Ionic Crosslinking of Carboxyl-Terminated Liquid Rubbers with Metal Oxides

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Synopsis

Ionic crosslinking of carboxyl-terminated liquid rubbers with metal oxides and metal carbonates, mainly with the former, were investigated. The liquid rubbers used were a polymer of butadiene (Hycar CTB 2000X162) and a copolymer of butadiene–acrylonitrile (Hycar CTBN 1300X8). The CTBN ionically crosslinked rubbers obtained showed higher tensile strength than the CTB series, due to the polarity effect of the nitrile groups. The ionic rubbers cured with MgO and CaO were studied in detail, and it was found that their tensile strength increased markedly with increase in the metal oxides used, and in addition white carbon and carbon black showed remarkable reinforcing effects. The properties such as tensile strength, elongation, Shore A hardness, and melt index are influenced by humidity. It is characteristic of these ionically crosslinked rubbers that they can be successfully reprocessed.

INTRODUCTION

There have been many studies on ionically crosslinked polymers having pendent carboxyl groups neutralized with metal ions. Well-known examples are studies on ionic crosslinking of butadiene copolymers,[1] ethylene–methacrylic (MAA) or acrylic acid (AA) copolymers,[2] and styrene–MAA copolymers.[3] It is generally known that ionic crosslinking improves tensile strength, clarity, adhesive properties, etc. More recently, interesting ionic elastomers have been reported[4] which contained roughly 1 mol % sulfonate groups appended to some of the unsaturated groups of an ethylene–propylene–diene terpolymer. They not only are new materials but also have recyclability.

On the other hand, only several reports of ionic polymers derived from divalent metal ions and dicarboxylic acids of low molecular weight have appeared so far.[5–7] In these studies, metal dimerates which were resinuous materials were obtained by the reaction of the potassium salt of dimerized fatty acids with a zinc, calcium, or magnesium salt,[5] and metal dicarboxylates were prepared by the reaction of organic dibasic acids with divalent metal ions.[6,7] Recently, a paper[8] has reported ionic crosslinking of adduct polymers prepared by addition reaction of acid anhydrides to hydroxyl-terminated liquid polybutadiene. However, ionic crosslinking of liquid polymers having terminal carboxyl groups has not been studied to any great extent so far.

Therefore, in the present study preparations of ionically crosslinked rubbers were investigated 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

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2000X162) and a copolymer of butadiene-acrylonitrile (HycarCTBN1300X8). The ionically crosslinked rubbers obtained were evaluated for physical and other properties.

EXPERIMENTAL

Materials

Hycar CTB 2000X162 (acid value 0.4248 eq/kg, MW 4708, by endgroup analysis) and Hycar CTBN 1300X8 (AN 18 mol %, acid value 0.5247 eq/kg, MW 3812, by endgroup analysis) (manufactured by B. F. Goodrich Chemical Co.) were kindly supplied by Ube Kosan Co. and were used as received. The microstructure of the butadiene part was as follows: cis-1,4 15%–25%, trans-1,4 60%–65%, and vinyl structure 10%–20%. MgO (guaranteed reagent), ZnO (technical grade), and CdO (chemical pure grade) were used as received. Na_2CO_3, K_2CO_3 (guaranteed reagents), CaO (extrapure grade), and BaO (anhydrous pure grade) were ground to pass a 115-mesh screen. White carbon, $SiO_2(H_2O)_n$ (Tokusil GU), carbon black (Asahi Carbon Black #70H), and $CaCO_3$ (activated calcium carbonate, Hakuenka CC) were obtained, respectively, from Tokuyama Soda Co., Asahi Carbon Co., and Shiraishi Calcium Co. Benzene and other reagents were also used as received.

Preparation of Ionically Crosslinked Rubbers

In a 300-ml separable flask were placed fixed amounts of liquid rubber and metal compound and the mixture was stirred at 140°C under a nitrogen stream. The viscosity of the mixture increased as the neutralization reaction proceeded. When the viscosity increase was slow (as is often the case with CaO), trace amounts (several drops) of water were added to promote the reaction effectively. The stirring was stopped when the mixture became too viscous to be stirred with a stirrer. Next, the mixture was kneaded on a mixing roll at 125–130°C for 10–35 min to allow further progress of the reaction. The mixture thus obtained was cut into small pieces and placed into a mold for sheet forming. The mold was put in an oven kept at 180°C under an atmosphere of nitrogen. The temperature of the mold increased gradually over about 1 hr up to 180°C. At 180°C it was kept for 1.5 hr for forming. The mold was then cold pressed at 50 kg/cm² to give a rubber sheet. When filler was used, it was mixed with the ionically crosslinked rubber at the time of kneading by a mixing roll at 125–130°C.

For comparison, MgO and CaO were incorporated into a polybutadiene rubber (98% cis-1,4 structure) without carboxyl groups (Nipol BR 1220, Japanese Geon Co.) as follows: the rubber and MgO or CaO were mixed on the mixing roll at 50°C and the mixture was placed into the mold, pressed at 10 kg/cm² for 25 min at 130°C, and then at 60 kg/cm² for 5 min at 130°C to give a rubber sheet.

Measurements

Infrared spectra were obtained using a Shimazu IR-400 with the KRS method. Samples were applied to the KRS plate generally by using chloroform (chloroform was removed by evaporation before the measurement).

