

# Moisture Effects during Cure of High-Performance Epoxy Matrices

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## Synopsis

The effects of absorbed moisture on the cure reactions and subsequent solid-state properties of a high-performance epoxy system were investigated in this study. The resin systems investigated were a model system, TGDDM–Novalac–DDS–BF<sub>3</sub>:MEA (TNDB), and its commercial analog, Hercules 3501-6. The samples were exposed to three environments: a liquid water environment at 50°C; an 85% relative humidity vapor environment at 50°C; and an evacuated, desiccated atmosphere at 22°C. Differential scanning calorimetry (DSC) thermograms were obtained for the Hercules 3501-6 formulation as well as various compositions of the TNDB system for samples exposed to each of the three environments. Moisture was found to accelerate the cure especially for formulations exposed to the vapor environment. Dynamic mechanical experiments were also performed on cured, thin film samples. The “wet” samples were produced by adding water to the resin mixture prior to B-staging. The moisture was shown to increase the extent of reaction, but produce a slightly lower degree of crosslinking as related to the sample’s glass transition. This has been attributed to chain-extension reactions, such as the hydroxyl–epoxide etherification reaction, which are favored in the presence of hydroxyl groups from water.

## INTRODUCTION

High-performance epoxy resins are the most commonly used matrix materials in continuous, carbon-fiber-reinforced composites for load-bearing structural applications. Numerous investigations have been reported in the literature in the area of sorption–desorption phenomena and how the absorbed moisture affects the physical and mechanical properties of the cured epoxy matrix material.<sup>1–5</sup> However, very few studies have focused on the understanding of how moisture, sorbed by the uncured monomers, affects the reaction kinetics of this system and its subsequent effect on the network structure and properties.<sup>6–8</sup> It is this effect which is investigated in this study.

The model high-performance epoxy system examined in this study consisted of a mixture of two epoxy resins, tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and poly(glycidyl ether) of bisphenol-A Novalac (Novalac), which is cured in the presence of an amine curing agent, 4,4'-diaminodiphenyl sulfone (DDS), and a catalyst, boron trifluoride monoethylamine (BF<sub>3</sub>:MEA) (Fig. 1). This epoxy system was selected because its composition approximates many systems of commercial importance to the aerospace industry. Previous investigations into the cure kinetics and solid-state properties of the catalyzed<sup>9</sup> as well as the uncatalyzed<sup>10</sup> epoxy systems

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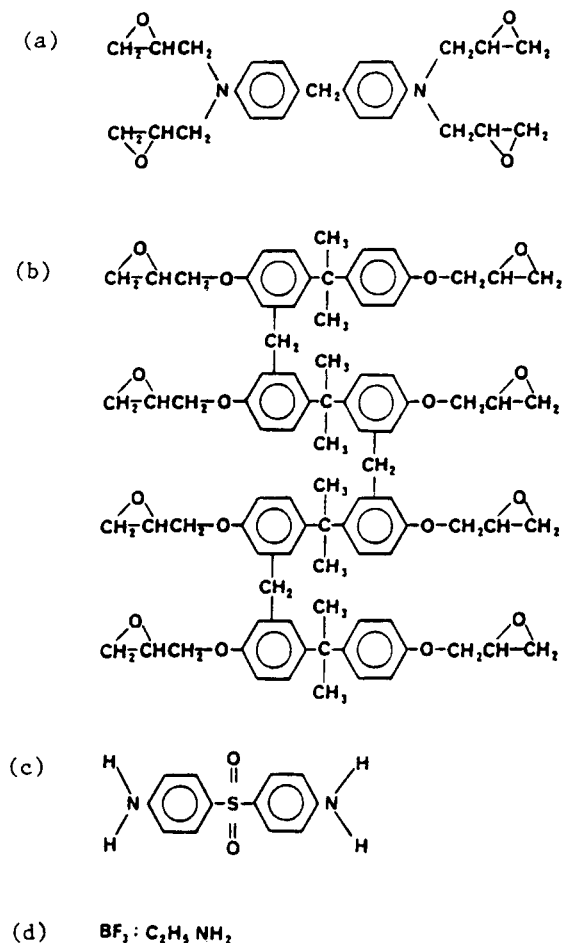


