

Stability, Cure Properties, and Applicability as One Part Adhesives of Systems of Divalent Metal Salts of Mono(hydroxyethyl) Phthalate-Anhydride-Bisepoxide

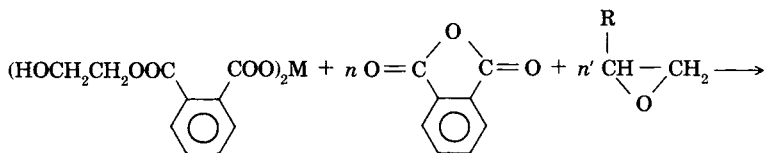
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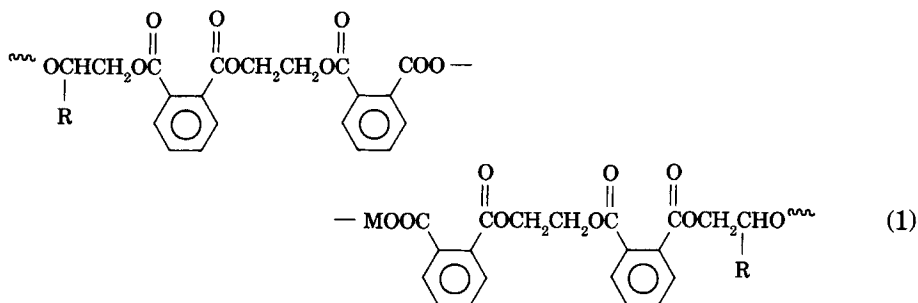
Synopsis

Heterogeneous curable compositions of divalent metal salts of mono(hydroxyethyl) phthalate-anhydride-bisphenol A diglycidyl ether (BADG) systems were prepared by merely mixing these components at room temperature. Stability at room temperature and cure properties at high temperature of the compositions were investigated for evaluating their applicability as one part adhesive. It was found that the systems containing Mg were generally more stable than those containing Ca. Similarly, at 150°C the Ca-containing systems showed generally shorter gelation time than the Mg-containing ones, due to the fact that the Ca salt dissolves more rapidly and enters into the addition reaction with the anhydride, leading to the faster appearance of the catalytic activities of the Ca carboxylate group. Among the various combinations of components, the metal salt-succinic anhydride (SA)-BADG systems were stable at room temperature for more than 6 months and rapidly cured at high temperature, showing excellent adhesive properties. This result indicates that the SA-containing systems should be of interest in applications to one part adhesives.

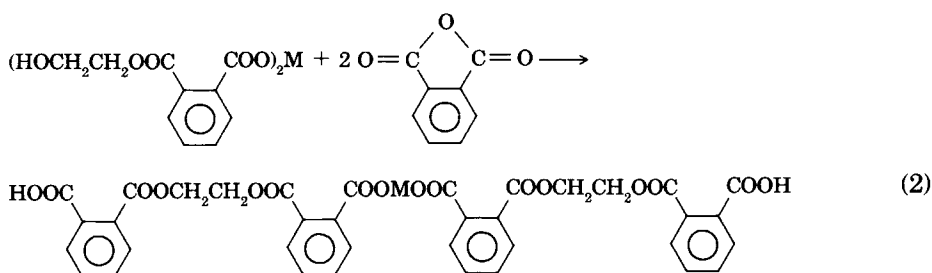
INTRODUCTION

Since 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) contain an ionic bond formed between $-\text{COO}^-$ and M^{++} , and two hydroxyl groups, the $(\text{HEP})_2\text{M}$ salts are useful starting materials for preparation of ionic polymers into which metal is firmly incorporated. Previously, we have reported¹ that metal-containing polyesters containing ionic links were synthesized by the $(\text{HEP})_2\text{M}$ -phthalic anhydride (PA)-monoepoxide reactions, as shown by eq. (1):





where M = Mg or Ca. Dimethylformamide (DMF) was used as a solvent in this case. The reactions were conducted by first producing *in situ* an adduct of (HEP—)₂M and PA, as shown by eq. (2), and then adding monoepoxide to the mixture of the produced adduct and PA:



It was found that, in the systems, the following main reactions occur: (1) the reaction of carboxyl group with epoxide group to form OH group; (2) the reaction of the OH group with acid anhydride group to form terminal carboxyl group; (3) the reaction of acid anhydride group with epoxide group to form ester linkage. In addition, interestingly the metal carboxylate group in (HEP—)₂M showed catalytic activities for the reactions.

