

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

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## Synopsis

Poly(ethylene glycol)s (PEG) were crosslinked with divalent metal salts of mono(hydroxyethyl) phthalate, anhydride, and bisepoxide to give metal-containing cured rubbers. As the anhydride, hexahydrophthalic anhydride was used, and bisphenol A diglycidyl ether was the bisepoxide used. As for the physical properties of the cured rubbers obtained, the rubbers containing Mg showed much better physical properties than those containing Ca. In addition, the rubbers with high hard block contents and high overall crosslinking densities exhibited high tensile strength and Shore A hardness, and so did the rubbers having a high degree of crystallinity of the PEG soft block. The occurrence of crystallization became easy as the soft block length became longer and the soft block content became higher, or as the crosslinking density of the hard block became lower. The PEG-based rubbers showed much higher water absorption than the previously reported poly(propylene glycol)-based rubbers, due to the much higher hydrophilicity of the PEG block. Resistance to chemical attack and stress-relaxation are also discussed.

## INTRODUCTION

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) are considered useful starting materials for preparations of ionic polymers into which metal is firmly incorporated. Previously, we have reported the preparation and properties of metal-containing cured rubbers by crosslinking of poly(propylene glycol) (PPG) with  $(\text{HEP})_2\text{M}$ , anhydride, and bisepoxide,<sup>1</sup> as shown by eq. (1). The metal-containing cured rubbers obtained consist of the following two main blocks: one is a soft block based on PPG and the other is a crosslinked block (hard block) from  $(\text{HEP})_2\text{M}$ , anhydride, and bisepoxide. This synthesis is an extension of the studies on synthesis of metal-containing cured rubbers from  $(\text{HEP})_2\text{M}$ , hydroxyl-terminated liquid polybutadiene, anhydride, and bisepoxide.<sup>2</sup>

Meanwhile, poly(ethylene glycol)s (PEG) have crystallinity and are more hydrophilic than PPG. It is expected that when PEG is used as the soft block in the above reaction of eq. (1) instead of PPG, the systems would give cured rubbers which show some interesting properties not observed for the cured rubbers based on PPG. Therefore, it seemed of interest to investigate the preparation and properties of novel metal-containing cured rubbers by crosslinking of PEG with  $(\text{HEP})_2\text{M}$ , anhydride, and bisepoxide.

As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used, and hexahydrophthalic anhydride (HPA) was the anhydride used.



Shore hardness, effects of water on weight change and physical properties, and resistance to chemical attack. Tear strengths and stress-relaxation were determined by the same methods as in the previous study.<sup>1</sup>

## RESULTS AND DISCUSSION

### Curing Reactions

Figure 1, as a typical example, shows results of the curing reaction for the system of (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG at a mole ratio of 5:5:60:30. The bath temperature was 140°C. The acidities shown were determined by non-aqueous titration and are due to anhydride and carboxyl groups. The reaction proceeded smoothly at 140°C. Gelation of the system occurred when conversions reached 59–64%. The decrease in epoxide value is consistently a little greater than the decrease in acidity. Thus, a slight degree of etherification of epoxide groups occurred as side reactions, but appears least serious in the present study.

The results of the curing reactions of the PEG-containing systems were almost similar to those of the curing reactions of the PPG-containing ones in the previous study.<sup>1</sup> That is, the Mg carboxylate group showed higher catalytic activities than the Ca carboxylate group toward the curing reaction. In case of the systems containing Ca, a considerable number of them did not become homogeneous during the curing reaction, especially so for the PEG3-containing systems. Meanwhile, the curing systems containing Mg were generally homogeneous.

The curing reactions for obtaining samples for determining physical and other properties were carried out, as in the previous study,<sup>1</sup> 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 I. The content of the PEG part

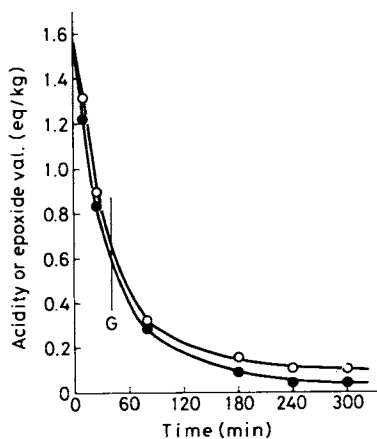


Fig. 1. Curing reaction of system of (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG (5:5:60:30). Bath temp = 140°C. G = gel point. (○) Acidity; (●) epoxide value.

