Crosslinking of Polypropylene Glycol with Divalent Metal Salts of Mono(hydroxyethyl) Phthalate, Anhydride, and Bisepoxide

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Synopsis

Crosslinking of polypropylene glycol with divalent metal salts of mono(hydroxyethyl) phthalate, anhydride, and bisepoxide is investigated. The anhydride and bisepoxide were hexahydrophthalic anhydride and bisphenol A diglycidyl ether. The metal carboxylate groups catalyzed the crosslinking reactions. The Mg carboxylate group showed higher catalytic activities than the Ca carboxylate group. The rubbers containing Mg showed much better physical properties than those containing Ca, due to higher interionic attraction of Mg^{++} and better homogeneity. In addition, tensile strength of the cured rubbers at about the same soft block contents depended largely upon that of the hard block. Resistances to water and chemical attack, stress-relaxation, and thermal behavior are also discussed.

INTRODUCTION

Divalent metal salts of mono(hydroxyethyl) phthalate (HEP) are considered useful starting materials for preparation of ionic polymers in which metal is firmly incorporated. Recently, we reported the preparation of metal-containing cured rubbers by crosslinking hydroxyl-terminated liquid polybutadiene (HTPB) with $(HEP—)_2M$, anhydride, and bisepoxide,[1] as shown by eq. (1). The metal-containing cured rubbers obtained consist of two main blocks: a soft block based on HTPB and a crosslinked hard block from $(HEP—)_2M$, anhydride, and bisepoxide. This synthetic route is an extension of studies on the synthesis of metal-containing cured resins by the $(HEP—)_2M$—anhydride—bisepoxide reactions.[2]

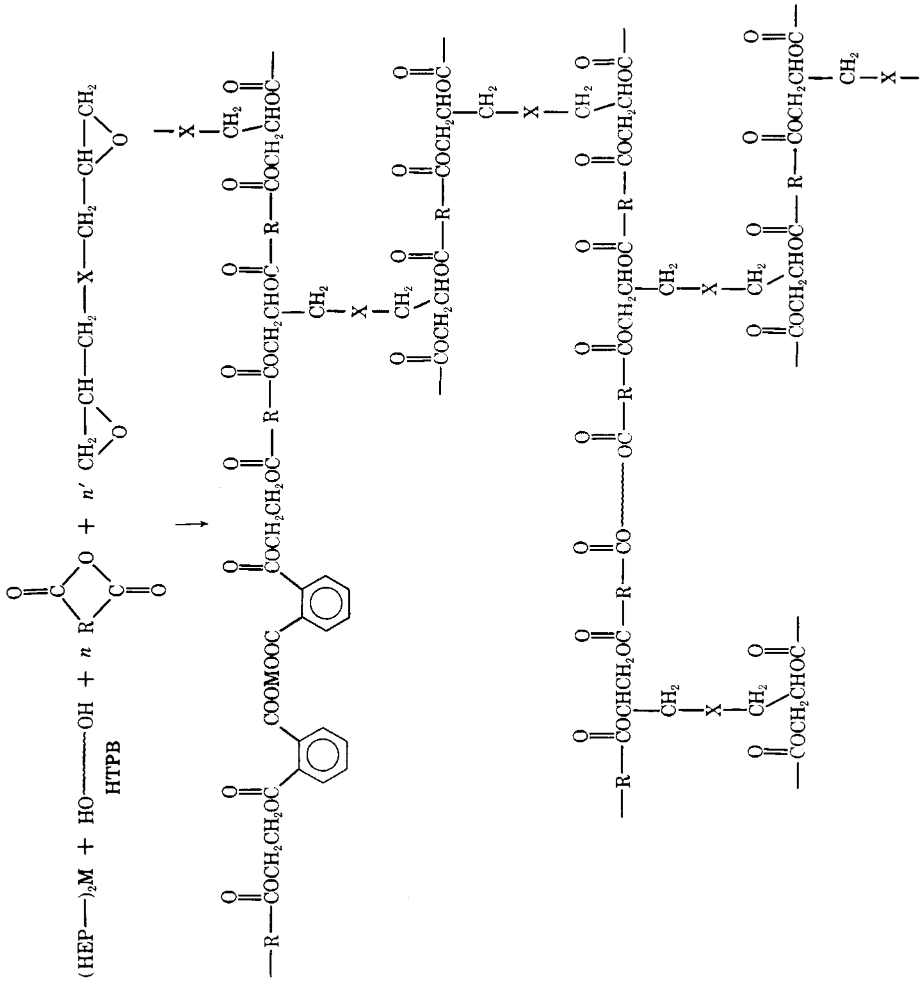
Polypropylene glycol (PPG) could be used as the soft block in eq. (1) instead of HTPB. Therefore, the preparation of novel metal-containing cured rubbers by crosslinking of PPG with $(HEP—)_2M$, anhydride, and bisepoxide was investigated. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used; hexahydrophthalic anhydride (HPA) was the anhydride used. Properties of the cured rubbers are discussed.

