Investigation of Polyamine Quinones as Hydrophobic Curatives for Epoxy Resins

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SYNOPSIS

Polyamine quinones (PAQs), which have been used previously to produce solvent-based coatings with exceptional durability in corrosive environments, were synthesized and blended with an aliphatic diamine (diethylenetriamine, DETA) to provide a liquid, epoxy curing agent. The PAQ–amine mixture was evaluated as a curing agent for an epoxy matrix resin system for glass-reinforced composites. After elevated temperature water exposure, short-beam shear and dynamic mechanical analyses were performed on the composites. The ability of PAQs to enhance fiber–resin bonding was evaluated. Dynamic mechanical analysis (DMA), which is a sensitive measurement of fiber–resin interactions, showed that the PAQ curative enhances strength retention of composites exposed to aggressive environments. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Erhan et al. pioneered much of the work with polyamine quinones (PAQs) by showing that these polymers have a great affinity toward metal and glass surfaces and are active enough to displace water from wet, rusted, steel surfaces.[1-3] The apparent mechanism for adhesion of these polymers occurs through chemisorption, mediated by the quinone and imino moieties. A similar mechanism of adhesion has also been suggested for the highly durable bioadhesives used by barnacles and mussels. The PAQ polymers developed thus far have been solid materials that are typically dissolved in an appropriate solvent for coatings applications. The PAQ is capable of cross-linking on heating alone, although compounding with epoxies or other amines has produced more durable coatings. Epoxy resins can react with PAQs providing toughness without diminishing the mechanical characteristics of the epoxy resin.[3]

During the 1920s, reactions between p-benzoquinone and amines were studied. This initial research resulted from the extensive use of quinone in tanning processes during this time.[4,5] Model studies were performed with several amines and quinones in order to discern the phenomenon of barnacle adhesion, where an amine–quinone reaction also occurs.[6] Figure 1 shows the proposed reaction of a diamine with benzoquinone yielding a PAQ polymer.[1-3]

In an effort to improve water-resistant characteristics of the PAQ polymers, Erhan also investigated several aromatic polyamines as starting materials. The aromatic polyamines investigated included 1,3-bis(3-aminophenoxy)-benzene, 4,4'-diaminodiphenylmethane (DADM), 3,3'-diaminobenzidine, and tetraminopyridine. The polymer produced from the first compound had lower moisture uptake than processable aromatic polyimides (0.1% w/w) while being unwettable by water. The DADM–benzoquinone polymer was a brown powder having a melting point of 178°C. Water absorption of the product was 0.34% after 48 h and 0.46% after 72 h.[2] Attempts at developing polymeric coatings with increased saltwater resistance led researchers to trials of the reaction product of PAQ polymers and epoxy resins. The addition of 1.5 mol of epoxy per mole of PAQ repeat unit (polyetheramine based) yielded a product with outstanding saltwater resistance.[3]

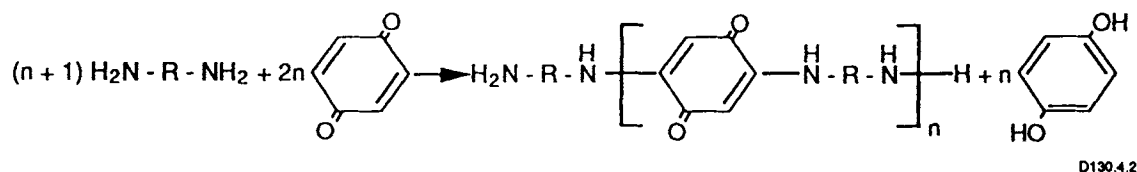* To whom correspondence should be addressed.

Figure 1   Reaction of a diamine with benzoquinone yielding a PAQ polymer.

The goal of the work that follows was based on the speculation that PAQs might enhance the adhesion of epoxy matrix resins in glass-fiber-reinforced composites. The purpose of this work has been to develop a liquid, epoxy curing agent with PAQ incorporated without the use of solvents. Although solvent-containing impregnation resins are often used for the preparation of preimpregnated reinforcements, our objective was to develop a more versatile solvent-free curative. Thus, in this work, several PAQs were synthesized and blended with an aliphatic diamine (diethylenetriamine, DETA) to provide liquid, epoxy curing agents. The PAQ–amine mixture was then used as a curing agent for an epoxy matrix resin system for glass-reinforced composites. After elevated temperature water exposure, mechanical analyses were performed on the composites. The ability of PAQs to enhance fiber–resin bonding was evaluated.