TABLE I  
Physical Properties of Metal-Containing Cured Rubbers from (HEP)<sub>2</sub>M, PEG, HPA, and BADG

Components	Mole ratio of components	Metal in cured rubber (%)	PEG in cured rubber (%)	Tensile strength (kg/cm <sup>2</sup> )	Elongation (%)	Shore A hardness	Tear strength (kg/cm)
(HEP) <sub>2</sub> Mg-PEG1-HPA-BADG	0:10:30:15	—	50.0	5	123	22	2
	3:7:30:15	0.39	38.2	0.4	1500<	23	0.6
	5:5:30:15	0.70	29.1	29	318	85	19
	0:10:40:20	—	42.8	14	87	48	4
	3:7:40:20	0.33	32.3	46	198	81	17
	5:5:40:20	0.59	24.3	237	194	99	91
	0:10:60:30	—	33.3	55	125	82	12
	3:7:60:30	0.25	24.7	244	149	99	119
	5:5:30:15	0.53	45.8	6	99	80	5
	7:3:30:15	0.87	32.2	2	863	63	4
(HEP) <sub>2</sub> Mg-PEG2-HPA-BADG	0:10:40:20	—	60.7	30	87	81	18
	5:5:40:20	0.46	39.9	7	343	32	4
	7:3:40:20	0.74	27.4	135	274	93	47
	0:10:60:30	—	50.8	10	85	47	2
	3:7:60:30	0.20	40.3	24	149	56	6
	5:5:60:30	0.37	31.9	96	188	87	17
	0:10:80:40	—	43.6	33	77	71	5
	3:7:80:40	0.17	34.1	60	115	81	12
	5:5:80:40	0.31	26.3	202	126	99	78

(HEP-)2Mg-PEG3-HPA-BADG	5:5:40:20	0.38	50.5	66	218	92	46
	6:4:40:20	0.50	44.2	22	381	52	8
	7:3:40:20	0.65	36.7	19	418	50	7
	8:2:40:20	0.83	27.3	124	374	93	50
	0:10:60:30	—	61.3	71	73	93	42
	3:7:60:30	0.17	50.9	15	116	48	5
	4:6:60:30	0.24	46.6	18	236	68	11
	5:5:60:30	0.32	41.6	27	190	56	7
	6:4:60:30	0.41	35.9	37	183	68	12
	0:10:80:40	—	54.3	37	78	88	13
	2:8:80:40	0.09	47.9	20	133	53	4
	5:5:80:40	0.27	35.4	85	141	85	18
(HEP-)2Ca-PEG1-HPA-BADG	3:7:40:20	0.55	32.2	6	348	25	3
	5:5:40:20	0.96	24.3	131	152	97	46
	3:7:60:30	0.42	24.7	48	151	93	16
(HEP-)2Ca-PEG2-HPA-BADG	7:3:40:20	1.22	27.3	88	150	88	19
	5:5:60:30	0.61	31.7	11	242	38	4
	3:7:80:40	0.28	34.0	4	213	18	2
	5:5:80:40	0.50	26.3	38	169	80	11

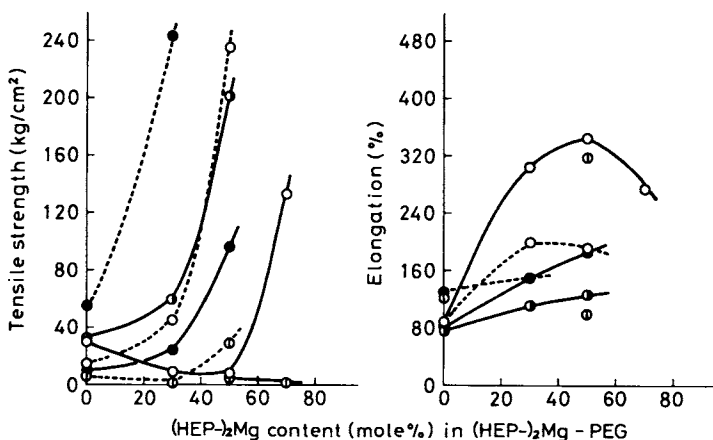


Fig. 2. Effect of  $(\text{HEP-})_2\text{Mg}$  content in  $(\text{HEP-})_2\text{Mg-PEG}$  on tensile strength and elongation for cured rubbers of  $(\text{HEP-})_2\text{Mg-PEG-HPA-BADG}$  at diols:HPA:BADG mole ratios of: ( $\oplus$ ) 10:30:15; ( $\circ$ ) 10:40:20; ( $\bullet$ ) 10:60:30; ( $\odot$ ) 10:80:40. (---) PEG1-containing systems; (—) PEG2-containing systems.

might be regarded as that of soft blocks. Reference cured rubbers were also prepared from PEG, HPA, and BADG, using *N,N*-dimethylbenzylamine as a catalyst. Since  $(\text{HEP-})_2\text{M}$  and PEG are regarded as diol, for example, the  $(\text{HEP-})_2\text{M-PEG-HPA-BADG}$  system at a mole ratio of 3:7:30:15 corresponds to the diols-HPA-BADG system at a mole ratio of 10:30:15. Also for the systems in the present study, increasing the  $(\text{HEP-})_2\text{M}$  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. Meanwhile, many of the systems containing Ca gave no acceptable cured rubber sheets because of the inhomogeneity caused by the mutual incompatibility of the components, especially so for the PEG3-containing systems. Hence, the number of acceptable samples was limited for the Ca-containing systems. On comparing the metal-containing cured rubbers at the same mole ratios, it is obvious that those containing Mg have much better physical properties than those containing Ca, due to higher interionic attraction of  $\text{Mg}^{++}$ , and further to the better homogeneity of the Mg-containing systems.