EXPERIMENTAL

Materials

Polypropylene glycols PPG1 and PPG2 (molecular weights 1025 and 2055, respectively, as determined by the endgroup analysis) were used, as received. $(HEP—)_2M$ salts were prepared according to the method reported in a previous

Journal of Applied Polymer Science, Vol. 27, 3877–3892 (1982)
CCC 0021-8995/82/103877-16$02.60



(1)

paper.[3] HPA was extra pure grade and was used as received. BADG, Epomik R 139, [epoxide value was 5.461 eq/kg (calcd = 5.875 eq/kg)] a product of Mitsui Petrochemical Epoxy Co., was used.

Curing Reactions

Given amounts of (HEP—$)_2$M and HPA were heated together with stirring at 140–160°C for 20–90 min. After adding a given amount of PPG, the mixture was heated and stirred at 100°C for 30–120 min. After cooling, a given amount of BADG was added, and the mixture was placed in a 18 × 180 mm test tube. The tube was placed in a constant temperature bath, and the mixture was stirred with a glass rod until gelation occurred. After a desired time, the mixture was analyzed acid and epoxide.

Rubber sheets for determining physical and other properties were prepared as follows: given amounts of (HEP—$)_2$M and HPA were heated together as above, and, then, a given amount of PPG was added; the mixture was heated and stirred at 140°C for 60 min. A given amount of BADG was added; the mixture was stirred until it became homogeneous, poured into molds, and cured at fixed temperatures for fixed periods.

Analytical Methods

Epoxide values were determined by the HBr method.[2,4–6] Acidities and infrared spectra were determined as reported earlier.[1]

Also, thermogravimetric (TGA) and differential thermal analyses (DTA) were conducted by the same methods as in the previous paper.[1]

Determination of Physical and Other Properties

The following properties were determined as in the previous papers[1,7]: tensile strength, elongation, Shore hardness, effects of water on weight change and physical properties, resistances to chemical attack.

Tear strengths were determined using a Shimazu Autograph IS-5000 at a strain rate of 100 mm/min.

Stress relaxation was determined on: dumbbell-shaped specimens strained to 50%, using the above autograph at a strain rate of 50 mm/min. When the elongation at break was below 100%, the specimens were strained to 50% of the elongation at break. The strained specimens were allowed to stand for 3 min, followed by determining the initial stress. The stress was recorded periodically.

RESULTS AND DISCUSSION

Curing Reactions

Figure 1 shows typical curing results for the system (HEP—$)_2$Mg—PPG2—HPA—BADG at a mole ratio of 4:6:40:20. The bath temperature was 140°C. The reaction is exothermic in the initial stages. The acidities shown were determined by nonaqueous titration and are due to anhydride and carboxyl

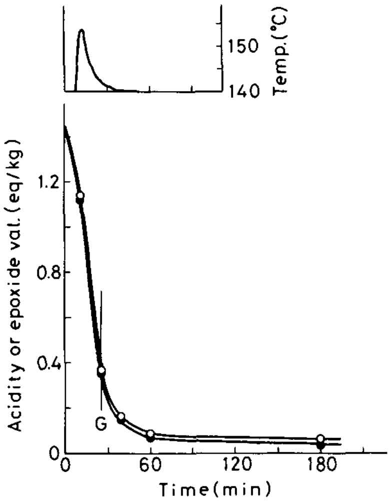


Fig. 1. Curing reaction of (HEP—)$_2$Mg—PPG2—HPA—BADG system (4:6:40:20). (○) Acidity; (●) epoxide value; bath temp = 140°C; G = gel point.

groups. The reaction proceeded smoothly at 140°C. Gelation occurred when the conversion reached 75–76%. The decrease in epoxide value is consistently slightly greater than the decrease in acidity. Thus, etherification of epoxide groups as side reactions appears less serious in the present study.

Also in the above curing system, the main reactions[2] are: 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 an ester linkage. The tendency for the metal carboxylate groups based on (HEP—)$_2$M to reequilibrate with any of the free carboxylic acids of the hexahydrophthalic group might also be possible.

Table I shows the curing reactions of various systems. Increase in temperature from 120°C to 140°C reduces the gel time and increases the exotherm peak temperature. Further, it is advantageous for the metal carboxylate groups to catalyze the curing reactions.[1,2,4,7] In comparing the cure of the systems at the same mole ratio of components, at the same temperature, the systems containing Mg showed shorter gel times and higher exotherm peak temperatures than those containing Ca. Thus, the Mg carboxylate group has higher catalytic activity than the Ca carboxylate group.

In most systems, the final conversions were 92–99%, and differences between acidity and epoxide value were generally very small. However, curing at 120°C of the systems containing Ca resulted in lower conversions because of the lower curing temperature and the lower catalytic activity of the Ca carboxylate group.