Fig. 1. Chemical structure of the catalyzed TGDDM–Novalac–DDS system constituents: (a) tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM); (b) poly(glycidyl ether) of bisphenol-A (Novalac); (c) 4,4'-diaminodiphenyl sulfone (DDS); (d) Boron trifluoride–monoethylamine ( $\text{BF}_3\text{:MEA}$ ).

have been presented elsewhere, but did not consider the effect of moisture exposure on these important characteristics of the polymer processing, structure, and properties. The monomers as well as different mixtures of these monomers were exposed to both liquid water and 85% relative-humidity environments in order to determine the effect of moisture absorbed during processing on the cure reactions and the resulting bulk properties. The effect of moisture on the cure kinetics was evaluated using differential scanning calorimetry (DSC), while dynamic mechanical experiments on cured samples were utilized to investigate the effect on the resulting network properties.

## EXPERIMENTAL

### Sample Preparation

The samples used for studying moisture effects during cure were prepared using TGDDM (Ciba-Geigy MY 720), Novalac (Celanese EPI-REZ-SU-8), DDS

(Ciba-Geigy HT 976), and  $\text{BF}_3\text{:MEA}$  (Miller-Stephenson Chemical Co.) in the quantities indicated in Table I. For DSC measurements, the samples containing TGDDM, a viscous liquid, were hand-mixed at  $50^\circ\text{C}$  until a homogeneous mixture was achieved, whereas the solid samples were hand-mixed at room temperature. All of the samples were stored at  $-17^\circ\text{C}$  until needed.

To prepare the cured, thin film samples required for dynamic mechanical experiments, the monomers, TGDDM, Novalac, and DDS were mixed at  $135^\circ\text{C}$ , cooled to about  $90^\circ\text{C}$ , and then  $\text{BF}_3\text{:MEA}$  was added and mixed to give TGDDM–Novalac–DDS– $\text{BF}_3\text{:MEA}$  (TNDB) system, according to the procedure of Munns and Seferis.<sup>9</sup> The composition chosen for these experiments contained 88.5% by weight TGDDM and 11.5% by weight Novalac with 25 phr DDS and 2 phr  $\text{BF}_3\text{:MEA}$ ; refers to part per hundred of epoxy present. This mixture closely approximates commercial resin formulations such as Hercules 3501-6. The moisture exposure for these samples was produced by adding 2 phr water and mixing it with the above TNDB system at  $90^\circ\text{C}$  to give the TGDDM–Novalac–DDS– $\text{BF}_3$ –water (TNDBW) system. Both the virgin and the water-containing epoxy resins were processed into void-free films using the melt-processing technique of Chu and Seferis<sup>11</sup> with a slight modification to avoid evaporation of the added water: The resins were degassed at  $90^\circ\text{C}$  for 30 min and cured between steel plates at  $177^\circ\text{C}$  for 2 h.<sup>9</sup> Hercules 3501-6 neat resin and cured, thin film samples were also studied for comparison to the model epoxy system outlined above.

### Moisture Treatment

The uncured samples were exposed to a liquid environment by submerging in deionized water held at  $50^\circ\text{C}$  using a constant temperature bath for 6 days. The solid samples were wrapped in filter paper to allow the weight to be accurately measured after the water had been removed, and then placed into test tubes. The viscous liquid samples were simply placed in the test tubes directly. The test tubes were then filled with deionized water, corked, and sealed with paraffin. The test tubes were then placed in a constant temperature bath at  $50^\circ\text{C}$  for 6 days. Weight measurements were taken daily. Fresh deionized water was used to replace the water removed before each weighing.

TABLE I  
Formulation of Samples Used for Studying Moisture Effects

Batch	TGDDM (wt %)	Constituent Concentration		
		Novalac (wt %)	DDS (phr)	$\text{BF}_3\text{:MEA}$ (phr)
1	0.0	100.0	25	0
2	0.0	100.0	0	2
3	0.0	100.0	25	2
4	0.0	100.0	0	0
5	100.0	0.0	0	0
6	100.0	0.0	25	0
7	100.0	0.0	0	2
8	100.0	0.0	25	2
9	88.5	11.5	0	0
10	88.5	11.5	25	0
11	88.5	11.5	0	2
12	88.5	11.5	25	2

A humidity chamber previously utilized for moisture sorption studies<sup>1</sup> was used to expose the samples to 85% relative humidity at 50°C for 6 days. The "dry" samples used for comparison were desiccated under a vacuum at room temperature in the presence of anhydrous calcium sulfate for eight to ten days. The samples were simply placed in open test tubes and then exposed to the appropriate environment.