Figures 2 and 3 show the effect of  $(\text{HEP-})_2\text{Mg}$  content in diols on tensile strength and elongation of the cured rubbers obtained. In case of the PPG-based cured rubbers in the previous study,<sup>1</sup> tensile strength increased markedly with increase in the  $(\text{HEP-})_2\text{Mg}$  content in diols, 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 exhibited higher tensile strengths at specific  $(\text{HEP-})_2\text{Mg}$  contents in diols, probably due to lower soft block content and to higher crosslinking density of the hard block. Similar tendencies are observed also for the PEG1- and PEG2-based cured rubbers at higher concentrations of HPA and BADG relative to that of diols (Fig. 2).

On the other hand, different trends are observed for the PEG3-based rubbers (Fig. 3). In this case, tensile strength has a minimum. Especially, the PEG3-

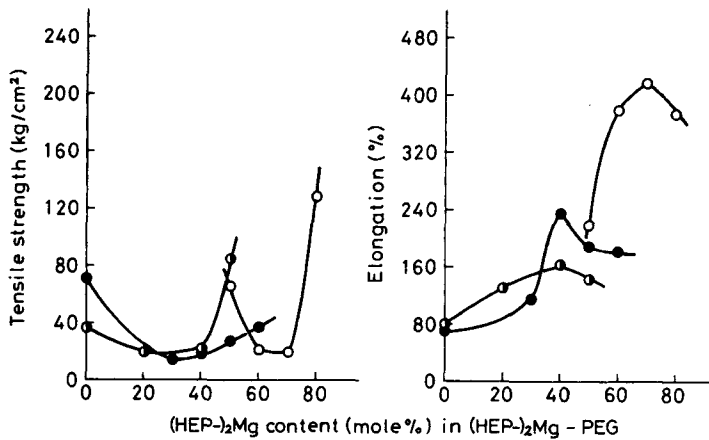


Fig. 3. Effect of (HEP-)<sub>2</sub>Mg content in (HEP-)<sub>2</sub>Mg-PEG3 on tensile strength and elongation for cured rubbers of (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG at diols:HPA:BADG mole ratios of (○) 10:40:20; (●) 10:60:30; (●) 10:80:40.

based rubbers at a diols:HPA:BADG mole ratio of 10:40:20 showed a curve having a distinct minimum. This is considered due to crystallization of the PEG block at lower (HEP-)<sub>2</sub>Mg contents in the diols. The PEG3-based rubbers with lower (HEP-)<sub>2</sub>Mg contents and those without (HEP-)<sub>2</sub>Mg showed an opaque or semitransparent appearance, suggesting the presence of crystallinity. This correlates well with the DTA curves in Figure 4. That is, the DTA curves of the PEG3-based rubbers at the ratio of 10:40:20 show an endothermic peak at about 40°C indicative of crystalline melting of the PEG soft block. The melting peak in pure PEG3 is known to occur at 51–55°C. Thus, it is shifted to lower temperature, the sharpness of the endothermic peak decreases with increasing the (HEP-)<sub>2</sub>Mg content in diols, and, at the highest (HEP-)<sub>2</sub>Mg content examined,

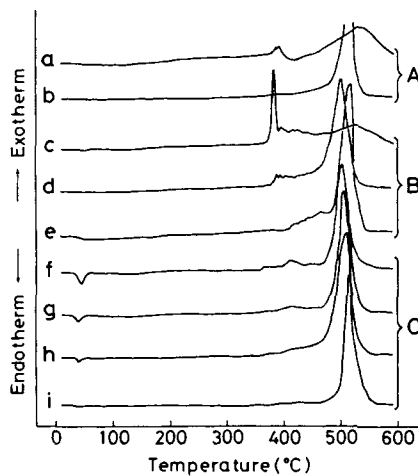


Fig. 4. DTA curves for cured rubbers. (A) (HEP-)<sub>2</sub>Mg-PEG1-HPA-BADG at mole ratios of: (a) 0:10:60:30; (b) 3:7:60:30. (B) (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG at mole ratios of: (c) 0:10:60:30; (d) 3:7:60:30; (e) 5:5:60:30. (C) (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG at mole ratios of (f) 5:5:40:20; (g) 6:4:40:20; (h) 7:3:40:20; (i) 8:2:40:20.