Tensile strength and elongation were determined at 23°C (R.H. 50%) using a Shimazu Autograph IS-5000 at a strain rate of 100 mm/min. Dumbbell-shaped specimens of JIS Z1702 were cut from the rubber sheets and used for the determinations. Tensile strengths were expressed as the maximum tensile stress sustained by the specimen during the tension test. Elongations were expressed as the percentage elongation at the moment of rupture of the test specimen. Unless otherwise specified, the samples were aged before testing for 24–72 hr at 23°C in a room of 50% R.H.

Acidities of samples were determined by titrating the solution of the sample in chloroform with $0.1N$ KOH–methanol using methyl red as indicator.

The benzene-soluble part was measured generally as follows: specimens of the rubbers (20 × 20 × about 2 mm, or about 1 g) were weighed and immersed in 100 g benzene at 23°C. After 96 hr, the specimens were separated from benzene phase. Benzene was removed by placing the specimens in a drier at 80°C and the samples were reweighed. The differences between the weights after benzene removal and the initial weight of the samples were regarded as the weight of the benzene-soluble part. Corrections were made for the amounts of excess metal compound and filler.

The apparent melting points were determined, using a Shimazu Micro Melting Point Determination Apparatus, by observing the state of the sample put between two cover glasses. The apparent melting point was taken as the temperature at which the rubbery state seemingly changed into the plastic state.

Shore A hardness was determined using UF Shore's Durometer Type A (Kamishima Seisakusho Co.) at 23°C.

Melt indexes (MI) were determined according to ASTM D-1238-62T using a Melt Indexer Type MX-101 (Takara Kogyo Co.), a weight of 2160 g being applied.
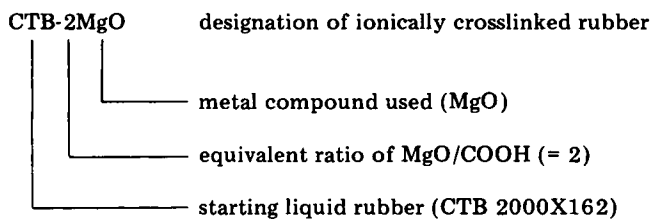
RESULTS AND DISCUSSION

Preparation of Ionically Crosslinked Rubbers with Metal Oxides and Metal Carbonates

Since carboxyl-terminated liquid rubbers have a low content of carboxyl groups and the reactivities of the carboxyl groups toward metal ions are low, it is difficult to carry out neutralization reactions of the carboxyl groups with metal ions under mild conditions such as room temperature. In the neutralization reaction, it is necessary that by-products produced from hydrogen of the carboxyl group and anion of the metal compound be removed effectively from the system. When metal oxides or metal carbonates are used, most simple by-products such as water and carbon dioxide are generated, which can be removed easily from the system. When metal acetates are used, acetic acid with higher boiling point is formed. Further, in the method for making sodium salt and treating with the desired metal halide, solvent is needed; in addition, it is generally awkward to thoroughly remove sodium halide as by-product from the system. Therefore, in the present study, metal oxides and metal carbonates, mainly the former, were used for the ionic crosslinking.

For preparation of ionically crosslinked rubbers, the procedures described in the experimental section were arrived at empirically as optimum from the results

of preliminary experiments. In the first step, the reaction mixture was stirred at 140°C until it became too viscous to be stirred with a stirrer. In the second step, kneading of the mixture by a mixing roll at 125–130°C was conducted for further progress of the reaction and also for removing volatile by-products such as water, etc.; especially when fillers are used the kneading is required. Finally, in the third step, the mixture was kept at 180°C to complete cure, being formed into sheets.

Neutralization of the liquid rubbers with various metal compounds was carried out at various equivalent ratios of the metal compound to the carboxyl group present. Thus, designations of ionically crosslinked rubbers obtained would become considerably long. Therefore, we simplify the designation by the method illustrated in the following example:

CTB-2MgO   designation of ionically crosslinked rubber

———————— metal compound used (MgO)

———————— equivalent ratio of MgO/COOH (= 2)

———————— starting liquid rubber (CTB 2000X162)

Infrared spectra of representative ionically crosslinked rubbers obtained by the above conditions are shown in Figures 1 and 2, together with those of the corresponding original liquid rubbers. In the spectra of the original liquid rubbers, absorption bands at 1710 cm^{-1}, due to carboxyl group, and at 1640 cm^{-1} (C=C) are noteworthy. In the spectra of the ionically crosslinked rubbers, the band at 1710 cm^{-1} has disappeared and the band at 1560 cm^{-1}, due to carboxylate, has newly appeared. This indicates that the neutralization reaction has proceeded, resulting in the formation of metal carboxylate groups. The unsaturated groups in the rubbers are considered stable under the above reaction conditions from the fact that the band at 1640 cm^{-1} has remained unchanged. Other ionically crosslinked rubbers showed similar spectra.
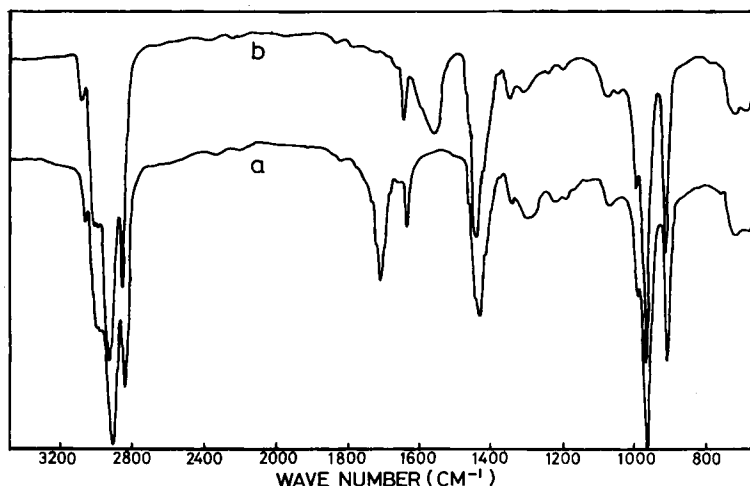