By applying the above reactions to the (HEP—)₂M–anhydride–bisepoxide systems without solvent, metal-containing cured resins with excellent physical properties have been prepared.² Further, adhesive properties were investigated for the cured resins from the homogeneous curable compositions prepared by adding bisepoxide to anhydride–adduct of (HEP—)₂M and the anhydride, and stirring the mixture at room or high temperature.³ It was found that the adhesive properties of the metal-containing systems were generally superior to those of the systems not containing metal, due to the polarity effect of the metal carboxylate groups.

On the other hand, research efforts have been made to develop latent curing agents for epoxy resins.^{4–8} Well-known examples of the latent curing agents investigated are imidazole derivatives, boron trifluoride amine salts, dicyandiamide, organic acid dihydrazides, and aminimides. Recently, aminimide compounds were found to be excellent curing agents, which are activated only at elevated temperatures, and to give cured epoxy resins with mechanical properties exhibiting a number of interesting characteristics.^{9,10}

In the present study, heterogeneous curable compositions of the $(\text{HEP—})_2\text{M}$ -anhydride-bisepoxide systems were prepared by merely mixing these components at room temperature without producing *in situ* the adduct of $(\text{HEP—})_2\text{M}$ and anhydride. We investigated stability at room temperature and cure properties at high temperature of the compositions for evaluating applicability as one part adhesives of the compositions. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used because bisphenol-type epoxy resins have been widely used.

EXPERIMENTAL

Materials

The $(\text{HEP—})_2\text{M}$ salts were prepared according to the method reported in a previous paper.¹¹ As the BADG, Epomik R 140 (Mitsui Petrochemical Epoxy Co.) was used: the epoxide value was 5.400–5.403 eq/kg (calcd = 5.875 eq/kg). Succinic anhydride (SA), hexahydrophthalic anhydride (HPA), PA, maleic anhydride, dodeceny succinic anhydride, and methyl nadic anhydride were of extra pure grade. Methylhexahydrophthalic anhydride and methyl-1,2,3,6-tetrahydrophthalic anhydride (MTPA) were of technical grade. They were used as received. Aerosil (silicic acid anhydride ($\text{SiO}_2 > 99.8\%$)) was obtained from Nippon Aerosil Co. Moreover, the $(\text{HEP—})_2\text{M}$ salts and SA were used in the form of powder which has passed through a 115-mesh screen.

Preparation of Heterogeneous Curable Compositions of $(\text{HEP—})_2\text{M}$ -Anhydride-Bisepoxide Systems

When HPA and MTPA were used as the anhydride, a fixed amount of $(\text{HEP—})_2\text{M}$ and Aerosil [for preventing sedimentation of $(\text{HEP—})_2\text{M}$] at an amount of 12 wt % based on BADG + anhydride were added to a mixture of BADG and anhydride in a mortar, and the content was kneaded thoroughly to obtain a heterogeneous curable composition. When SA was used as the anhydride, fixed amounts of $(\text{HEP—})_2\text{M}$ and SA, and further Aerosil at an amount of 10 wt % based on BADG were added to a given amount of BADG in the mortar, and the content was kneaded thoroughly to obtain a heterogeneous curable composition. The compositions thus obtained were evaluated for stability, viscosity, and adhesive properties.

Moreover, in the case of investigations of gelation time and gel state, the compositions not containing Aerosil were used.