### Experimental Techniques

DSC experiments were performed for all of the desiccated and moisture-exposed samples at a heating rate of 5°C/min using a DuPont 910 DSC module attached to the 1090 Thermal Analysis System. The size of the samples used was kept at  $5.0 \pm 0.3$  mg.

Dynamic mechanical experiments were performed on the cured samples at a heating rate of 1°C/min in the temperature range  $-150$ – $320$ °C with a constant frequency of 11 Hz using a Rheovibron model DDV-II modified according to the procedure of Wedgewood and Seferis.<sup>12</sup>

## RESULTS AND DISCUSSION

### Moisture Absorption Characterization

The results of the moisture exposure outlined in the experimental section indicate that the individual components of the TGDDM–Novalac–DDS–BF<sub>3</sub>:MEA (TNDB) epoxy system and mixtures of these constituents absorbed a significant amount of moisture. The percent, by weight, of moisture absorbed from the liquid environment during the 6-day exposure at 50°C is shown in Table II for the pure components and the various resin compositions that were investigated. As can be seen in Table II, the DDS absorbed a significant amount of moisture due to its crystalline form and due to the

TABLE II  
Percent Moisture Absorbed from Liquid Water Environment for Various Resin Compositions

Batch	TGDDM (wt %)	Constituent Concentration			Wt % of Moisture Absorbed
		Novalac (wt %)	DDS (wt %)	BF <sub>3</sub> :MEA (phr)	
1	0.0	100.0	25	0	49.7
2	0.0	100.0	0	2	84.8
3	0.0	100.0	25	2	63.0
4	0.0	100.0	0	0	39.3
5	100.0	0.0	0	0	0.7
6	100.0	0.0	25	0	4.9
7	100.0	0.0	0	2	17.8
8	100.0	0.0	25	2	11.6
9	88.5	11.5	0	0	8.7
10	88.5	11.5	25	0	9.7
11	88.5	11.5	0	2	31.2
12	88.5	11.5	25	2	17.6

presence of hydrogen-bonding amine and sulfone groups. In general, comparison of pure epoxy component absorption results showed that the Novalac absorbed much more moisture than the TGDDM with the mixed TGDDM–Novalac systems absorbing intermediate amounts. Novalac systems absorb more moisture because their high functionality provides more absorbing sites for water than TGDDM. Furthermore, because Novalac is a solid, more surface area is available for moisture absorption than for the viscous, liquid TGDDM.

The addition of DDS and  $\text{BF}_3\text{:MEA}$  to the epoxy mixture increased the amount of moisture absorbed by the mixtures, due to the high moisture affinity of both DDS and  $\text{BF}_3\text{:MEA}$ . The addition of  $\text{BF}_3\text{:MEA}$  caused the largest increase in absorbed moisture due to the hydrophilic nature of the  $\text{BF}_3\text{:MEA}$  complex. DDS increased the moisture content to a lesser extent than the  $\text{BF}_3\text{:MEA}$ . When both  $\text{BF}_3\text{:MEA}$  and DDS were added, the moisture content was intermediate to the  $\text{BF}_3\text{:MEA}$ -modified and DDS-modified epoxies.

The weight percent of moisture absorbed from the vapor environment by the pure constituents during the 6-day exposure is shown in Table III. As in the liquid environment, the Novalac epoxy absorbed significantly more moisture than the TGDDM due to the large surface area and greater number of diffusive sites available in the Novalac. The DDS and  $\text{BF}_3\text{:MEA}$  samples gained less weight in the vapor environment than in the liquid water.