Fig. 1. Infrared spectra of (a) liquid CTB 2000X162 rubber and (b) ionically crosslinked CTB–1.5CaO rubber.
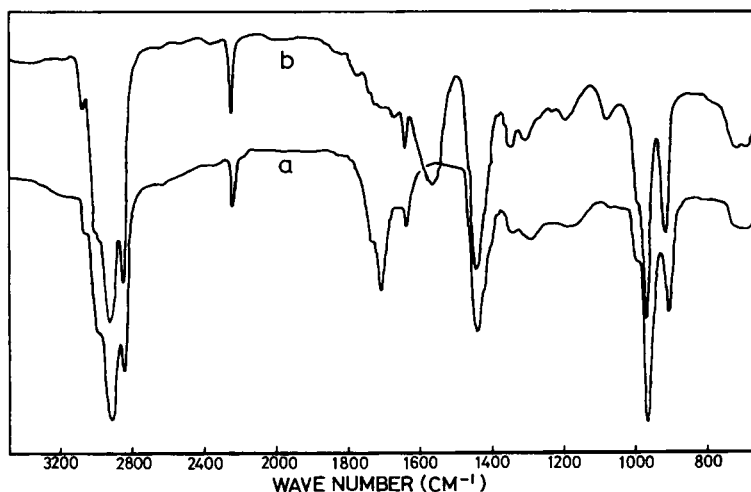
Fig. 2. Infrared spectra of (a) liquid CTBN 1300X8 rubber and (b) ionically crosslinked CTBN–1CaO rubber.

The results of preparations of ionically crosslinked rubbers with various metal ions are summarized in Tables I and II. When the equivalent ratio of M_2CO_3 or MO/COOH was 1, the ionically crosslinked rubbers obtained showed generally extremely low tensile strengths. However, as the ratio increased to 2, the tensile strength increased, especially so in the rubbers cured with MgO, CaO, or BaO. A similar tendency was observed also for the apparent melting point. As will be shown later, at the ratio of 1, neutralization proceeds with greater difficulty than at the ratio of 2, probably due to a difficulty of effective diffusion of the metal compounds.

Curing with Zn^{2+} or monovalent metal ions such as Na^+ and K^+ gave ionically crosslinked rubbers with very low tensile strength and apparent melting point. Especially the ionically crosslinked rubbers obtained with a ratio of 1 showed slight fluidity at room temperature. It has generally been known[9] that fluidity can appear with greater ease in polymers crosslinked with monovalent metal ions than in those with divalent metal ions. Moreover, among the rubbers cured with the divalent metal ions at a ratio of 2, tensile strength decreased in the order Ba $\geqq$ Ca > Mg > Cd > Zn. However, in the BaO-cured rubbers dispersion of excess unreacted BaO was not good. In addition, the CTB–2BaO rubber had poor processability, and hence additional 2 hr at 200°C was necessary to obtain acceptable sheets.

On the other hand, elongation and benzene-soluble part decreased with increase in the metal compound used, especially the elongation. The benzene-insoluble parts lost their original form in benzene and became generally very viscous oily substances. The infrared spectra of the benzene-soluble and insoluble parts were essentially identical, indicating that the benzene-soluble parts also contain ionized parts. The benzene-soluble parts are considered to consist of ionized linear polymers not taking part in crosslinking, intramolecularly ionized compounds and small portion of polymers containing unreacted carboxyl groups.

However, the CTBN–1CdO rubber swelled in benzene instead of turning into an oily state. It also showed unexpectedly high tensile strength for the equivalent

TABLE I
Neutralization of CTB 2000X162 Liquid Rubber[a] by Metal Oxides and Carbonates

M_2CO_3 or MO	Equivalent ratio of M_2CO_3 or MO:COOH	Reaction condition				Product			
		First stirring		Time of kneading by roll at 125–130°C, min	Time of forming at 180°C, hr	Tensile strength,[b] kg/cm^2	Elongation,[b] %	Benzene-soluble part,[c] %	Apparent melting point, °C
		Temp., °C	Time, hr						
Na_2CO_3	1:1	140	2.5	30	1.5	—	—	89	<25
	2:1	140	1.5	30	1.5	0.3	396	85	42–44
K_2CO_3	1:1	140	2.5	30	1.5	—	—	84	<25
	2:1	140	1.33	30	1.5	0.3	633<	80	44–46
MgO	1:1	140	4.0	30	1.5	0.3	615<	99	45–48
	2:1	140	0.42	30	1.5	3.5	63	39	106–108
CaO	1:1	140	2.5	30	1.5	0.5	309	71	44–46
	2:1	140	1.0	30	1.5	7.0	34	18	75–78
ZnO	1:1	140	4.75	30	1.5	0.3	650<	94	<25
	2:1	140	1.5	30	1.5	0.5	171	93	54–56
CdO	1:1	140	3.0	30	1.5	0.4	274	63	56–59
	2:1	140	1.0	30	1.5	2.3	72	30	95–100
BaO	1:1	140	3.0	30	1.5	0.6	317	82	32–35
	2:1	140	1.5	30	1.5[d]	10.9	7	12	173–176

