Modification of Epoxy Polymer by Plasticizing, Blending, or Reinforcing

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Synopsis

Epoxy polymer (EP) was modified by incorporation of DBP, PVC, PVA, and glass fiber reinforcement. The morphology of the unmodified polymer and the various blends was studied by SEM, dispersive X-ray analysis, and DSC. Results indicated that EP and DBP are miscible in the proportions used in this work (up to 10% of DBP). PVA added to cured EP in a concentration of 10% occurs as a separate phase. The morphology of EP–PVC blends is relatively complex: EP and PVC are immiscible at low concentrations of the second component (up to 10% of PVC), but become mutually and increasingly more miscible as the concentration of PVC increases. Incorporation of DBP into EP causes a marked reduction in the heat distortion temperature (HDT), whereas addition of PVC has only a moderate effect. Modified EP containing small amounts of DBP (up to 4%) has moderately lower bond strength than the unmodified polymer, as evidenced by lower ultimate tensile strength of the adhesion sandwich specimens mounted on aluminum substrate. However, as the concentration of DBP in the blend increases, the ultimate tensile strength is slightly higher than that of the unmodified EP. Blending of EP with PVC, PVA, and glass fibers has generally a detrimental effect on the ultimate tensile strength. Outdoor exposure for 100 days (between January and April) generally caused deterioration of the tensile strength of all samples. EP-based blends containing DBP, however, had better resistance to deterioration in outdoor exposure than the other blends, including unmodified EP.

INTRODUCTION

Despite their relatively high cost, epoxies are now firmly established in many important applications. They are used in surface coatings, encapsulation of electronic components, adhesives, castings, composites, etc. The modern adhesives technology has led to the development of many types of epoxy and modified epoxy-based adhesive systems. The variation of properties with formulation accounts for the wide range of applications for which epoxy type adhesives can be designed. The curing process of an epoxy adhesive involves the transformation of the system from a viscous liquid to a gelled rubber and finally to a solid state (hard glass).

Only a few papers deal with blends of epoxy polymers and other high polymers, including diallyl phthalate–epoxy interpenetrating polymer network,[1] nylon–epoxy blends,[2] and epoxy-modified polyethylene.[3] Most of these papers are discussing different aspects of rubber modified epoxies.[4-10]

In previous papers,[11,12] results of a study on the morphology and properties of some modified polyurethanes were reported. A similar study was subsequently carried out on an epoxy polymer modified by plasticizing with dibutyl phthalate, blending with PVC, PVA and reinforcing with glass fibers. Fur-

thermore, the effect of the outdoor exposure in the Canadian climate and that of aging by immersion in some liquid chemical environments on some of these blends was also investigated. The properties of the epoxy resin and modified epoxy blend were assessed by scanning electron microscope, energy dispersive X-ray analysis, DSC measurements, heat distortion measurements, and mechanical testing. This paper reports results of this study, which is part of a research project on the durability of polymeric materials used as adhesives, plastics or sealants.

EXPERIMENTAL

Materials. The epoxy polymer (EP) was a commercial, thixotropic structural adhesive grade (Araldite CA-1200) supplied by Ciba-Geigy, cured with an aliphatic diamine, using the weight ratio of 100:11 (EP:amine). The other materials were also commercial, as follows: dibutyl phthalate (DBP) (J. T. Baker Chemical Co.), poly(vinyl alcohol) (PVA) (Anachemia), and poly(vinyl chloride) (PVC) (B. F. Goodrich). The reinforcement consisted of short glass fibers with a length distribution in the range of 10–15 mm.

To prepare the epoxy-based blends, the appropriate amount of the second component (e.g., DBP, polymer or reinforcement) was mixed with the epoxy polymer at room temperature and the product was stirred vigorously (5–10 min); then the hardener was added, and stirring was continued for another 5 min without heating. The unmodified epoxy resin (control) sample was prepared in a similar manner. The various samples were kept at 22°C for 24 h to allow for completion of the curing reaction.

Apparatus and Procedures. Fracture surfaces of the various samples were observed with a Cambridge Stereoscan S250 Scanning Electron Microscope (SEM) operated at 20 kV and tilt angle of 45°. The fracture surfaces were obtained by using a chisel and hammer to split the sample at 22°C. The specimens were coated with carbon and then with gold to prevent electrical charging. The DSC curves were recorded with a DuPont 1090 Thermal Analyzer over a temperature range of −110°C to 160°C under nitrogen, using approximately 29 mg of sample.

To determine the approximate amount of PVC at the different micro sites of the EP–PVC blend specimens, an X-ray energy dispersive attachment (on the SEM), equipped with a lithium drifted detector, Si (Li), was used. The Si (Li) detector is able to detect sodium and elements with atomic number greater than sodium, but does not see elements with lower atomic number (e.g., C, N, O, etc.).

Tensile stress–strain measurements were carried out at 22°C, using an Instron Model 1125 Universal Testing Machine at a crosshead speed of 5 mm/min and chart speed of 100 mm/min. The test specimens ($12.5 \times 12.5 \times 50.0$ mm) consisted of a bead of material (cured control or modified epoxy) cast between two prismoidal pieces of substrate (portland cement mortar, California redwood, aluminum). The values used for plotting the stress–strain curves are averages of 5–10 successful determinations. To measure the heat distortion temperature, the Wallace apparatus was used.

To assess the effect of the outdoor weather on the properties of modified cured epoxy materials, samples were exposed in a highly polluted area in Montreal

TABLE I
Results of SEM Observations of Fracture Surfaces of Modified Epoxy Resin

Sample	Amount of modifier (%)	Observations	Sample	Amount of modifier (%)	Observations
EPOXY (EP)	—	Material of fracture surface has rough texture, consisting of two phases: highly crosslinked microgel particles (micelles) embedded in a continuous phase of low crosslink density	EP–PVC EP–PVC	10 20	In blends containing between 10% and approximately 40% PVC, three types of material occur: pure PVC occurring as discrete particles, PVC mixed with EP resin, and pure EP resin
EP–DBP EP–DBP	2 4	Morphology of surface material similar to that of unmodified EP resin; observation by SEM did not reveal the occurrence of an additional	EP–PVC EP–PVC	30 40	
EP–DBP EP–DBP	6 10	phase; thus DBP is completely miscible with the epoxy resin	EP–PVC	50	Blends of equal proportions of the two components also consist of three types of materials: pure EP phase, particles of PVC containing small proportions of EP, and a solid phase of well-mixed EP and PVC
EP–PVA	10	PVA occurs as a separate phase; good adhesion between the two blend components			
EP–PVC EP–PVC	2 5	At the lower concentrations (up to 5%) PVC is a separate phase, consisting of particles which are aggregates of approximately spherical granules	EP–GF[a] EP–GF[a]	1 2	Fibers well distributed throughout the blend; weak adhesion between glass fiber and resin

[a] GF designates glass fiber.