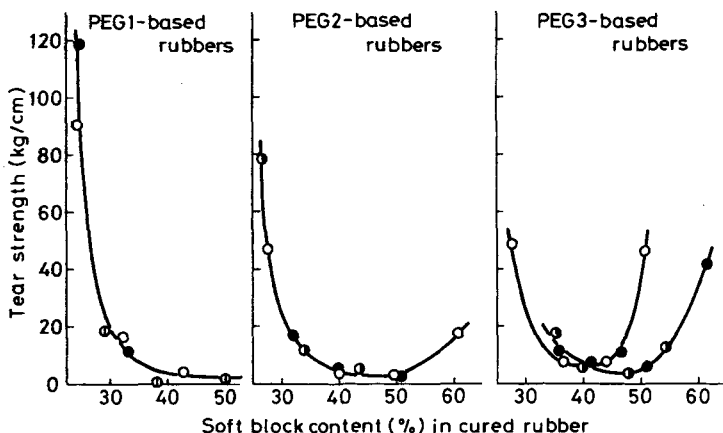


Fig. 5. Effect of soft block content on tear strength for cured rubbers of  $(\text{HEP})_2\text{Mg}$ -PEG-HPA-BADG at diols:HPA:BADG mole ratios of (○) 10:30:15; (◻) 10:40:20; (●) 10:60:30; (◼) 10:80:40.

no endothermic peak is observed. The crystalline region would act as a crosslink and restrict the macromolecular mobility, leading to higher tensile strength and hardness, and lower elongation. Above the  $(\text{HEP})_2\text{Mg}$  content where the minimum tensile strength is observed, tensile strength increases markedly with increase in the  $(\text{HEP})_2\text{Mg}$  content, due to the decrease in the soft block content and also to the increase in the ionic crosslinking and overall crosslinking density.

Though not shown here, also other series of PEG3-based rubbers (those at the ratios of 10:60:30 and of 10:80:40), and the PEG2-based ones at the ratio of 10:40:20 showed an endothermic melting peak at zero or lower  $(\text{HEP})_2\text{Mg}$  contents in diols. However, the sharpness of the peaks was less distinct, especially for the latter PEG2-based ones. Meanwhile, as shown in Figure 4, the PEG1- and PEG2-based rubbers at the ratio of 10:60:30 show no endothermic peak, indicating the absence of crystallinity. It is considered that the occurrence of crystallization becomes easy as the soft block becomes longer and the soft block content becomes higher, or as the crosslinking density of the hard block becomes lower.

As shown in Table I, the cured rubbers at  $(\text{HEP})_2\text{Mg}$ :PEG2:HPA:BADG mole ratios of 5:5:40:20 and of 3:7:60:30 have about the same soft block content of about 40%; however, the tensile strengths were lower ( $7 \text{ kg/cm}^2$ ) for the former with the lower HPA and BADG contents, and higher ( $24 \text{ kg/cm}^2$ ) for the latter with the higher HPA and BADG contents, hence with the higher crosslinking density of the hard block, though the former contains higher Mg content. Thus, 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; that is, tensile strength depends upon the crosslinking density of the hard block to a larger extent than upon the metal content, a trend observed also for the PPG-based cured rubbers.<sup>1</sup> Naturally, higher crosslinking density of the hard block leads to higher overall crosslinking density of the rubber. The same tendency is observed also on comparing the PEG2-based rubbers at the ratios of 7:3:30:15 and of 5:5:60:30 and the PEG3-based ones at the ratios of 6:4:60:30 and of 5:5:80:40.



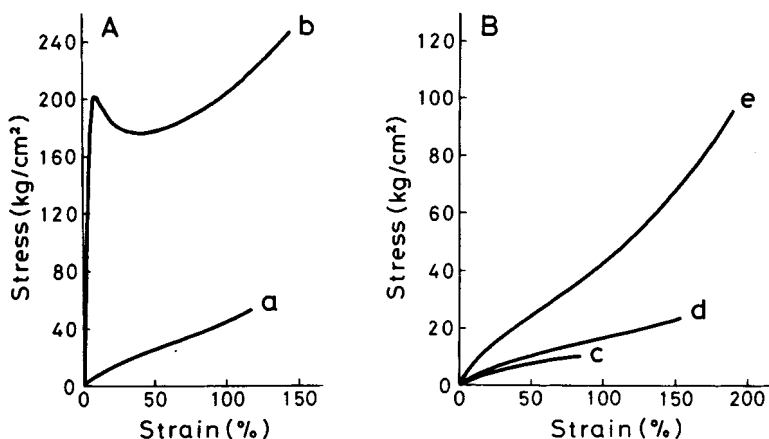


Fig. 6. Stress-strain curves for PEG1- and PEG2-series-cured rubbers. (A) (HEP-)<sub>2</sub>Mg-PEG1-HPA-BADG at mole ratios of: (a) 0:10:60:30; (PEG1-HPA-BADG at 10:60:30); (b) 3:7:60:30. (B) (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG at mole ratios of: (c) 0:10:60:30 (PEG2-HPA-BADG at 10:60:30); (d) 3:7:60:30; (e) 5:5:60:30.

