

Crosslinking of Partially Neutralized Liquid Rubbers Containing Terminal and Pendent Carboxyl Groups with Anhydride and Bisepoxide

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

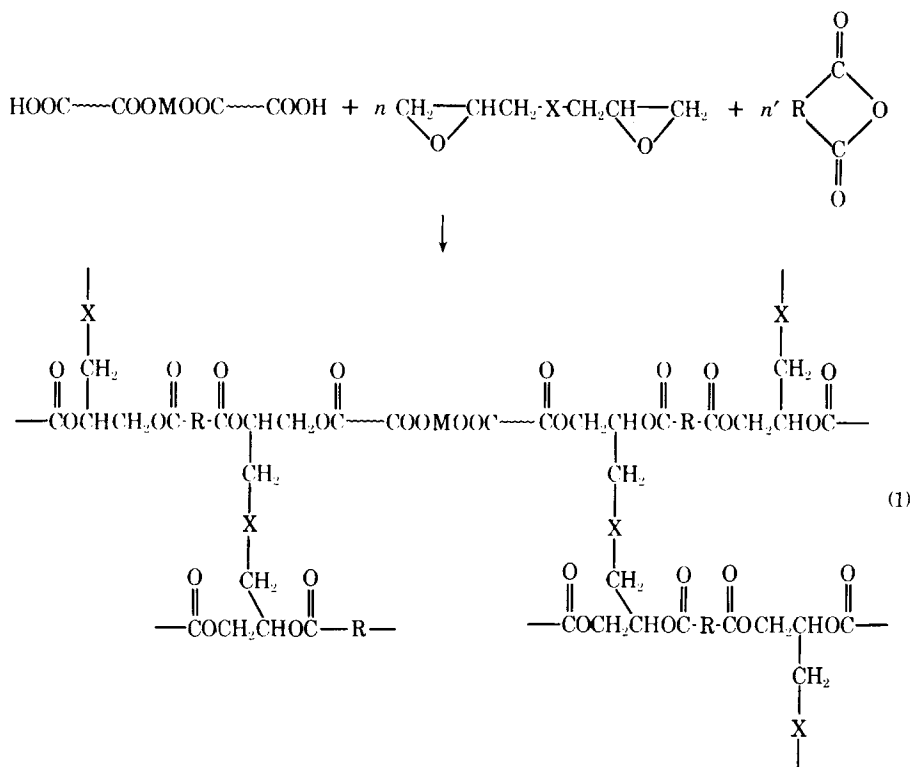
Synopsis

Crosslinking of partially neutralized liquid rubbers containing terminal and pendent carboxyl groups with anhydride, and bisepoxide was investigated by the carboxyl-anhydride-epoxide reaction. The partially neutralized liquid rubbers were prepared by the partial neutralization with MgO and CaO from a butadiene (BD)-acrylonitrile (AN) copolymer (Hycar CTBNX 1300X9) with the functionality of 2.4. Bisphenol-A diglycidyl ether (BADG) was the bisepoxide used, and hexahydrophthalic anhydride (HPA) was the anhydride used. The metal carboxylate groups in the system catalyzed the curing reaction. The metal-containing cured rubbers obtained showed considerably higher tensile strength than the previously reported metal-containing cured rubbers based on CTBN 1300X8 (BD-AN copolymer) with the lower functionality of 1.8. In addition, the cured rubbers generally showed higher water resistance, and lower weight gains in benzene, dioxane, and *n*-hexane than the CTBN-series ones. Thermal behavior and stress relaxation are also discussed.

