

# Adhesives from Divalent Metal Salts of Mono(hydroxyethyl)phthalate, Anhydrides, and Bisepoxides

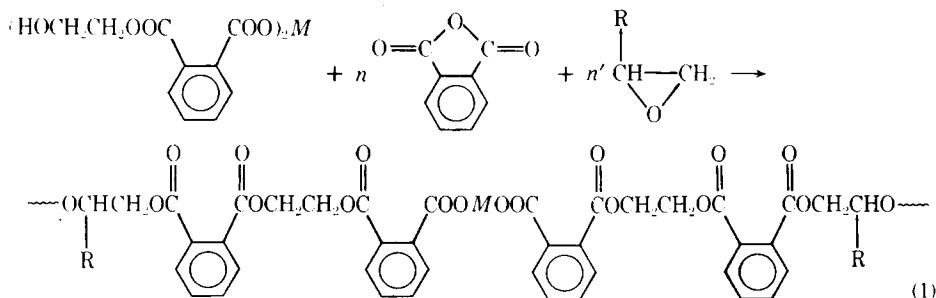
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## Synopsis

Systems of divalent metal salts of mono(hydroxyethyl)phthalate-anhydride-bisepoxide were evaluated as adhesives. The bisepoxides, bisphenol A diglycidyl ether (BADG) and hexahydrophthalic acid diglycidyl ester and the anhydrides, maleic anhydride and hexahydrophthalic anhydride (HPA) were used. The adhesive properties of the above metal-containing systems were generally superior to those of the systems not containing metal, due to the polarity effect of metal carboxylate groups. The effect of introducing metal (ionic links) on tensile shear and peel strengths clearly appeared, especially in the metal salt-HPA-BADG systems.

## INTRODUCTION

Divalent metal salts of mono(hydroxyethyl)phthalate (HEP), that is  $(\text{HEP}-)_2M$  (where HEP— denotes the HEP residue and  $M$  is a divalent metal such as Mg or Ca) are of interest as ionic monomers from the scientific and industrial standpoints. Previously it was found<sup>1</sup> that metal-containing polyesters containing ionic links were synthesized by the  $(\text{HEP}-)_2M$ -phthalic anhydride (PA)-epoxide reactions, as shown by eq. (1):



By applying the above reaction to  $(\text{HEP}-)_2M$ -anhydride-bisepoxide systems, metal-containing cured resins have been prepared.<sup>2</sup> The metal carboxylate groups of the  $(\text{HEP}-)_2M$  effectively catalyzed the curing reaction. Among the cured resins, generally those based on bisphenol A diglycidyl ether (BADG) and on hexahydrophthalic acid diglycidyl ester (HPDG) showed good physical properties.

It is well known that epoxy resins are useful as adhesives, especially the resins based on bisphenol A that are commercially available. It is generally considered that OH groups existing in the epoxy resins or produced by the reaction of the

epoxy group with the active hydrogen of the hardener form hydrogen bonds with the surface to be bonded, resulting in high adhesive strength.

It was expected that the introduction of ionic links into the epoxy resin systems would enhance adhesive properties. Therefore, we investigated the adhesive properties of (HEP—)<sub>2</sub>M-anhydride-bisepoxide systems. BADG and HPDG were selected as the bisepoxides. The anhydrides used were maleic anhydride (MA) and hexahydrophthalic anhydride (HPA). The above systems are expected to have potential application as useful adhesives.

## EXPERIMENTAL

### Materials

(HEP—)<sub>2</sub>M were prepared according to the method reported in a previous paper.<sup>3</sup> MA, HPA, and PA were of extra-pure grade and used as received. Ethylene glycol dipththalate (EGDP) was prepared by the reaction of ethylene glycol (EG) with PA. BADG was prepared by the reactions of bisphenol A and epichlorohydrin (Ep) and NaOH (epoxide value = 5.589–5.779 eq/kg. Calcd. = 5.875 eq/kg). HPDG was prepared by the reaction of di K salt of hexahydrophthalic acid with Ep (epoxide value = 6.702–6.756 eq/kg. Calcd. = 7.035 eq/kg).

