

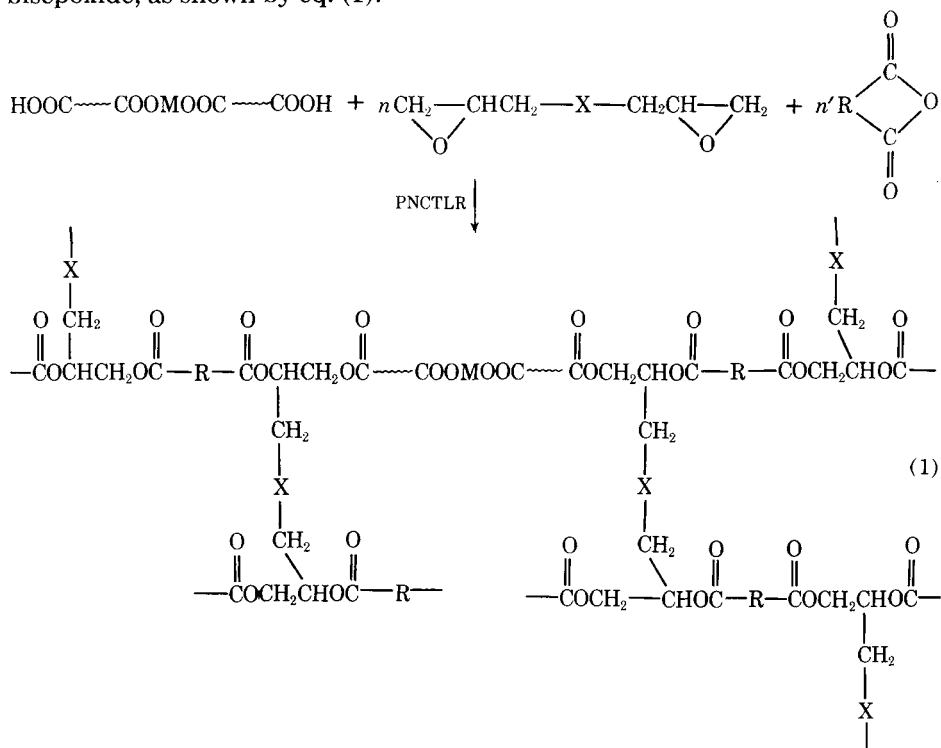
# Adhesive Properties of Systems of Partially Neutralized Carboxyl-Terminated Liquid Rubber-Anhydride-Bisepoxide

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## Synopsis

Systems of partially neutralized carboxyl-terminated liquid rubber (PNCTLR)-anhydride-bisepoxide were evaluated for adhesive properties. The PNCTLRs were prepared by the partial neutralization with MgO and CaO from a polymer of butadiene (BD) (Hycar CTB 2000X162) and copolymers of BD-acrylonitrile (Hycar CTBN 1300X8 and CTBNX 1300X9). As the bisepoxide, bisphenol A diglycidyl ether was used, and hexahydrophthalic anhydride was the anhydride used. The adhesive properties of the metal-containing systems were superior to those of the reference systems not containing metal, owing to the polarity effect of the metal carboxylate groups. Further, the CTBN- and CTBNX-series systems showed higher tensile shear and peel strengths than the CTB-series systems, owing to the enhanced polarity effect of the nitrile groups.

Partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) are useful starting materials for the preparations of ionic cured rubbers into which metal is firmly incorporated. In previous reports<sup>1,2</sup> it has been shown that ionic cured rubbers were prepared by crosslinking (curing) of PNCTLR with anhydride and bisepoxide, as shown by eq. (1):



where M = Mg or Ca. The carboxyl-terminated liquid rubbers used to prepare PNCTLR were a polymer of butadiene (BD) (Hycar CTB 2000X162 with functionality of 2.01) and copolymers of BD-acrylonitrile (Hycar CTBN 1300X8 (functionality of 1.8) and CTBNX 1300X9 (functionality of 2.4)). As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used, and hexahydrophthalic anhydride (HPA) was the anhydride used.