TABLE II
Data on the Chemical Stability of EP[a]

Chemical	Weight loss		Ultimate tensile strength (MPa)
	g	%	
Water	0.36	0.20	5.28
Air	—	—	5.12
Benzene	0.20	0.13	5.12
Acetone[b]	—	—	—
DMF[b]	—	—	—
NaCl[c] (aqueous solution)	—	—	—
CaCl_2[c] (aqueous solution)	—	—	—
Methanol	0.18	0.12	2.56

[a] Specimens similar to those used for tensile testing were immersed for 120 days at room temperature.

[b] Samples decomposed after 7 days (in DMF) and 14 days (in acetone).

[c] Adhesive bond has broken under its own weight.

(Canada) for 100 days between January and April 1982. The low and high temperatures recorded during the period were −26°C (January 26) and 22°C (April 15), respectively. Control samples were kept in the laboratory at 22°C and 20–50% relative humidity for 200 days. A detailed description of the various samples is given in Table I.

To determine the chemical stability, epoxy blends and control specimens (unmodified EP) were immersed in organic solvents and aqueous solutions of some salts for 120 days at room temperature (22°C), after which they were removed and allowed to dry for 14 days at 22°C.

RESULTS AND DISCUSSION

Morphology of Epoxy-Based Blends. Selected SEM photomicrographs are presented in Figures 1 and 2 and 4–10 to illustrate the morphology of epoxy and epoxy polymer modified by plasticizing with DBP, blending with PVC, PVA and by reinforcing with glass fibers.
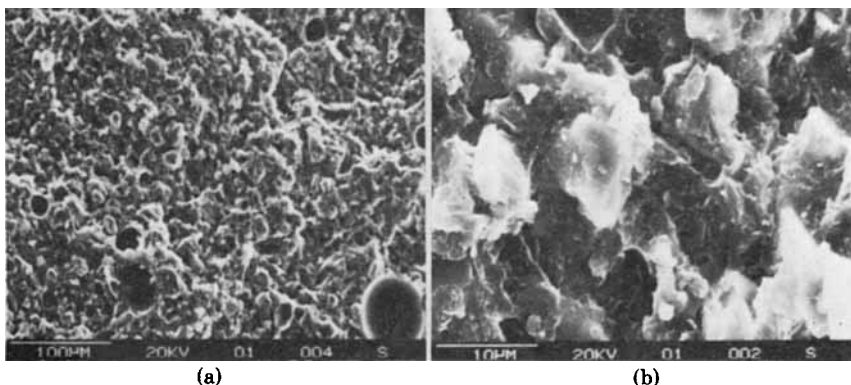

(a)   (b)
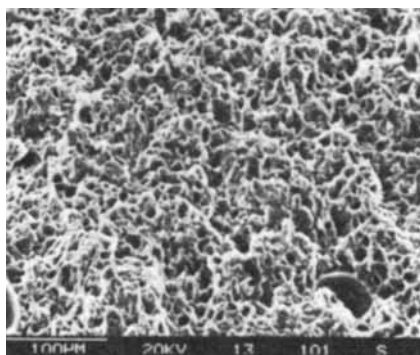Fig. 1. SEM photomicrographs of fracture surface of epoxide EP resin.

Fig. 2. Fracture surface of EP–DBP blend (10% of DBP).

Dibutyl Phthalate (DBP)-Modified Epoxy Polymer (EP). The fracture surface of unmodified and DBP-modified cured epoxy polymer is shown in Figures 1 and 2, respectively. SEM observations indicate that cured unmodified epoxy polymer is a two-phase solid. This is in agreement with literature reports in which it is shown that cured epoxy polymers consist of highly crosslinked microgell particles (micelles) embedded in a continuous phase of lower crosslink density.[13,14] In the SEM photomicrographs, these micelles are irregularly shaped and appear brighter than the continuous phase, owing to the stronger electron capture by the more highly crosslinked material and thus having a higher nitrogen content. The unmodified epoxy material contains also a very small number of voids, probably due to the presence of air bubbles introduced by stirring during mixing.

Addition of DBP plasticizer to epoxy polymer, followed by subsequent curing,
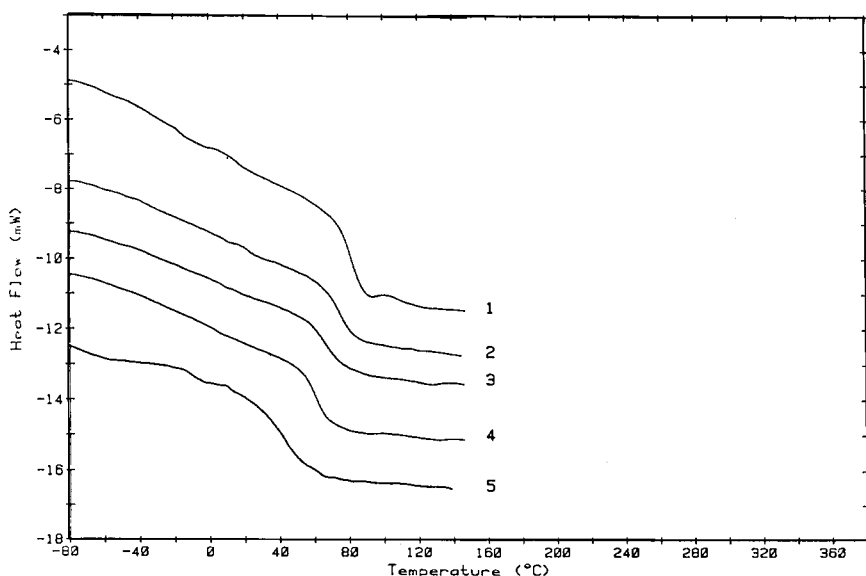
Fig. 3. DSC curves of epoxy (EP) and epoxy–dibutyl-phthalate (DBP) blends: (1) EP, (2) EP–DBP (2%); (3) EP–DBP (4%); (4) EP–DBP (6%); (5) EP–DBP (10%).
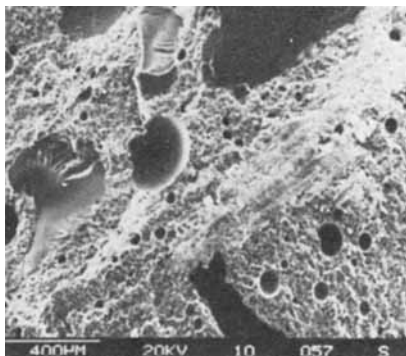
Fig. 4. EP–PVA (10% of PVA).