[a] Acid value 0.4248 eq/kg; molecular weight 4708.
[b] Determined at 23°C.
[c] Soluble part (%) obtained from about 1 g product/100 g benzene.
[d] Additional 2 hr at 200°C was applied.

TABLE II
Neutralization of CTBN 1300X8 Liquid Rubber[a] by Metal Oxides and Carbonates

M₂CO₃ or MO	Equivalent ratio of M₂CO₃ or MO:COOH	Reaction condition				Product			
		First stirring		Time of kneading by roll at 125–130°C, min	Time of forming at 180°C, hr	Tensile strength[b], kg/cm²	Elongation[b], %	Benzene-soluble part[c], %	Apparent melting point, °C
		Temp., °C	Time, hr						
Na₂CO₃	1:1	140	2.5	30	1.5	—	—	92	<25
	2:1	140	0.67	30	1.5	1.1	650<	56	24–27
K₂CO₃	1:1	140	2.17	30	1.5	0.3	650<	100	<25
	2:1	140	1.0	30	1.5	1.3	268	25	33–35
MgO	1:1	140	3.5	35	1.5	0.6	167	95	51–54
	2:1	140	0.67	20	1.5	4.5	86	9	127–130
CaO	1:1	140	7.0	30	1.5	0.4	800<	17	47–49
	2:1	140	1.17	15	1.5	11.7	53	7	96–99
ZnO	1:1	140	3.5	30	1.5	—	—	100	<25
	2:1	140	1.5	30	1.5	1.1	236	67	69–73
CdO	1:1	140	4.0	15	1.5	3.2	273	3	98–102
	2:1	140	1.67	15	1.5	3.3	70	60	78–82
BaO	1:1	140	3.0	30	1.5	0.4	590<	65	72–75
	2:1	140	1.0	15	1.5	11.6	29	3	134–139

[a] Acid value 0.5247 eq/kg; molecular weight 3812.
[b] Determined at 23°C.
[c] Soluble part (%) obtained from about 1 g product/100 g benzene.

ratio of 1. These tendencies seem to be due to a slight degree of heat polymerization of the double bonds of the vinyl structure under high temperatures.

As for the structure of ionomers, Macknight et al.[10] proposed that the salt groups are largely concentrated in spherical clusters 8–10 Å in radius in the amorphous hydrocarbon phase and that these clusters contain the carboxylate groups associated with the metal ion. Furthermore, it has recently been reported[11] that, in the telechelic polybutadiene–methacrylic acid copolymer containing 2 mol % acid and neutralized by alkali ions such as Na^+, K^+, and Cs^+, salt groups form clusters and the ionic groups may form small bilayer disks.

Generally, the ionically crosslinked rubbers were elastic when subjected to a rapid impact, however, they showed a tendency to slowly relax over a long time because of reorganization of the metal carboxylate bonds.

The CTBN ionic cured rubbers showed higher tensile strength than the CTB series. The increase in the strength of the former might be due to a polarity effect of nitrile groups.

Next, MgO and CaO were selected for the preparation of ionic rubbers cured at various equivalent ratios of MO/COOH, and the ionic cured rubbers obtained were evaluated for various properties.

Effect of Equivalent Ratio of MO/COOH on Properties of Ionic Rubbers Cured with MgO or CaO

Figure 3 shows stress–strain curves of representative CTBN ionic rubbers cured with CaO. The ionic cured rubber of CTBN–1.5 CaO prepared at a low equivalent ratio of CaO/COOH was soft and showed high elongation but low tensile strength. With increase in the amount of CaO used, elongation decreased and tensile strength increased. The rubber of CTBN–10CaO reinforced with carbon black (50 phr) was hard, showing high tensile strength but very low elongation. Other series of ionic cured rubbers showed similar stress–strain curves.
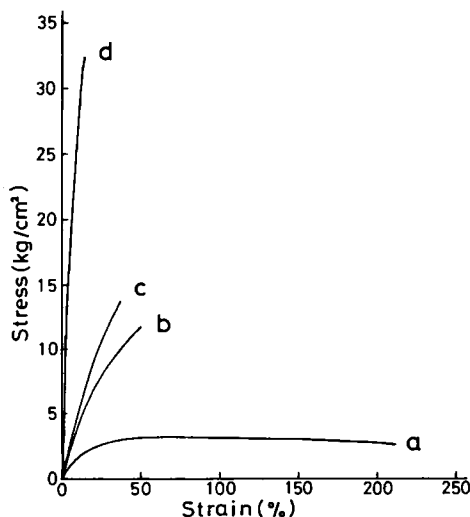

Fig. 3. Stress–strain curves of ionically crosslinked rubbers of (a) CTBN–1.5CaO; (b) CTBN–2CaO; (c) CTBN–10CaO; (d) CTBN–10CaO + carbon black (50 phr).

