Property - Structure Relationships in Epoxy Resin Systems

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ABSTRACT

An investigation is conducted into some of the properties of epoxy resin formulations. Diglycidyl ether of bisphenol A epoxy resin is cured with an amine, an anhydride/catalyst and a polyamide as curing agents. Water absorptions of the cured resins are compared with each other. The chemical resistance of cured epoxy/diethylene triamine and epoxy/polyamide systems is studied in acetone, sulphuric acid and sodium hydroxide solutions. The properties of epoxy/polyamide system show similar trend in comparison with epoxy/diethylene triamine system but they are different in magnitudes. Thermal oxidation of cured epoxy/diethylene triamine system is studied by measuring the carbonyl group formation index. Water absorption of the oxidized resin showed some differences from the unoxidized sample.

INTRODUCTION

Epoxies are utilized by the aerospace and marine industries primarily in the form of materials for composites and as adhesives. A number of studies have indicated that the absorbed moisture under service conditions can cause significant changes in the mechanical properties of these materials. A thorough literature survey indicates that, for most neat as well as the graphite fibre-reinforced epoxy resins, the rate of moisture diffusion is adequately described by Fick's second law of diffusion or Fick's law with a constant diffusion coefficient [1]. The absorbed moisture plasticizes the epoxy resin with a resultant depression in the glass transition temperature. Several research studies [2,3] have used the equations based on the free volume concept [4] or classical thermodynamics [5] to pre-

dict the extent of plasticization of neat and reinforced epoxy resins. However, it has been pointed out that these predictions are questionable [6,7], or only qualitatively applicable, with the condition that the higher the crosslink density, the more accurate the equation [3].

The crosslinked network structure, involving hydrophilic groups, such as hydroxyl groups, is expected to have water uptake. One of the objectives of this study is to confirm the hydrophilic character of the crosslinked polymer and as well as the effect of initial stages of thermal oxidation on water absorption. Kinetics and mechanism of epoxy/dodecylsuccinicanhydride and epoxy/polyamide systems have been described in an earlier publication [8]. The understanding of the mechanism and kinetics of cure reactions are the first essential step in the evaluation of processing-

Table 1. Chemical structure of epoxy resin and curing agents.
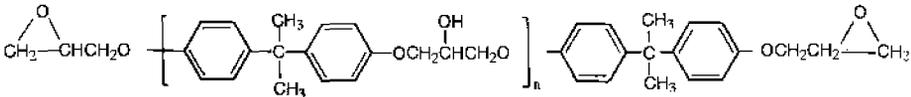
Typical diglycidal ether of bisphenol A (DGEBA) resin

$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$
Diethylene triamine (DETA) curing agent
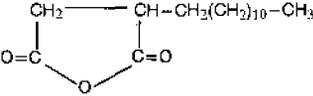
Dodecyl succinic anhydride (DDSA) curing agent
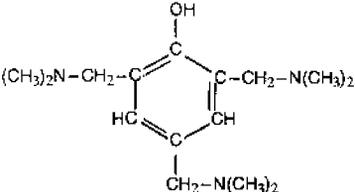
2,4,6-Tris(dimethylaminomethyl)phenol (DMP-30) as a catalyst
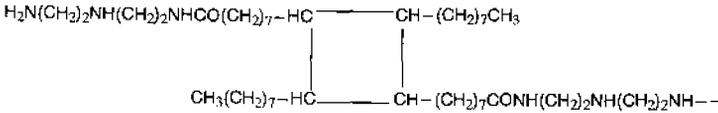
Polyamide curing agent

morphology-property relationships of the thermosets and their composites [9].