For systems containing Ca, a considerable number did not become homogeneous during the curing reaction, especially for the PPG2-containing systems. Also, the curing systems containing Mg were generally homogeneous. Therefore, cure properties were further investigated of the Mg-containing systems over a wide range of compositions at 140°C. Figure 2 shows the effect of Mg content

TABLE I
Curing Reactions of (HEP—)$_2$M—PPG—HPA—BADG Systems

Components	Mole ratio of components	Cure conditions		Cure properties			Final conversions	
		Temp[a] (°C)	Time (min)	Gel time (min)	Exotherm peak temp (°C)	Exotherm time[b] (min)	Epoxide value (%)	Acidity (%)
(HEP—)$_2$Mg—PPG1—HPA—BADG	3:7:30:15	140	240	15	155	11.9	92	93
	5:5:30:15	140	240	11.8	171	9	95	94
	2:8:40:20	120	360	50	122	24.2	94	93
	2:8:40:20	140	240	23	153	16	97	97
(HEP—)$_2$Ca—PPG1—HPA—BADG	3:7:30:15	120	360	124	121	23.1	90	89
	3:7:30:15	140	240	70	144	16.3	95	96
	5:5:30:15	140	240	26	156	11.2	93	92
(HEP—)$_2$Mg—PPG2—HPA—BADG	2:8:40:20	120	360	90	121	27	94	93
	2:8:40:20	140	240	31	144	17.8	98	97
	6:4:40:20	140	240	11.3	168	9.6	99	94
	5:5:60:30	140	240	16	164	13.4	95	94
(HEP—)$_2$Ca—PPG2—HPA—BADG	6:4:40:20	140	240	25	152	12.5	94	95
	5:5:60:30	120	360	71	120	54.6	88	88
	5:5:60:30	140	240	39	143	15.5	92	93

[a] Bath temperature.

[b] Time required to reach peak exotherm temperature.

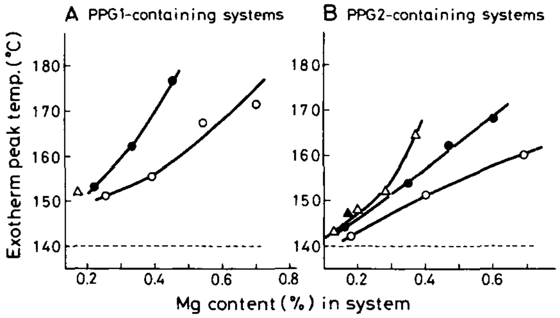


Fig. 2. Effect of Mg content in system on exotherm peak temperature for (HEP—$)_2$Mg—PPG—HPA—BADG systems at diols:HPA:BADG mole ratios of (○) 10:30:15; (●) 10:40:20; (△) 10:60:30; (▲) 10:80:40; (- - - - - -) bath temp.

on the exotherm peak temperature. Exotherm peak temperature increases markedly with increase in the Mg content, again indicating the clear catalytic activity of the metal carboxylate group. In addition, PPG1-containing systems show higher exotherm peak temperatures. Naturally, the concentrations of anhydride and epoxide groups at specific compositions of diols increase, depending on the diols:HPA:BADG mole ratio, in the order: 10:30:15 < 10;40:20 < 10:60:30 < 10:80:40. Thus higher concentrations of these functional groups exhibited higher exotherm peak temperatures at specific Mg concentrations, especially at higher Mg levels. Thus, the curing reaction also depends on the concentrations of these functional groups. Further, Figure 3 shows the effect of (HEP—$)_2$Mg content in diols on gel time at 140°C. Gel time decreases with increase in the (HEP—$)_2$Mg content in diols, due to the increase in the reaction rates. Moreover, the PPG1-containing systems show considerably shorter gel times.

The curing reactions were further examined by determining infrared spectra. Absorption bands at 1850 and 1780–1790 cm^{-1} (characteristic of the anhydride) and 860 cm^{-1} (epoxy ring) are of particular interest. In spectra of cured rubbers, these bands have disappeared, indicating that polyesterification had proceeded.

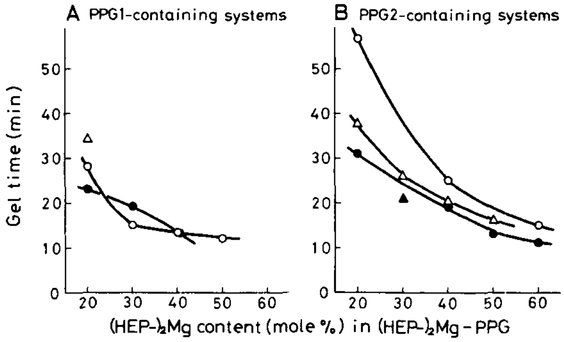


Fig. 3. Effect of (HEP—$)_2$Mg content in (HEP—$)_2$Mg—PPG on gel time at 140°C for (HEP—$)_2$Mg—PPG—HPA—BADG systems at diols:HPA:BADG mole ratios of (○) 10:30:15; (●) 10:40:20; (△) 10:60:30; (▲) 10:80:40.

Curing reactions were also carried out under the following conditions: 100°C for 30 min, 120°C for 1 h, and 140°C for 5 h.

Physical Properties

Physical properties of the metal-containing cured rubbers of various combinations of components are summarized in Table II. Reference cured rubbers were also prepared from PPG, HPA, and BADG, using *N*,*N*-dimethylbenzylamine as a catalyst. The variation in the mole ratio of components brings about considerable changes in metal content and concentration of the PPG part in the cured rubber. The concentration of the PPG part might be regarded as that of the soft blocks. Since (HEP—)$_2$M and PPG are regarded as diol, for example, the (HEP—)$_2$M—PPG—HPA—BADG system at a mole ratio of 3:7:40:20 corresponds to the diols—HPA—BADG system at a mole ratio of 10:40:20. It is apparent that increasing the (HEP—)$_2$M content in diols at the same diols: HPA:BADG mole ratios results in an increase in the overall crosslinking density; similarly, increasing the concentrations of HPA and BADG relative to that of diols leads to an increase in the crosslinking density of the hard block.