did not induce any significant changes in the morphology of the resulting blends. Indeed, SEM observations did not reveal the occurrence of a new phase, indicating only the occurrence of a slightly higher proportion of void. Therefore, it may be concluded that the DBP is completely miscible with the epoxy polymer system. Probably, mixing of the plasticizer occurred mostly in the continuous phase, as it has less crosslinks, and, hence, the network is less tight. Thus, the continuous phase may be more easily penetrated by the plasticizer molecules. The good miscibility of the DBP with the cured EP network was confirmed by DSC measurements. As shown in Figure 3, incorporation of DBP into the cured EP system causes a lowering of T_g from 72°C (unmodified EP) to 23°C (modified EP containing 10% DBP). Thus, for each of these blends, there is a single T_g, with values intermediate between those corresponding to the two components (72°C for EP vs. −85°C for DBP).

Poly(vinyl Alcohol) (PVA)-Modified EP. When incorporated into cured EP polymer system at a concentration of 10%, PVA occurs as a separate phase, as illustrated in the SEM photomicrographs of Figure 4; the smooth regions of the fracture surface represent cross sections of discrete particles of PVA, very similar in texture to particles of pure PVA (Fig. 5). Also, SEM observations of the fracture surface indicate that the adhesion between the two components is good. The DSC results could not be used to draw a conclusion on the miscibility
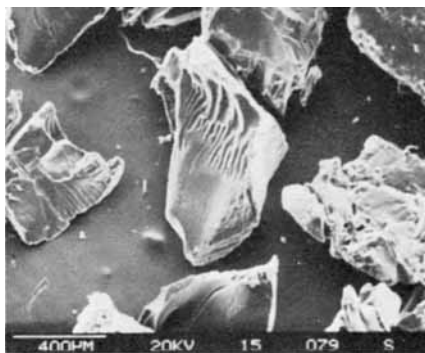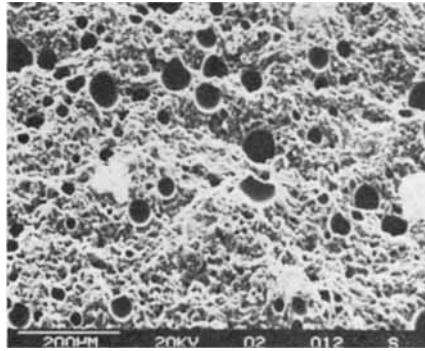

Fig. 5. PVA particles.

Fig. 6. EP–PVC (2% of PVC).

of the components, because the corresponding T_g's were not sufficiently far apart.

Poly(Vinyl Chloride) (PVC)-Modified EP. The morphology of EP–PVC blends has been assessed by SEM and energy-dispersive X-ray analysis (EDXA). In blends of low concentrations (up to approximately 10% of PVC), the PVC polymer is readily distinguishable as dispersed particles, represented in the SEM photomicrographs as white patches varying in shape and size (Fig. 6).
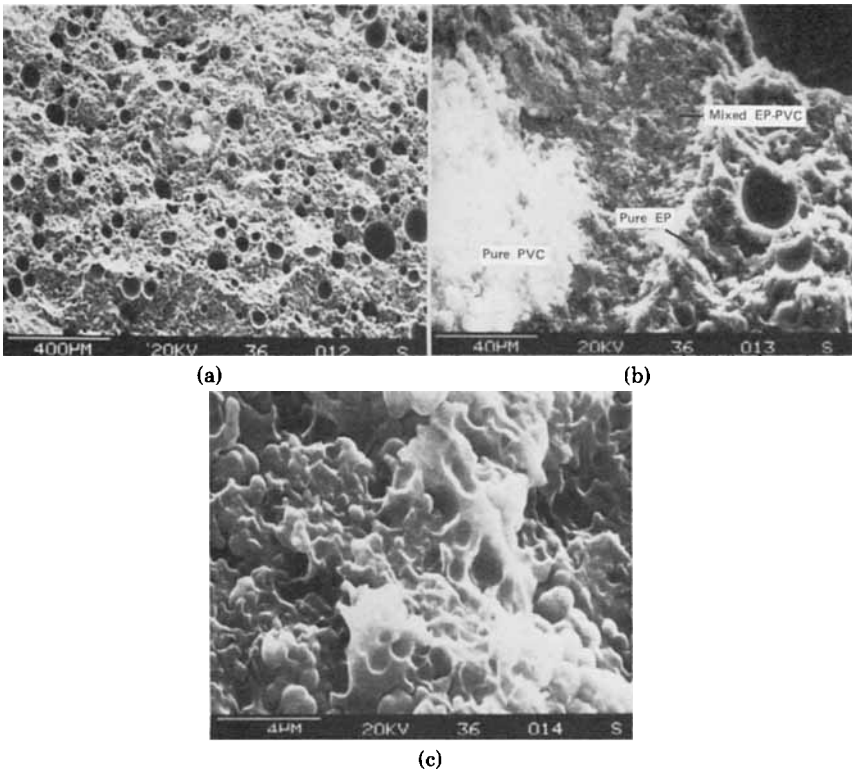

(a)   (b)

(c)

Fig. 7. EP–PVC (20% of PVC). Region of mixed polymers.
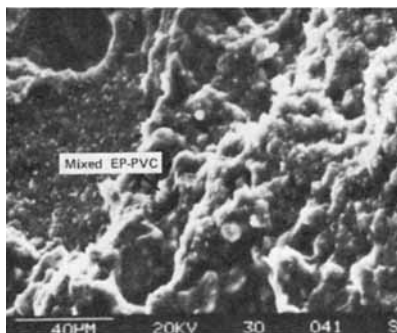
Fig. 8. EP–PVC (50% of PVC).