Determination of Stability of Heterogeneous Curable Compositions at 50°C

About 3 g of the above compositions was placed in a polyethylene bag, and the bag was sealed. It was kept in a room maintained at 50°C, and the days up to the time of gelation were determined.

Determination of Gelation Time

About 3 g of the above composition was placed in a test tube, and the test tube was placed in a constant-temperature bath maintained at 150°C while stirring the composition with a glass rod. The stirring was continued until gelation occurred. At the gelation point, the state of the gel was observed.

Physical Testing

Tensile shear strength was determined, as in the previous paper,³ on steel with reference to ASTM-D 1002-64. Similarly, peel strength was determined, as in the previous paper,³ on aluminum foil according to ASTM-D 1876-61 T. Moreover, viscosity was determined at 50°C by using a B-type viscosimeter.

RESULTS AND DISCUSSION

Screening of Anhydrides Suitable for One Part Adhesives of (HEP—)₂M-Anhydride-Bisepoxide Systems

In one part adhesives of epoxy resin compositions, respective components must be inactive with each other at room temperature. The (HEP—)₂M salts are insoluble in ordinary organic solvents and generally inactive at room temperature.

At first, for screening anhydrides which are comparatively stable at room temperature when mixed with the bisepoxide, eight anhydrides were mixed with BADG (when the anhydrides are solid at room temperature, they were dispersed in the powdery state in the mixture) and epoxide value vs. storage time of the mixtures was followed at 23°C. The epoxide values were determined by the HBr method.^{12,13} The results are shown in Figure 1. As a result of the observation for six months, it was found that the mixtures containing SA, HPA, MTPA, dodecenylsuccinic anhydride, or methylnadic anhydride exhibited low decrease in epoxide value and were stable. Meanwhile, the

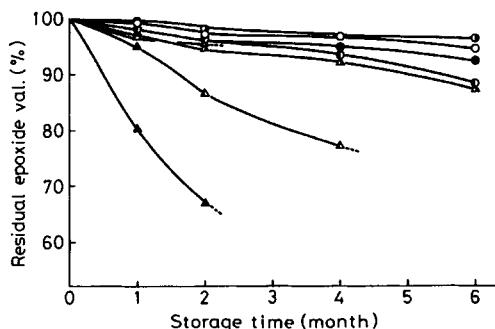


Fig. 1. Epoxide value vs. storage time at 23°C for mixtures of anhydride-BADG: (○) SA; (◐) HPA; (◑) MTPA; (●) dodecenylsuccinic anhydride; (◔) methylnadic anhydride; (◕) methylhexahydrophthalic anhydride; (△) phthalic anhydride; (▲) maleic anhydride.

mixture containing methylhexahydrophthalic anhydride spread a film on the surface of the mixture and showed a viscosity increase. Further, those containing phthalic anhydride or maleic anhydride gelled on the way.

Since, in the heterogeneous compositions of the $(\text{HEP}-)_2\text{M}$ -anhydride-bisepoxide systems, the curing starts with the addition reaction of $(\text{HEP}-)_2\text{M}$ and anhydride, it is very important for the addition reaction to proceed smoothly at high temperature. Then, using the above five stable anhydrides, $(\text{HEP}-)_2\text{M}$ -anhydride mixtures at a mole ratio of 1:10 were prepared, and reactivity of the mixtures was examined at 140°C; as a result, SA, HPA, and MTPA gave homogeneous adducts, however, the mixtures containing dodecenylsuccinic anhydride or methyl nadic anhydride were heterogeneous at 140°C and the addition reaction did not proceed enough.

As a summary of the results described above, SA, HPA, and MTPA were selected as the anhydrides suitable for the investigation of one part adhesives of the $(\text{HEP}-)_2\text{M}$ -anhydride-bisepoxide systems.