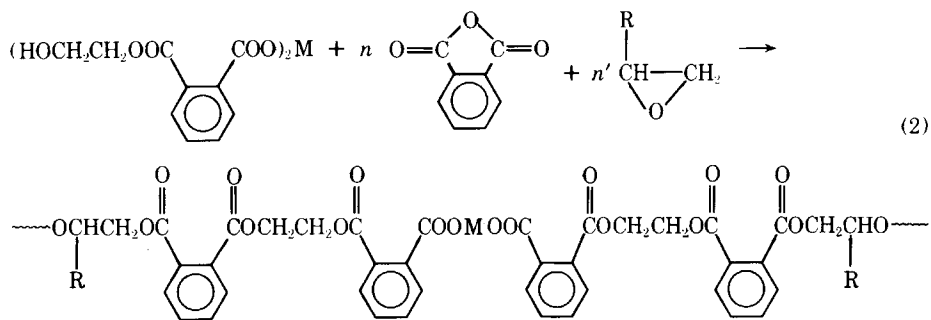
INTRODUCTION

Recently, studies on curing of liquid rubbers have attracted considerable interest from the scientific and industrial standpoints. Previously, the author has reported¹ preparation of ionic cured rubbers by crosslinking (curing) of partially neutralized carboxyl-terminated liquid rubbers with anhydride and bisepoxide, as shown by eq. (1). Bisphenol-A diglycidyl ether (BADG) was used as the bisepoxide, and hexahydrophthalic anhydride (HPA) was the anhydride used [see eq. (1)]. Interestingly, the metal carboxylate groups in the partially neutralized liquid rubbers were found to have catalytic activities for the curing reactions. This synthetic route is an extension of the studies on syntheses of metal-containing polyesters² and cured resins³ by using divalent metal salts of

mono(hydroxyethyl) phthalate, as shown by eq. (2).



where M is Mg or Ca.



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The carboxyl-terminated liquid rubbers used in the previous study¹ were a polymer of butadiene (BD) (Hycar CTB 2000X162) and a copolymer of BD-acrylonitrile (AN) (Hycar CTBN 1300X8). The functionalities of carboxyl group are 2.01 for CTB 2000X162 and 1.8 for CTBN 1300X8.⁴ The CTBN-series cured rubbers obtained in the above curing reaction showed better physical properties than the CTB-series ones, because of a polarity effect of nitrile group in the former rubbers.

It is expected that liquid BD-AN copolymer with higher functionality would

impart further improved physical and other properties to cured rubbers. Hycar CTBNX 1300X9 is a liquid BD-AN copolymer with the higher functionality of 2.4, having pendent carboxyl groups in addition to terminal carboxyl groups.⁴ It contains 18-19 mole % AN and has molecular weight of 3400; the microstructure of the BD part is as follows: *cis*-1,4 = 16.3%, *trans*-1,4 = 68.7%, and vinyl structure = 15.0%.

Therefore, in the present study, the author investigated preparation and properties of cured rubbers by crosslinking of partially neutralized CTBNX 1300X9 with anhydride and bisepoxide.

EXPERIMENTAL

Materials

The liquid rubber containing terminal and pendent carboxyl groups, Hycar CTBNX 1300X9 (acid value = 0.6827 equiv/kg) (manufactured by B. F. Goodrich Chemical Co.) was kindly supplied by Ube Kosan Co., and used as received. HPA, BADG, MgO, and CaO were the same as those used in the previous study.¹

Preparation of Partially Neutralized CTBNX 1300X9

The degree of neutralization of CTBNX 1300X9 was 50%. Hereafter, the partially neutralized CTBNX 1300X9 will be denoted by CTBNX(0.5 M). That is, CTBNX(0.5 Mg) and CTBNX(0.5 Ca) indicate that CTBNX 1300X9 was neutralized with MgO and CaO, respectively, to the degree of neutralization = 50%.

In the case of the neutralization, a mixture of a fixed amount of the CTBNX 1300X9 and a quantity of MgO or CaO such as 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 4.5 hr for CaO. In the case of MgO, a suitable amount of water was added to the mixture to allow the reaction to proceed smoothly. The system was demoiatured during the reaction. The acid value of CTBNX(0.5 Mg) was 0.3510 equiv/kg, and that of CTBNX(0.5 Ca) was 0.3456 equiv/kg.