EXPERIMENTAL

Synthesis of PAQ Compounds

The PAQ synthesis was performed by dissolving 0.08 mol of diamine in 150 mL ethanol in a 500-mL reaction vessel equipped with a mechanical stirrer. To this solution 0.12 mol of p-benzoquinone was slowly added. After heating the mixture at reflux for 4 h, the ethanol was removed on a rotary evaporator. The syrup was poured into cold water to precipitate the product. This material was dissolved in acetone then washed with cold water, followed by hot water. The dissolving and reprecipitating purification procedure was repeated until the wash water was colorless. The product was then dried in a vacuum oven for 6 h.

Preparation of PAQ-Liquid Amine Blends

An amine blend containing PAQ was prepared by heating DETA to 60°C followed by adding the PAQ product, which resulted from the reaction of polyetherdiamine and benzoquinone. This mixture was found to be stable with no precipitation for up to 6 months at room temperature. It was designated as PAQ-E1—the solid product from the reaction of a polyetherdiamine (Jeffamine D-230 supplied by Texaco Chemical Corp.) and benzoquinone (2 : 3), dissolved in DETA at a concentration of 20% by weight.

Specimen Preparation and Characterization

Glass-reinforced epoxy composites were prepared for short-beam shear strength and dynamic mechanical analysis using five plies of a woven glass cloth with a weight of 6 ounces per square yard and 18 strands per inch. The sizing treatment on the reinforcement as received was removed by heating to 600°C for 1 h. The composites were then fabricated by a hand lay-up process. Neat specimens were cast in an aluminum mold. Epon 828 (EEW = 188) epoxy resin, supplied by Shell Chemical Company, was used for preparation of both neat and composite specimens. This resin was cured with either PAQ-E1 or DETA.

The stoichiometry used for the DETA-cured specimens was 11 parts DETA to 100 parts epoxy. The stoichiometric ratio used with the PAQ-E1 curing agent was 13 parts to 100 parts epoxy resin. The cure cycle for both neat and composite specimens was 24 h at room temperature followed by 2 h at 200°C.

Differential scanning calorimetry (DSC) was used to characterize the curing behavior of PAQs with epoxy resin in both the neat and blended (PAQ-E1) form. These tests were performed with a DuPont 9900/912 instrument. The curing agents were mixed with epoxy resin and allowed to cure at room temperature overnight. The DSC analysis was then performed on the material in order to determine residual exotherm behavior. The heating rate was 10°C per minute.

Fourier transform infrared (FTIR) analysis was performed to determine the relative conversion of epoxide in the presence of the pure PAQ product and the PAQ-E1 blend. These determinations were made with a Nicolet SX-20 spectrophotometer. A

thin film specimen was scanned 32 times in the transmission mode. Resolution was 2 cm^{-1}. The absorption band at 915 cm^{-1} was observed at three stages of the curing reaction: initially after mixing the epoxy with amine, and at two additional times during the cure. By observing this absorption band, which is associated with epoxide functionality, the extent of conversion was determined.

Water absorption was performed on both neat and composite specimens. Replicate specimens of each type were exposed to deionized water at 25°C. Weight gain was monitored as a function of exposure time.

Dynamic mechanical analysis (DMA) was performed at room temperature on composite specimens in order to ascertain the degree of matrix–fiber bonding. The instrument used for this analysis was a DuPont 9900/983. The dynamic shear loss modulus, G'', and tan δ, were measured before and after exposure of the specimens to deionized water at 70°C. Measurements were made at room temperature over a range of 0.25–2.0 Hz. Investigations into the use of DMA for characterization of a fiber-glass–polyester interphase showed that energy dissipation, measured in terms of tan Δ was affected by the type of silane coated on the glass fiber.[7] Kennedy et al. recently reported that DMA tests readily detected the difference in fiber–matrix bonding of PAN-based and pitch-based fibers. The results also indicated an ability to isolate fiber–matrix interface effects from matrix and fiber effects using DMA.[8] During deformation, a composite material with poor interfacial bonding will likely dissipate more energy than the same composite with good interfacial bonding. Therefore, decreases in the adhesion between fiber and matrix should be evidenced by an increase in the values of the loss shear modulus G'' and tan δ.