### Preparation of Adhesives (Curable Mixtures)

(HEP—)<sub>2</sub>M and anhydride were mixed at a mole ratio of 1:10, except in case of the (HEP—)<sub>2</sub>Ca—HPA system, where the ratio was 1:6. The mixture was heated at 130°C with stirring until it became homogeneous. Next, given amounts of bisepoxide and, if necessary, anhydride were added to a desired mole ratio, and in case of the systems containing MA, the mixture was stirred at 60–100°C until it became homogeneous. The curable mixture thus obtained was used as adhesive. Meanwhile, for systems containing EGDP, curable mixtures were generally obtained by heating all components at 80–100°C until the systems became homogeneous. *N,N*-Dimethylbenzylamine (DMBA) was used as a catalyst, usually at an amount of about 1 wt % based on bisepoxide, except in cases cured for obtaining time-strength curves, where the amount was 0.05–0.1 wt % based on bisepoxide.

### Physical Testing

The adhesives were tested at 23°C, unless otherwise specified, using a Shimazu 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. Test specimens were 25.4 × 101.6 × 1.6 mm. The surface to be bonded was first polished by abrasive cloth No. 80 and then by abrasive paper No. 240 and was further treated with trichloroethylene. The adhesive was applied with a spatula to both surfaces to be bonded. The bonded area was 13 mm and was clamped at each edge with a small spring clip. The samples were cured at fixed temperature for fixed periods. A crosshead speed of 2.5 mm/min was applied in the tensile shear strength determinations.

The peel strength was determined on aluminum foil (Tokai Kinzoku Co. IN 30-H 18, 50  $\mu\text{m}$  thick) according to ASTM-D 1876-61 T. The surface to be bonded was polished by abrasive paper No. 240 and then treated with trichloroethylene. The samples were cured under a heated press at approximately 3.2 kg. A constant head speed of 260 mm/min was applied in the determination.

## RESULTS AND DISCUSSION

As stated above, the  $(\text{HEP})_2M$ -anhydride-bisepoxide systems, when cured, give metal-containing crosslinked resins containing ionic links. In these systems the following main reactions have been found to occur:<sup>2</sup> (1) the reaction of the carboxyl group with the epoxide group to form an OH group; (2) the reaction of the OH group with the acid anhydride group to form a terminal carboxyl group; and (3) the reaction of the acid anhydride group with the epoxide group to form an ester linkage.

Meanwhile, when EGDP is used in the curing reactions instead of  $(\text{HEP})_2M$ , the EGDP-anhydride-bisepoxide systems are expected to give cured resins whose structure is about the same as that of the former cured resins, except for the fact

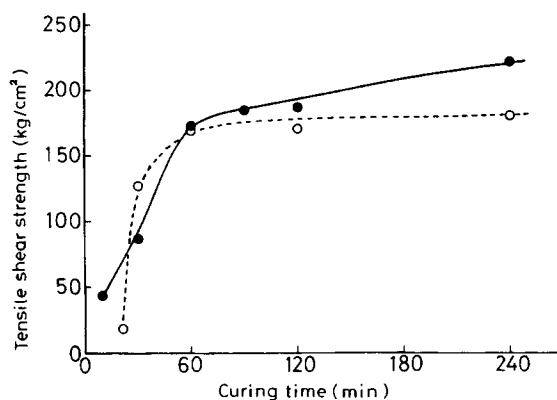


Fig. 1. Tensile shear strength (on steel) vs curing time at 120°C for systems of  $(\text{HEP})_2\text{Mg}$ -MA-BADG (1:10:5) (●) and EGDP-MA-BADG (1:8:5) with DMBA (○).