In blends containing between 15 and 40 per cent of PVC, three types of materials have been observed: pure PVC occurring as discrete particles [Fig. 7(a)]; a transition material consisting of PVC mixed with EP polymer and pure EP polymer [Figs. 7(b) and 7(c)]. Blends of equal proportions of EP and PVC (50%) consist of particles of PVC containing a small proportion of EP polymer surrounded by a phase of well-mixed EP and PVC (Fig. 8), and a phase of pure EP (not shown). Also, incorporation of PVC in the EP system resulted in an increased number of voids [Figs. 6 and 7(a)]. Thus, observations by SEM and results from EDXA technique indicate that EP and PVC are immiscible at lower concentrations of PVC (up to 10%), but that they become mutually and increasingly more miscible with increased concentration of the second component.

Reinforced Epoxy Resin. Reinforcing of epoxy polymer with 1% and 2% of glass fibers did not significantly change the morphology of the matrix in the resulting blends. The glass fibers were distributed relatively well. However, the adhesion between the glass fiber reinforcement and epoxy polymer was weak. Indeed, SEM examination of the surface material indicates that the fibers readily undergo "pullout" during the fracture process. The surface of the fibers is smooth and free of polymer, indicating that the cleavages of the bond between reinforcement and polymer occurred at the glass surface. This is illustrated in
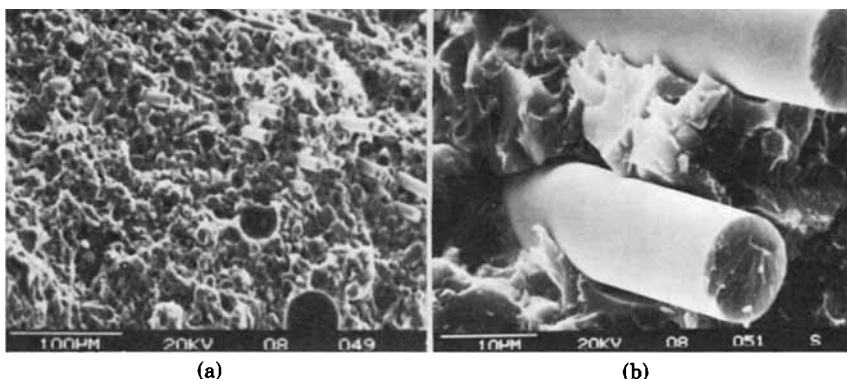

(a)   (b)

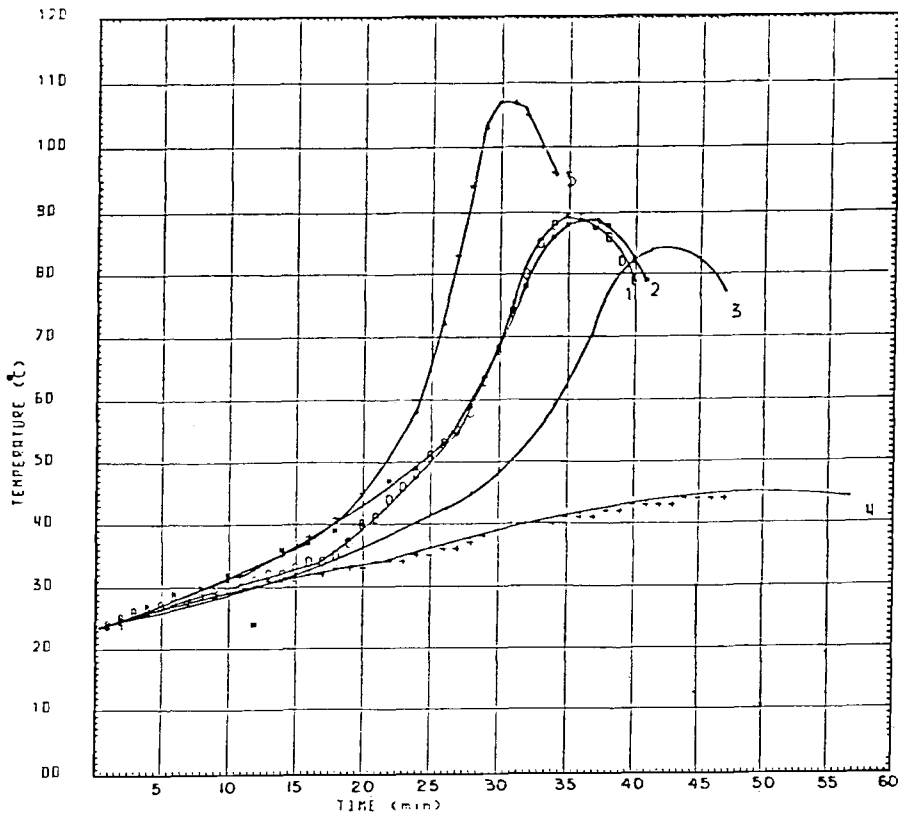Fig. 9. EP reinforced with glass fibers (2% of GF).

Fig. 10. Effect of additives on the curing temperature of epoxy resin: (1) EP, (2) EP–PVC (10% of PVC); (3) EP–DBP (5% of DBP); (4) EP–DBP (12.6 DBP); (5) EP–GF (5.6%).

Figures 9(a) and 9(b) under two different magnifications. DSC measurements indicated that the thermal behavior of cured epoxy was not affected by the presence of glass fiber reinforcement (1 or 2%).