Curing Reactions

Curing reactions were carried out by the same methods as described in the previous study.¹

Analytical Methods

Epoxy values were determined, as in previous articles,^{2,3} by the HBr method.^{5,6} Acidities and infrared spectra were determined by the methods reported in a previous article.¹

Also, the thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out by the same methods as in the previous article.¹

Determination of Physical and Other Properties

The following properties were determined by the same methods as in the previous article¹: tensile strength, elongation, effects of water on physical properties and weight change, resistances to chemical attack, and stress relaxation.

Shore A or D hardness was determined using UF. Shore's durometer type A or D (Kamishima Seisakusho Co.) at 23°C (relative humidity, 50%).

RESULTS AND DISCUSSION

Preparation of Partially neutralized CTBNX 1300X9 [CTBNX(0.5M)]

As in the case of CTB 2000X162 and CTBN 1300X8,⁷ while complete neutralization of terminal and pendent carboxyl groups of CTBNX 1300X9 is difficult because of low reactivities of the carboxyl groups toward metal ions, partial neutralization is comparatively easy. The partially neutralized products, that is, CTBNX(0.5M) were slightly brownish viscous materials. The viscosity was higher in CTBNX(0.5 Mg) than in CTBNX(0.5 Ca).

Figure 1 shows infrared spectra of CTBNX(0.5M), together with that of the original rubber, namely, CTBNX 1300X9. In the spectra of CTBNX 1300X9, absorption bands at 1710 cm^{-1} owing to carboxyl group, at 1640 cm^{-1} (C=C), and at 2250 cm^{-1} (nitrile group) are noteworthy. On the other hand, in the spectra of CTBNX(0.5M), the bands at about 1600 cm^{-1} for CTBNX(0.5 Mg) and at 1560 cm^{-1} for CTBNX(0.5 Ca) owing to the carboxylate group have newly appeared. In addition, the presence of considerable concentration of carboxyl groups is confirmed by the band at 1710 cm^{-1} remained almost unchanged, indicating that CTBNX 1300X9 was partially neutralized.

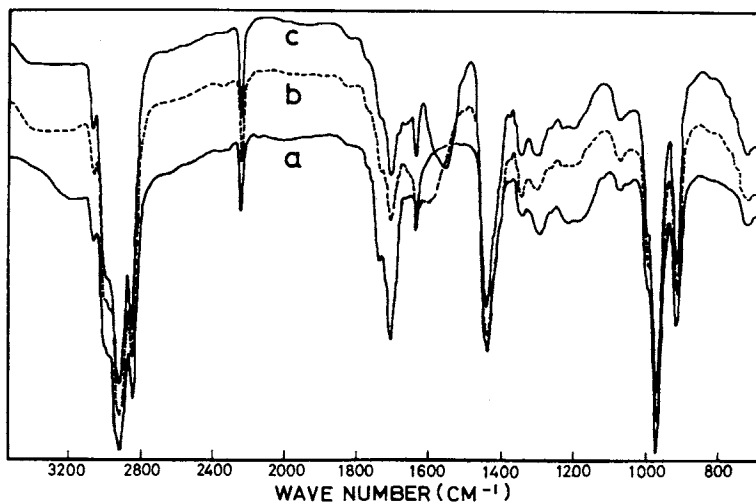
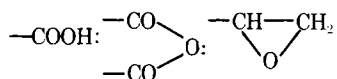


Fig. 1. Infrared spectra of (a) CTBNX 1300X9; (b) CTBNX(0.5 Mg); (c) CTBNX(0.5 Ca).

Curing Reactions

In the present study, the compositions of components were expressed by equivalent ratio of



in the system

Figure 2 shows, as a typical example, results of the curing reaction of the system of CTBNX(0.5 Ca)-HPA-BADG at an equivalent ratio of 1:5:6. The curing reaction proceeded smoothly at 160°C. Also in this case, the decrease in epoxide value is consistently a little greater than that in acidity determined by non-aqueous titration. That is, etherification of epoxide groups as side reaction occurred to a slight degree, but appears least serious. The conversions reached nearly maximum conversions attainable after about 240 min.

