGA and DTA curves of cured rubbers. (—) CTB(0.5 Ca)-HPA-BADG (1:20:11); (---) CTBN(0.5 Mg)-HPA-BADG (1:10:6).

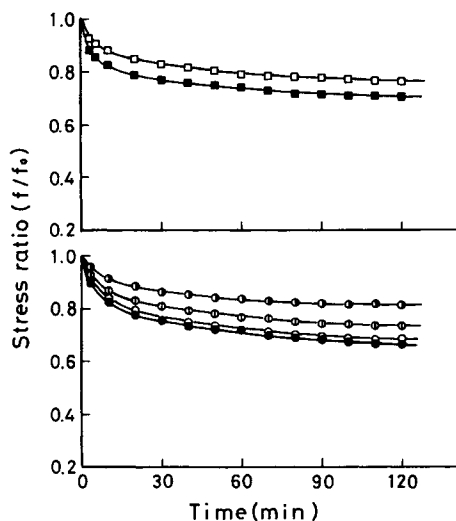


Fig. 10. Stress relaxation of cured rubbers. (■) CTB(0.5 Mg)-HPA-BADG (1:20:11); (□) CTB(0.5 Ca)-HPA-BADG (1:20:11); (●) CTBN(0.5 Mg)-HPA-BADG (1:10:6); (●) CTBN(0.5 Mg)-HPA-BADG (1:20:11); (○) CTBN(0.5 Ca)-HPA-BADG (1:20:11); (◇) CTBN 1300X8-HPA-BADG (1:10:6).

Resistance of Cured Rubbers to Chemical Attack

Table III shows the resistance of the cured rubbers to chemical attack. The cured rubbers showed much higher weight gains in benzene and dioxane than in *n*-hexane. The metal-containing cured rubbers, in which the PNCTLR: HPA:BADG mole ratio is 1:20:11, showed considerably lower weight gains than those with a ratio of 1:10:6, indicating that the overall crosslinking density is higher in the former than in the latter. Benzene- and dioxane-soluble parts were generally very small. Most of the polymer molecules are considered to have taken part in the crosslinking. It is noteworthy that the soluble parts in *n*-hexane are considerably smaller in the CTBN-series rubbers than in the CTB-series rubbers.

Thermal Behavior

Figure 9 shows TGA and DTA curves in air of representative cured rubbers as typical examples. In the TGA curves, the cured rubbers are thermally stable up to about 300°C, above which gradual weight loss begins; above about 400°C, destruction proceeds rapidly. The plateaus observed above 530°C correspond to the formation of MgO for Mg and to the formation of CaCO₃ for Ca. The DTA curves show several exothermic peaks, probably as a result of degradations occurring via oxidative modes.

Moreover, below 300°C, the DTA curves show no sharp endothermic peaks indicating that the hard block domains in the polymer matrix have no melting point.

Other cured rubbers show similar TGA and DTA curves.

TABLE III
Resistance of Cured Rubbers to Chemical Attack

Components	Mole ratio of components	Benzene		Dioxane		n-Hexane	
		Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)
CTB(0.5 Mg)-HPA-BADG	1:10:6	216	4.8	167	1.7	58	3.6
	1:20:11	154	3.4	127	0.3	39	2.6
CTB(0.5 Ca)-HPA-BADG	1:10:6	258	8.8	187	5.5	68	6.1
	1:20:11	179	5.0	140	3.2	43	4.0
CTB 2000X162-HPA-BADG ^a	1:10:6	203	6.4	156	3.8	49	4.0
	1:10:6	179	2.4	202	0.9	17	1.4
CTBN(0.5 Mg)-HPA-BADG	1:16:9	132	2.4	150	0.8	15	1.0
	1:20:11	116	2.2	140	0.7	13	1.0
CTBN(0.5 Ca)-HPA-BADG	1:10:6	201	4.5	229	2.8	16	2.0
	1:16:9	134	2.9	147	1.3	14	1.0
CTBN 1300X8-HPA-BADG ^a	1:20:11	129	2.4	140	0.9	13	1.0
	1:10:6	122	1.6	146	2.5	12	1.8

^a Reference cured rubber cured at 160°C for 4-5 hr. Catalyst: DMBA (0.15 wt % based on BADG).

Stress Relaxation

Figure 10 shows the stress relaxation behavior of representative cured rubbers. At first, remarkable relaxation occurred, and then it gradually moderated. It is known that ionically crosslinked rubbers have a tendency to slowly relax because of reorganization of metal carboxylate bonds. In the CTB-series cured rubbers, that containing Mg showed higher relaxation than that containing Ca. The difference is very small in the CTBN-series rubbers at the same mole ratio. Further, in this series, the CTBN(0.5 Mg)-HPA-BADG rubber at a mole ratio of 1:10:6, which contains higher soft block content, showed considerably lower relaxation than that at a ratio of 1:20:11, though the former contains a higher concentration of metal carboxylate groups than the latter.

The reference cured rubber showed an intermediate stress relaxation. It appears that the soft block content has higher effect on the stress relaxation of the cured rubbers in the present study than the metal carboxylate groups.

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