Effect of Additives on the Curing Reaction. The effect of various additives (plasticizer, polymers, and reinforcement) on the temperature evolution during curing (crosslinking reaction) is illustrated in Figure 10. The temperature during crosslinking reaction of the unmodified epoxy polymer reaches a maximum (peak exotherm) at 90°C after 35 min. Addition of 10% of PVC to EP polymer does not have any significant effect on the temperature maximum (Fig. 10, curve 2). However, incorporation of only 5.6% of glass reinforcement causes the maximum to reach 108°C at a faster rate than in the unmodified EP (Fig. 10, curve 5), probably due to low thermal conductivity of the reinforcement that that of the polymer ($K = 0.036$ w/m·°K vs $K = 0.271$) and which acts as a thermal insulator. Addition of DBP to EP in low concentrations (5%) results in diminished rates of temperature rise (Fig. 10, curve 3). This increases the time required to reach reaction maximum (90°C). At higher concentrations of DBP (12.6%), the temperature rise of the blends is very gradual throughout the curing and does not have a maximum (Fig. 10, curve 4).
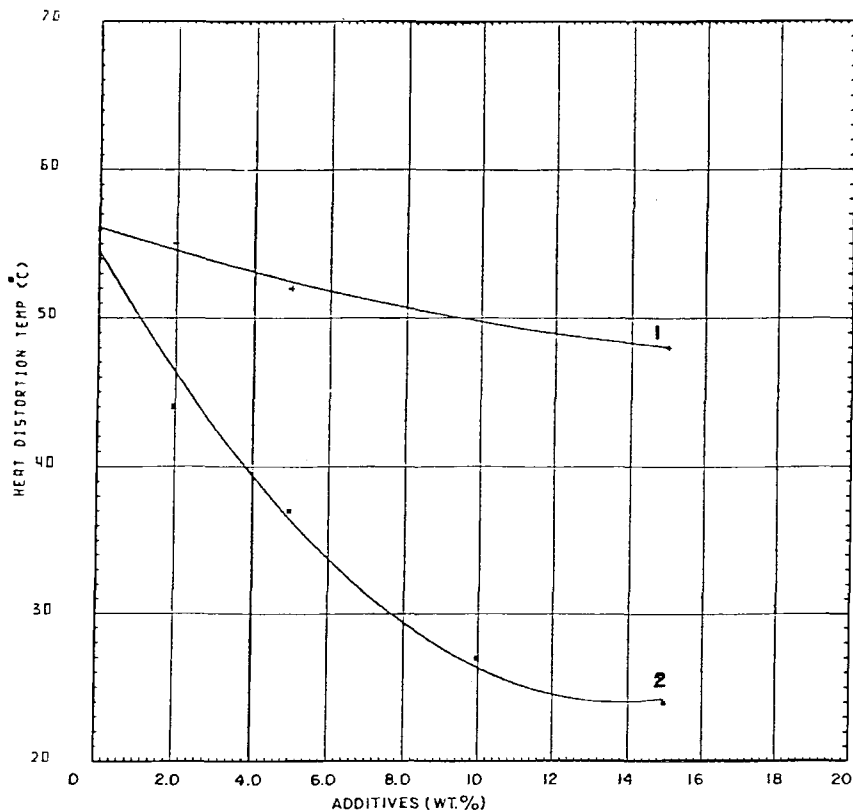
Fig. 11. Effect of additives [(1) PVC or (2) DBP] on the heat distortion temperature.

Effect of Additives on the Heat Distortion Temperature (HDT). In Figures 11 and 12 are shown plots of heat distortion temperatures (HDT) versus concentration of DBP and PVC of EP-based blends. Incorporation of DBP into EP causes a marked reduction in HDT. For example, the value of HDT decreases from approximately 55°C for unmodified EP to about 22°C for a blend containing 15% of DBP (Fig. 11). Addition of PVC to EP has only a moderate effect in decreasing HDT of the resulting blends (Figs. 11 and 12). The rate of decrease in HDT of EP–PVC blends is greater at lower than at higher PVC concentrations (Fig. 12).

Effect of Substrate on Adhesive Properties of EP. The effect of substrate on the adhesion strength of EP is illustrated in Figure 13 for three different substrate materials, namely, aluminum, redwood, and mortar. Under normal conditions, EP (unmodified) has considerably better adhesion to aluminum than to mortar or redwood substrate, as assessed by ultimate tensile test measurements. The ultimate tensile strength of specimens mounted on aluminum is 6.5 and 11.7 times greater than that of specimens bonded to mortar and redwood substrate, respectively.

Effect of Additives on the Ultimate Tensile Strength. Blends of modified EP containing small amounts of DBP (2–4 wt %) have moderately lower ultimate tensile strength (7.80–8.30 MPa) than that (9.80 MPa) of the unmodified poly-
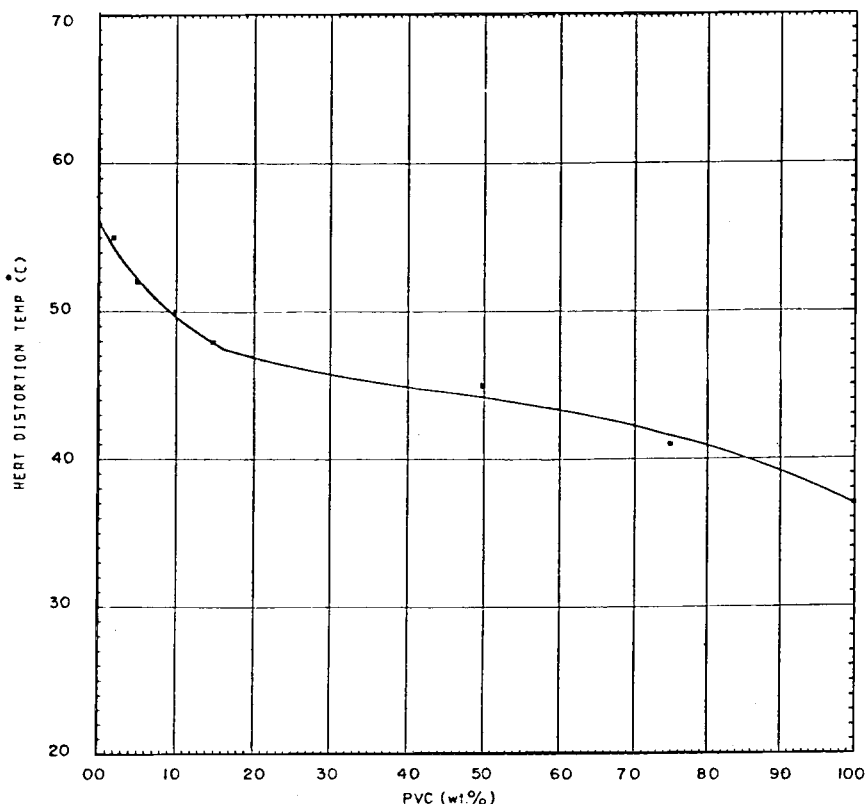
Fig. 12. Variation of heat distortion temperature with PVC concentration in EP–PVC blends.

mer. However, an increase in the concentration of DBP in the blend to 6% results in slightly higher value than that of the unmodified EP, for both the ultimate tensile strength (9.90 MPa) and strain (Fig. 14).