EXPERIMENTAL

Materials
Epon 828, Shell's liquid diglycidyl ether of bisphenol A (DGEBA) epoxy resin with the epoxy equivalent of 170 was used in this study. Diethylene triamine (DETA), dodecylsuccinic anhydride (DDSA) and a polyamide were used as curing agents and tris(dimethylaminomethyl) phenol (DMP-30) was used with DDSA as a catalyst. The curing agents, catalyst, and other chemicals were supplied by Fluka. Chemical structures of the epoxy resin and curing agents are shown in Table 1.
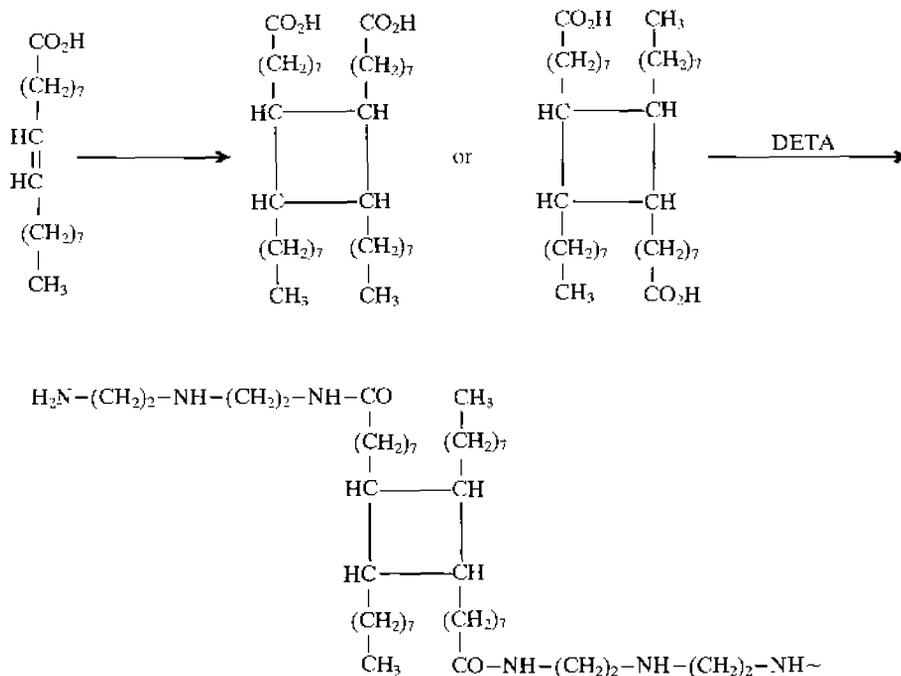
Scheme I

Synthesis

The polyamide curing agent was synthesized from a known procedure [10]. A mixture of 10 mg oleic acid and 0.1 g aluminium chloride was heated at 110 °C in a three-necked round bottom flask under nitrogen atmosphere for 1 h. A yellowish viscous liquid obtained in which distinct IR absorption bands of oleic acid at 960–970 cm⁻¹ and 1295–1310 cm⁻¹ related to C–H bending of unsaturation disappeared. There is an absorption at 1720 cm⁻¹ which relates to carbonyl group. The amount of 1.61 g of the viscous liquid and 0.53 g of DETA were mixed and heated at 60 °C in a flask under nitrogen atmosphere for 2 h. A yellow liquid product was obtained with absorptions at 1580 and 1480 cm⁻¹ which are related to the amide

(–CONH–) linkage and N–H bending, respectively. Scheme I shows the reactions and proposed structure of the product which was directly used as curing agent.

Different oligomers were formed according to the above reaction and the product was used as curing agent without further purification.

These curing agents are aminopolyamides, produced from the reaction of dimerized fatty acids with polyamides. From the simplified structure of the polyamide, it can be seen that it contains not only amide but also primary and secondary amino groups, and it is the latter which is responsible for the curing reaction. In fact, the polyamides available commercially are complex mixtures of substances containing additionally free carboxyl

groups and ring structures [11,12]. They are not unpleasant to handle, and are compatible with the resin and their mixing ratios are not critical [11]. We have used several concentrations of the polyamide with the resin to study their effects on the cure rate [8], and one of the concentration, 50 phr, was used for water absorption and chemical resistance tests.

Sample Preparation

Samples for water absorption and for chemical resistance tests were prepared as follows [8]: three mixtures of 1.70 g Epon 828/0.30 g DETA; 1.00 g Epon 828/0.30 g DDSA/0.05 g DMP-30; and 1.00 g Epon 828/0.5 g polyamide were each mixed thoroughly and the subsequent curing took place at room temperature for a week. Water absorption tests were conducted in distilled water and in a 10% solution of salt as well.

Chemical resistance tests were carried out in acetone, 50% solution of sodium hydroxide and 30% solution of sulphuric acid.