A variation of ASTM Test Method for Apparent Horizontal Shear Strength of Reinforced Plastics by Short-Beam (D2344) was also used to evaluate fiber–resin adhesion. Because of complex, nonshear related stresses, resulting in multiple failure modes,

the short-beam shear test is used primarily for approximating interfacial interply adhesion. Failure may either be at the fiber–matrix interphase or exclusively within the matrix. Failure within the matrix is evidence that the interphase is stronger than the matrix. A span to thickness ratio of 5 was used with a sample thickness of 1.4 mm and a width of 11.5 mm. Crosshead speed during the test was maintained at 1 mm/min.

RESULTS AND DISCUSSION

Several PAQ materials were synthesized, including those resulting from the following precursors: 1,3-diaminocyclohexane, bis (para-aminocyclohexyl) methane, and a polyetherdiamine (Jeffamine D-230®). The products resulting from the first two precursors were found to have limited solubility (5% by weight) in aliphatic diamine curing agents such as DETA.

The PAQ product resulting from the polyetherdiamine had a much higher solubility, up to 20% by weight in DETA. This blend was used for further evaluation as an epoxy curing agent. Figure 2 depicts the molecular structure of the PAQ product from the reaction between the polyetherdiamine (D-230) and benzoquinone.

The n value in the structure in Figure 2 is, of course, a result of the degree of polymerization of the polyetherdiamine starting material. For the 230-g/mol material used here, n has an average value of 3.4. The m value is the degree of polymerization during the reaction between the polyetherdiamine and the benzoquinone. This value is difficult to determine either theoretically or experimentally. The value of m has an influence on the epoxy reaction stoichiometry. Consequently, an evaluation was conducted of the effect of changes in PAQ molecular weight (caused by changes in the degree of polymerization, m) on the amine equivalent weight (AEW) of the blend. Since the secondary amines
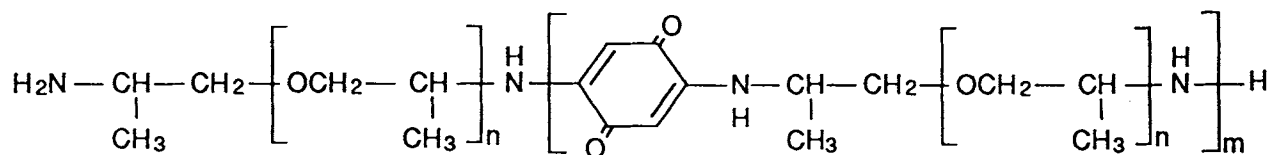
D130.4.3

Figure 2 Molecular structure of the PAQ product from the reaction between polyetherdiamine (D-230) and benzoquinone.

adjacent to the benzoquinone are also active in epoxy chemistry, they also must be considered. In Table I are given values of the degree of polymerization, m, and the calculated PAQ molecular weight. From the listed number of active hydrogens the amine equivalent weight is calculated.

The AEW of the mixture of PAQ with DETA can be calculated by

$$\text{AEW of mix} = \frac{\text{Total weight}}{\left(\dfrac{\text{Wt } a}{\text{AEW } a}\right) + \left(\dfrac{\text{Wt } b}{\text{AEW } b}\right)}$$

The PAQ product had a solubility of 20% in the DETA. With these relative weights, the AEW of the blend is calculated and is shown on Table I, column 5. The weight of the blend required to cure 100 parts of the epoxy can be calculated from this and the 188-g/equivalents for the epoxy used here. This curative weight is seen to change only very slightly with the change in degree of polymerization m. Thus for further work, a mix ratio of 13 parts of the PAQ-E1 blend to 100 parts of epoxy was selected.

Figure 3 shows the DSC scan of a sample composed of epoxy resin mixed with pure PAQ product (D-230 : PAQ, 2 : 3) at a level of 50 phr. The results show an endothermic melting peak at 154°C identified with the PAQ compound. This is followed by the onset of an exothermic peak associated with the reaction between epoxide and PAQ at 224°C.

A DSC comparison between the PAQ-E1 blend and DETA was also performed. The specimens used for this test were cured 24 h at room temperature prior to the DSC tests. As seen in Figure 4, the PAQ-E1/epoxy mixture produced a higher exotherm than the control that contained DETA alone. This behavior may result from the PAQs lower reactivity at room temperature compared to DETA. Therefore, the PAQ-E1/epoxy had a higher residual cure exotherm.