Incorporation of PVC into the cured EP has generally a detrimental effect on the ultimate tensile strength of the corresponding blends (Fig. 15). The tensile strength of blends containing 2–5% of PVC is only approximately 35–50% of that of unmodified EP. A concentration of 10% of PVC in the EP–PVC blend causes a reduction of 10% in the ultimate tensile strength (Fig. 15). PVA has a greater effect than PVC in causing a lowering of ultimate tensile strength of EP–PVA blends. A 10% concentration of PVA induces a reduction in ultimate tensile strength greater than 36% (Fig. 15).

Reinforcing with glass fibers (1% or 2%) caused a marked decrease in ultimate tensile strength and strain (Fig. 16). For example, the ultimate tensile strength of blends containing 1% and 2% of glass fibers is only 30% and 50%, respectively, of that of unreinforced EP.

Effect of Outdoor Exposure and the Ultimate Tensile Strength. The resistance of EP adhesive material (unmodified and modified) to outdoor exposure was assessed on sandwich specimens. Aluminum was used as a substrate, as this material was found to have a better adhesion to cured EP.

At the end of 100 days of outdoor exposure, the various specimens were tested
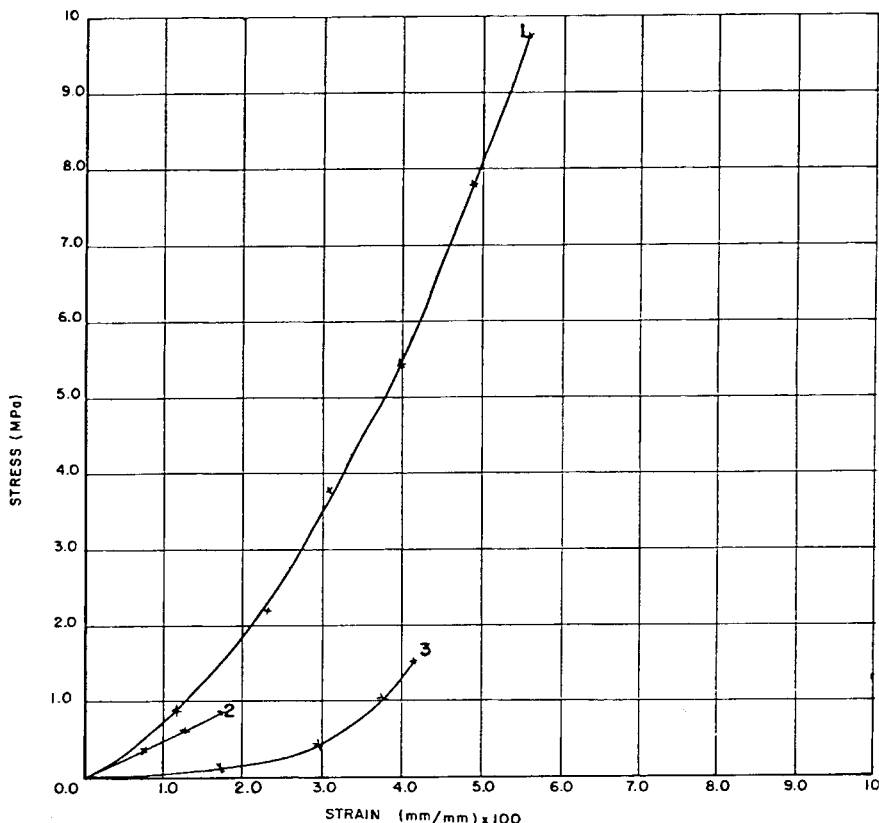
Fig. 13. Effect of substrate on the ultimate tensile strength: (1) EP and aluminum substrate; (2) EP and wood substrate; (3) EP and mortar substrate.

for ultimate tensile strength to assess the change in bond strength. Results are presented in Figure 17.

Outdoor exposure for 100 days causes a considerable deterioration in the tensile strength of unmodified EP. The exposed specimens retain only approximately 43% (curve 2) of the ultimate tensile strength of the unexposed material (curve 1). It is believed that the deterioration is caused by a cryolitic process (mechanochemical degradation as a result of freeze–thaw cycles) occurring within the epoxy network, similar to that described previously for polyurethanes[15] and occurring very frequently in the Canadian climate during March and April. It is known that freeze–thaw cycling induces the formation of localized forces, which cause the mechanical degradation of the polymer chain, resulting in a decrease of the molecular mass. For example, water, which is liquid during the warmer period of the cycle, is converted into ice crystals at the freezing temperature and thus produces considerable localized stresses as a result of its volume increase. In addition to mechanochemical degradation, EP resin may also undergo chemical degradation induced by chemical pollutants.

EP-based blends containing 6% of DBP have better resistance to deterioration by freeze–thaw cycles in outdoor exposure than unmodified resin. For example,
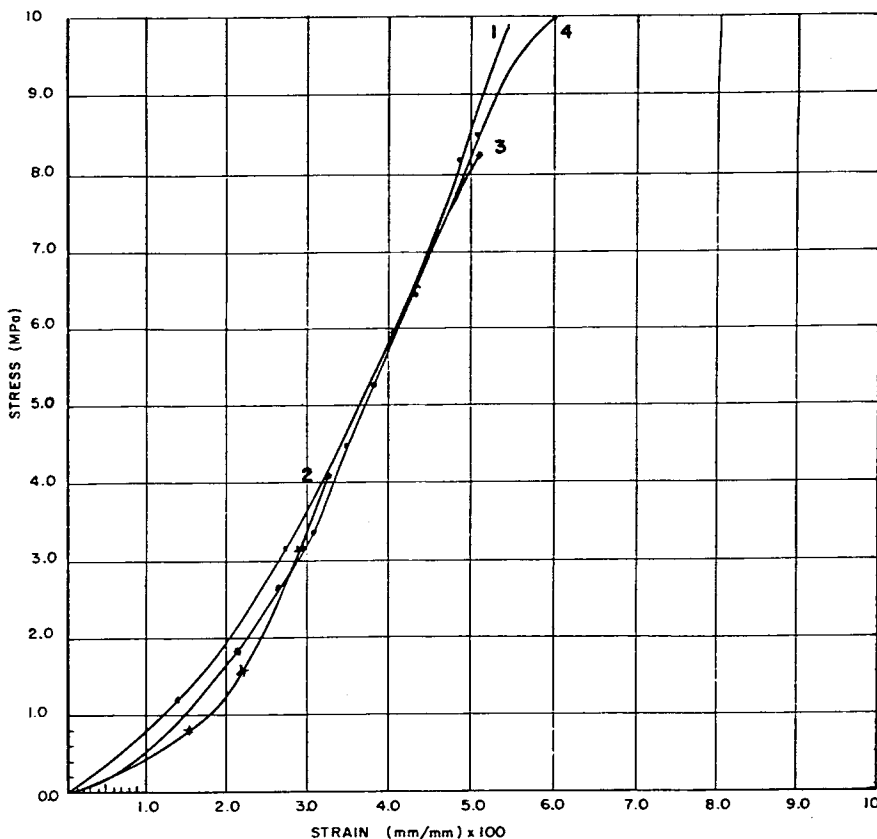
Fig. 14. Effect of DBP on the ultimate tensile strength: (1) EP; (2) EP–DBP (2% of DBP); (3) EP–DBP (4% of DBP); (4) EP–DBP (6% of DBP). Aluminum substrate.