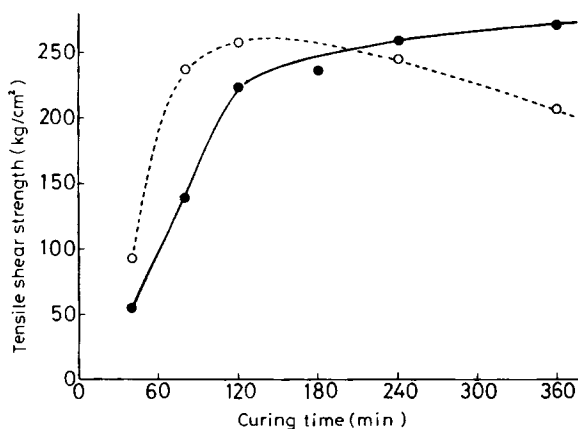


Fig. 2. Tensile shear strength (on steel) vs curing time at 140°C for systems of  $(\text{HEP})_2\text{Ca}$ -HPA-BADG (1:20:10) (●) and EGDP-HPA-BADG (1:18:10) with DMBA (○).

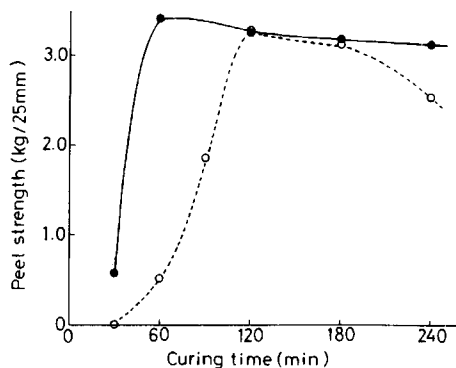
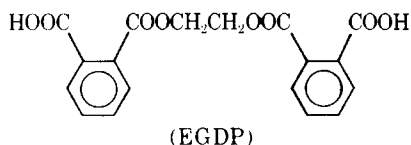


Fig. 3. Peel strength (on aluminum foil) vs curing time at 120°C for systems of  $(\text{HEP-})_2\text{Mg-MA-BADG}$  (1:10:5) (●); and  $\text{EGDP-MA-BADG}$  (1:8:5) with DMBA (○).

that the resins have no ionic links:



Therefore, for comparison, the systems containing EGDP were also used as the reference systems. In this case, for instance, the EGDP-MA-BADG system at a mole ratio of 1:8:5 corresponds to the EG-PA-MA-BADG system at a ratio of 1:2:8:5; that is, glycol:anhydride:bisepoxide = 1:10:5 (mole ratio). Similarly, the system of EGDP-HPA-BADG (1:18:10) corresponds to the system of EG-PA-HPA-BADG (1:2:18:10); that is, glycol:anhydride:bisepoxide = 1:20:10 (mole ratio).

Since bisphenol-type epoxide resins have been widely used, the systems containing BADG are considered to be important. First, the effect of curing time on the adhesive properties was investigated on representative  $(\text{HEP-})_2\text{M}$ -anhydride-BADG systems. The results are shown in Figures 1-4, together with the results on reference systems not containing metal. DMBA was usually used as the catalyst in preparing the reference systems.

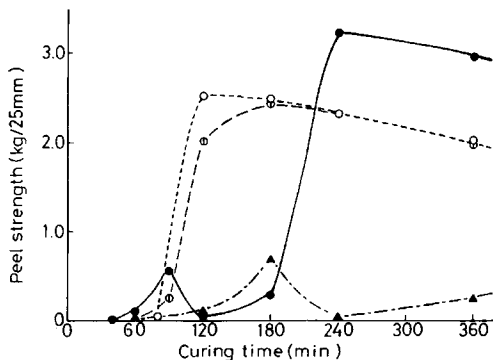


Fig. 4. Peel strength (on aluminum foil) vs curing time at 140°C for the systems of  $(\text{HEP-})_2\text{Ca-HPA-BADG}$  (1:20:10) (●),  $\text{EGDP-HPA-BADG}$  (1:18:10) with DMBA (○),  $\text{EGDP-HPA-BADG}$  (1:18:10) without DMBA (▲), and  $\text{HPA-BADG}$  (2:1) with DMBA (⊙).