Generally, the systems containing Mg gave acceptable homogeneous cured rubbers. Many of the systems containing Ca gave unacceptable cured rubber sheets because of the inhomogeneity caused by mutual incompatibility of the components, especially for the PPG2-containing systems. Hence, the number of acceptable samples was limited for the Ca-containing systems and the obtained rubber sheets were generally semitransparent. Such was the case also with the reference cured rubbers. As is obvious in comparing the metal-containing cured rubbers at the same mole ratios, those containing Mg have much better physical properties than those containing Ca, due to higher interionic attraction of Mg^{++}, and better homogeneity of the Mg-containing systems. In metal-containing HTPB-based cured rubbers, the range of variation of compositions was not wide because of limited mutual compatibility of components.[1]

Figure 4 shows the effect of (HEP—)$_2$Mg content in diols on tensile strength and elongation of the cured rubbers. Tensile strength increases markedly with increase in the (HEP—)$_2$Mg content due to the decrease in the soft block content and also to the increase in the ionic crosslinking and overall crosslinking density. Further, higher concentrations of HPA and BADG give higher tensile strengths at specific (HEP—)$_2$Mg contents in diols. This is probably due to lower soft block content and to higher crosslinking density of the hard block. On the other hand, for ordinary vulcanizates tensile strength shows a peak at a low crosslinking density, and then decreases rapidly with increase in the crosslinking density; elongation at break decreases with increase in the crosslinking density.[8–10] In the cured rubbers (Table II), at about the same soft block contents, the rubbers with higher concentrations of HPA and BADG exhibited higher tensile strengths, due to higher crosslinking density of the hard block. For example, the cured rubbers at (HEP—)$_2$Mg:PPG2:HPA:BADG mole ratios of 6:4:40:20 and of 3:7:80:40 have the same soft block content of 33.7%. The tensile strengths were lower (121 kg/cm^2) for the former with the lower HPA and BADG contents and higher (187 kg/cm^2) for the latter with the higher HPA and BADG contents, though the former contains higher Mg content than the latter. A similar trend is also observed when comparing the PPG2-based rubbers at the ratios of 5:5:

TABLE II

Physical Properties of Metal-Containing Cured Rubbers from (HEP—)$_2$M, PPG, HPA, and BADG

Components	Mole ratio of components	Metal in cured rubber (%)	PPG in cured rubber (%)	Tensile strength (kg/cm^2)	Elon-gation (%)	Shore A or D hardness	Tear strength (kg/cm)
(HEP—)$_2$Mg—PPG1—HPA—BADG	2:8:30:15	0.25	42.7	20	444	A 39	5
	3:7:30:15	0.39	38.5	32	470	A 53	9
	4:6:30:15	0.54	34.1	85	400	A 82	20
	5:5:30:15	0.70	29.4	109	365	A 95	39
	2:8:40:20	0.22	36.3	85	225	A 77	16
	3:7:40:20	0.33	32.6	104	200	A 90	27
	4:6:40:20	0.45	28.7	228	201	A 98	66
	2:8:60:30	0.17	28.0	216	129	D 70	82
(HEP—)$_2$Ca—PPG1—HPA—BADG	3:7:30:15	0.64	38.4	26	334	A 47	9
	4:6:30:15	0.89	34.0	40	280	A 76	16
	5:5:30:15	1.14	29.2	73	284	A 92	25
	3:7:40:20	0.55	32.6	17	198	A 66	6
	4:6:40:20	0.75	28.6	47	125	A 92	19
PPG1—HPA—BADG[a]	10:30:15	—	50.3	6	120	A 31	3
	10:40:20	—	46.8	18	115	A 53	5
	10:60:30	—	33.6	111	99	A 96	27
(HEP—)$_2$Mg—PPG2—HPA—BADG	6:4:30:15	0.69	39.2	10	156	A 82	—
	7:3:30:15	0.88	31.8	23	128	A 94	—
	2:8:40:20	0.16	53.4	19	205	A 43	5
	3:7:40:20	0.25	49.3	29	235	A 52	8
	4:6:40:20	0.35	44.7	43	280	A 69	14
	5:5:40:20	0.47	39.6	62	234	A 85	25
	6:4:40:20	0.60	33.7	121	205	A 97	49
	2:8:60:30	0.13	43.8	74	131	A 88	13
	3:7:60:30	0.20	40.0	114	135	A 96	27
	4:6:60:30	0.28	35.9	154	139	A 98	44
	5:5:60:30	0.37	31.4	191	138	D 67	65
	2:8:80:40	0.11	37.1	139	110	A 98	33
	3:7:80:40	0.17	33.7	187	110	D 64	51
(HEP—)$_2$Ca—PPG2—HPA—BADG	6:4:40:20	0.98	33.6	80	145	A 96	25
	4:6:60:30	0.47	35.8	60	71	A 91	16
	5:5:60:30	0.61	31.3	113	74	A 97	37
PPG2—HPA—BADG[a]	10:80:40	—	43.2	82	70	A 89	12

[a] Reference cured rubber cured at 100°C for 30 h, 120°C for 1 h, and 140°C for 5 h. Catalyst = *N*,*N*-dimethylbenzylamine (1.5 wt % based on BADG).