the ultimate tensile strength of the blend at the end of 100 days of outdoor exposure (Fig. 17, curve 3) is 78% of that of the unexposed sample (control) and 1.8 times higher than that of the unmodified EP exposed outdoors under similar conditions (Fig. 17, curve 1).

The PVC-modified EP samples had slightly better resistance to outdoor exposure at low concentrations (2% of PVC) (Fig. 17, curve 4), but they underwent a marked deterioration in ultimate tensile strength with increasing concentration. The tensile strength of EP blends containing 5% and 10% of PVC (Fig. 17, curves 5 and 6) was only 36% and 29%, respectively, of the value of unexposed (control) blend.

Chemical Stability of EP. As shown in Table II, cured EP has good resistance to tap water and benzene, but it is very susceptible to deterioration by DMF, acetone and aqueous solutions of sodium and calcium chlorides. EP used in adhesion specimens, mounted on aluminum substrate and immersed for 120 days at room temperature in DMF (dimethylformamide) or acetone, decomposed after only 14 days. Immersion of similar EP specimens in aqueous solutions of either sodium chloride or calcium chloride resulted in the weakening of the adhesive bond so as to break under its own weight. Although long contact (120
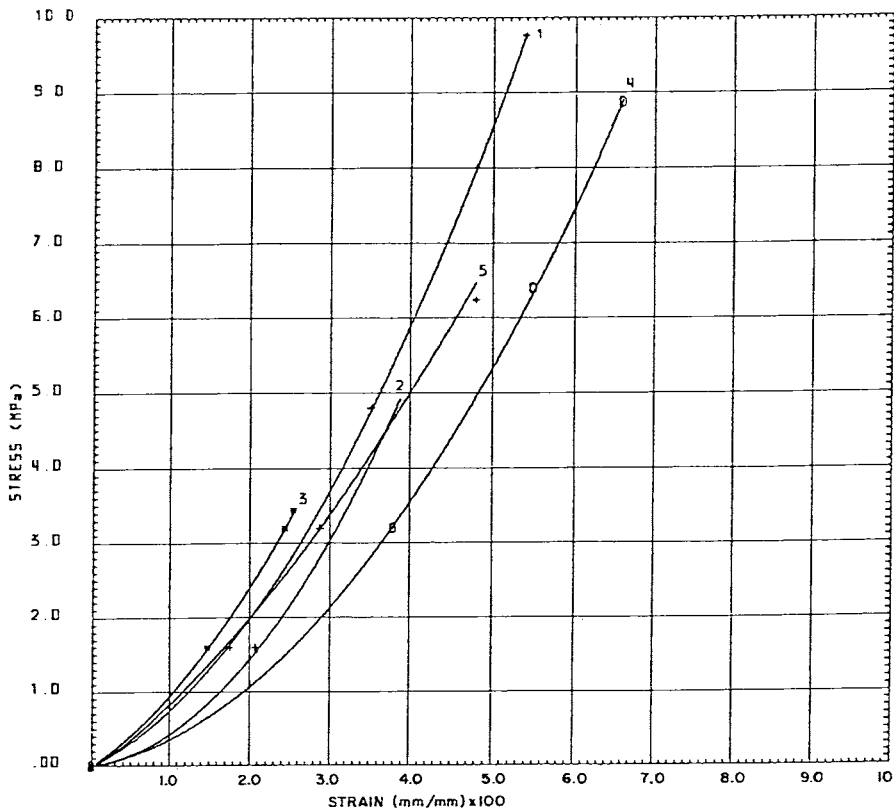
Fig. 15. Effect of PVC and PVA on the strength of EP-based blends: (1) EP; (2) EP–PVC (2% of PVC); (3) EP–PVC (5% of PVC); (4) EP–PVC (10% of PVC); (5) EP–PVA (10% of PVA). Aluminum substrate.

days) with methanol is less detrimental than the other chemicals, the EP adhesion specimens had only 50% of the ultimate tensile strength of the unimmersed (control) specimens (Table II).

CONCLUSIONS

SEM observations indicate that incorporation of DBP up to 10 wt % into the cured EP resin system does not induce any significant changes in the morphology of the resulting blends; no additional solid phase was detected. Thus, the two components of these blends are miscible in these proportions. The miscibility of EP and DBP was confirmed by DSC measurements. PVA added to EP in a concentration of 10 wt % occurs as a separate phase, but the adhesion of the two components in the corresponding blends is good. The DSC measurements could not be used to determine the miscibility, as the glass transition endotherms of the two components overlapped.