The cured rubbers obtained consist of the following two main blocks: one is a soft block based on PNCTLR, and the other is a hard block from anhydride and bisepoxide. The metal-containing cured rubbers showed better physical properties than the reference ones (those not containing metal). Thus, the effect of introducing metal on the physical properties became evident.

Previously, systems of divalent metal salts of mono(hydroxyethyl) phthalate-anhydride-bisepoxide were evaluated for adhesive properties. It was found that the adhesive properties of the metal-containing systems were generally superior to those of the systems not containing metal, owing to the polarity effect of metal carboxylate groups.<sup>3</sup> In the present study, we investigated the adhesive properties of the PNCTLR-anhydride-bisepoxide systems.

## EXPERIMENTAL

### Materials

Hycar CTB 2000X162 (acid value 0.3900 equiv/kg, cis-1,4 22.1%, trans-1,4 53.4%, and vinyl 24.5%), CTBN 1300X8 (AN 18–19%, acid value 0.5215 equiv/kg, cis-1,4 23.8%, trans-1,4 64.2%, and vinyl 12.0%), and CTBNX 1300X9 (AN 18–19%, acid value 0.6827 equiv/kg, cis-1,4 16.3%, trans-1,4 68.7%, and vinyl 15.0%) were B.F. Goodrich Chemical Co. products and used as received. CTBNX 1300X9 contains pendent carboxyl groups in addition to the terminal ones. The PNCTLR from them were prepared by the same method as in the previous reports.<sup>1,2</sup> While complete neutralization of the terminal carboxyl groups is difficult,<sup>4</sup> partial neutralization is comparatively easy. The degree of neutralization of the PNCTLR was 50%. Also in this study, a coded system for the PNCTLR will be used. For example, CTB (0.5 Mg) indicates that CTB 2000X162 was neutralized with MgO to the degree of neutralization = 50%. The acid values were 0.1995 equiv/kg for CTB (0.5 Mg), 0.2644 equiv/kg for CTBN (0.5 Mg), 0.3499 equiv/kg for CTBNX (0.5 Mg), 0.1926 equiv/kg for CTB (0.5 Ca), 0.2638 equiv/kg for CTBN (0.5 Ca), and 0.3456 equiv/kg for CTBNX (0.5 Ca).

HPA was of extrapure grade and used as received. As the BADG, Epomik R 139 (Mitsui Petrochemical Epoxy Co.) was used; the epoxide value was 5.478 equiv/kg (calc = 5.875 equiv/kg).

### Preparation of Adhesives (Curable Mixtures)

A mixture of PNCTLR, HPA, and BADG at a desired equivalent ratio was heated at 160°C with stirring until it became homogeneous. The curable mixture thus obtained was used as adhesive. Similarly, reference curable mixtures were prepared from original liquid rubber, HPA, and BADG. In this case, *N,N*-dimethylbenzylamine (DMBA) was used as a catalyst at an amount of 0.1 wt % based on BADG.

### Physical Testing

The adhesives were tested by the same methods as in the previous study<sup>3</sup> at 23°C, unless otherwise specified, using a Shimadzu autograph IS-5000. Tensile shear strength was determined on steel (Sumitomo Kinzoku Co. SS 41, 1.6 mm thick) with reference to ASTM-D 1002-64 (crosshead speed 2.5 mm/min). Peel strength was determined on aluminium foil (Tokai Kinzoku Co. AIN 30-H, 50  $\mu$ m thick) according to ASTM-D 1876-61 T (crosshead speed 260 mm/min).