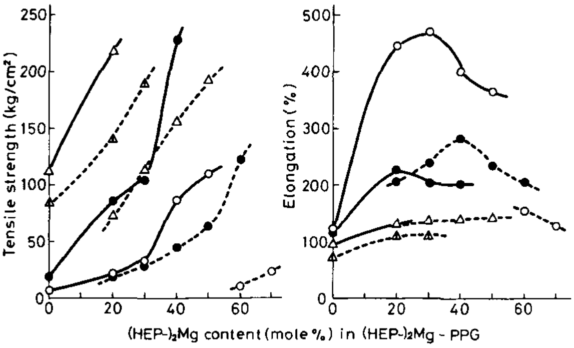


Fig. 4. Effect of (HEP—$)_2$Mg content in (HEP—$)_2$Mg—PPG on tensile strength and elongation for cured rubbers of (HEP—$)_2$Mg—PPG—HPA—BADG at diols:HPA:BADG mole ratios of (○) 10:30:15; (●) 10:40:20; (△) 10:60:30; (▲) 10:80:40. (——) PPG1-containing systems; (- - - -) PPG2-containing systems.

40:20 and of 3:7:60:30. Thus, with the same soft block contents, tensile strength depends upon the crosslinking density of the hard block to a larger extent than upon the metal content. Naturally, higher crosslinking density of the hard block leads to higher overall crosslinking density of the rubber.

The previous study[2] indicated that the (HEP—$)_2$M—anhydride—BADG-cured resins in which the mole ratio of (HEP—$)_2$M:anhydride:BADG was 1:20:10 showed higher tensile strength than those in which the ratio was 1:10:5, due to higher crosslinking density of the former resins. Thus, higher crosslinking density results in higher tensile strength. These three components constitute the hard block of the cured rubbers in the present study. It follows from the above that tensile strength of the above-cured rubbers at about the same soft block contents depends upon that of the hard block to a larger extent. Similar tendencies were also observed for Shore hardness.

On the other hand, elongation at break generally increases with increase in the (HEP—$)_2$Mg content in the diols. For some of the cured rubbers, elongation has a peak. The appearance of the peak might be due to shifting of rubbery state to glassy state with increase in the (HEP—$)_2$Mg content. At specific (HEP—$)_2$Mg contents, lower concentrations of HPA and BADG exhibited higher elongation. The PPG1-containing cured rubbers at a diols:HPA:BADG mole ratio of 10:30:15 showed highest elongations.

Figure 5 shows the effect of soft block content on tear strength for the cured rubbers. Interestingly, the data for the respective PPG1- and PPG2-containing series lie upon a curve which decreases markedly with increase in the soft block content. In addition, the PPG2-containing series showed considerably higher tear strengths than the PPG1-containing series at specific soft block contents. Thus, the soft block with the longer chain length imparts higher tear strength to the rubber.

Figures 6 and 7 show stress–strain curves of the representative Mg-containing cured rubbers. Tensile modulus, tensile strength, and elongation at break depend strongly on the composition of the rubber. With increase in the (HEP—$)_2$Mg content and/or in the concentrations of HPA and BADG, tensile modulus and tensile strength generally increase, while elongation at break de-

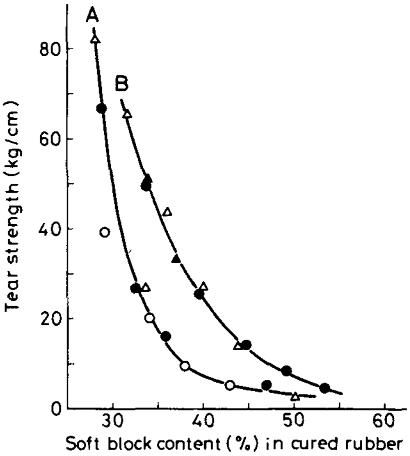


Fig. 5. Effect of soft block content on tear strength for cured rubbers of (HEP—$)_2$Mg—PPG—HPA—BADG at diols:HPA:BADG mole ratios of (○) 10:30:15; (●) 10:40:20; (△) 10:60:30; (▲) 10:80:40. (A) PPG1-containing systems; (B) PPG2-containing systems.

creases, especially for the PPG1-containing series. Further; the curves of the cured rubbers with low soft block content and high overall crosslinking density show a deviation from the behavior of usual vulcanizates; the (HEP—$)_2$Mg—PPG1—HPA—BADG (2:8:60:30) rubber shows a yield point in the curve. The tendency for the curves to become steeper at high elongations might be due to molecular orientation. For normal vulcanizates, the tendency for stress–strain curves to become steeper at higher elongations would be due to crystallization caused by molecular orientation or non-Gaussian behavior of molecular chain segments extended to their limit of extensibility.[11]

Figure 8 shows temperature dependence of tensile strength of the representative cured rubber. Tensile strength decreases markedly with increase in temperature and at 90°C the strength approaches that of the reference rubber. However, the effect of introducing metal on the strength still remains at 90°C, especially for the (HEP—$)_2$Mg—PPG1—HPA—BADG (4:6:40:20) rubber.