The results of curing reactions carried out on various combinations of components are shown in Table I. Cure properties are influenced by metal content and temperature. Further, Mg has higher catalytic activities than Ca has toward the curing reaction. The system of CTBNX(0.5 Ca)-HPA-BADG showed no exotherm at 140°C. The gel times were generally shorter than those of the CTBN series in the previous study,¹ probably because of the higher functionality of the original liquid rubber, CTBNX 1300X9.

The final conversions were 92-100% and conversions differences between acidity and epoxide value were below 5%. Curing at 160°C resulted in higher final conversions than curing at 140°C.

Figure 3 shows, as a typical example, the infrared spectra of the system of CTBNX(0.5 Mg)-HPA-BADG (1:5:6). The absorption bands at 1850 and 1780 cm^{-1} , characteristic of the anhydride, and at 860 cm^{-1} , characteristic of the epoxy ring, which are observed in the spectrum (a) of the initial curable mixture, have disappeared in the spectrum (b) of the cured rubber. Moreover, the band at 3450

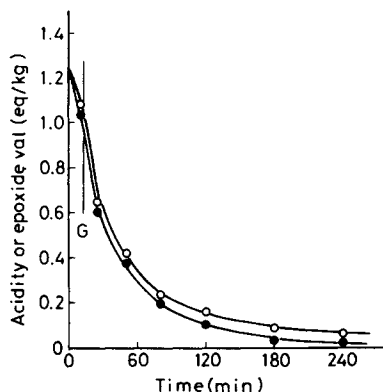
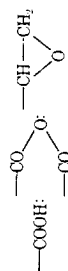


Fig. 2. Curing reaction of system of CTBNX(0.5 Ca)-HPA-BADG at an equivalent ratio of $\text{---COOH:} \begin{array}{c} \text{---CO} \quad \text{---CH---CH}_2 \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \quad \text{O} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{---CO} \quad \text{---O} \end{array} = 1:5:6$; bath temperature: 160°C; G: Gel point; (○) acidity; (●) epoxide value.

TABLE I
Curing Reactions of Systems of CTBNX(0.5M)-HPA-BADG

Components	Equiv ratio of components ^a	Cure conditions		Cure properties			Final conversions	
		Temperature ^b (°C)	Time (min)	Gel time (min)	Exotherm peak temperature (°C)	Exotherm time ^c (min)	Epoxide value (%)	Acidity (%)
CTBNX(0.5 Mg)-HPA-BADG	1:5:6	140	180	19.5	145.6	11.3	96	92
	1:5:6	160	180	7.3	179.7	10.5	100	95
	1:10:11	140	180	25.7	144.5	12.7	96	94
CTBNX(0.5 Ca)-HPA-BADG	1:10:11	160	180	11.7	175.2	13	99	95
	1:5:6	140	240	32.2	—	—	95	92
	1:5:6	160	240	13	164.7	14.1	99	95
	1:10:11	140	240	40.5	—	—	96	93
	1:10:11	160	240	17.6	168.2	18	99	95

^a Equivalent ratio of



^b Bath temperature.

^c Time required to reach peak exotherm temperature.