## RESULTS AND DISCUSSION

The PNCTLR–anhydride–bisepoxide systems, when cured, give metal-containing cured rubbers having ionic links. In these systems, the following main reactions<sup>5</sup> are believed to occur: reaction of the carboxyl group with the epoxide group to form OH group; reaction of the OH group with acid anhydride group to form a terminal carboxyl group; reaction of an acid anhydride group with an epoxide group to form ester linkage. Moreover, there might possibly be a tendency for the metal carboxylate groups in PNCTLR to reequilibrate with any of the free carboxylic acids of the hexahydrophthalic group. It is advantageous that the metal carboxylate groups in the system catalyze this type of polyesterification.<sup>1,2,5</sup>

On the other hand, the original liquid rubber–anhydride–bisepoxide systems give cured rubbers whose structures are about the same as that of the former cured rubbers, except for the fact that the rubbers have no ionic links. Therefore, for comparison, the systems containing the original liquid rubber were also used as the reference systems.

The concentration of the PNCTLR part might be regarded as that of the soft blocks; similarly, the concentration of the liquid rubber part in the reference cured rubber might be regarded as that of the soft blocks. Hence, the PNCTLR–HPA–BADG systems at an equivalent ratio of 1:5*n*:5*n* + 1 contain about the same concentration of soft blocks as the reference ones of the original liquid rubber–HPA–BADG at a ratio of 1:2.5*n*:2.5*n* + 1 contain. For example, the CTBN (0.5 Ca)–HPA–BADG system at a ratio of 1:20:21 (*n* = 4) contains 36% soft block, and the CTBN 1300X8–HPA–BADG system at a ratio of 1:10:11 contains 35% soft block.

First, the effect of curing time on the adhesive properties was investigated on representative systems. The results are shown in Figures 1 and 2. As shown in Figure 1, tensile shear strength increased rapidly with curing time at 160°C and reached a constant value of 157 kg/cm<sup>2</sup> after 180 min and did not increase even if the curing time increased for the CTBN (0.5 Mg)–HPA–BADG (1:20:21) system. For the reference system CTBN 1300X8–HPA–BADG (1:10:11), tensile shear strength reached a constant value after 120 min at 160°C; however, the value is much smaller than that of the metal-containing system. For both systems, the type of failure was cohesive failure in the initial stages and, after about 120 min, a mixture of cohesive and interfacial failures (mixed failure).

As shown in Figure 2, the initial rapid rise of peel strength started earlier in the reference system than in the metal-containing system. The former system however, showed a peak of peel strength at about 60 min at 160°C; and even after about 120 min, the strength showed a tendency to decrease gradually. At the

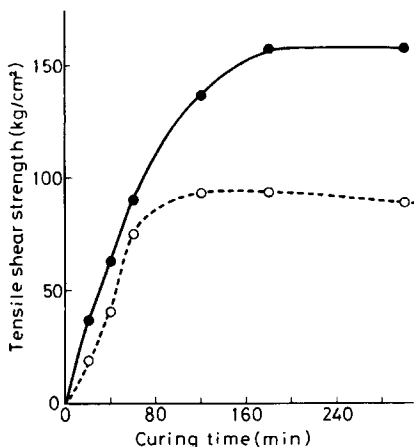


Fig. 1. Tensile shear strength (on steel) vs. curing time at 160°C for systems of (●) CTBN (0.5 Mg)-HPA-BADG (1:20:21) and (○) CTBN 1300X8-HPA-BADG (1:10:11).

time when the peak value was obtained, the type of failure was a mixed type; and after the peak, an interfacial failure. Meanwhile, for the latter system, peel strength reached a constant value of 2.4 kg/25 mm after 180 min at 160°C. The infrared spectrum of the system after 60 min showed the existence of unreacted anhydride and epoxy groups; however, these groups decreased with further curing time. The type of failure at 90 min was mixed failure; and after about 120 min, interfacial failure.

Next, adhesive properties were tested on various combinations of components. For obtaining ultimate adhesive strengths, sufficient curing conditions of 160°C for 3–5 h were applied.