The FTIR analysis was performed on a sample prepared with 13 parts PAQ-E1 with 100 parts epoxy resin. The absorption band at 915 cm^{-1} was observed at three stages of the curing reaction: initially after mixing the epoxy with amine, after 24 h at room temperature, and 24 h at room temperature plus 1 h at 100°C. In the same manner, a sample prepared using the pure PAQ product (PAQ : D-230 2 : 3) was prepared and scanned initially after mixing, after curing 30 min at 200°C, and finally after curing 30 min at 200°C plus 30 min at 250°C. As seen in Figures 5 and 6, a higher cure temperature is required to achieve epoxide conversion with the mixture containing only pure PAQ. This was expected because of the presence of DETA in the PAQ-E1. These results do show clearly the ability of PAQs to cure epoxy resin in both the neat and blended form.

Water absorption was performed on both neat and composite specimens. The neat epoxy specimens were cured with PAQ-E1 and compared to specimens cured with DETA for a control. As shown in Figure 7, the neat DETA-cured control absorbed 40% more water than the PAQ-E1 material. The composite DETA samples absorbed 20% more water than the PAQ-E1 cured composite samples as depicted in Figure 8. This amount is even more dramatic compared to the neat specimens, considering that the matrix resin composes a smaller percentage of the tested specimens in the case of the composites.

Table I Effect of PAQ Molecular Weight on the Amine Equivalent Weight of the Final PAQ-E1 Blend

m	PAQ Molecular Weight	PAQ Active Hydrogens	PAQ Amine Equivalent Weight	PAQ-E1 Amine Blend Equivalent Weight	phr[a] PAQ-E1
0	564	6	94	24.4	13.0
1	896	8	112	24.6	13.0
2	1230	10	123	24.7	13.2
3	1564	12	130	24.8	13.2
4	1898	14	136	24.8	13.2
5	2232	16	140	24.8	13.2
6	2566	18	143	24.9	13.2
7	2900	20	145	24.9	13.2
8	3234	22	147	24.9	13.2
9	3568	24	149	24.9	13.2
10	3902	26	150	24.9	13.2

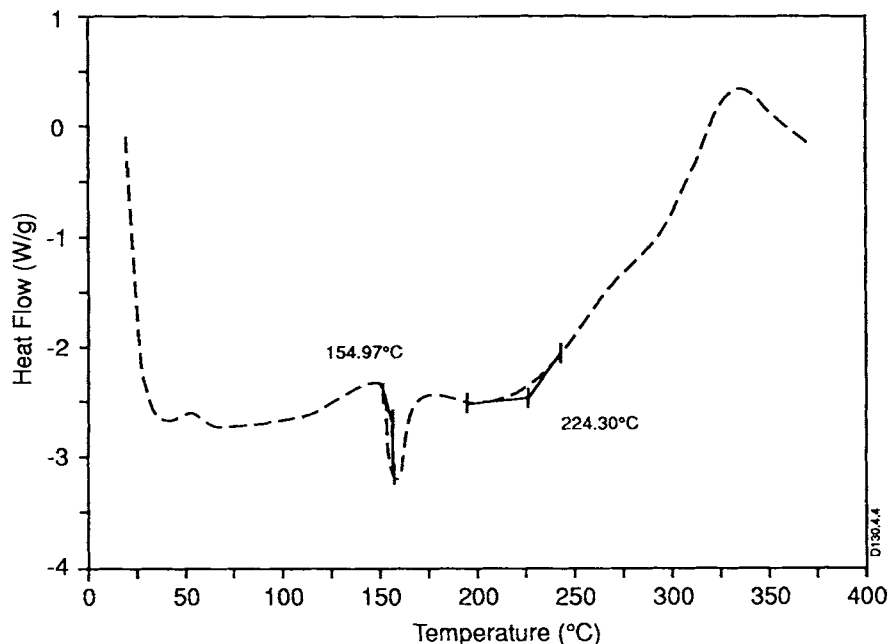[a] phr indicates parts of PAQ-E1 per hundred parts of epoxy resin.

Figure 3 DSC scan of epoxy resin mixed with pure PAQ product (D-230 : PAQ, 2 : 3).