Possessing molecular weight of 103 and five active hydrogen atoms per molecule, DETA should be used at a concentration of about 12 phr with the liquid resin for stoichiometric value to be obtained. We have used 15 phr DETA for compensation of weighing errors and evaporation. DDSA was used at 30 phr in the presence of 5 phr DMP-30 [11]. Samples of the same size were used for water absorption and chemical resistance tests. All the measurements were made at room temperature and before weighing the surface of the sample was dried by a clean tissue.

One drop of viscous mixture of epoxy resin and DETA hadener on KBr pellet was cured at room temperature and thermal oxidation was followed by measuring carbonyl absorption at 1720 cm^{-1} during heating in an oven at 150 °C. Water absorption of oxidized sample was measured in distilled water.

RESULTS AND DISCUSSION
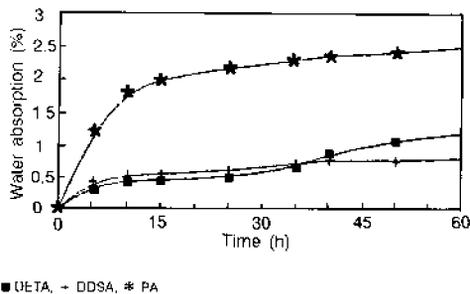
Figure 1, shows the water absorption for three

■ DETA, + DDSA, ✱ PA

Figure 1. Water absorption of cured epoxy resin at 25 °C in distilled water.

cured epoxy resins under investigation. As it is seen, the water absorption of the two cured systems with DETA and DDSA is the same whereas the water absorption of the resin cured with polyamide is almost 5 times higher. This could be due to the presence of more hydrophilic groups in the chemical structure of polyamide. The primary goal of this study was to describe the interactions between the absorbed moisture and the epoxy network. The transport of moisture through the epoxy network involves cooperative motion of water molecules and the 3-dimensional resin network. The equilibrium water absorption of Epon 828/DETA and Epon 828/DDSA systems was almost 0.6% and 1% by weight, respectively, while that of Epon 828/polyamide system was 2.5% by weight. These support the view that one of the major factors affecting water absorption is the presence or absence of hydrophilic groups in the crosslinked network. However, there are other relevant factors to consider, notably free volume, which generally increases with crosslink density because of the development of a rigid macromolecular framework. Figure 2 indicates the water absorption of the two Epon 828/DETA and DDSA systems in 10% salt solution. In comparison with the results in Figure 1, the water absorption is lower and it also shows that the water absorption of a cured resin/hardener system varies slightly from one sample to another.
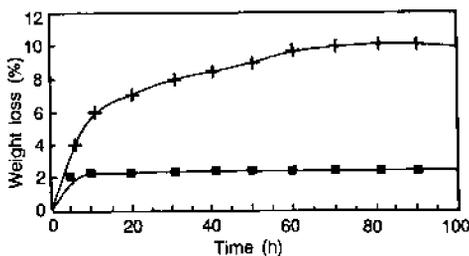
Figure 3 compares the chemical resistance of the two systems, Epon 828/DETA and Epon
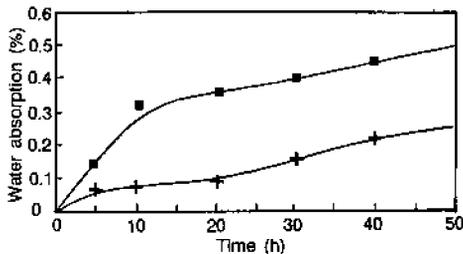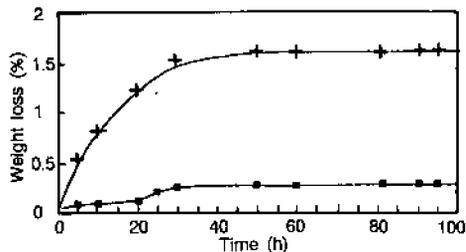
■ DETA,+ DDSA.

Figure 2. Water absorption of cured epoxy resin at 25 °C in 10% salt solution.

■ DETA, + PA.

Figure 4. Chemical resistance of cured epoxy resin in 50% NaOH solution at 25 °C.