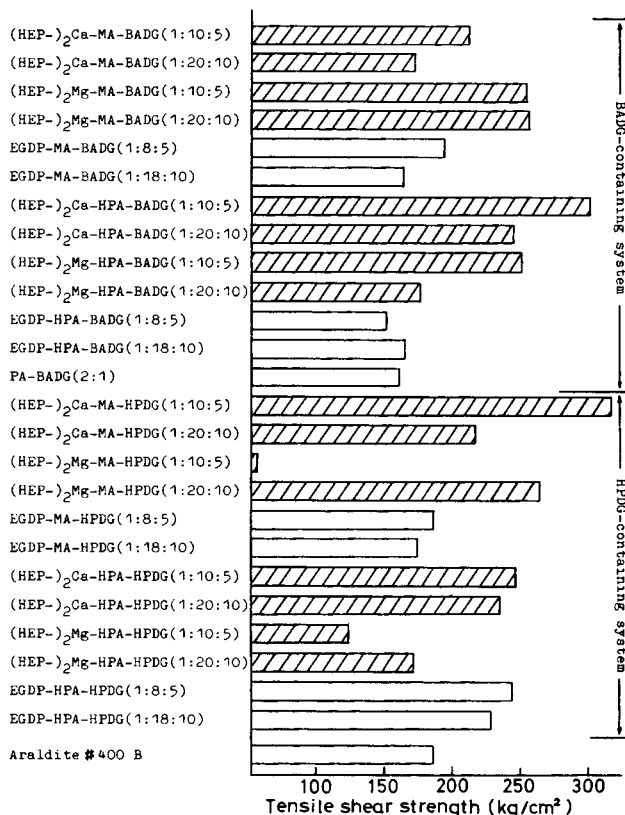


Fig. 5. Tensile shear strength (on steel) of metal-containing cured resin (▨) and reference resins (□).

As shown in Figures 1 and 2, tensile shear strength initially increased rapidly with curing time and reached a value of 172 kg/cm<sup>2</sup> after 60 min at 120°C for (HEP—)<sub>2</sub>Mg-MA-BADG (1:10:5) and 224 kg/cm<sup>2</sup> after 120 min at 140°C for (HEP—)<sub>2</sub>Ca-HPA-BADG (1:20:10), with the strength gradually increasing with further curing time. For the reference system EGDP-MA-BADG (1:8:5), tensile shear strength reached a constant after 60 min at 120°C and did not increase even if the curing time increased; for EGDP-HPA-BADG (1:18:10), the strength peaked at about 120 min at 140°C and then decreased gradually with further curing time. At the time when the peak value was obtained, the infrared spectrum showed the existence of unreacted anhydride and epoxy groups, which decreased with further curing time. Thus in this case the tensile shear strength decreased with further decreases in these functional groups in the curing system. Generally the type of failure was mixed state of contact and cohesive failures.

As shown in Figure 3, the initial rapid rise of peel strength started considerably earlier in (HEP—)<sub>2</sub>Mg-MA-BADG (1:10:5) than in the reference system; however, a reverse trend was observed for systems containing HPA, as can be seen in Figure 4. The system of HPA-BADG (2:1) showed a result almost similar to that of the EGDP-HPA-BADG (1:18:10) system. The EGDP-HPA-BADG (1:18:10) system without DMBA was also tested, with a result that peel strength was almost negligible because of an incomplete cure.