The dynamic mechanical properties (G'', G', and tan δ) of composite samples prepared with both PAQ-E1 and DETA were measured at room temperature at 0.25, 0.50, 1.0, and 2.0 Hz fixed frequencies. Ten samples were tested of each curing agent type. Half of the specimens of each type were sub-jected to elevated temperature exposure in water (70°C for 60 days) before testing. In Figure 9 the average loss shear modulus (G'') of the specimens made using the PAQ-E1 curing agent is compared to that obtained from specimens produced using DETA curing agent. The plot also shows the effect
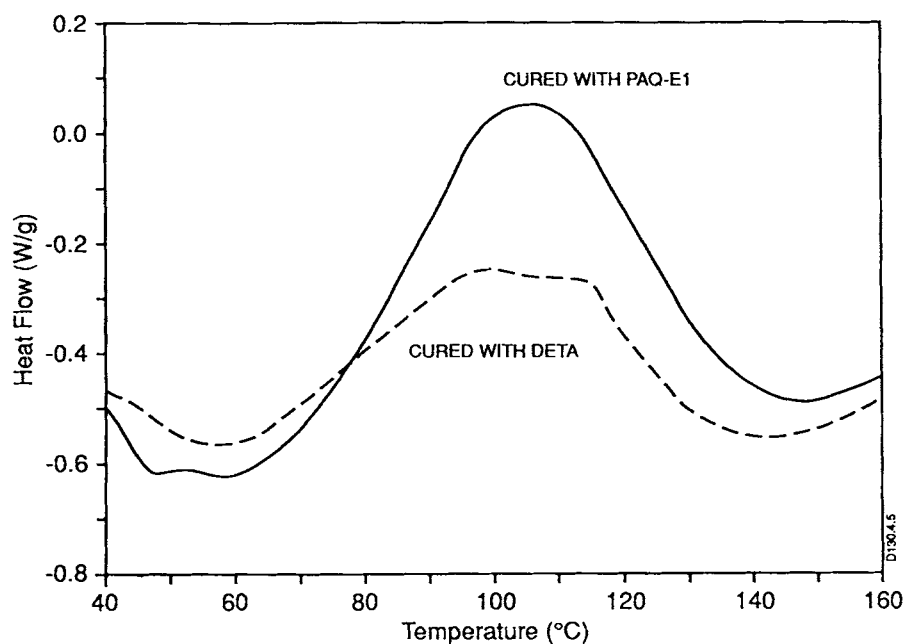
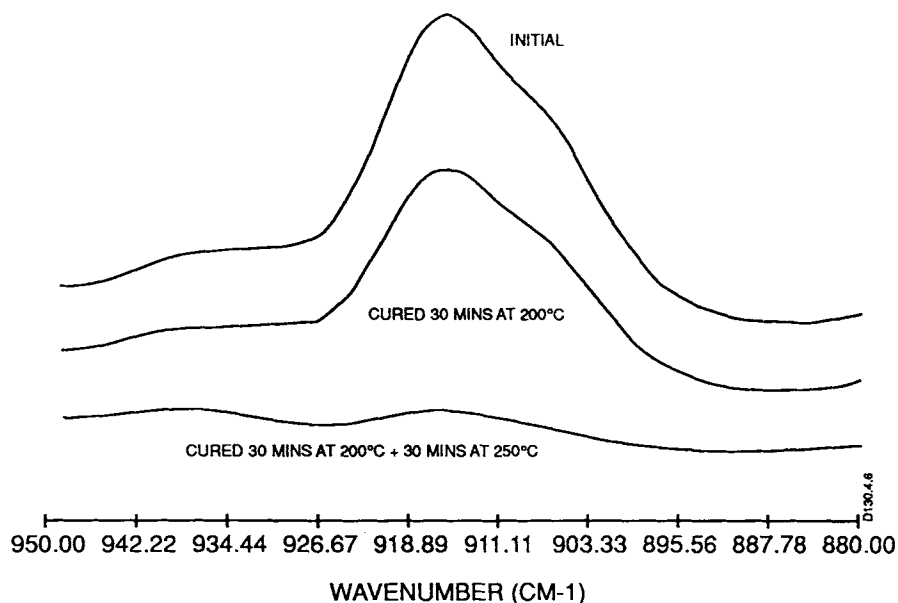**Figure 4** DSC comparison of epoxy resin cured with PAQ-E1 and DETA.