Figure 3 shows tensile shear strengths of the PNCTLR-HPA-BADG systems at equivalent ratios of 1:20:21 and 1:30:31, together with those of their corresponding reference systems. The CTB-series systems showed generally very low tensile shear strength; the type of failure was that of cohesive failure. But

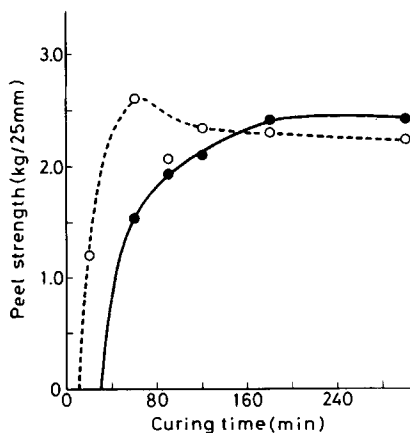


Fig. 2. Peel strength (on aluminium foil) vs. curing time at 160°C for systems of (●) CTBN (0.5 Mg)-HPA-BADG (1:20:21) and (○) CTBN 1300X8-HPA-BADG (1:10:11).

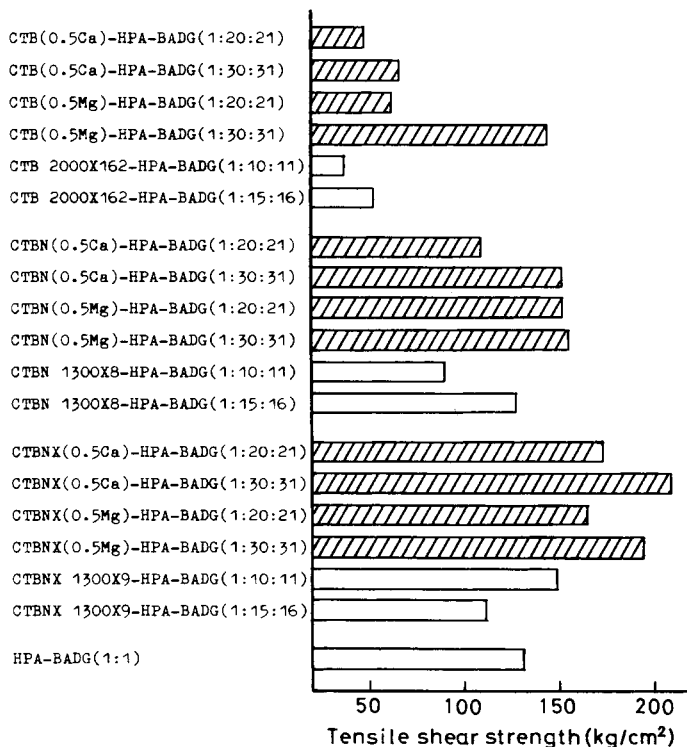


Fig. 3. Tensile shear strength (on steel) of (▨) metal-containing systems and (□) reference systems.

the CTB (0.5 Mg)-HPA-BADG (1:30:31) system showed mixed failure and the tensile shear strength was considerably higher. On the other hand, the CTBN- and CTBNX-series systems showed much higher tensile shear strength than the CTB-series systems, and the type of failure was mixed failure. This correlates well with the fact<sup>1,2</sup> that the former cured systems gave higher tensile strength than the latter cured systems, owing to the polarity effect of the nitrile groups. Further, the strength is generally higher in the metal-containing systems than in the reference systems. This tendency is remarkable, especially in the CTBNX series; for example, the CTBNX (0.5 Ca)-HPA-BADG (1:30:31) system gave a value of 209 kg/cm<sup>2</sup>. Thus, the effect of introducing metal (ionic links) is apparent. This may be due to further increase in polarity, resulting in a cured resin which is more firmly bound to the surface to be bonded.

HPA is a typical anhydride-type curing agent, hence the HPA-BADG (1:1) system was also cured with DMBA as a catalyst for testing. It was found that many of the metal-containing systems gave higher tensile shear strength than the HPA-BADG (1:1) system.