828/polyamide, in acetone. As it is seen, Epon 828/ polyamide system shows a much higher reduction in weight and this can be due to the presence of some unreacted starting materials and/or by-products formed during synthesis of polyamide which are washed out of the resin by acetone. The polyamide curing agent was used as was prepared without any purification. It can be suggested that since the functionality of polyamide is high, the free volume increases with increasing crosslinking density. The more complex network structure in epoxy resin/polyamide system the longer it takes for acetone to diffuse in and it reaches an equilibrium after about 80 h immersion. Figure 4 shows the chemical resistance of both systems in 50% solution of sodium hydroxide. In this case the weight reduction is noticed and it is more pronounced with epoxy resin/polyamide system. This can also be due to the presence of some

unreacted materials in polyamide which are washed out into the water phase. Figure 5 shows the chemical resistance of the two systems in 30% solution of sulphuric acid. As it is seen, here we have a weight gain and this can be due to the reaction of unreacted amine groups with sulphuric acid. Because of the existance of more amine groups in polyamide, there is a sharp increase in weight gain in first 10 h of immersion. An investigation of the reaction was carried out to determine whether oxidation had occurred. The IR spectra of heat-aged and virgin samples were obtained by curing thin films of the polymer onto a KBr pellet, recording the IR spectra, and then heating the films at 150 °C in a circulating air oven. The principal difference after heat ageing was the appearance of a new peak at 1720 cm^{-1}, presumably caused by the oxidation of benzyl ether groups to phenyl benzoate type structures.
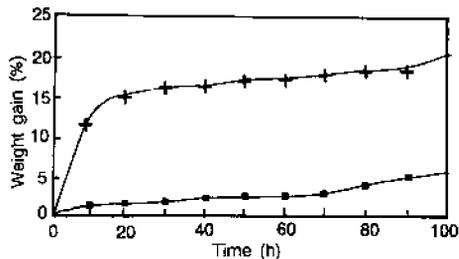

■ DETA, + PA.

Figure 3. Chemical resistance of cured epoxy resin in acetone at room temperature.

■ DETA, + PA.
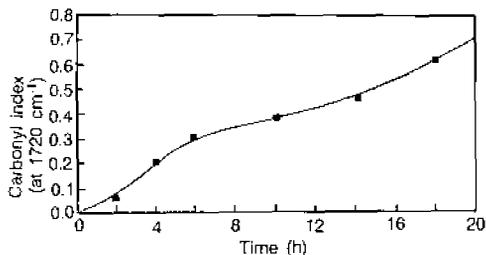
Figure 5. Chemical resistance of cured epoxy resin in 30% H$_2$SO$_4$ solution at 25 °C.

Figure 6. Thermal degradation of cured epoxy resin at 150 °C.

Figure 6 shows the increase in carbonyl index which is calculated by using an ether absorbance band at 1200 cm^{-1} as a reference. This latter peak is constant during thermal oxidation. There is also a slight weight reduction (1.5%) in Epon 828/DETA system during thermal oxidation at 150 °C after 22 h. Weight reduction for Epon 828/polyamide system is almost 15% at 150 °C after 20 h. These results also show that resin/polyamide system contains some products which are not involved in the formation of the network structure.

The oxidation of methylene groups to ketonic ones is well known [13]. The oxidation of ethers to produce hydroperoxides and finally peroxides is widely attributed to the formation of a hydroperoxide on the methylene group, followed by decomposition to ketonic species. The ketonic group can be oxidized further with chain cleavage to an acid and a diketonic species. It is proposed, however, that the initial stage of oxidation involves proton abstraction by radical species from the labile methylene ether group, followed by the addition of oxygen to form a peroxide radical. This can abstract a proton from another benzyl ether group or methylene group to form a hydroperoxide and an oxidizable radical R that can re-enter the cycle, as shown in Scheme II.

The hydroperoxide and the peroxide are both thermally unstable. On decomposition they produce RO and hydroxyl radicals which can further enter the auto-oxidation cycle. The hydroxyl radicals readily abstract protons to form water, i.e.,

$$\dot{O}H + RH \longrightarrow H_2O + \dot{R}$$

and again a reactive radical species is produced. The breakdown of peroxy radicals to yield ester groups and hydroxyl radicals is another alternative mechanism (Scheme III).