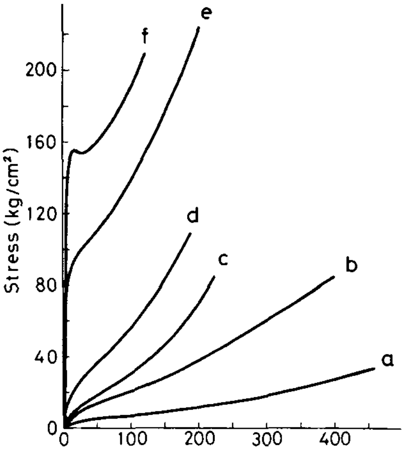


Fig. 6. Stress–strain curves for cured rubbers of (HEP—$)_2$Mg—PPG1—HPA—BADG at mole ratios of: (a) 3:7:30:15; (b) 4:6:30:15; (c) 2:8:40:20; (d) 3:7:40:20; (e) 4:6:40:20; (f) 2:8:60:30.

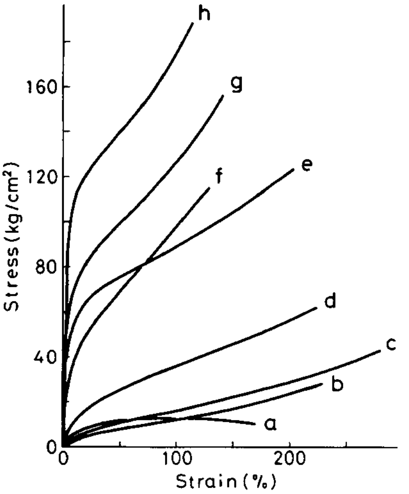


Fig. 7. Stress–strain curves for cured rubbers of (HEP—$)_2$Mg—PPG2—HPA—BADG at mole ratios of: (a) 6:4:30:15; (b) 3:7:40:20; (c) 4:6:40:20; (d) 5:5:40:20; (e) 6:4:40:20; (f) 3:7:60:30; (g) 4:6:60:30; (h) 3:7:80:40.

Water Resistance of Cured Rubbers

Figure 9 shows the effect of water on weight change of representative cured rubbers. Increasing the HPA and BADG concentrations resulted in a decrease in water absorption, due to the increase in the hard block content and also its crosslinking density. However, with an increase in the (HEP—$)_2$Mg content in the diols at the same diols:HPA:BADG mole ratio, water absorption increased in spite of the increase in the hard block content, due to the increase in the ionic links. Thus, the effect of the ionic links on the water absorption is evident in this case. The above-cured rubbers showed considerably higher water absorption than the previously reported Mg-containing cured rubbers based on HTPB.[1] This is due to the increased hydrophylicity by the ether oxygens of PPG.

Tensile strength decreased with water absorption (Fig. 10). In the PPG1-based rubbers, the decrease was greater for those with low hard block contents.

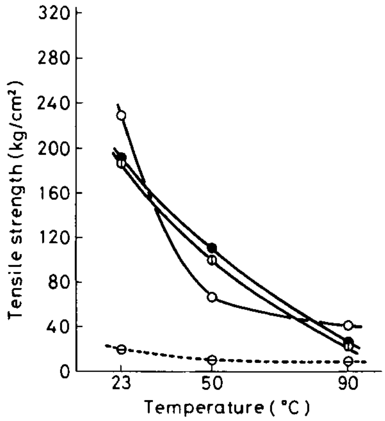


Fig. 8. Temperature dependence of tensile strength of cured rubbers: (○) (HEP—$)_2$Mg—PPG1—HPA—BADG (4:6:40:20); (●) (HEP—$)_2$Mg—PPG2—HPA—BADG (5:5:60:30); (⦶) (HEP—$)_2$Mg—PPG2—HPA—BADG (3:7:80:40); (⊖) PPG1—HPA—BADG (10:40:20).

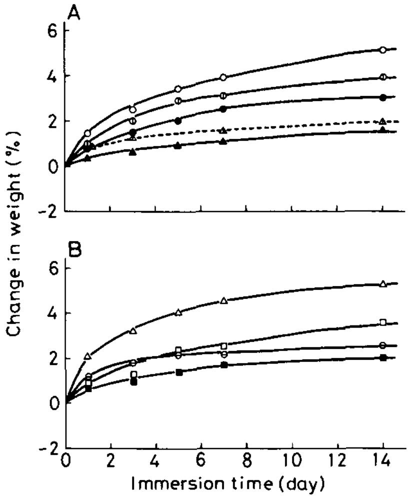


Fig. 9. Effect of water on weight change of cured rubbers. (A) (HEP—$)_2$Mg—PPG1—HPA—BADG at mole ratios of: (○) 2:8:30:15; (●) 2:8:40:20; (◑) 4:6:40:20; (△) 0:10:40:20 (PPG1—HPA—BADG at 10:40:20); (▲) 2:8:60:30. (B) (HEP—$)_2$Mg—PPG2—HPA—BADG at mole ratios of (△) 2:8:40:20; (⊖) 2:8:60:30; (□) 5:5:60:30; (■) 3:7:80:40.

Meanwhile, the reference cured rubbers whose water absorption was low showed little decrease in tensile strength; however, the strength was already very low (18 kg/cm^2).