However, in the case of the Ca-containing cured rubbers, a reverse trend is observed because of their heterogeneity. For example, the rubbers at (HEP-)<sub>2</sub>Ca:PEG1:HPA:BADG ratios of 5:5:40:20 and of 3:7:60:30 have about the same soft block content, but the tensile strengths were higher for the former and lower for the latter, due to the higher degree of inhomogeneity of the latter.

On the other hand, the rubbers at (HEP-)<sub>2</sub>Mg:PEG3:HPA:BADG ratios of 5:5:40:20 and of 3:7:60:30 have about the same soft block content (about 51%); however, the tensile strengths were higher (66 kg/cm<sup>2</sup>) for the former and lower (15 kg/cm<sup>2</sup>) for the latter, due to the much higher crystallinity of the former. Thus, at about the same soft block contents, the high degree of crystallinity of the soft block has greater effect on tensile strength than crosslinking density of the hard block has. Very recently, a paper<sup>9</sup> on cured polyacrylourethane films based on poly(ethylene adipate) and toluene diisocyanate has appeared, reporting that the solid state polymerized films showed a low elongation, a high modulus, and a high breaking strength due to their crystallinity.

Similar tendencies are observed also for Shore A hardness. Meanwhile, elongation at break generally increases with increase in the (HEP-)<sub>2</sub>Mg content in the diols, and, for many of the cured rubbers, elongation has a peak. The (HEP-)<sub>2</sub>Mg-PEG1-HPA-BADG (3:7:30:15) rubber showed a highest elongation of above 1500%.

Figure 5 shows the effect of soft block content on tear strength for the cured rubbers. The previous study<sup>1</sup> indicated that, for the PPG-based cured rubbers, the data of tear strength lie upon a curve which decreases markedly with increase in the soft block content. The same tendency is observed also for the PEG-1 based rubbers having no crystallinity. Meanwhile, for the PEG2- and PEG3-based rubbers, tear strength decreases markedly with increase in the soft block content, reaching a minimum, and then increases again, especially markedly for the latter cured rubbers, again indicating the effect of crystallinity at higher soft block contents. In the case of the PEG3-based rubbers, two curves, each having a distinct minimum, were obtained; one shown by the data for the cured rubbers

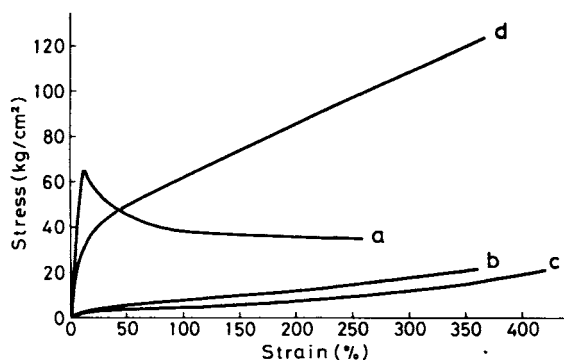


Fig. 7. Stress-strain curves for cured rubbers of  $(\text{HEP-})_2\text{Mg-PEG3-HPA-BADG}$  at mole ratios of: (a) 5:5:40:20; (b) 6:4:40:20; (c) 7:3:40:20; (d) 8:2:40:20.

at a diols:HPA:BADG mole ratio of 10:40:20, and the other shown by the data for those at the ratios of 10:60:30 and of 10:80:40. At about 51% soft block content, the rubber at the ratio of 10:40:20 shows much higher tear strength than the other one, due to much higher crystallinity of the former rubber. It is considered that the crystalline region is able to share load and resist crack propagation.

Figures 6 and 7 show stress-strain curves of the representative Mg-containing cured rubbers. Also from these, it is apparent that tensile modulus, tensile strength, and elongation at break depend strongly on the composition of the rubber. The  $(\text{HEP-})_2\text{Mg-PEG1-HPA-BADG}$  (3:7:60:30) rubber with low soft block content and high overall crosslinking density showed a yield point in the curve. After the yield point, a sharp decrease in the tensile stress was observed, and, finally, the stress increased to the breaking point. The  $(\text{HEP-})_2\text{Mg-PEG2-HPA-BADG}$  (5:5:60:30) rubber showed the stress-strain behavior close to that of usual unfilled vulcanizates. With increase in the chain length of the soft block, elongation at break increased. In the PEG3-based rubbers, that at a mole ratio of 5:5:40:20 exhibited a yield point, though the overall crosslinking density was very low (curve a in Figure 7). This is considered to be due to the