Figure 5 FTIR scan of epoxy resin during cure with pure PAQ-D230 product.

of elevated water temperature exposure on G''. The average loss shear modulus for the PAQ-E1-cured samples is less than the DETA-cured specimens. In addition, the PAQ-E1-cured samples show much less degradation of interfacial bonding as evidenced by the small difference in G'' after exposure compared to the DETA specimens. The shear storage modulus,

G', showed only minor differences for the PAQ-E1-cured specimens compared to the DETA specimens.

Tan δ was also significantly lower for both the wet and dry specimens prepared with PAQ-E1 compared to DETA-cured samples. Table II shows a notable increase in tan δ for the DETA-prepared specimens after water exposure. Table II also shows the
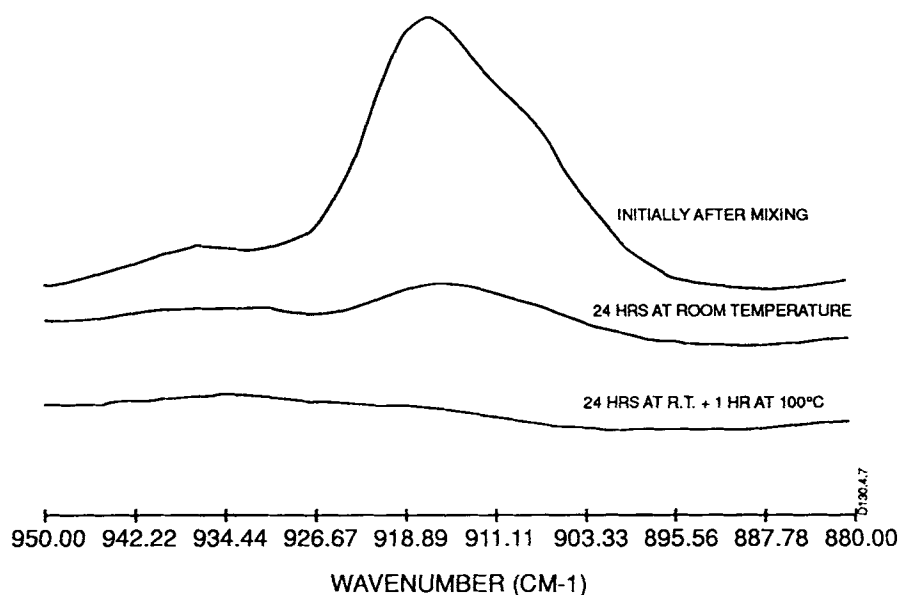

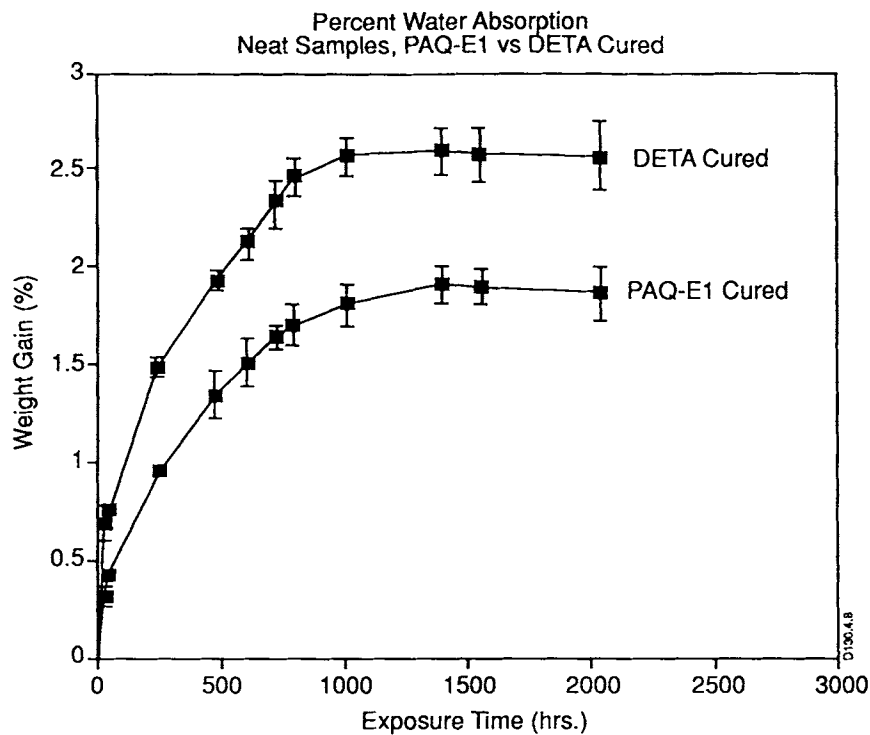**Figure 6** FTIR scan of epoxy resin during cure with PAQ-E1.