As shown in Figure 4, also for peel strength the CTBN- and CTBNX-series systems showed considerably higher values than the CTB-series systems, and, further, peel strength is generally higher in the metal-containing systems. The CTB-series systems showed cohesive failure, except for the CTB (0.5 Mg)-HPA-BADG (1:20:21 or 1:30:31) systems, which showed interfacial failure. Moreover, the type of failure for the CTBN- and CTBNX-series systems was

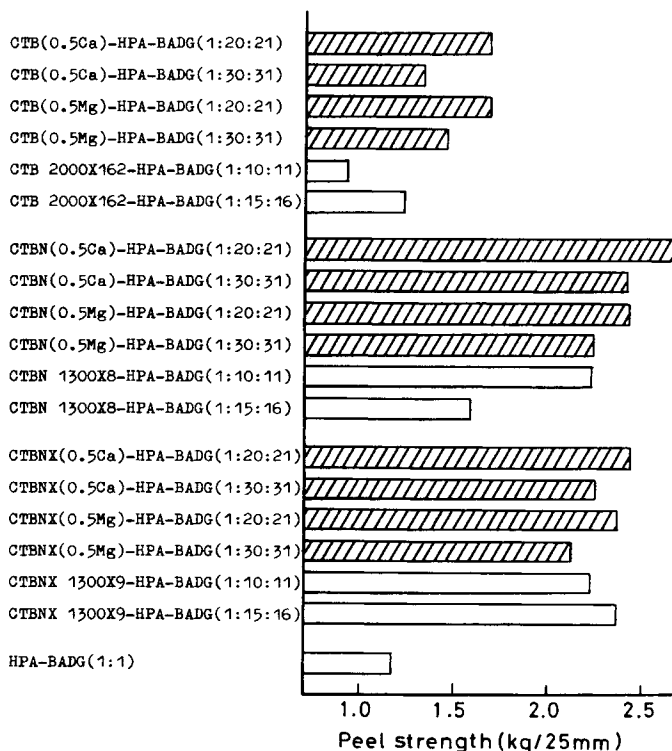


Fig. 4. Peel strength (on aluminium foil) of (▨) metal-containing systems and (□) reference systems.

interfacial failure. The effect on peel strength of introducing metal is remarkable, especially for the CTBN-series systems; for example, the CTBN (0.5 Ca)-HPA-BADG (1:20:21) system gave a value of 2.7 kg/25 mm. It is noteworthy that the peel strength of the HPA-BADG (1:1) system which showed interfacial failure is very low, almost corresponding to that of the reference system CTB 2000X162-HPA-BADG (1:15:16), which showed cohesive failure.

Next, adhesive properties were tested over a wide range of soft block contents on representative systems, varying the equivalent ratio of the PNCTLR-HPA-BADG systems.

Figures 5 through 7 show tensile shear and peel strengths of the representative PNCTLR-HPA-BADG systems at equivalent ratios of  $1:5n:5n + 1$ , together with those of the reference systems of original liquid rubber-HPA-BADG at ratios of  $1:2.5n:2.5n + 1$ , where  $n = 0, 1, 2, 4, \dots, 10$ . As  $n$  increases, soft-block content decreases and crosslinking density increases. Meanwhile, the systems at  $n = 0$  consist of PNCTLR-BADG (1:1), which contains the highest soft block content studied. As shown in Figure 5, in the CTB series, the Mg-containing systems showed cohesive failure above the soft block content of about 43% in the tensile shear strength test; while in the reference systems, cohesive failure was observed over the wide range of soft block content. The Mg-containing systems with a soft block content of 23–33% showed mixed failure, and the tensile shear strengths were much higher than those of the reference ones. Thus, the effect of introducing metal appears marked in this case. The difference in strength between