### Investigation of Moisture Effects on Cure

The DSC results for TGDDM resin alone in each of the environments are provided in Figure 2. These results indicate that the extent of reaction which occurred during exposure increased as the amount of moisture that was absorbed increased. The extent of reaction was greatest for the sample exposed to a liquid environment and least for the desiccated sample, as shown in Figure 2. The sample exposed to a vapor environment had an extent of reaction between the liquid-soaked and desiccated values. These results indicate that the presence of water accelerates the cure of the TGDDM. From previous work, the reaction of the TGDDM alone may be attributed to epoxide–epoxide homopolymerization and hydroxyl–epoxide etherification reactions.<sup>10</sup> These reactions are accelerated by the presence of hydroxyl groups, such as those in water. However, Novalac does not exhibit either of these reactions, and even with moisture exposure Novalac

TABLE III  
Percent Moisture Absorbed from Water Vapor Environment for Epoxy Resin Constituents

Constituent	Wt % of Moisture Absorbed
TGDDM	7.7
Novalac	38.8
DDS	20.4
$\text{BF}_3\text{:MEA}$	15.4 <sup>a</sup>

<sup>a</sup> Not saturated at the end of 6-day exposure.

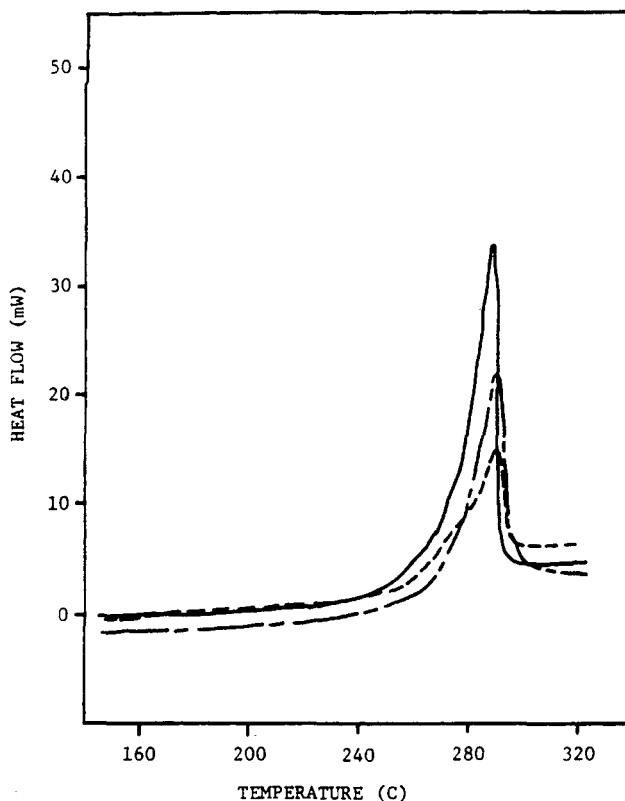


Fig. 2. DSC thermograms for desiccated (—), liquid-water exposed (---), and humidity-exposed (- · - ·) TGDDM.

shows no effect indicating that even in the presence of an accelerating agent, i.e., water, neither reaction is evident.

The DSC thermograms for DDS showed little effect due to moisture absorbed from the vapor environment; however, in the liquid environment the moisture led to a broad, endothermic peak in the DSC thermogram at approximately 70°C as can be seen in Figure 3. This endothermic peak is probably due to the melting of a DDS complex formed with the moisture during exposure. In addition, a significant reduction in the magnitude of the crystalline melting endotherm was also identified. This reduction may be explained as a decrease in the amount of pure DDS crystals due to the formation of a DDS-water complex.

The behavior of the  $\text{BF}_3\text{:MEA}$  catalyst, as shown by the DSC thermograms in Figure 4, was found to be significantly different after exposure to the humid environment. Several exothermic reaction peaks in the DSC thermogram appear as a result of exposing the  $\text{BF}_3\text{:MEA}$  to the vapor environment. These reaction peaks may be a result of reaction among complexes formed when the  $\text{BF}_3\text{:MEA}$  contacts the water. Other researchers have shown that ethylammonium tetrafluoroborates and hydroxyfluoroborates are present in the catalyst after synthesis and will form as a result of reactions with water.<sup>7,13</sup>