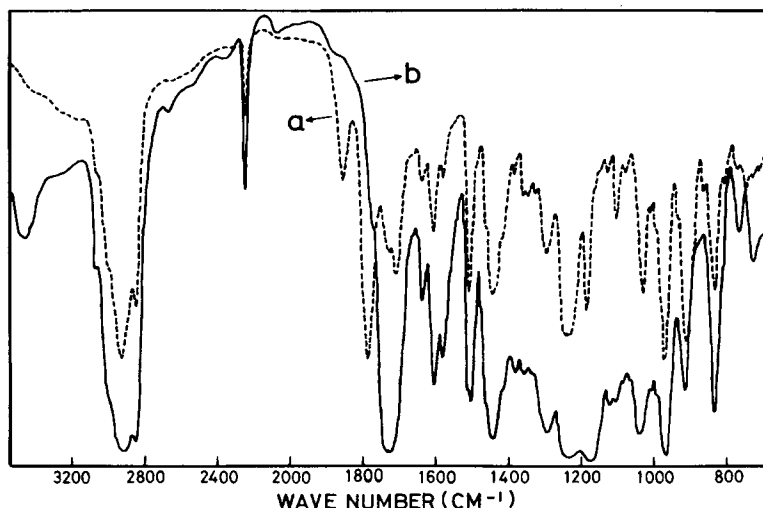


Fig. 3. Infrared spectra of system of CTBNX(0.5 Mg)-HPA-BADG at an equivalent ratio of $-\text{COOH} : -\text{CO} : -\text{CH}-\text{CH}_2 = 1:5:6$. (a) Initial curable mixture; (b) cured at 160°C for 3 hr.

cm^{-1} owing to the OH group has newly appeared; it is somewhat stronger than that of the CTBN series.¹ This indicates that the cured rubber contains higher concentration of OH groups than the CTBN series.

Based on these results, curing reactions for obtaining samples for determining physical and other properties were further carried out as follows: for the systems containing Mg, 160°C for 3 hr; for the systems containing Ca, 160°C for 4 hr.

Physical Properties

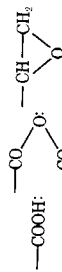
In Table II are summarized physical properties of the cured rubbers of various combinations of components. Further, Figure 4 shows stress-strain curves of the cured rubbers. Reference cured rubbers also were prepared from CTBNX 1300X9, HPA, and BADG using *N,N*-dimethylbenzylamine (DMBA) as a catalyst. The cured rubbers are considered to consist of the following two main blocks: one is soft block based on CTBNX(0.5M) and, the other is hard block from HPA and BADG. Similarly, the concentration of the CTBNX 1300X9 part in the reference cured rubber might be regarded as that of the soft blocks. The metal-containing cured rubbers of CTBNX (0.5M)-HPA-BADG at equivalent ratios of 1:5:6, and 1:10:11, respectively, contain about the same concentration of the soft blocks as the reference ones of CTBNX 1300X9-HPA-BADG at the ratios of 1:2.5:3.5 and 1:5:6 contain.

The cured rubbers in which the equivalent ratio is 1:10:11 showed much higher tensile strength and Shore hardness than those in which the ratio is 1:5:6. This tendency is similar to that observed in the previous study¹; that is, this is probably due to lower concentration of the soft blocks and also to higher crosslinking densities of the hard blocks in the former rubbers. Further, it is noteworthy that the CTBNX(0.5 Mg)-HPA-BADG (1:10:11) rubber showed a very high tensile strength of 249 kg/cm^2 . Meanwhile, the highest tensile strength observed in

TABLE II
Physical Properties of Cured Rubbers from CTBNX (0.5M), HPA, and BADG

Components	Equip ratio of components ^a	Metal in cured rubber (%)	CTBNX (0.5M) in cured rubber (%)	Tensile strength (kg/cm ²)	Elongation (%)	Shore hardness (A or D)
CTBNX (0.5 Mg) - HPA - BADG	1:5:6	0.25	61.1	88	70	A 96
	1:10:11	0.19	45.2	249	34	D 75
CTBNX (0.5 Ca) - HPA - BADG	1:5:6	0.42	61.2	74	75	A 89
	1:10:11	0.31	45.3	178	45	D 66
CTBNX 1300X9 - HPA - BADG ^b	1:2.5:3.5	—	58.8 ^c	83	86	A 88
	1:5:6	—	43.9 ^c	193	50	D 65

^a Equivalent ratio of



^b Reference cured rubber cured at 160°C for 3 hr. Catalyst: *N,N*-dimethylbenzylamine (0.15 wt % based on BADG).

^c Concentration of CTBNX 1300X9 part in the cured rubber.