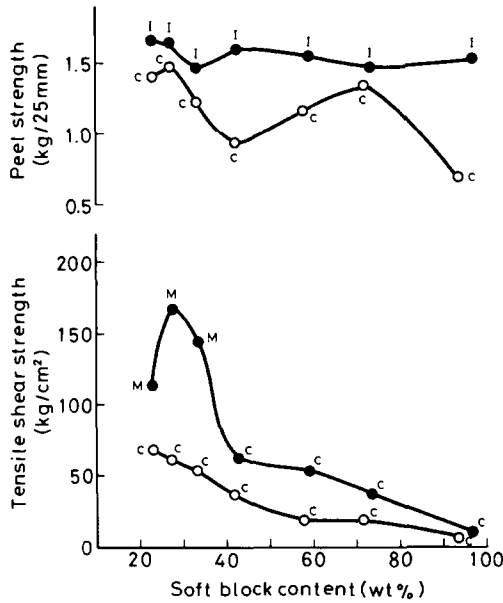


Fig. 5. Effect of soft block content on tensile shear and peel strengths for (●) CTB (0.5 Mg)-HPA-BADG systems and (○) reference systems (CTB 2000X162-HPA-BADG). I = Interfacial failure; C = cohesive failure; M = mixed failure.

the Mg-containing systems and the reference ones above the soft block content of about 43% seems to reflect a difference in cohesive force between the former and the latter cured systems. Meanwhile, in the peel strength test, all the Mg-containing systems showed interfacial failure, while all the reference systems

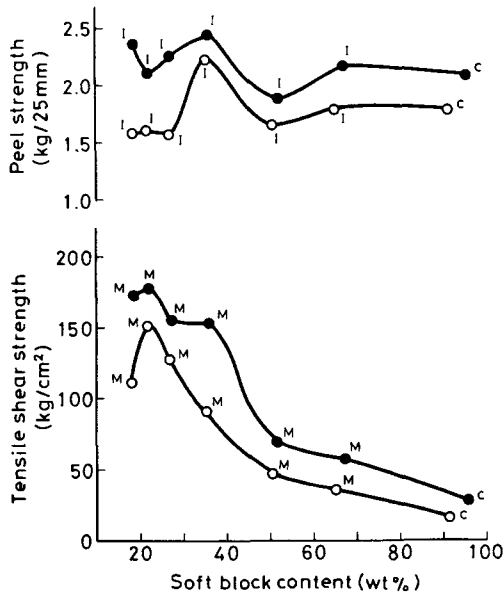


Fig. 6. Effect of soft block content on tensile shear and peel strengths for (●) CTBN (0.5 Mg)-HPA-BADG systems and (○) reference systems (CTBN 1300X8-HPA-BADG). I = Interfacial failure; C = cohesive failure; M = mixed failure.

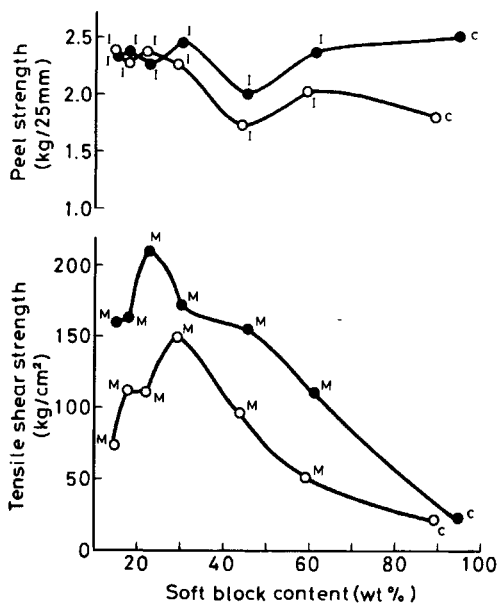


Fig. 7. Effect of soft block content on tensile shear and peel strengths for (●) CTBNX (0.5 Ca)-HPA-BADG systems and (○) reference systems (CTBNX 1300X9-HPA-BADG). I = Interfacial failure; C = cohesive failure; M = mixed failure.

displayed cohesive failure, and the former gave consistently higher peel strength than the latter.