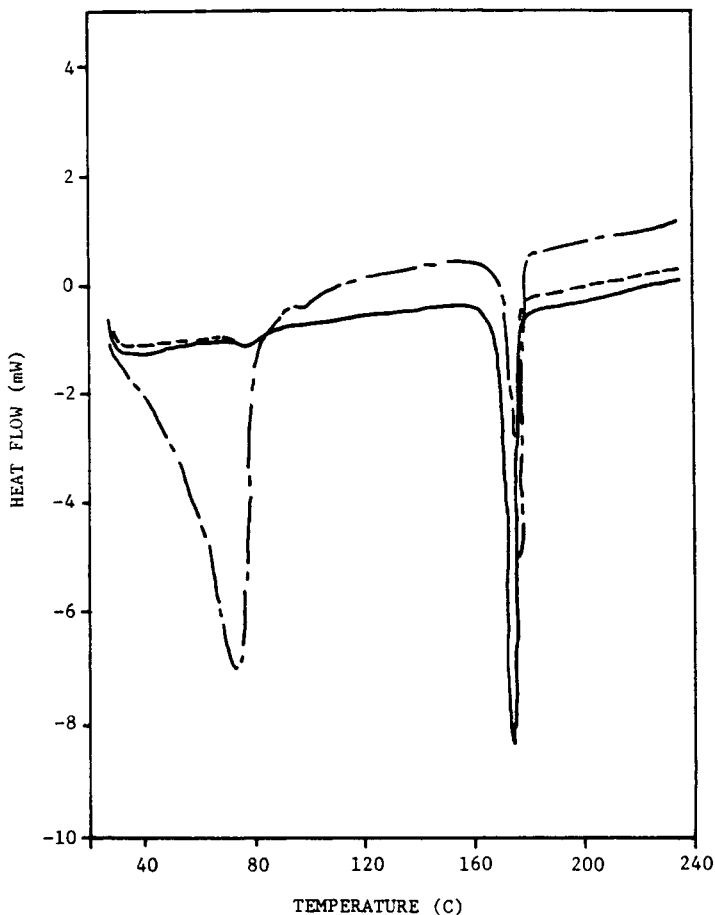


Fig. 3. DSC thermograms for desiccated (—), liquid-water exposed (---), and humidity-exposed (- · -) DDS.

In general, DSC results for mixed, resin systems exhibited an increased extent of reaction as a result of exposure to a liquid water environment. For the moisture-conditioned Novalac- $\text{BF}_3$ :MEA and Novalac-DDS- $\text{BF}_3$ :MEA systems, a significant decrease in catalyzed reaction during the DSC experiment was observed as shown in Figures 5 and 6. The low-temperature reaction peaks in the DSC thermograms shown in Figure 7 for the TGDDM-Novalac-DDS- $\text{BF}_3$ :MEA epoxy system were not observed for the liquid-soaked sample. The low-temperature reaction peaks have been attributed to  $\text{BF}_3$ :MEA-catalyzed reactions.<sup>9</sup> The decrease in catalyzed reactions for the Novalac- $\text{BF}_3$ :MEA, Novalac-DDS- $\text{BF}_3$ , and TGDDM-Novalac-DDS- $\text{BF}_3$  systems could be due to a decrease in the catalytic activity of the  $\text{BF}_3$ :MEA because of the reactions with water observed for the catalyst. The increase in the extent of reaction during moisture exposure may be due to moisture-initiated reactions.

As shown in Figures 8 and 6 respectively, the DSC thermograms for the Novalac-DDS and Novalac-DDS- $\text{BF}_3$ :MEA systems had a broad, endo-