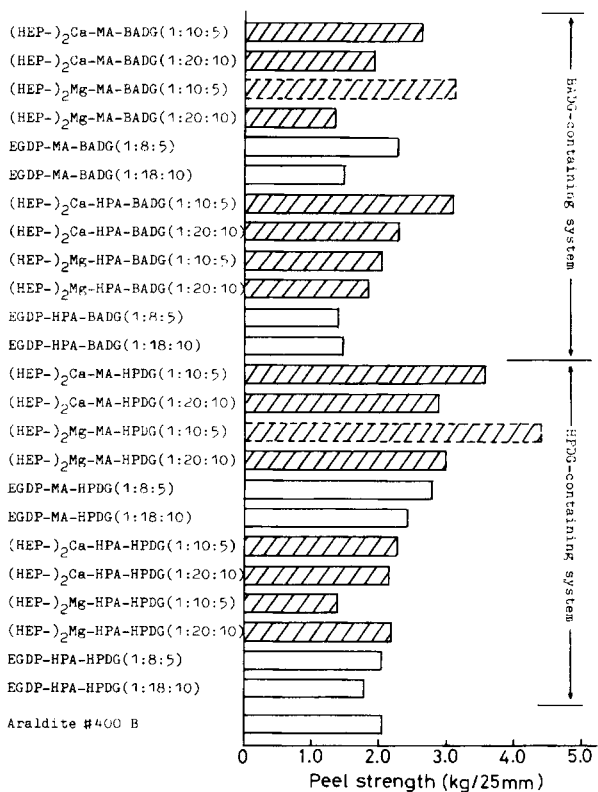


Fig. 6. Peel strength (on aluminum foil) of metal-containing cured resins (▨) and reference resins (□). Some test specimens broke during the peel strength measurements (≡).

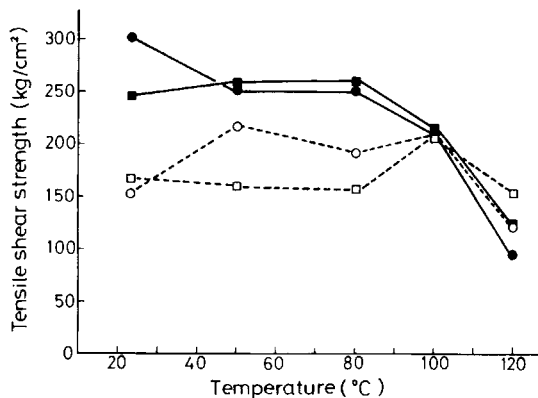


Fig. 7. Temperature dependence of tensile shear strength (on steel) for the (HEP-)2Ca-HPA-BADG systems and the reference systems: (HEP-)2Ca-HPA-BADG (1:10:5) (●), (HEP-)2Ca-HPA-BADG (1:20:10) (■), EGDP-HPA-BADG (1:8:5) (○), and EGDP-HPA-BADG (1:18:10) (□).

Generally peel strength showed a peak at a certain curing time, after which the strength showed a tendency to decrease gradually. This tendency was remarkable in the EGDP-MA-BADG (1:8:5) system. In the initial stages, the type of failure was cohesive failure and after peak, contact failure. A similar tendency

has been found for the peel strengths of bisphenol-type epoxy resins cured with polyamines or polyamides.<sup>4</sup>

For systems containing HPDG, the rates of adhesion were generally higher than those of systems containing BADG.

Next adhesive properties were tested on various combinations of components. In order to obtain ultimate adhesive strengths, sufficient curing was considered necessary. Curing conditions were as follows: in case of the tensile shear strength measurements, 100°C for 3 hr and 160°C for 1 hr for the (HEP—)<sub>2</sub>M-MA-HPDG systems; for other systems, 120°C for 1–3 hr and 160°C for 1–4 hr; for the peel strength measurements, 80°C for 1 hr, 120°C for 3 hr, and 160°C for 1 hr for the (HEP—)<sub>2</sub>M-MA-BADG systems and 60°C for 1 hr, 100°C for 3 hr, and 160°C for 1 hr for the (HEP—)<sub>2</sub>M-MA-HPDG systems; for other systems, 120°C for 1–2 hr and 160°C for 1–4 hr.

As shown in Figure 5, tensile shear strength of BADG-containing systems is generally higher in the metal-containing cured resins than in the reference resins. This tendency is remarkable especially in the resins based on HPA; for example, the (HEP—)<sub>2</sub>Ca-HPA-BADG (1:10:5) system showed a value of 301 kg/cm<sup>2</sup>. Thus the effect of introducing metal (ionic links) is apparent. This may be due to the increase in polarity resulting in a cured resin which is more firmly bound to the surface to be bonded.