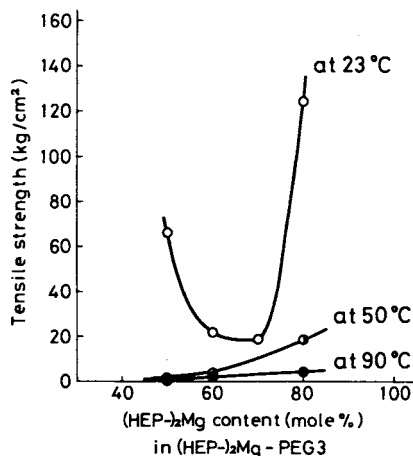


Fig. 8. Effect of temperature on relationship between  $(\text{HEP-})_2\text{Mg}$  content in  $(\text{HEP-})_2\text{Mg-PEG3}$  and tensile strength for cured rubbers of  $(\text{HEP-})_2\text{Mg-PEG3-HPA-BADG}$  at diols:HPA:BADG mole ratio of 10:40:20.

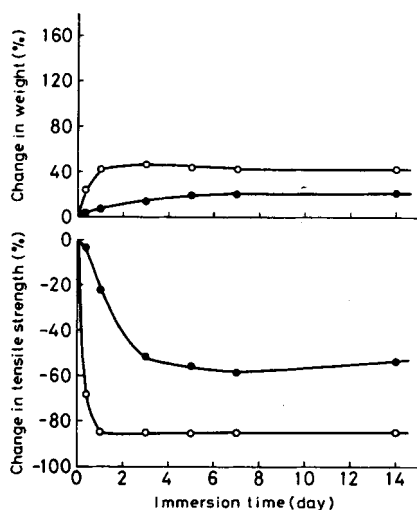


Fig. 9. Effects of water on weight change and tensile strength of cured rubbers of (HEP-)<sub>2</sub>Mg-PEG1-HPA-BADG at mole ratios of: (O) 5:5:40:20; (●) 3:7:60:30.

high degree of crystallinity of the soft block. The high crystallinity would have contributed to the high initial modulus. After the yield point, the stress decreased sharply, and high elongation followed; finally, the specimen broke without stress increase because of the very low overall crosslinking density. With decrease in the crystallinity, the modulus decreased, though the hard block content increased (curves b and c in Fig. 7). But, the rubber at the ratio of 8:2:40:20, which had no crystallinity, showed again high tensile modulus, due to very high overall crosslinking density (curve d in Fig. 7). It has generally been known that polymer materials with a very high degree of crystallinity often show stress-strain curves characteristic of brittle materials.<sup>10-12</sup>

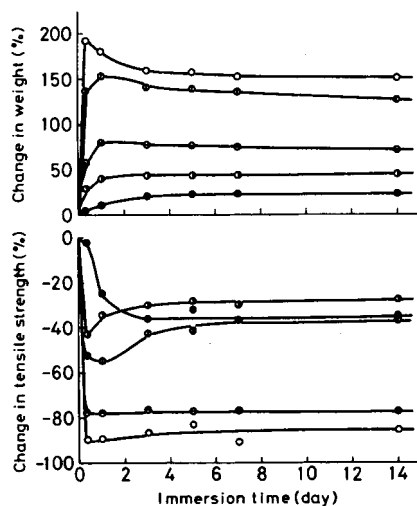


Fig. 10. Effects of water on weight change and tensile strength of cured rubbers of (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG at mole ratios of: (O) 0:10:40:20; (⊕) 5:5:40:20; (⊖) 7:3:40:20; (⊙) 5:5:60:30; (●) 5:5:80:40.

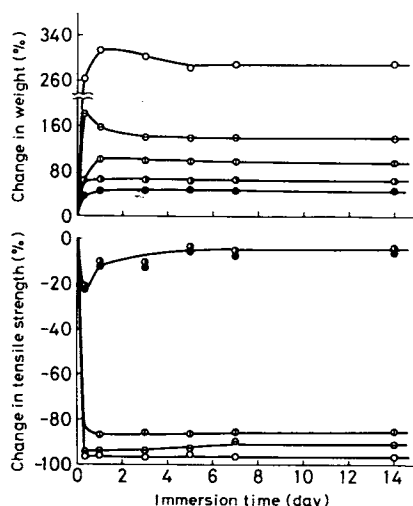


Fig. 11. Effects of water on weight change and tensile strength of cured rubbers of  $(\text{HEP-})_2\text{Mg-PEG3-HPA-BADG}$  at mole ratios of: (O) 5:5:40:20; ( $\oplus$ ) 8:2:40:20; ( $\ominus$ ) 0:10:60:30; ( $\odot$ ) 6:4:60:30; ( $\bullet$ ) 5:5:80:40.