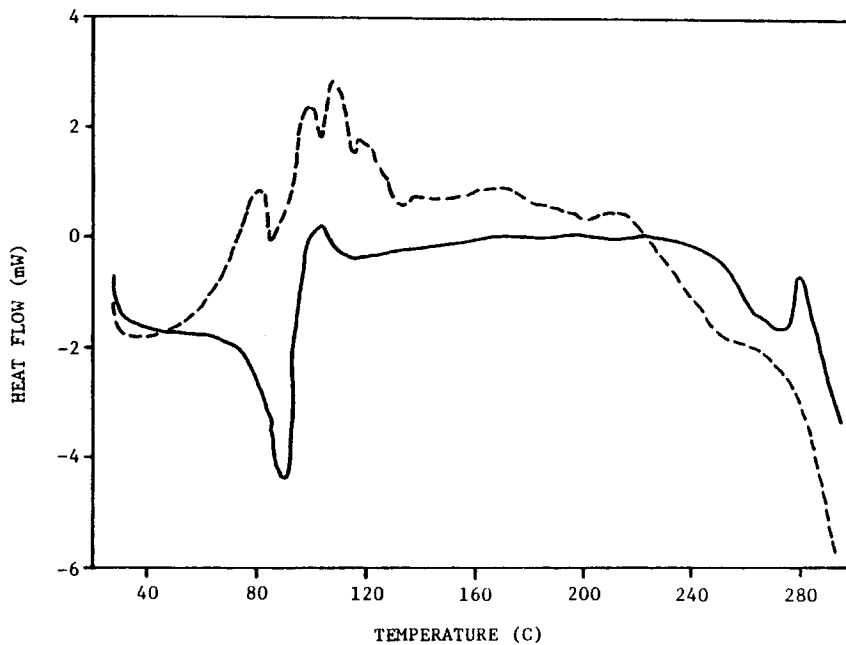


Fig. 4. DSC thermograms for desiccated (—) and humidity-exposed (- - -)  $\text{BF}_3 \cdot \text{MEA}$ .

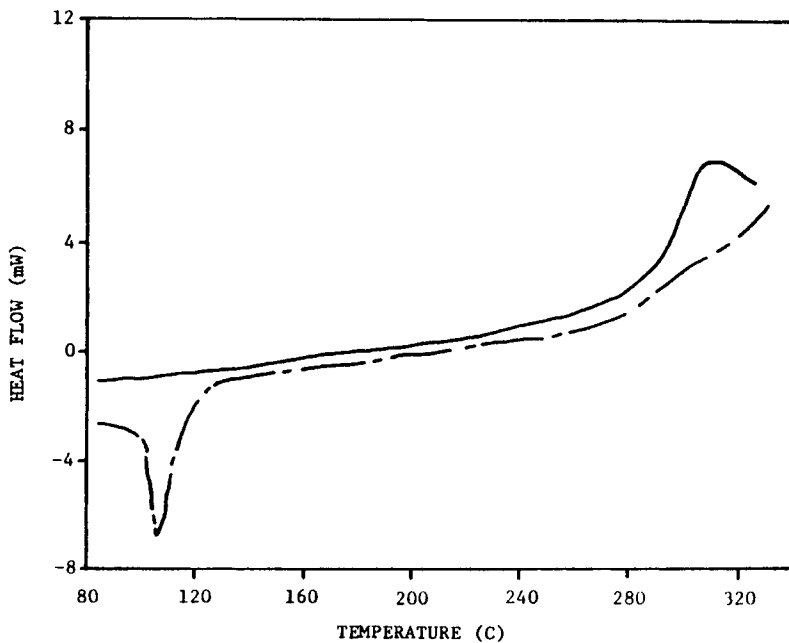


Fig. 5. DSC thermograms for desiccated (—) and liquid-water exposed (- - -) Novalac- $\text{BF}_3 \cdot \text{MEA}$ .