Figures 4 and 5 show the effect of equivalent ratio of MO/COOH on physical properties of ionic rubbers cured with MgO or CaO, together with the effect of MO on tensile strength of Nipol BR 1220 rubber for comparison (polybutadiene rubber with 98% *cis*-1,4 structure, Japanese Geon Co.). Generally, tensile strength of the ionic cured rubbers increased markedly with increase in the metal oxides used. The effect of increasing CaO was remarkable up to an equivalent ratio of about 2, and further increase of CaO showed no significant effect. At the equivalent ratio of 10, tensile strength was about 8 kg/cm^2 for the CTB series and about 14 kg/cm^2 for the CTBN series. As a whole, the tensile strengths of the CaO-cured ionic rubbers were higher than those of the MgO-cured ones. A reverse trend was observed for elongation. That is, elongation decreased markedly with increase in the metal oxides used up to an equivalent ratio of about 2, above which only a slight decrease was observed even if the ratio increased up to 10.

No effect of addition of metal oxides was observed for the reference rubber Nipol BR 1220 without terminal carboxyl groups. This rubber showed very high elongation of above 1000%. From this it is apparent that the increase in tensile strengths of the CTB and CTBN rubbers with increase in metal oxides is due to the chain extension through ionic links based on carboxylate anions neutralized with Mg^{2+} or Ca^{2+}.

Table III shows the effect of equivalent ratio of MO/COOH on residual acid value of the ionic cured rubbers. At lower equivalent ratios, residual acid value decreased with increase in the equivalent ratio; and at the ratio of about 2, it generally reached almost the minimum acid value attainable. In the CTBN rubbers cured with MgO, acid value continued to decrease gradually with increase
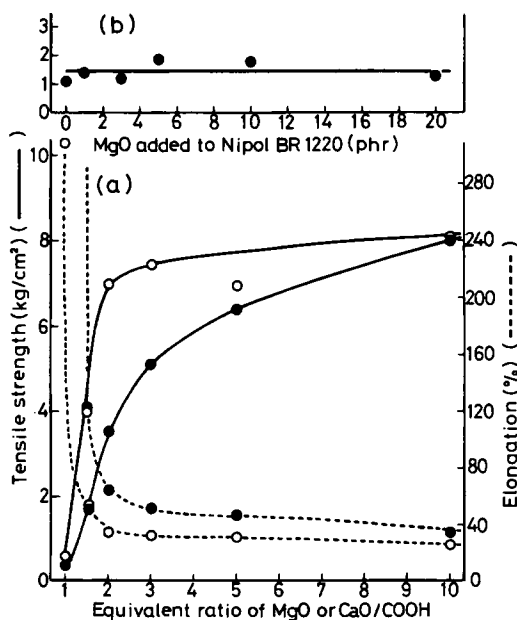

Fig. 4. (a) Effect of equivalent ratio of MO/COOH on physical properties of CTB series ionic rubbers cured with MgO or CaO: (●) MgO; (○) CaO. (b) Effect of MgO on tensile strength of Nipol BR 1220 rubber.
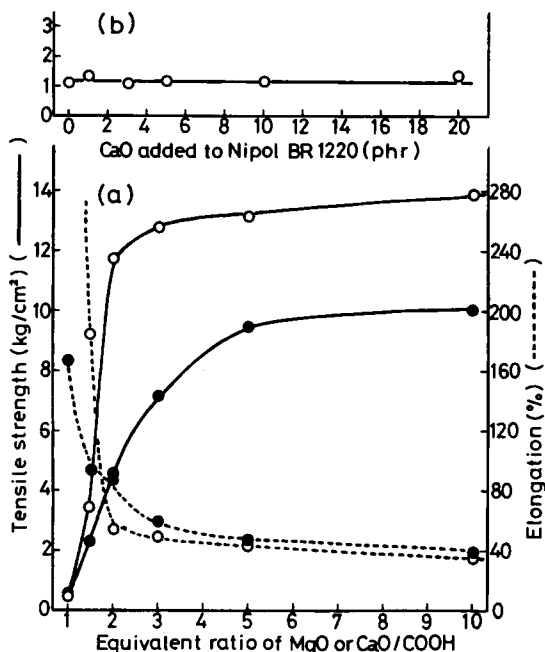
Fig. 5. (a) Effect of equivalent ratio of MO/COOH on physical properties of CTBN series ionic rubbers cured with MgO or CaO: (●) MgO; (○) CaO. (b) Effect of CaO on tensile strength of Nipol BR 1220 rubber.

TABLE III

Effect of Equivalent Ratio of MO/COOH on Acid Value of CTB Series[a] and CTBN Series[b] Ionic Rubbers Cured with MgO or CaO

Ionically crosslinked rubber	MO	Acid value, eq/kg					
		MO/COOH					
		1	1.5	2	3	5	10
CTB series	MgO	0.1378	0.1168	0.0818	0.0921	0.0877	0.0695
CTB series	CaO	0.0525	0.0168	0.0123	0.0260	0.0305	0.0144
CTBN series	MgO	0.1908	0.1807	0.1199	0.0859	0.0514	0.0428
CTBN series	CaO	0.0789	0.0188	0.0189	0.0155	0.0104	0.0108

[a] Acid value of CTB 2000X162 = 0.4248 eq/kg.