Figure 8 shows the effect of temperature on the relationship between  $(\text{HEP-})_2\text{Mg}$  content in diols and tensile strength for the PEG3-based rubbers at a diols:HPA:BADG mole ratio of 10:40:20. Tensile strength decreases markedly with increase in temperature. The marked decrease above  $50^\circ\text{C}$  at the low  $(\text{HEP-})_2\text{Mg}$  content would reflect the disappearance of the crystallinity of the soft block.

### Water Resistance of Cured Rubbers

Figures 9–11 show the effect of water on weight change and tensile strength for representative cured rubbers. They showed much higher water absorption than the previously reported PPG-based cured rubbers.<sup>1</sup> This is attributed to the much higher hydrophilicity of the PEG soft block. Generally, increasing the HPA and BADG concentrations results in a decrease in water absorption, due to the increase in the hard block content and also its crosslinking density. At about the same soft block contents, the rubbers with higher crosslinking density of hard block showed lower water absorption. This is clearly demonstrated in the PEG1-based rubbers in Figure 9. Similarly, with increase in the  $(\text{HEP-})_2\text{Mg}$  content in the diols at the same diols:HPA:BADG mole ratio, water absorption decreases in spite of the increase in the ionic links, due to the decrease in the soft block content. This is contrary to the tendency for the PPG-based rubbers.<sup>1</sup> Thus, in the PEG-based rubbers, the hydrophilicity of the soft block has greater effect on water absorption than the ionic links.

The  $(\text{HEP-})_2\text{Mg-PEG3-HPA-BADG}$  (5:5:40:20) rubber exhibited the highest water absorption of about 300%. With the water absorption, this rubber lost the crystallinity. However, the crystallinity could reappear by removing water from the rubber.

Generally, the samples of the rubbers with lower soft block content and with higher overall crosslinking density became white with the water absorption.

Meanwhile, the rubbers of (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG (0:10:40:20) and of (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG (0:10:60:30) showed a distinct maximum in water absorption with time. This might probably be due mainly to removal of some hydrophilic part rich in PEG block with immersion time.

Tensile strength generally decreased with the water absorption. In the rubbers at a diols:HPA:BADG mole ratio of 10:40:20, the decrease was remarkable. However, it is noteworthy that the rubbers of (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG (6:4:60:30 or 5:5:80:40) exhibited lowest decrease in tensile strength of about 5% after 14 days water immersion. In addition, these two rubbers and that of (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG (5:5:60:30) showed a distinct minimum in tensile strength with time. The strength increase with time after the minimum might presumably be due to orientation of the hard block phase by its extension, caused by water absorption of hydrophilic soft (PEG) blocks dispersed in the hard block phase.

### Resistance of Cured Rubbers to Chemical Attack

Table II shows the resistance of representative cured rubbers to chemical attack. They showed much higher weight gain in benzene and dioxane than in *n*-hexane. At the same (HEP-)<sub>2</sub>Mg:PEG:HPA:BADG mole ratios, the rubbers based on the longer PEG showed higher weight gain. This indicates that the overall crosslinking density decreases with increase in the chain length of the PEG soft block. Except for some, they showed very small benzene- and dioxane-soluble parts, indicating that most of the polymer molecules have taken part in the crosslinking.

The (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG (5:5:40:20) rubber disintegrated in dioxane and exhibited a soluble part of 35%, showing that the overall crosslinking density is very low. Also from this, it is apparent that the above observed fact that this rubber exhibited high tensile strength, Shore A hardness, and high tear strength is due to the high degree of crystallinity of the soft block. The same may be said of the PEG3-based rubber at a mole ratio of 0:10:60:30.

### Stress-Relaxation

Figure 12 shows stress-relaxation behavior of the representative cured rubbers. In case of the PEG1- and PEG2-based rubbers, at the same diols:HPA:BADG mole ratios, increasing the (HEP-)<sub>2</sub>Mg content generally results in an increase in the stress-relaxation, probably due to the increase in the hard block content, and ionic crosslinking which has a tendency to reorganize. Such a trend was observed also in the previous study.<sup>1</sup> However, it is noteworthy that the above cured rubbers with the higher soft block contents broke under stress because of the initial low strengths. Moreover, it has been reported<sup>8,13</sup> that, for the cured rubbers prepared from partially neutralized carboxyl-terminated liquid rubbers, bisepoxide, and anhydride, the ratio of soft block to hard block contents has a higher effect on stress-relaxation than the metal carboxylate groups.