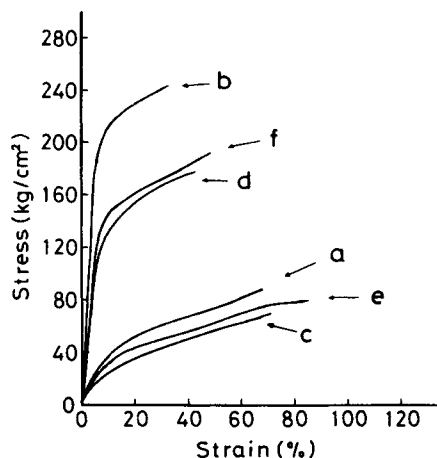


Fig. 4. Stress-strain curves of cured rubbers of (a) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (b) CTBNX(0.5 Mg)-HPA-BADG (1:10:11); (c) CTBNX(0.5 Ca)-HPA-BADG(1:5:6); (d) CTBNX(0.5 Ca)-HPA-BADG (1:10:11); (e) CTBNX 1300X9-HPA-BADG (1:2.5:3.5); (f) CTBNX 1300X9-HPA-BADG (1:5:6).

the previous study¹ was 166 kg/cm² as shown by the CTBN(0.5 Mg)-HPA-BADG rubber at a mole ratio of 1:20:11. Thus, the effect of increasing the functionality of original liquid rubber appears clearly. The CTBNX (0.5M)-HPA-BADG (1:10:11) rubbers showed Shore A hardness of above 100, hence Shore D hardness was determined for these rubbers. On the other hand, an almost reverse trend was observed for elongation.

As for the metal species, at the same equivalent ratio, the rubbers containing Mg showed better physical properties than the rubbers containing Ca, because of the higher interionic attraction of Mg²⁺. Moreover, the Mg-containing cured rubbers show higher tensile strength and Shore hardness than the reference ones do, especially so for the CTBNX(0.5 Mg)-HPA-BADG (1:10:11) rubber. Thus, the effect of introducing metal appears clearly in this case.

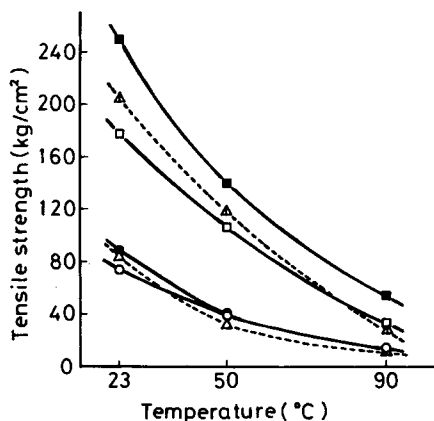


Fig. 5. Temperature dependence of tensile strength of cured rubbers. (●) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (■) CTBNX(0.5 Mg)-HPA-BADG (1:10:11); (○) CTBNX(0.5 Ca)-HPA-BADG (1:5:6); (□) CTBNX(0.5 Ca)-HPA-BADG (1:10:11); (Δ) CTBNX 1300X9-HPA-BADG (1:2.5:3.5); (▲) CTBNX 1300X9-HPA-BADG (1:5:6).

Figure 5 shows temperature dependence of tensile strength. The tensile strength decreases markedly with temperature increase. However, it is noteworthy that the CTBNX(0.5 Mg)-HPA-BADG (1:10:11) rubber still retains the effect of introducing Mg on the strength at 90°C, showing 55 kg/cm², a value considerably higher than that of the CTBN series.¹

Water Resistance of Cured Rubbers

As shown in Figure 6, increasing the metal content in the cured rubber resulted in the increase in the water absorption. On comparing the cured rubbers with about the same concentration of the soft blocks, the metal-containing cured rubbers showed higher water absorption than their corresponding reference rubbers. However, the water absorption of the former rubbers were generally lower than the metal-containing CTBN series ones in the previous study,¹ an effect of increasing the functionality of original liquid rubber. Further, it should be noted that the CTBNX(0.5 Mg)-HPA-BADG (1:5:6) rubber showed remarkably higher water absorption than the other cured rubbers; the water absorption after 14 days was almost the same as that of the CTBN(0.5 Mg)-HPA-BADG rubber at a mole ratio of 1:10:6 in the previous study.¹