Figure 7   Water absorption at 25°C of neat epoxy specimens cured with PAQ-E1 and DETA.
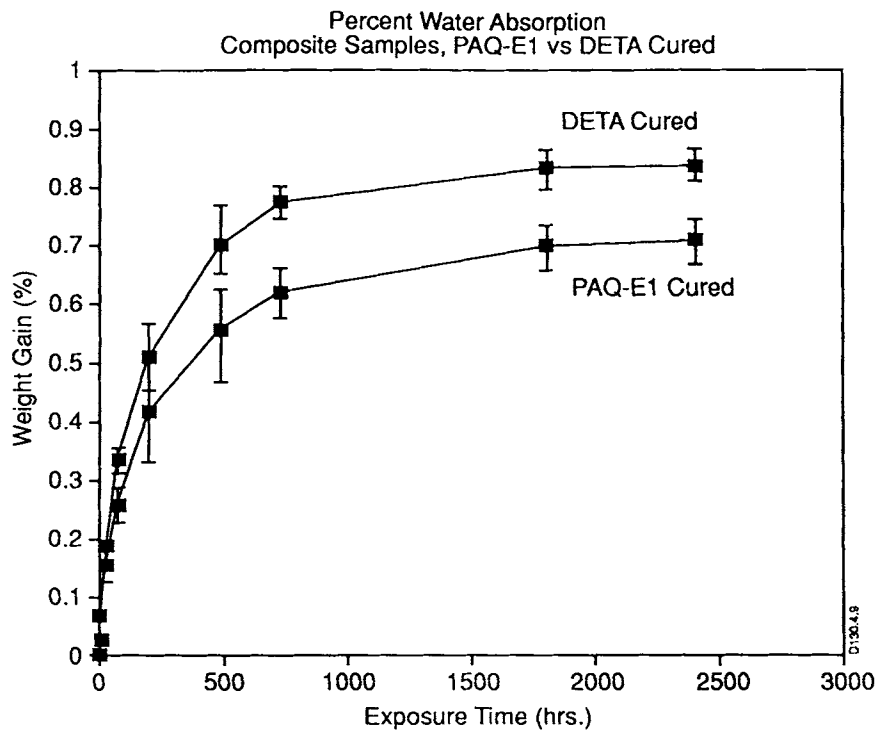

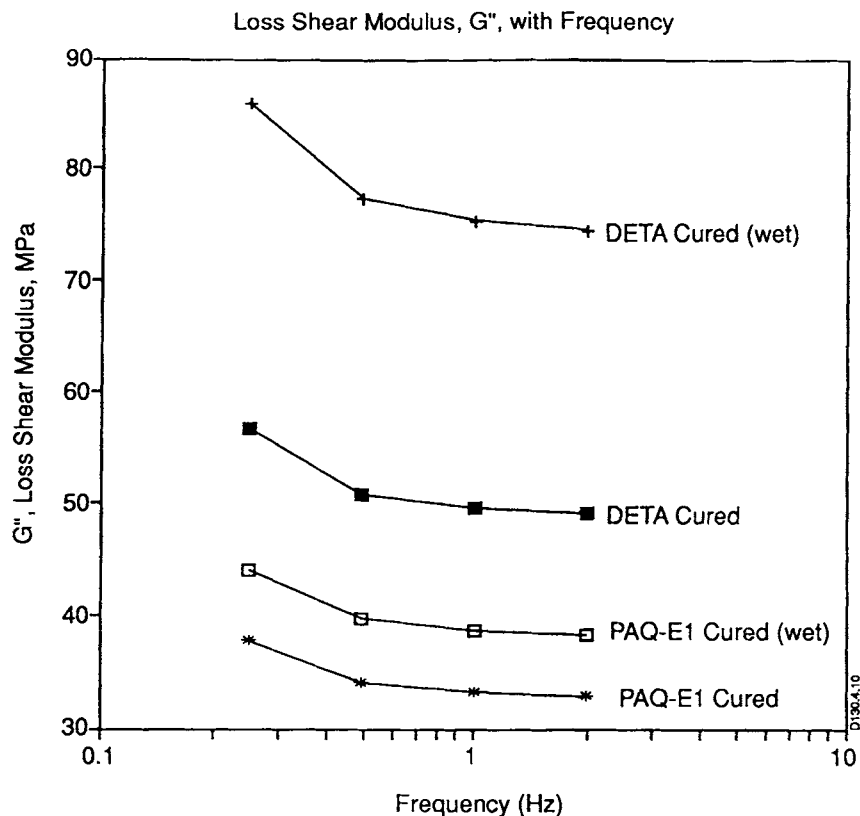**Figure 8**   Water absorption at 25°C of epoxy composite specimens cured with PAQ-E1 and DETA.