Resistance of Cured Rubbers to Solvents

Table III shows the resistance of representative cured rubbers to solvents. They show much higher weight gains in benzene and dioxane than in *n*-hexane. As is obvious on comparing the cured rubbers at the same (HEP—$)_2$Mg:PPG:

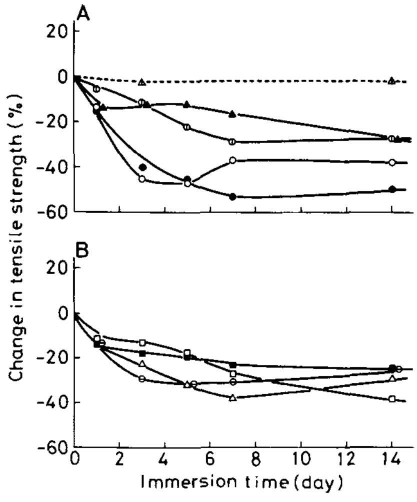


Fig. 10. Effect of water on tensile strength of cured rubbers. (A) (HEP—$)_2$Mg—PPG1—HPA—BADG at mole ratios of: (○) 2:8:30:15; (●) 2:8:40:20; (◑) 4:6:40:20; (△) 0:10:40:20 (PPG1—HPA—BADG at 10:40:20); (▲) 2:8:60:30. (B) (HEP—$)_2$Mg—PPG2—HPA—BADG at mole ratios of: (△) 2:8:40:20; (⊖) 2:8:60:30; (□) 5:5:60:30; (■) 3:7:80:40.

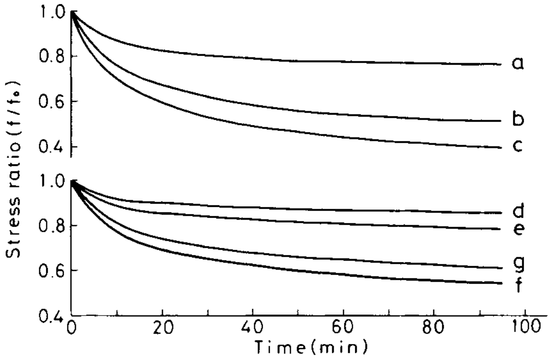


Fig. 11. Stress–relaxation of cured rubbers of (HEP—$)_2$Mg—PPG1—HPA—BADG at mole ratios of: (a) 2:8:30:15; (b) 3:7:30:15; (c) 5:5:30:15; (d) 2:8:40:20; (e) 3:7:40:20; (f) 4:6:40:20; (g) 2:8:60:30.

HPA:BADG mole ratios, the rubbers based on PPG1 show generally lower weight gain than those based on PPG2. The former have higher overall crosslinking densities than the latter. Generally, benzene– and dioxane–soluble fractions were very small, and most of the polymer molecules took part in the crosslinking.

Stress Relaxation

Figures 11–13 show stress relaxation behavior of the representative cured rubbers. At first considerable relaxation occurred, and then it gradually moderated. At the same diols:HPA:BADG mole ratios, increasing the (HEP—$)_2$M content resulted in an increase in stress–relaxation, probably due to the increase in the hard block content, and ionic crosslinking. Ionically crosslinked rubbers have a tendency to slowly relax because of reorganization of metal carboxylate bonds. In comparing the rubbers with similar soft block contents, those with higher ionic links contents showed higher stress relaxation. For example, the (HEP—$)_2$Mg—PPG2—HPA—BADG rubbers at mole ratios of 5:5:40:20 and of 3:7:60:30 have similar soft block contents (÷40%) (Table II); however, (Fig. 12) the former with the higher Mg content (0.47%) showed higher stress–relaxation than the latter with the lower Mg content (0.20%) (curve d vs. curve f). A

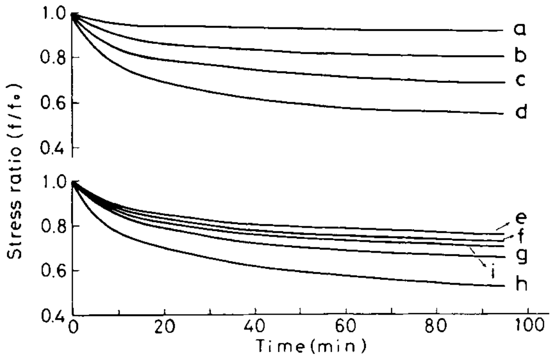


Fig. 12. Stress–relaxation of cured rubbers of (HEP—$)_2$Mg—PPG2—HPA—BADG at mole ratios of: (a) 2:8:40:20; (b) 3:7:40:20; (c) 4:6:40:20; (d) 5:5:40:20; (e) 2:8:60:30; (f) 3:7:60:30; (g) 4:6:60:30; (h) 5:5:60:30; (i) 3:7:80:40.