Stability of Heterogeneous Compositions of $(\text{HEP}-)_2\text{M}$ -Anhydride-BADG Systems

Table I shows stability of the heterogeneous compositions of the $(\text{HEP}-)_2\text{M}$ -anhydride-BADG systems. The stability at 50°C increased, depending on the species of anhydride, in the order MTPA < HPA < SA. It is noteworthy that the SA-containing systems were most stable at 50°C, showing no gelation for more than about 1 month. This is considered due to the fact that, below the melting point (119.6°C), SA is dispersed in the powdery state in the system, thereby causing the system hardly to react at low temperatures.

As for the influence of the metal species, at 50°C the Mg-containing systems were generally more stable than the Ca-containing ones, as in the case at 150°C, which will be mentioned later. On the other hand, the effect of the mole ratio of the components on the stability was negligible.

TABLE I
Stability of Heterogeneous Compositions of $(\text{HEP}-)_2\text{M}$ -Anhydride-BADG Systems

Components	Mole ratio of components	Stability at 50°C (day)
$(\text{HEP}-)_2\text{Ca}$ -SA-BADG	1:10:5	29
	1:20:10	37
$(\text{HEP}-)_2\text{Mg}$ -SA-BADG	1:10:5	37
	1:20:10	37
$(\text{HEP}-)_2\text{Ca}$ -HPA-BADG	1:10:5	23
	1:20:10	24
$(\text{HEP}-)_2\text{Mg}$ -HPA-BADG	1:10:5	25
	1:20:10	27
$(\text{HEP}-)_2\text{Ca}$ -MTPA-BADG	1:10:5	14
	1:20:10	14
$(\text{HEP}-)_2\text{Mg}$ -MTPA-BADG	1:10:5	21
	1:20:10	19

TABLE II
Cure Properties of Heterogeneous Compositions of (HEP—)₂M-Anhydride-BADG Systems

Components	Mole ratio of components	Gelation time at 150°C (min)	External appearance of cured resin
(HEP—) ₂ Ca-SA-BADG	1:10:5	10	Semitransparent
	1:20:10	70	Almost transparent
(HEP—) ₂ Mg-SA-BADG	1:10:5	18	A little turbid
	1:20:10	25	Semitransparent
(HEP—) ₂ Ca-HPA-BADG	1:10:5	8	Semitransparent
	1:20:10	23	Almost transparent
(HEP—) ₂ Mg-HPA-BADG	1:10:5	20	A little turbid
	1:20:10	29	A little turbid
(HEP—) ₂ Ca-MTPA-BADG	1:10:5	15	Turbid
	1:20:10	28	A little turbid
(HEP—) ₂ Mg-MTPA-BADG	1:10:5	33	Turbid
	1:20:10	44	Turbid

Cure Properties of Heterogeneous Compositions of (HEP—)₂M-Anhydride-BADG Systems

Table II shows cure properties at 150°C of the heterogeneous compositions of the (HEP—)₂M-anhydride-BADG systems. On comparing the systems containing the same species of metal and anhydride, the systems in which the mole ratio of (HEP—)₂M:anhydride:BADG is 1:10:5 exhibited shorter gelation time than those in which the ratio is 1:20:10. That is, with increase in the metal content, the gelation time became shorter, indicating the catalytic effect of the metal carboxylate group.^{1,2} On the other hand, when comparing the systems with the same anhydride and at the same mole ratio, the Ca-containing systems showed shorter gelation time than the Mg-containing ones, except for the systems of (HEP—)₂M-SA-BADG (1:20:10). This tendency is contrary to that observed for the previous studies,^{2,14} which disclosed that, in the homogeneous compositions from (HEP—)₂M, anhydride, and bisepoxide, or from (HEP—)₂M, bisester anhydride, and monoepoxide, the Mg carboxylate group has higher catalytic activities than the Ca carboxylate group toward the curing reactions.