Prolonged heating of the polymer in air would, therefore, introduce hydrophilic carbonyl groups and promote chain cleavage, with the emission of water (Scheme IV).

Figure 7 shows water absorption of cured resin with DETA system before and after thermal oxidation at 150 °C for different lengths of time. As can be seen, the difference in water absorption is not very significant.

CONCLUSION

The results show that the water absorption of epoxy/polyamide system is almost 5 times higher than that of epoxy/DETA system. The water absorption of the two cured systems with DETA and DDSA is the same. The higher water absorption of epoxy/polyamide system can be due to the presence of more hydrophilic groups in this system. As the diffusion of a liquid into a network structure is a cooperative motion of liquid molecules and the three-dimensional structure, the higher the crosslinking density the higher will be the free volume and the longer it will take for acetone to diffuse in the epoxy/polyamide network. The study of chemical resistance of the epoxy systems shows that the amine type curing agents gain weight in
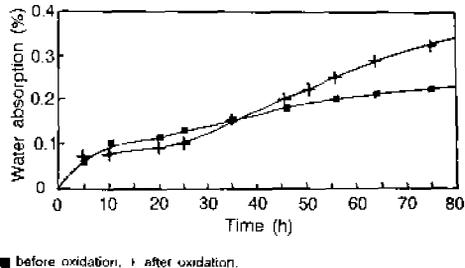
■ before oxidation, + after oxidation.

Figure 7. Water absorption of cured resin/DETA system before and after thermal oxidation.

$$ph-C(CH_3)_2-\underset{\text{(ring)}}{}-OCH_2-\underset{\underset{OH}{|}}{CH}-CH_2\sim \; + \; \dot{R} \longrightarrow RH +$$

$$ph-C(CH_3)_2-ph-O-\dot{C}H-\underset{\underset{OH}{|}}{CH}-CH_2\sim$$

$$\underset{ph-C(CH_3)-ph-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2\sim}{\overset{\dot{C}H_2}{\overset{|}{\,}}}$$

$$ph-C(CH_3)_2-ph-O-CH_2-\underset{\underset{OH}{|}}{\dot{C}}-CH_2\sim$$

$$ph-C(CH_3)_2-ph-O-CH_2-\underset{\underset{OH}{|}}{CH}-\dot{C}H\sim$$

$$\xrightarrow{O_2} \; ph-C(CH_3)_2-ph-O-\underset{\underset{H\;\;OH}{|\;\;|}}{\overset{\overset{O-\dot{O}}{|}}{C}}-CH-CH_2\sim \qquad \xrightarrow{RH}$$

$$ph-C(CH_3)_2-ph-O-\underset{\underset{H\;\;OH}{|\;\;|}}{\overset{\overset{O-OH}{|}}{C}}-CH-CH_2\sim \longrightarrow \dot{O}H + ph-C(CH_3)_2-ph-\dot{O} + HOC-\underset{\underset{OH}{|}}{CH}-CH_2\sim$$

<center>Scheme II</center>

$$ph-C(CH_3)_2-ph-O-\underset{\underset{OH}{|}}{\overset{\overset{O-OH}{|}}{CH}}-CH-CH_2\sim \longrightarrow \dot{O}H + ph-C(CH_3)_2-ph-O-\underset{\underset{H\;\;OH}{|\;\;|}}{\overset{\overset{O}{|}}{C}}-CH-CH_2\sim$$

<center>Scheme III</center>

$$ph-C(CH_3)_2-ph-O-\underset{\underset{OH}{|}}{\overset{\overset{O-OH}{|}}{CH}}-CH-CH_2\sim \longrightarrow H_2O + ph-C(CH_3)_2-ph-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{C}}-CH-CH_2\sim$$

<center>Scheme IV</center>

acids such as sulphuric acid which could be due to chemical reaction between the acid and amine.

Thermal oxidation of epoxy system at high temperature shows the gradual development of a dark colour accompanies the formation of carbonyl group at 1720 cm^{-1} band. For the time and temperature of oxidation used in this experiment, the water absorption showed a slight increase in comparison with the unoxidized sample.

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