PA is a typical anhydride-type curing agent, and hence the PA-BADG (2:1) system was also cured with DMBA for testing. It was found that this system gave about the same tensile shear strength as those shown by the reference systems EGDP-HPA-BADG (1:8:5 or 1:18:10) and EGDP-MA-BADG (1:18:10). Moreover, the systems of (HEP—)<sub>2</sub>M-PA-bisepoxide did not become homogeneous at high curing temperatures, and hence they were excluded from the study.

As for the mole ratio of components, the systems in which the ratio of (HEP—)<sub>2</sub>M:anhydride:BADG was 1:10:5 generally showed higher tensile shear strengths than those in which the ratio was 1:20:10. This might be attributed to the greater polarity effect of the former resins with their higher metal content.

Glycidyl esters are known to offer greater adhesive properties than glycidyl ethers due to the higher polarity of the ester groups.<sup>5</sup> Similarly, it has been reported that tensile shear strength increases with epoxy content of starting resins.<sup>6</sup> HPDG has two ester groups and a higher epoxy content than BADG. Therefore, it was thought that replacing BADG by HPDG would enhance the adhesive properties. Indeed, this seems to be well reflected in the fact that the reference systems containing HPDG gave generally higher tensile shear strengths than those containing BADG, the strengths of the EGDP-HPA-HPDG systems being considerably higher. The same may be said of peel strength, which will be discussed below. In HPDG-containing systems, the tensile shear strengths of the systems of (HEP—)<sub>2</sub>M-MA-HPDG, except for (HEP—)<sub>2</sub>Mg-MA-HPDG (1:10:5), were fairly higher than those of the reference systems EGDP-MA-HPDG.

Araldite (standard) # 400 B (epoxide value = 3.938 eq/kg; Ciba Geigy Co.) is a well-known, commercially available, strong epoxy adhesive. For comparison, this adhesive was also cured, for testing, with a polyamide-type curing agent as prescribed (80 °C for 1 hr). As shown in Figure 5, many of the metal-containing systems gave higher tensile shear strength than the Araldite # 400 B.

About the same tendencies as presented above were obtained on peel strength (Fig. 6). For the systems of  $(\text{HEP—})_2\text{Mg-MA-BADG}$  (1:10:5) and  $(\text{HEP—})_2\text{-Mg-MA-HPDG}$  (1:10:5), the test specimens of aluminum foil broke during the peel strength measurements. All of the systems of  $(\text{HEP—})_2\text{M-HPA-BADG}$  and of  $(\text{HEP—})_2\text{M-MA-HPDG}$  gave higher peel strength than the corresponding reference systems; thus the effect of introducing metal clear. The fact that the  $(\text{HEP—})_2\text{M-MA-HPDG}$  systems gave the highest peel strength may be due to a polarity effect of the ionic links in addition to the enhanced concentrations of ester and epoxy groups of the starting HPDG.

In summary, the adhesive properties of the metal-containing systems are generally superior to those of the corresponding reference systems, except for the  $(\text{HEP—})_2\text{M-HPA-HPDG}$  systems. Especially in case of the  $(\text{HEP—})_2\text{-M-HPA-BADG}$  systems, the effect of introducing metal on tensile shear and peel strengths is apparent.

Figure 7 shows the temperature dependences of tensile shear strength for the  $(\text{HEP—})_2\text{Ca-HPA-BADG}$  systems in which the effect of introducing metal is apparent, together with those for the reference systems. Up to about 100°C, the tensile shear strengths of the metal-containing cured resins were higher than those of the reference resins. Thus the effect of introducing metal appears up to about 100°C, at which the values of 208–215 kg/cm<sup>2</sup> were obtained.

In case of the HPDG-containing systems, on the other hand, somewhat poor results were obtained; for instance, the systems of  $(\text{HEP—})_2\text{Mg-MA-HPDG}$  (1:20:10) and of  $(\text{HEP—})_2\text{Ca-MA-HPDG}$  (1:20:10) gave tensile shear strengths at 80°C of 110 and 105 kg/cm<sup>2</sup>, respectively.

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