TABLE III
(HEP—)₂M-Anhydride Reaction at 140°C

Components	Mole ratio of components	Time required to become homogeneous (min)
(HEP—) ₂ Ca-SA	1:10	15
(HEP—) ₂ Mg-SA	1:10	45
(HEP—) ₂ Ca-HPA	1:10	40
(HEP—) ₂ Mg-HPA	1:10	120
(HEP—) ₂ Ca-MTPA	1:10	60
(HEP—) ₂ Mg-MTPA	1:10	150

As stated earlier, in the previous studies,¹⁻³ the epoxide compounds were added to the system after making $(\text{HEP}-)_{2}\text{M}$ react with anhydride to produce *in situ* the adduct with good solubility. Meanwhile, in the present study, since the curing of the heterogeneous systems in which the $(\text{HEP}-)_{2}\text{M}$ salts were dispersed in the powdery state starts with the addition reaction of $(\text{HEP}-)_{2}\text{M}$ and anhydride, the rate of the addition reaction is considered to significantly influence on the gelation time. Then, Table III shows times required for the $(\text{HEP}-)_{2}\text{M}$ -anhydride (1:10) mixtures to become homogeneous at 140°C. On comparing the mixtures with the same anhydride, the Ca-containing mixtures required shorter time to become homogeneous than the Mg-containing ones. That is, the addition reaction of the former mixtures proceeded more rapidly than that of the latter mixtures. This is considered due to the difference of the solubilities of $(\text{HEP}-)_{2}\text{Ca}$ and $(\text{HEP}-)_{2}\text{Mg}$, that is, to the higher solubility of the former. Therefore, it is considered that, in the curing of the $(\text{HEP}-)_{2}\text{M}$ -anhydride-BADG systems, $(\text{HEP}-)_{2}\text{Ca}$ dissolves more rapidly and enters into the addition reaction with the anhydride, leading to the faster appearance of the catalytic activities of the Ca carboxylate group. Meanwhile, $(\text{HEP}-)_{2}\text{Mg}$ dissolves more slowly in the system, thereby causing the slower appearance of the catalytic activities, resulting in the longer gelation time.

As for the state of the gels, the Mg-containing systems were a little more turbid than the Ca-containing ones, indicating that $(\text{HEP}-)_{2}\text{Mg}$ is comparatively difficult to incorporate smoothly into the cured resin. Moreover, MTPA, as compared with SA and HPA, gave turbid gels.

Tensile Shear Strengths of $(\text{HEP}-)_{2}\text{M}$ -Anhydride-BADG Systems

Figure 2 shows tensile shear strengths of the $(\text{HEP}-)_{2}\text{M}$ -anhydride-BADG systems. The previous study³ indicated that the systems in which the mole ratio of $(\text{HEP}-)_{2}\text{M}$:anhydride:BADG was 1:10:5 generally showed higher tensile shear strengths than those in which the ratio was 1:20:10, probably due to the greater polarity effect of the former resins with their higher metal content. Such a tendency is observed for the systems containing HPA or MTPA in the present study.

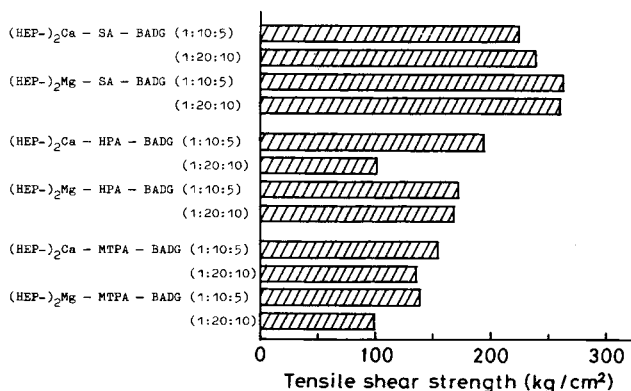


Fig. 2. Tensile shear strength for systems of $(\text{HEP}-)_{2}\text{M}$ -anhydride-BADG. Cure condition = 150°C for 3 h.