However, as is clear from Figure 7, the CTBNX(0.5 Mg)-HPA-BADG (1:5:6) rubber retained 85% of the initial tensile strength after 14 days, while the CTBN rubber lost 29% of the initial value.¹ In addition, the former showed rather lower tensile strength decrease than the CTBNX(0.5 Ca)-HPA-BADG (1:5:6) rubber which showed lower water absorption. In the CTBN-series rubbers, the decrease in tensile strength became remarkable nearly in the order of water absorption. Interestingly, such a trend is not observed for the metal-containing cured rubbers based on CTBNX 1300X9 with the higher functionality. In this case, the crosslinking density due to covalent bonds is considered to be so high as to mask the decreasing effect by water of interionic attraction.

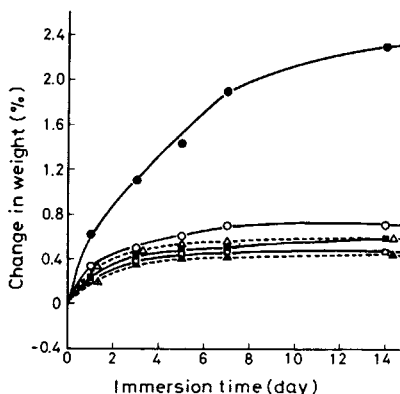


Fig. 6. Effect of water on weight change of cured rubbers. (●) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (■) CTBNX(0.5 Mg)-HPA-BADG (1:10:11); (○) CTBNX(0.5 Ca)-HPA-BADG (1:5:6); (□) CTBNX(0.5 Ca)-HPA-BADG (1:10:11); (Δ) CTBNX 1300X9-HPA-BADG (1:2.5:3.5); (▲) CTBNX 1300X9-HPA-BADG (1:5:6).

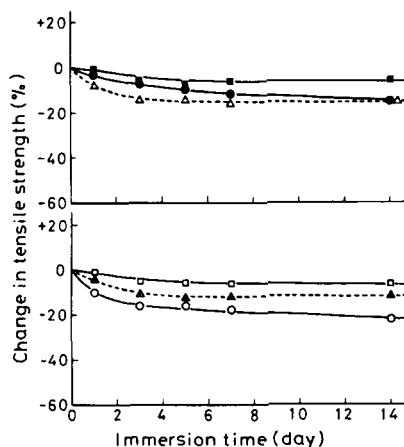


Fig. 7. Effect of water on tensile strength of cured rubbers. (●) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (■) CTBNX(0.5 Mg)-HPA-BADG (1:10:11); (○) CTBNX(0.5 Ca)-HPA-BADG (1:5:6); (□) CTBNX(0.5 Ca)-HPA-BADG (1:10:11); (△) CTBNX 1300X9-HPA-BADG (1:2.5:3.5); (▲) CTBNX 1300X9-HPA-BADG (1:5:6).

Resistance of Cured Rubbers to Chemical Attack

As shown in Table III, the cured rubbers showed much higher weight gains in benzene and dioxane than in *n*-hexane. The cured rubbers in which the equivalent ratio is 1:10:11 showed considerably lower weight gain than those in which the ratio is 1:5:6. Thus, the overall crosslinking density is considered to be higher in the former than in the latter. Further, the weight gains, in respective chemicals, of the above cured rubbers were generally lower than those of the CTBN-series rubbers in the previous study,¹ especially so in benzene and dioxane. Also from this, it is apparent that the cured rubbers in the present study have higher overall crosslinking densities than the CTBN-series ones. The soluble parts of the CTBNX(0.5 Mg)-HPA-BADG (1:10:11) rubber were extremely small (below 1%). Hence, almost all of the polymer molecules are considered to have taken part in the crosslinking.

On the other hand, the cured rubbers were unaffected in external appearance by 5% H₂SO₄, and 5% NaOH, while some of the CTBN-series ones became white.