TABLE III
Resistance of Cured Rubbers to Solvents

Components	Mole ratio of components	Benzene: Change in wt (%)	Benzene: Soluble part (%)	Dioxane: Change in wt (%)	Dioxane: Soluble part (%)	*n*-Hexane: Change in wt (%)	*n*-Hexane: Soluble part (%)
(HEP—)$_2$Mg—PPG1—HPA—BADG	2:8:30:15	211	7.4	641	39.5	6.3	1.2
	5:5:30:15	190	12.7	409	4.7	1.4	0.7
	2:8:40:20	128	2.6	204	2.5	3.5	1.1
	3:7:40:20	118	2.3	212	3.3	2.1	0.9
	4:6:40:20	112	3.3	—	—	1.0	1.0
	2:8:60:30	138	6.4	123	2.0	0.8	1.1
(HEP—)$_2$Ca—PPG1—HPA—BADG	3:7:30:15	188	18.6	430	20.1	4.4	1.9
PPG1—HPA—BADG[a]	10:40:20	88	0.0	198	5.5	9.0	1.1
(HEP—)$_2$Mg—PPG2—HPA—BADG	2:8:40:20	229	14.3	323	12.5	15.6	5.4
	4:6:40:20	184	7.6	289	9.7	11.6	3.2
	6:4:40:20	138	2.4	232	3.6	7.8	1.2
	2:8:60:30	129	3.1	167	3.7	30.3	1.0
	5:5:60:30	105	1.4	161	2.0	8.6	0.4
	3:7:80:40	95	1.2	124	2.7	9.6	0.2

[a] Reference cured rubber cured at 100°C for 30 h, 120°C for 1 h, and 140°C for 5 h. Catalyst = *N*,*N*-dimethylbenzylamine (1.5 wt % based on BADG).

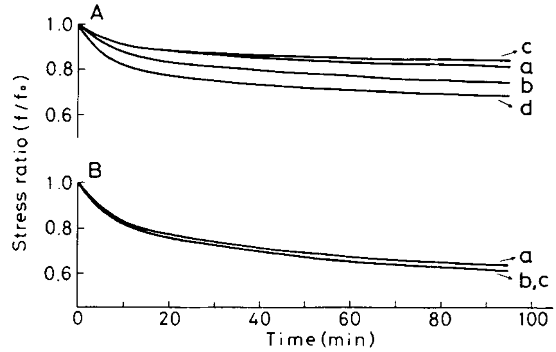


Fig. 13. Stress–relaxation of Ca-containing cured rubbers. (A) (HEP—$)_2$Ca—PPG1—HPA—BADG at mole ratios of: (a) 3:7:30:15; (b) 5:5:30:15; (c) 3:7:40:20; (d) 4:6:40:20. (B) (HEP—$)_2$Ca—PPG2—HPA—BADG at mole ratios of: (a) 6:4:40:20; (b) 4:6:60:30; (c) 5:5:60:30.

similar tendency was also observed when comparing the curves c with f, and f with g (Fig. 11).

At the same (HEP—$)_2$Mg:PPG:HPA:BADG mole ratios, the PPG2-based rubbers with the lower overall crosslinking density showed lower relaxation than the PPG1-based ones, due to a higher soft block content of the former. Thus, the ratio of soft block to hard block contents has a greater effect on the stress–relaxation of the cured rubbers than the overall crosslinking density. As for the influence of the metal species, when comparing the same PPG-based rubbers at the same mole ratio, Mg imparted higher relaxation than Ca to the rubbers, a tendency also observed in the previous studies.[1,7,12]

Thermal Behavior

Figure 14 shows TGA and DTA curves in air of the representative metal-containing cured rubber and the reference one. In the TGA curves, they are thermally stable up to about 240°C, above which gradual weight loss begins. Above about 350°C destruction proceeds rapidly. The DTA curve of the metal-containing rubber showed sharp exothermic peaks at 510–530°C, probably due to degradation occurring via oxidative modes. Moreover, the DTA curves showed no sharp endothermic peak below 300°C, indicating that both the soft block and the hard block domains in the polymer matrix have no melting point.

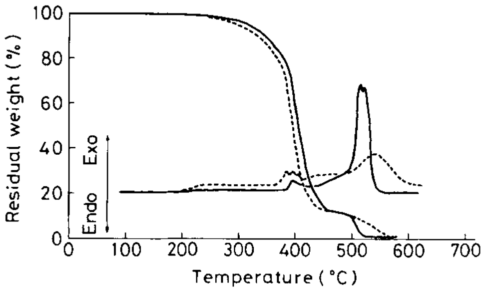
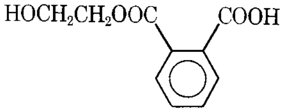


Fig. 14. TGA and DTA curves of cured rubbers. (—) (HEP—$)_2$Mg—PPG1—HPA—BADG at mole ratio of 2:8:40:20; (- - - -) PPG1—HPA—BADG at mole ratio of 10:40:20.

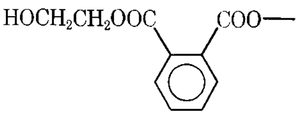
Other metal-containing cured rubbers showed similar TGA and DTA curves. However, the PPG2-based rubbers are thermally slightly less stable than the PPG1-based ones.

NOMENCLATURE

HEP = mono(hydroxyethyl)phthalate =



HEP— = HEP residue =



$(HEP\text{—})_2M$ = divalent metal salts of HEP

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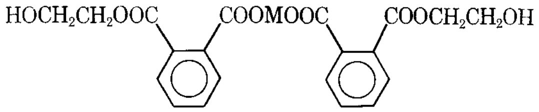

where M = divalent metal (Mg or Ca).

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Received December 3, 1981
Accepted April 23, 1982