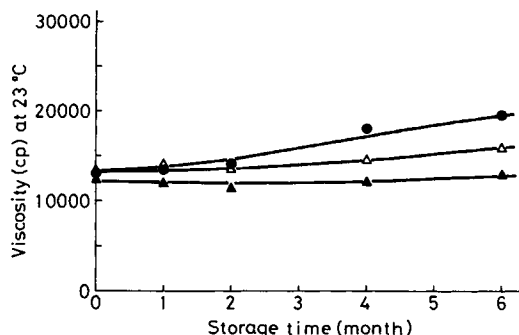


Fig. 3. Viscosity vs. storage time at 23°C for heterogeneous compositions of $(\text{HEP-})_2\text{M-SA-BADG}$ systems: (●) $(\text{HEP-})_2\text{Ca-SA-BADG}$ (1:20:10); (△) $(\text{HEP-})_2\text{Mg-SA-BADG}$ (1:10:5); (▲) $(\text{HEP-})_2\text{Mg-SA-BADG}$ (1:20:10).

On comparing the systems with the same metal and at the same mole ratio, the tensile shear strength generally increased, depending on the species of anhydride, generally in the order $\text{MTPA} < \text{HPA} < \text{SA}$. Especially, the systems containing SA showed high tensile shear strengths of above 200 kg/cm^2 .

In view of the observations described above, it could be said that, among the $(\text{HEP-})_2\text{M-anhydride-BADG}$ systems, those containing SA have high stability at low temperature and good cure properties at high temperature, exhibiting high adhesive strength when cured. Therefore, the SA-containing systems were further examined for evaluating the applicability as one part adhesives.

Viscosity and Adhesive Strength Change with Time of $(\text{HEP-})_2\text{M-SA-BADG}$ Systems

Figure 3 shows viscosity at 23°C vs. storage time for the heterogeneous compositions of the $(\text{HEP-})_2\text{M-SA-BADG}$ systems. The viscosity increased very gradually with the storage time for the systems of $(\text{HEP-})_2\text{Ca-SA-BADG}$ (1:20:10) and of $(\text{HEP-})_2\text{Mg-SA-BADG}$ (1:10:5), and the Ca-containing system exhibited higher increase than the Mg-containing one; however,

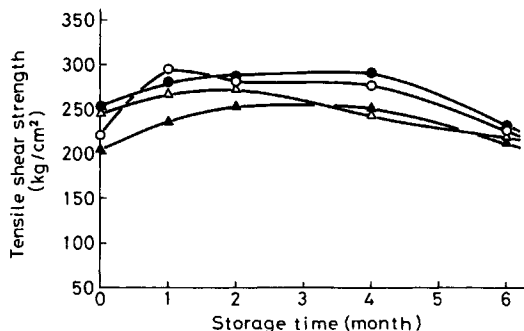


Fig. 4. Tensile shear strength vs. storage time at 23°C for systems of $(\text{HEP-})_2\text{M-SA-BADG}$: (○) $(\text{HEP-})_2\text{Ca-SA-BADG}$ (1:10:5); (●) $(\text{HEP-})_2\text{Ca-SA-BADG}$ (1:20:10); (△) $(\text{HEP-})_2\text{Mg-SA-BADG}$ (1:10:5); (▲) $(\text{HEP-})_2\text{Mg-SA-BADG}$ (1:20:10).

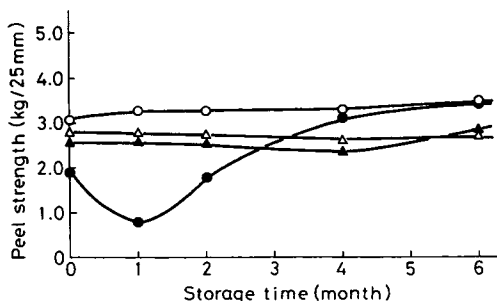


Fig. 5. Peel strength vs. storage time at 23°C for systems of (HEP-)2M-SA-BADG: (O) (HEP-)2Ca-SA-BADG (1:10:5); (●) (HEP-)2Ca-SA-BADG (1:20:10); (Δ) (HEP-)2Mg-SA-BADG (1:10:5); (▲) (HEP-)2Mg-SA-BADG (1:20:10).

the viscosity increase was very small even after 6 months. As for the mole ratio of components, the Mg-containing system in which the ratio of (HEP-)2Mg:SA:BADG was 1:10:5 showed slightly higher viscosity increase than that in which the ratio was 1:20:10, probably due to the higher metal content of the former. Moreover, the (HEP-)2Ca-SA-BADG (1:10:5) system was too viscous (> 100,000 cP) to measure its viscosity with the B-type viscosimeter.