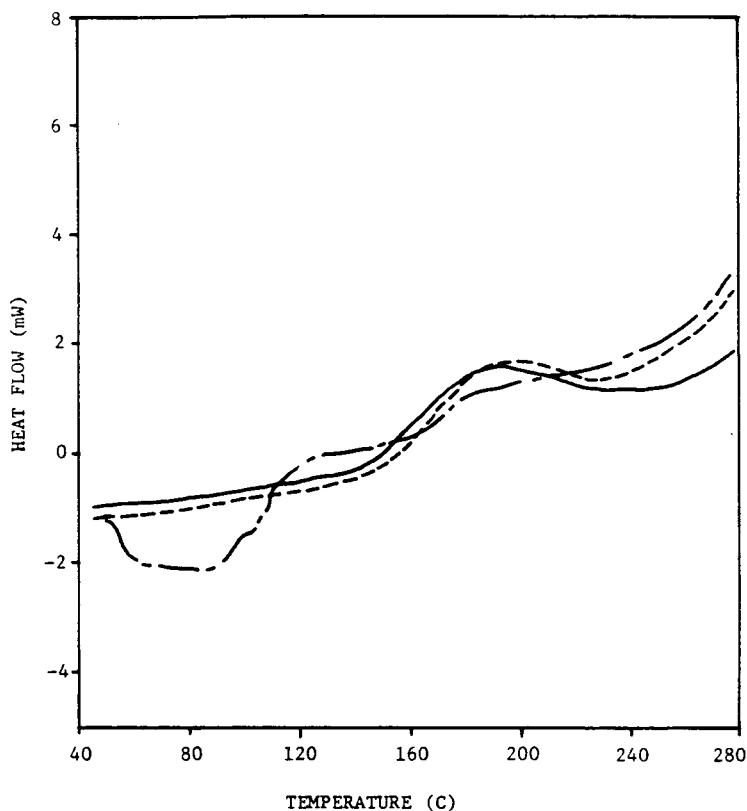


Fig. 6. DSC thermograms for desiccated (—), liquid-water exposed (---), and humidity-exposed (- · -) Novalac-DDS-BF<sub>3</sub>:MEA.

thermic peak at approximately 80°C for the liquid-exposed samples. These peaks correspond to the endothermic peak observed in DDS that was attributed to the complexing of the DDS with water.

The DSC thermograms for the Hercules 3501-6 are shown in Figure 9 demonstrating that exposure to the liquid water environment accelerates the onset of the curing reactions as with the model systems. The disappearance of the minor, low-temperature peaks shows that the moisture exposure reduced the catalytic activity of the BF<sub>3</sub>:MEA, possibly due to complexing of the catalyst with the water.

### Effects on Cured Samples

Dynamic mechanical results for the dry and moisture-modified cured TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA samples are shown in Figure 10 in  $\tan \delta$  form. For the dry film, two viscoelastic transitions were observed in  $\tan \delta$  as have been discussed in detail in earlier publications.<sup>14</sup> The low temperature  $\beta$ -transition is attributed to the molecular motions of the groups that result from amine-epoxide and hydroxyl-epoxide reactions. Because the magnitude and breadth of the  $\beta$ -transition increases with increasing extent

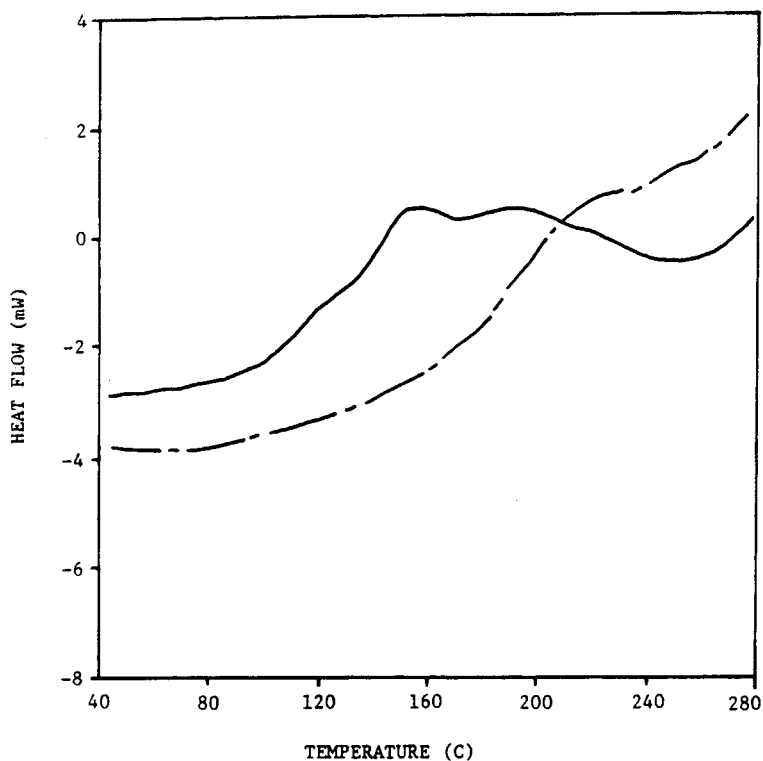


Fig. 7. DSC thermograms for desiccated (—) and liquid-water exposed (- - -) TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA.

of amine-epoxy reactions, the relative extent of amine-epoxy reaction can be determined from this transition. The high-temperature  $\alpha$ -transition split into two peaks,  $\alpha_1$  and  $\alpha_2$ , for partially cured materials.<sup>14</sup> The  $\alpha_1$  peak which appears around 190°C has been attributed to the glass transition of the original material with a superimposed effect of additional curing taking place during the experiment. After the additional cure has occurred, and as the temperature of the experiment is further increased, the glass transition temperature for the additionally cured system ( $\alpha_2$  peak) is reached.