The morphology of EP–PVC blends is relatively complex. Observation by both SEM and energy dispersive X-ray analysis indicates that the EP and PVC
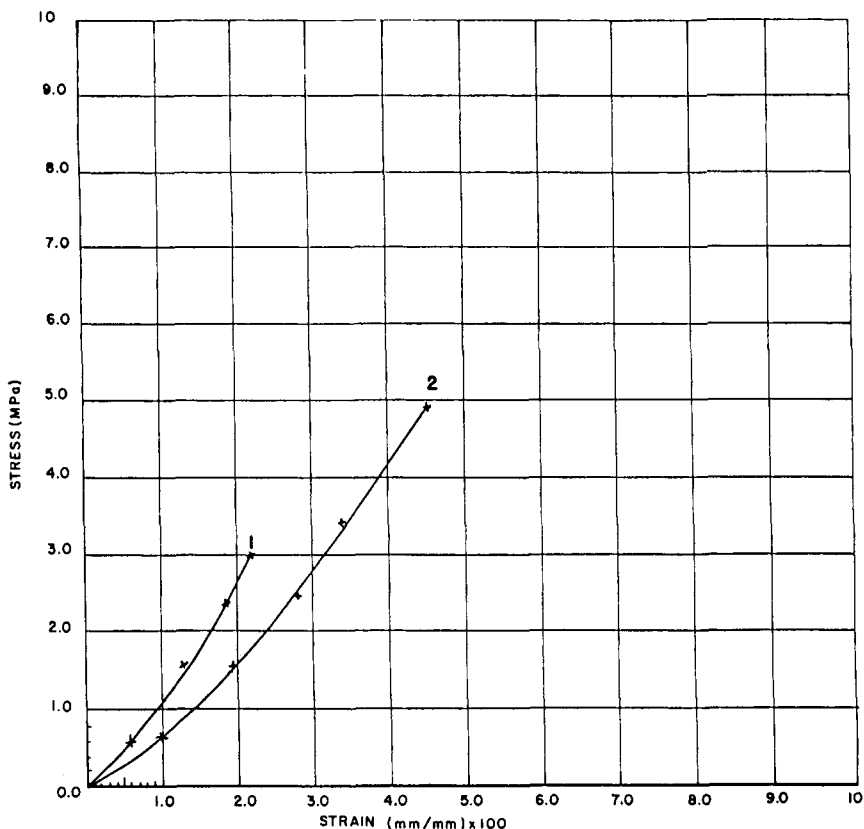
Fig. 16. Effect of glass fiber (GF) reinforcement on the ultimate tensile strength: (1) EP–GF (1% of GF); (2) EP–GF (2% of GF).   Aluminum substrate.

are immiscible at lower concentrations of the second component (up to 10%), but that they become mutually and increasingly more miscible as the concentration of PVC becomes higher.   Reinforcing with glass fibers (1% or 2%) did not change the morphology of the resulting blends.   Adhesion between glass fibers and epoxy matrix was relatively weak, as evidenced by the occurrence of "pullouts" in the fracture surface.

Incorporation of DBP into EP causes a marked reduction in the heat distortion temperature.   Addition of PVC to EP has generally a moderate influence in lowering the heat distortion temperature, this effect being much smaller at higher than at lower PVC concentrations.

Modification of EP by blending with PVC, PVA, and DBP in small concentrations (up to 4% of DBP) does not result in improvement of mechanical properties or better weatherability of the products.   The deterioration of mechanical properties of EP and modified EP blends by outdoor exposure in the Canadian climate is believed to be caused by a cryolitic process.   However, slight improvement in mechanical properties and in weatherability was found for EP blend containing a higher concentration of DBP (6%).   Cured EP has good chemical resistance to drinkable water and benzene; it has low stability in
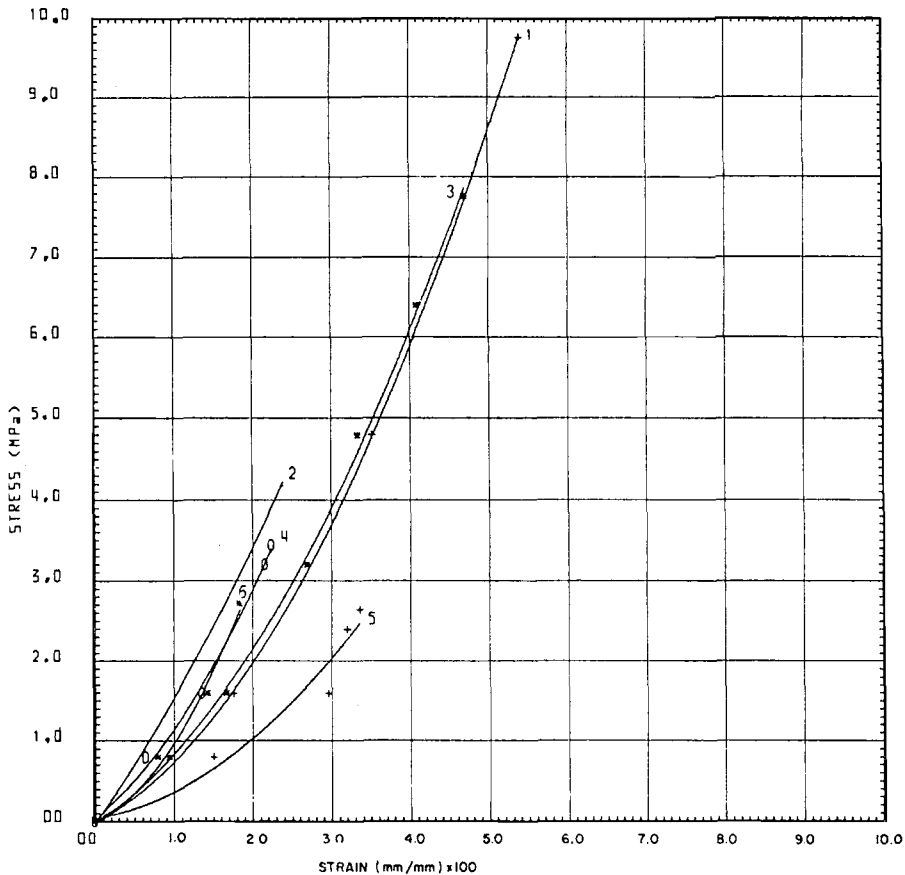
Fig. 17. Effect of outdoor exposure on the ultimate tensile strength of EP and EP-based blends: (1) EP (control); (2) exposed EP; (3) EP–DBP (6% of DBP); (4) EP–PVC (2% of PVC); (5) EP-PVC (5% of PVC); (6) EP-PVC (10% of PVC). Aluminum substrate.

methanol, and it is highly susceptible to deterioration in DMF, acetone and aqueous solutions of sodium and calcium chlorides.

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