Tensile shear and peel strengths change with storage time are shown in Figures 4 and 5, respectively. For the all systems, initially the tensile shear strength increased slightly with the storage time and subsequently it decreased gradually with the time; however, the strengths after 6 months were almost equal to or only slightly lower than their initial values. Meanwhile, the peel strength exhibited little change through 6 months, except for the (HEP-)2Ca-SA-BADG (1:20:10) system whose peel strength decreased markedly after 1 month and subsequently increased again with the time. Therefore, this system was considered unsuitable for one part adhesives and was not examined further.

Effect of Curing Time on Tensile Shear Strength for (HEP-)2M-SA-BADG Systems

Figure 6 shows tensile shear strength vs. curing time at 150°C for the (HEP-)2M-SA-BADG systems. The tensile shear strength first increased

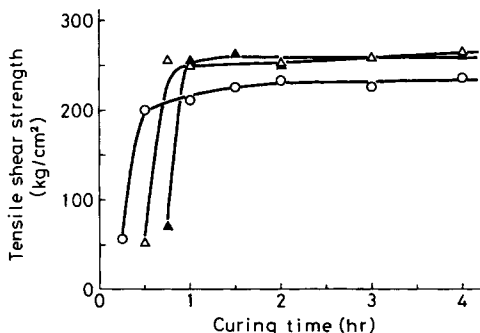
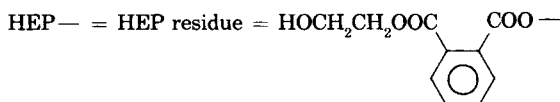
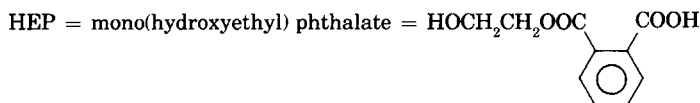


Fig. 6. Tensile shear strength vs. curing time at 150°C for systems of (HEP-)2M-SA-BADG: (O) (HEP-)2Ca-SA-BADG (1:10:5); (Δ) (HEP-)2Mg-SA-BADG (1:10:5); (▲) (HEP-)2Mg-SA-BADG (1:20:10).

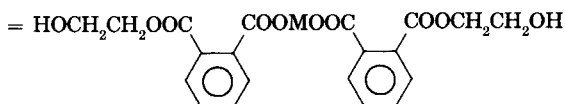
rapidly with the curing time, reaching a final value within 1 h. The (HEP—)₂Ca-SA-BADG (1:10:5) system exhibited a value of 200 kg/cm² after 30 min, the (HEP—)₂Mg-SA-BADG (1:10:5) system 257 kg/cm² after 45 min, and the (HEP—)₂Mg-SA-BADG (1:20:10) system 252 kg/cm² after 60 min. Thus, the rapid curing and the very high adhesive strengths (especially those shown by the latter two systems) are characteristics of the present compositions. Moreover, the rising of the strength was earlier for the systems containing Ca or with the higher Mg content than for those containing Mg or with the lower Mg content, a tendency similar to that observed for the gelation times at 150°C (in Table II).

As a summary of the results described above, it may be concluded that the heterogeneous compositions of the (HEP—)₂M-SA-BADG systems are stable at room temperature for more than 6 months and rapidly cure at high temperature, showing excellent adhesive properties. These properties are considered to be favorable for the application to one part adhesives.

APPENDIX: NOMENCLATURE



(HEP—)₂M = divalent metal salts of HEP



where M = divalent metal (Mg or Ca)

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