It is generally known that polar groups in adhesives have effects on adhesive strengths. For example, deBruyne<sup>6</sup> found that adhesive (tensile shear) strength of phthalic anhydride-cured epoxide resins (with varying OH concentrations) on  $\text{Al}_2\text{O}_3$  increases with increase in the OH concentration. However, in this case it is pointed out that the tendency for internal stress to decrease with increase in the OH concentration also cannot be disregarded. Similarly, McLaren et al.<sup>7</sup> measured adhesive (peel) strength of vinyl acetate-vinyl chloride-maleic anhydride copolymers (with varying COOH concentration) on cellophane and found that the strength increases with increase in the COOH concentration. In addition, glycidyl esters are known to offer greater adhesive properties than glycidyl ethers due to the higher polarity of the ester groups.<sup>8</sup> Meanwhile, it has been reported<sup>9</sup> that peel strength of a series of methacrylic copolymers with varying chemical compositions and viscoelastic properties on cellophane (or aluminium) depends on the viscoelastic properties of the adhesive polymers to a greater extent than on the chemical structures of the polymers.

As shown in Figures 6 and 7, in the CTBN- and CTBNX-series, all systems showed mixed failure in the tensile shear strength test and interfacial failure in the peel strength test, except for the PNCTLR-BADG (1:1) systems. Tensile shear strength showed a peak at a soft block content of 20–30%. With further increase in the soft block content, the strength decreases, though the concentration of ionic links in the cured system increases; at highest soft block content, cohesive failure was observed. This is probably due to a decrease in cohesive force of the cured system with decrease in the crosslinking density and also to a decrease in adhesive force at the interface with decrease in the concentration



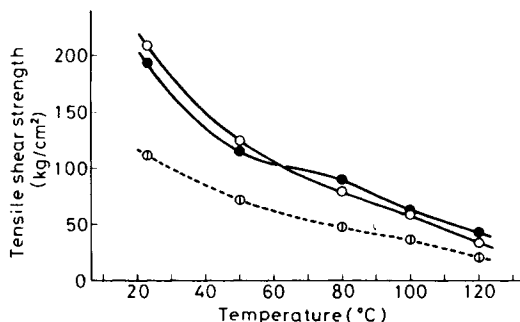


Fig. 8. Temperature dependence of tensile shear strength (on steel) for CTBNX (0.5 M)-HPA-BADG systems and reference system: (○) CTBNX (0.5 Ca)-HPA-BADG (1:30:31); (●) CTBNX (0.5 Mg)-HPA-BADG (1:30:31); (⊙) CTBNX 1300X9-HPA-BADG (1:15:16).

of polar ester groups. Meanwhile, the tendency for the strength to decrease with further decrease in the soft block content below 20–30% might be due to an increase in internal stress with decrease in soft block content and with increase in crosslinking density. Over the wide range of soft block contents studied, however, the metal-containing systems showed consistently higher strengths than their corresponding reference systems, again indicating the effect of the ionic links.

On the other hand, peel strength did not decrease even if the soft block content increased. It is considered that the peel strength depends largely on the viscoelastic properties of the cured systems. But the effect of introducing ionic links was observed over a wide range of soft block content.

On the whole, the adhesive properties of the metal-containing systems in the present study increase in the order CTB- < CTBN- < CTBNX-series.

More recently, it was reported<sup>10</sup> that peel strength of bisphenol-type epoxide resins cured with tertiary amine catalyst markedly increased upon modification with carboxyl-terminated polybutadiene, while no effect was observed on tensile shear strength. However, the peel strengths were 0.6–2 kg/25 mm at 10–50 phr added modifier. For tensile shear strength, these cured resins always gave values below 100 kg/cm<sup>2</sup>, much lower values than those shown by the above metal-containing systems (with soft block content of 20–30%).

Figure 8 shows the temperature dependence of tensile shear strength for the CTBNX (0.5 M)-HPA-BADG (1:30:31) systems which showed high strength, together with that for the reference system. Over the wide temperature range studied, the strengths of the metal-containing systems were consistently higher than that of the reference system. Thus, the effect of introducing metal appears clearly up to about 120°C.

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