For the PEG3-based rubbers, stress-relaxation increases with increase in the (HEP-)<sub>2</sub>Mg content in the diols, except for the (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG (5:5:40:20) rubber with the highest crystallinity. On comparing the rubbers at mole ratios of 5:5:40:20 and of 6:4:40:20, it is of interest to note that the former

TABLE II  
Resistance of Cured Rubbers to Chemical Attack

Components	Mole ratio of components	Benzene		Dioxane		<i>n</i> -Hexane	
		Change in wt (%)	Soluble part (%)	Change in wt (%)	Soluble part (%)	Change in wt (%)	Soluble part (%)
(HEP) <sub>2</sub> Mg-PEG1-HPA-BADG	0:10:40:20	99	9.0	215	9.5	0.5	1.8
	5:5:40:20	71	2.8	219	5.2	0.2	1.4
	0:10:60:30	78	3.9	140	4.0	0.1	1.7
	3:7:60:30	67	1.5	128	2.4	0.3	1.4
	0:10:40:20	146	25.8	314	38.0	0.1	3.8
(HEP) <sub>2</sub> Mg-PEG2-HPA-BADG	5:5:40:20	108	8.0	312	11.8	0.7	2.9
	7:3:40:20	79	4.5	273	7.6	0.3	2.0
	0:10:60:30	106	14.3	208	14.6	0.3	5.0
	5:5:60:30	78	3.3	142	4.0	0.2	2.6
	0:10:80:40	89	8.1	151	8.7	0.3	4.0
(HEP) <sub>2</sub> Mg-PEG3-HPA-BADG	5:5:80:40	66	2.2	113	3.3	0.3	1.6
	5:5:40:20	138	25.4	—	—	0.0	3.4
	8:2:40:20	82	4.9	383	9.9	0.3	1.5
	0:10:60:30	117	34.4	767	39.0	0.0	5.6
	5:5:60:30	98	8.5	226	9.4	0.1	5.2
0:10:80:40	6:4:60:30	88	5.6	194	7.5	0.5	3.6
	0:10:80:40	110	18.6	—	—	0.0	5.0
	5:5:80:40	83	3.7	148	5.2	0.6	3.1

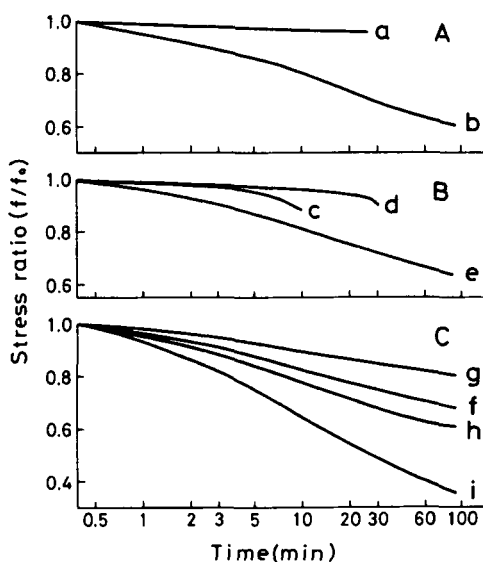
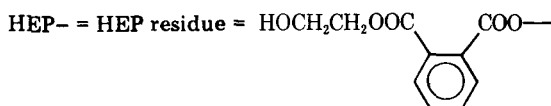
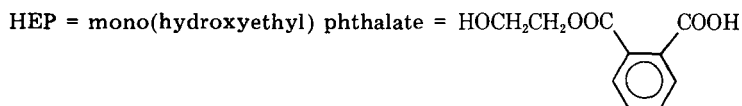


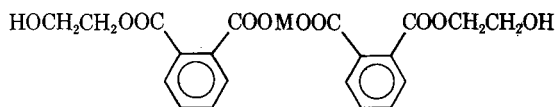
Fig. 12. Stress-relaxation of cured rubbers. (A) (HEP-)<sub>2</sub>Mg-PEG1-HPA-BADG at mole ratios of: (a) 0:10:60:30; (b) 3:7:60:30. (B) (HEP-)<sub>2</sub>Mg-PEG2-HPA-BADG at mole ratios of: (c) 0:10:80:40; (d) 3:7:80:40; (e) 5:5:80:40. (C) (HEP-)<sub>2</sub>Mg-PEG3-HPA-BADG at mole ratios of: (f) 5:5:40:20; (g) 6:4:40:20; (h) 7:3:40:20; (i) 8:2:40:20.

with the higher soft block content exhibited higher stress-relaxation than the latter with the lower soft block content, though the metal content was lower in the former. This is presumably due to the much higher crystallinity of the soft block in the former. That is, the higher stress-relaxation observed above would result from an arrangement of the crystalline part<sup>14</sup> of the soft block, in addition to the plastic deformation of the hard block. Thus, the crystallinity of the soft block seems to have considerable influence on the stress-relaxation of the cured rubbers.

#### APPENDIX: IDENTIFICATION



(HEP-)<sub>2</sub>M = divalent metal salts of HEP =



where M = divalent metal (Mg or Ca).

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