[b] Acid value of CTBN 1300X8 = 0.5247 eq/kg.

in the equivalent ratio up to 10.   These tendencies correlate well with the changes in the physical properties in Figures 4 and 5.   Further, it should be noted that the residual acid values of the MgO-cured rubbers are considerably greater than those of the CaO-cured ones.   Thus, CaO has higher reactivities for the terminal carboxyl groups of the liquid rubbers than MgO.

It has been shown[12] by creep measurements that interionic attraction increases in the order $Pb^{2+} < Zn^{2+} < Ca^{2+} < Mg^{2+}$.   The reverse trend observed with regard to the effect of Mg^{2+} and Ca^{2+} on the tensile strengths of the CTB and CTBN ionic cured rubbers is considered due to the lower degree of neutralization of the MgO-cured rubbers.   From the above observations it was found that the remarkable effects of increasing the amount of the metal oxides appear up to the equivalent ratios of 2–3.

Effect of Fillers on Properties of Ionic Rubbers Cured with MgO or CaO

As stated above, there were limits in the effects of increasing the metal oxide amounts. Next, the effects of various fillers were investigated on the ionic rubbers cured with MgO or CaO. First, the effects of the amount of various fillers on tensile strength of the ionic cured rubber of CTB–2MgO were studied, and the results are shown in Figure 6. Tensile strength increased markedly with increase in the amount of filler, especially so for white carbon and carbon black, and it generally showed a peak at 50 phr; further increase (to 70 phr) of filler showed a tendency for difficulty in processing. Thus, the use of 50 phr fillers seemed to be optimum.

The properties of ionic cured rubbers with 50 phr of various fillers are summarized in Table IV. Interestingly, white carbon and carbon black showed remarkable reinforcing effects. Also in this case the CTBN ionic cured rubbers showed generally higher tensile strength than the CTB series when comparing the rubbers containing the same filler, probably due to the polarity effect of the nitrile groups in addition to the reinforcing effects of the filler.

The ionic cured rubbers reinforced with carbon black showed no apparent melting point. However, in benzene they lost their original form instead of becoming gel-like, indicating the absence of covalent crosslinks. Carbon black is known to contain carboxyl, hydroxyl, ketone, ester, aldehyde, quinone, hydroquinone, lactone, and unsaturated groups.[13] Hence, it can be considered that these functional groups, especially carboxyl and carbonyl groups, on the surface of the filler particles will take part in some interactions with metal oxide and metal carboxylate groups, thus resulting in an increase in intermolecular attraction. Further, Table IV shows that the effect of the fillers on the thermal stability in terms of apparent melting point decreases in the order carbon black > white carbon > $CaCO_3$.

As is obvious when comparing rubbers having the same filler, the CTBN rubbers showed generally a smaller benzene-soluble part than the CTB series.
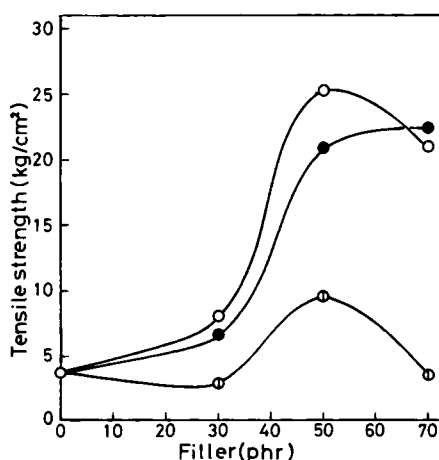

Fig. 6. Effect of fillers on tensile strength of ionically crosslinked CTB–2MgO rubber: (○) white carbon; (●) carbon black; (◑) $CaCO_3$.

TABLE IV
Effect of Various Fillers on Properties of Ionic Rubbers Cured with MgO or CaO

Ionically crosslinked rubber	Filler[a]	Tensile strength,[b] kg/cm^2	Elongation,[b] %	Benzene soluble part, %	Apparent melting point, °C
CTB–2MgO	white carbon	25.3	23	68	154–161
CTB–2CaO	white carbon	20.1	63	58	160–165
CTBN–2MgO	white carbon	35.5	38	56	174–179
CTBN–2CaO	white carbon	22.5	47	18	147–151
CTB–2MgO	CaCO$_3$	9.5	28	39	135–141
CTB–2CaO	CaCO$_3$	8.3	46	32	91–97
CTBN–2MgO	CaCO$_3$	12.1	36	17	113–116
CTBN–2CaO	CaCO$_3$	9.8	75	15	94–98
CTB–2MgO	carbon black	20.7	14	32	—
CTB–2CaO	carbon black	21.1	29	29	—
CTBN–2MgO	carbon black	36.0	26	13	—
CTBN–2CaO	carbon black	33.0	26	24	—
CTB–10MgO	white carbon	23.5	16	54	160–163
CTB–10CaO	white carbon	25.5	15	52	166–168
CTBN–10MgO	white carbon	33.8	18	11	—
CTBN–10CaO	white carbon	37.6	19	11	181–185
CTB–10MgO	CaCO$_3$	6.2	14	24	147–149
CTB–10CaO	CaCO$_3$	7.2	41	46	97–99
CTBN–10MgO	CaCO$_3$	9.5	16	10	176–178
CTBN–10CaO	CaCO$_3$	15.9	25	10	134–136
CTB–10MgO	carbon black	22.4	17	17	—
CTB–10CaO	carbon black	23.7	14	23	—
CTBN–10MgO	carbon black	21.3	10	9	—
CTBN–10CaO	carbon black	31.8	15	11	—

[a] The amount of filler was 50 phr.