Figure 9   Loss shear modulus, G'', of epoxy composite specimens cured with PAQ-E1 and DETA, wet and dry, test performed at 30°C.

glass transition temperatures as determined from a separate DMA analysis. The decreases in the T_g after water exposure are probably a result of plasticization. The PAQ-E1-cured material showed a smaller decrease in T_g compared to the DETA-cured specimens, another indication of moisture resistance.

Five composite samples of each type were cured and conditioned as shown in Table III. These specimens were tested using the short-beam shear test. The interlaminar shear strength of the dry DETA-

and PAQ-E1-cured specimens is comparable. After 70°C water exposure for 60 days, the PAQ-E1-cured samples retained slightly more shear strength compared to the DETA-cured samples.

CONCLUSIONS

This investigation into the use of polyamine quinones as epoxy curing agents has shown that it is

Table II   Tan δ and T_g for DETA- and PAQ-E1-Cured Composites, Wet and Dry

	Tan δ 40°C	T_g (°C)
DETA cure (dry)	0.0118	127
DETA cure (wet)	0.0167	101
PAQ-E1 cure (dry)	0.0108	121
PAQ-E1 cure (wet)	0.0118	107

Table III   Interlaminar Shear Strength, τ, of Epoxy Fiberglass Composites Cured with Either DETA or PAQ-E1, Wet and Dry

Sample Type	τ, MPa
DETA cured (dry)	44.5 ± 5
DETA cured (wet)	31.8 ± 3
PAQ-E1 (dry)	45.2 ± 4
PAQ-E1 (wet)	34.6 ± 5

possible to prepare liquid PAQ–amine curing agent blends. One of the more significant results thus far has been the improved water absorption performance of epoxy resin cured with PAQ blends. The DSC and FTIR data indicate that the PAQ is actively participating in the cure of the resin, although the exact mechanism of cure has not yet been determined. Short-beam shear strength of the PAQ-E1-cured epoxy–fiberglass composite was at least as good as the composite cured with the conventional DETA curing agent. Wet interlaminar shear strength retention was also improved with the PAQ-E1 blend. The DMA was shown to be a practical method of investigating matrix–reinforcement adhesion and durability in composite materials. The DMA also indicated an improvement in interfacial adhesion and durability achieved through the use of the PAQ-blended curing agent.

REFERENCES

1. K. Kaleem, F. Chertok, and S. Erhan, *Progr. Org. Coat.,* **15,** 63, 1987.
2. K. Kaleem, F. Chertok, and S. Erhan, *New Polym. Mat.,* **1,** 265, 1990.
3. V. S. Nithianandam, F. Chertok, and S. Erhan, *J. Coat. Technol.,* **63,** 47, 1991.
4. S. Hilpert and F. Brauns, "Quinone Tannage," Collegium 64–74 (1925).
5. K. H. Gustafson, *The Chemistry of Tanning Processes,* Academic Press, New York, 1985.
6. E. Lindner and C. A. Dooley, "Proc. 4th Int. Cong. Marine Corrosion and Fouling," Juan-Les-Pins, France, P. 333, Centre de Recherche et d'Etude Oceanographie, Boulogne, 1976.
7. Chua, Ping Seng, "Characterization of the Interfacial Adhesion Using Tan Delta," 42nd Annual Conference, Composites Institute, The Society of the Plastics Industry, Inc., February 2–6, 1987.
8. J. M. Kennedy, D. D. Edie, A. Banerjee, and R. J. Cano, *J. Comp. Mat.,* **26** (1992).