Thermal Behavior

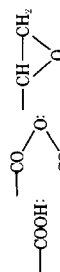
Figure 8 shows, as the typical examples, TGA and DTA curves in air of representative cured rubbers. Almost same tendencies as in the previous study¹ were observed. That is, the cured rubbers are thermally stable up to about 300°C, above which gradual weight loss begins. The exothermic peaks shown by the DTA curves are probably due to degradations occurring via oxidative modes.

Also in this case, the DTA curves show no sharp endothermic peak below 300°C. Hence, the hard block domains in the polymer matrix have no melting point.

TABLE III
Resistance of Cured Rubbers to Chemical Attack

Components	Equiv ratio of components ^a	Benzene		Dioxane		<i>n</i> -Hexane	
		Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)
CTBNX(0.5 Mg)-HPA-BADG	1:5:6	135	1.3	109	0.5	14	0.6
	1:10:11	85	0.7	97	0.5	10	0.1
CTBNX(0.5 Ca)-HPA-BADG	1:5:6	126	2.7	167	1.6	24	0.7
	1:10:11	96	2.7	157	1.3	7	0.9
CTBNX 1300X9-HPA-BADG ^b	1:2.5:3.5	144	1.5	170	1.1	14	1.0
	1:5:6	93	1.2	109	0.8	10	0.6

^a Equivalent ratio of



^b Reference cured rubber cured at 160°C for 3 hr. Catalyst: *N,N*-dimethylbenzylamine (0.15 wt % based on BADG).

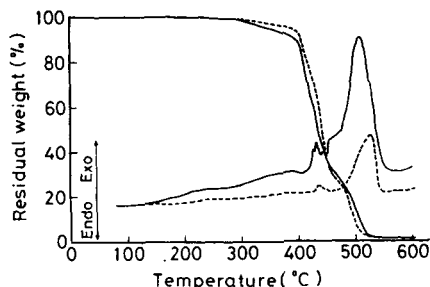


Fig. 8. TGA and DTA curves of cured rubbers. (—) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (---) CTBNX(0.5 Ca)-HPA-BADG (1:5:6).

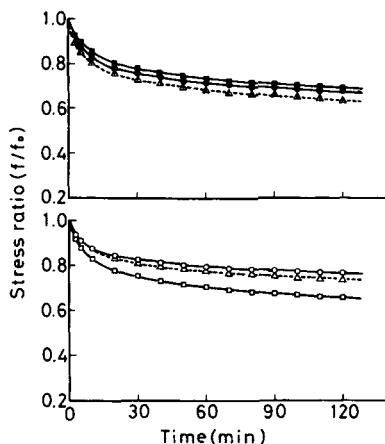


Fig. 9. Stress relaxation of cured rubbers. (●) CTBNX(0.5 Mg)-HPA-BADG (1:5:6); (■) CTBNX(0.5 Mg)-HPA-BADG (1:10:11); (○) CTBNX(0.5 Ca)-HPA-BADG (1:5:6); (□) CTBNX(0.5 Ca)-HPA-BADG (1:10:11); (Δ) CTBNX 1300X9-HPA-BADG (1:2.5:3.5); (▲) CTBNX 1300X9-HPA-BADG (1:5:6).

Stress Relaxation

Figure 9 shows the stress relaxation behavior of the cured rubbers. The previous study¹ indicated that the ratio of soft block to hard block content has higher effect on stress relaxation of the cured rubbers than the metal carboxylate groups. This tendency was observed in the Ca-containing cured rubbers. That is, the CTBNX(0.5 Ca)-HPA-BADG rubber at an equivalent ratio of 1:5:6, which contains lower hard block content, showed lower relaxation than that at a ratio of 1:10:11, though the former contains higher concentration of metal carboxylate groups than the latter. The effect of the ratio of soft block to hard block content on the stress relaxation is observed also in the reference cured rubbers.

Further, in the CTBNX(0.5M)-HPA-BADG (1:5:6) rubbers, that containing Mg showed higher relaxation than that containing Ca. However, it is noteworthy that the CTBNX(0.5 Mg)-HPA-BADG (1:10:11) rubber showed almost the same relaxation as the CTBNX(0.5 Mg)-HPA-BADG (1:5:6) rubber.

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