[b] Determined at 23°C.

In the corresponding series of rubbers the benzene-soluble part generally decreased in the order white carbon > CaCO$_3$ > carbon black. Moreover, increasing the equivalent ratio of MO/COOH from 2 to 10 resulted in a decrease in the benzene-soluble part and elongation when comparing the same series of rubbers having the same filler.

In summary, it can be said that the ionic cured rubbers reinforced with carbon black showed the best balance of properties investigated.

Effect of Humidity on Properties of Ionic Rubbers Cured with MgO or CaO and Water Resistance

Ionomers are generally known to be sensitive to moisture and water. Therefore, the effects of relative humidity (R.H.) on properties were evaluated for representative ionic rubbers. Table V shows the results. Initial values of properties were determined (at 23°C, R.H. 50%) at about 24 hr after preparation of the samples (rubber sheets). Properties such as tensile strength, elongation, Shore A hardness, and melt index (MI) are influenced by R.H. That is, tensile strength and Shore A hardness decreased with increase in R.H.; however, the reverse trend was observed for elongation and MI. These tendencies correlate

TABLE V
Effect of Relative Humidity (R.H.) on Properties of Ionically Crosslinked Rubbers

Ionically crosslinked rubber	Properties	Initial value	After one week at 23°C			After two weeks at 23°C		
			R.H. 17%–30%	50%	80%	R.H. 17%–30%	50%	80%
CTBN–2MgO	Tensile str., kg/cm^2	4.8	5.2	3.2	1.7	6.5	3.5	2.1
	Elongation, %	77	58	109	194	45	90	153
	Shore A hardness	60	56	54	49	56	53	53
	MI at 150°C, g/10 min	39		33		26	37	44
	Change in weight, %	—	−0.04	+0.23	+0.80	−0.14	+0.27	+1.10
CTBN–2CaO	Tensile str., kg/cm^2	10.7	9.2	5.8	2.8	7.2	4.2	1.3
	Elongation, %	55	52	66	136	61	69	594
	Shore A hardness	65	65	63	60	62	61	53
	MI at 150°C, g/10 min	6		13		10	17	18
	Change in weight, %	—	+0.16	+0.51	+0.87	+0.20	+0.58	+1.07
CTB–10CaO	Tensile str., kg/cm^2	7.9	8.0	6.7	5.1	7.5	4.9	4.2
	Elongation, %	26	29	28	30	35	30	30
	Shore A hardness	63	68	66	63	65	63	60
	MI at 150°C, g/10 min	0.2		1.1		1.0	4	6
	Change in weight, %	—	+0.51	+1.40	+1.91	+0.97	+2.01	+2.51
CTBN–10MgO	Tensile str., kg/cm^2	10.7	12.8	10.7	7.9	13.8	8.5	7.2
	Elongation, %	36	43	39	48	40	30	44
	Shore A hardness	71	73	71	70	70	69	62
	MI at 150°C, g/10 min	3		3		2	5	9
	Change in weight, %	—	−0.12	+0.23	+1.00	−0.15	+0.27	+1.37
CTB–2MgO + 50 phr carbon black	Tensile str., kg/cm^2	20.3	19.2	13.6	13.3	20.0	13.9	12.8
	Elongation, %	34	28	30	38	33	30	33
	Shore A hardness	82	82	82	81	86	83	82
	MI at 180°C, g/10 min	0.4		0.3		0.9	0.6	0.5
	Change in weight, %	—	−0.10	+0.17	+0.43	−0.10	+0.21	+0.51
CTBN–2CaO + 50 phr carbon black	Tensile str., kg/cm^2	30.1	25.3	20.7	10.5	24.7	19.3	8.2
	Elongation, %	24	23	29	154	25	31	288
	Shore A hardness	87	87	85	80	87	86	77
	MI at 180°C, g/10 min	0.4		0.7		0.3	0.2	0.3
	Change in weight, %	—	−0.10	+0.25	+0.80	−0.09	+0.29	+0.93

well with weight gain, which increased with increase in R.H. The MgO-cured rubbers such as CTBN–2MgO and CTBN–10MgO showed only slight weight decrease at the low R.H. of 17%–30%, probably due to trace amounts of water adsorbed in the rubber. Interestingly, tensile strength showed a tendency to increase only slightly with weight decrease. However, the CaO-cured rubbers

such as CTBN–2CaO and CTB–10CaO showed slight weight gain even at a R.H. of 17%–30%. Thus, the CaO-cured rubbers are more hygroscopic than the MgO-cured ones.

Both the MgO- and CaO-cured rubbers reinforced with carbon black showed only a slight weight decrease at the R.H. of 17%–30%. This might be due mainly to trace amounts of water adsorbed in the carbon black. The carbon black-reinforced rubbers showed extremely low MI which were little influenced by R.H.

Table VI shows the water resistance of representative ionic cured rubbers. Generally, the ionic cured rubbers became white in external appearance. Weight gain continued to increase with immersion time. Increasing the amount of the metal oxides used resulted in increase in the water absorption, especially for MgO. Further, the CTBN rubbers showed considerably higher water absorption than the CTB series. It is of interest to note that MgO imparted higher water absorption than CaO, contrary to the case of the above hygroscopic character. As for the water absorption, a similar trend has been observed also for unsaturated polyester resins thickened with MgO and CaO.[14]

On the other hand, reinforcing with carbon black reduced the water gain of the ionic cured rubbers considerably and did not affect external appearance.

Reprocessability of Ionic Rubbers Cured with MgO or CaO

Since the ionic cured rubbers described above have no covalent crosslinks, it is expected that they could be reprocessed. Some experiments on reprocessability were carried out as follows: Sample rubber sheets were cut into pieces, kneaded by a roll at 130°C for 5 min, preheated in the mold at 130–150°C for 15 min, and then pressed at 50 kg/cm^2 for 5 min at 130–150°C. The reprocessed ionic cured rubbers thus obtained were evaluated for various properties. As shown in Table VII, the results indicate that they can be successfully reprocessed. It is of interest to note that the residual acid values of the rubbers decreased gradually with the number of recycle times; that is, the degree of neutralization

TABLE VI
Water Resistance of Ionically Crosslinked Rubbers

Ionically crosslinked rubber	Change in weight, %, and external appearance[a]			
	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks
CTB–2MgO	+3.82 (UA)	+4.96 (SW)	+7.55 (SW)	+8.40 (SW)
CTB–10MgO	+6.29 (W)	+9.25 (W)	+14.59 (W)	+21.89 (W)
CTB–2CaO	+3.82 (SW)	+4.35 (W)	+5.30 (W)	+5.80 (W)
CTB–10CaO	+4.09 (W)	+5.04 (W)	+6.20 (W)	+6.50 (W)
CTBN–2MgO	+18.26 (W)	+34.01 (W)	+50.55 (W)	+67.61 (W)
CTBN–2CaO	+17.29 (W)	+27.96 (W)	+35.33 (W)	+43.37 (W)
CTB–2MgO + 50 phr carbon black	+2.03 (UA)	+2.75 (UA)	+3.33 (UA)	+3.97 (UA)
CTBN–2CaO + 50 phr carbon black	+14.22 (UA)	+18.32 (UA)	+21.90 (UA)	+25.31 (UA)

[a] Weight change (%) obtained from about 1 g sample/100 g water, temperature 23°C; UA = unaffected; SW = sample became slightly white; W = sample became white.

TABLE VII
Reprocessability of Ionically Crosslinked Rubbers

Ionically crosslinked rubber	Properties	Initial value	Recycle[a]	
			1st	2nd
CTB–2MgO	Tensile str., kg/cm^2	3.6	4.7	4.8
	Elongation, %	38	58	58
	Shore A hardness	54	58	58
	MI at 150°C, g/10 min	33	27	18
	Acid value, eq/kg	0.0754	0.0608	0.0406
CTBN–2MgO	Tensile str., kg/cm^2	4.8	5.4	6.3
	Elongation, %	77	75	76
	Shore A hardness	60	60	61
	MI at 150°C, g/10 min	39	18	9
	Acid value, eq/kg	0.1112	0.0689	0.0493
CTBN–2CaO	Tensile str., kg/cm^2	10.7	9.8	8.8
	Elongation, %	55	50	60
	Shore A hardness	65	65	66
	MI at 150°C, g/10 min	6	4	4
	Acid value, eq/kg	0.0161	0.0067	0.0000
CTB–10CaO	Tensile str., kg/cm^2	7.9	8.4	7.1
	Elongation, %	26	28	32
	Shore A hardness	63	69	66
	MI at 150°C, g/10 min	0.2	1.6	3
	Acid value, eq/kg	0.0149	0.0000	0.0000
CTB–2MgO + 50 phr carbon black	Tensile str., kg/cm^2	20.3	19.8	14.4
	Elongation, %	34	36	20
	Shore A hardness	81	79	81
	MI at 180°C, g/10 min	0.4	0.3	1.0
CTBN–2CaO + 50 phr carbon black	Tensile str., kg/cm^2	30.1	30.1	26.0
	Elongation, %	24	31	18
	Shore A hardness	87	87	83
	MI at 180°C, g/10 min	0.4	—	—

[a] Samples were kneaded by roll at 130°C for 5 min, preheated in the mold at 130–150°C for 15 min, and pressed at 50 kg/cm^2 for 5 min at 130–150°C.

further increased gradually. Furthermore, in MgO-cured rubbers having considerable residual acid value (such as CTB–2MgO and CTBN–2MgO), this gradual increase in the degree of neutralization resulted in a slight increase in tensile strength and in a decrease in MI. Generally, at least two recycles are possible for the ionic cured rubbers without filler.

On the other hand, the ionic cured rubbers reinforced with carbon black generally retained almost initial values of the properties in the first recycle; however, tensile strength and elongation decreased slightly in the second recycle. Thus, at least two recycles are possible also for the ionic cured rubbers reinforced with carbon black. Moreover, carbon black imparts extremely low MI to the ionic cured rubbers. That is, MI could not be determined at 150°C because of extremely high viscosity; even at 180°C the MI values were generally negligible.

However, the reprocessability has a tendency to decrease with the number of recycle times after the third recycle.

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