As shown in Figure 10, the addition of water to the TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA system caused a decrease in the magnitude of the  $\beta$ -transition, indicating a lower extent of amine-epoxide reactions. The  $\alpha_1$  peak disappeared for the moisture-modified system, which indicates a higher extent of cure for the water-modified epoxy. Hence, by considering the  $\beta$ - and  $\alpha_1$ -transitions, it may be concluded that besides amine-epoxide reactions, other reactions such as water-initiated etherifications should have occurred to give rise to the greater extent of the curing reaction. Finally, the water-modified epoxy system displays a glass transition temperature that has shifted to a slightly lower temperature and a higher  $\tan \delta$  maximum in comparison to the dry sample. This also supports the results that the presence of water during cure may give rise to a somewhat less highly crosslinked network structure.

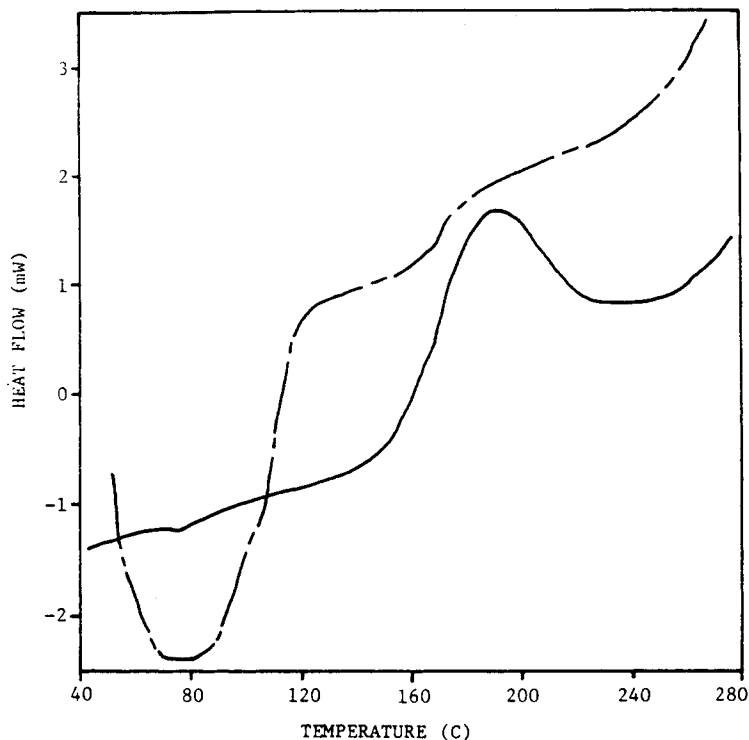


Fig. 8. DSC thermograms for desiccated (—) and liquid-water exposed (- - -) Novalac-DDS.

An additional transition was observed at approximately 80°C for the water-modified system. The  $\omega$  peak has been identified by Keenan et al.<sup>14</sup> and has been attributed to the presence of water in the epoxy. The magnitude of the  $\omega$ -transition has been shown to be related to the amount of moisture absorbed by the epoxy network and/or heterogeneities present in the samples as a result of regions of high and low crosslink density.

The dynamic mechanical results for the "as received" and moisture-modified Hercules 3501-6 resin after cure with our standard procedure<sup>9</sup> are shown in Figure 11 in terms of the  $\tan \delta$  results. Upon the addition of moisture to the resin system, the  $\omega$ -transition increased in magnitude, which is indicative of an increase in the heterogeneity which results from the moisture present in the system. In addition, the temperature of the  $\alpha$  peak maximum decreased for the moisture-modified epoxy system, indicating a lower extent of crosslinking.

The storage-modulus results are also plotted in Figure 12 for the Hercules 3501-6 system to provide a comparison for the mechanical behavior of samples cured with and without the presence of moisture. As expected, the modulus was unaffected by the presence of moisture in the glassy region below the glass transition temperature, while significant differences were observed at the onset and above the system's glass transition. Further, these results indicate that the "wet" cured sample exhibited a slightly lower glass

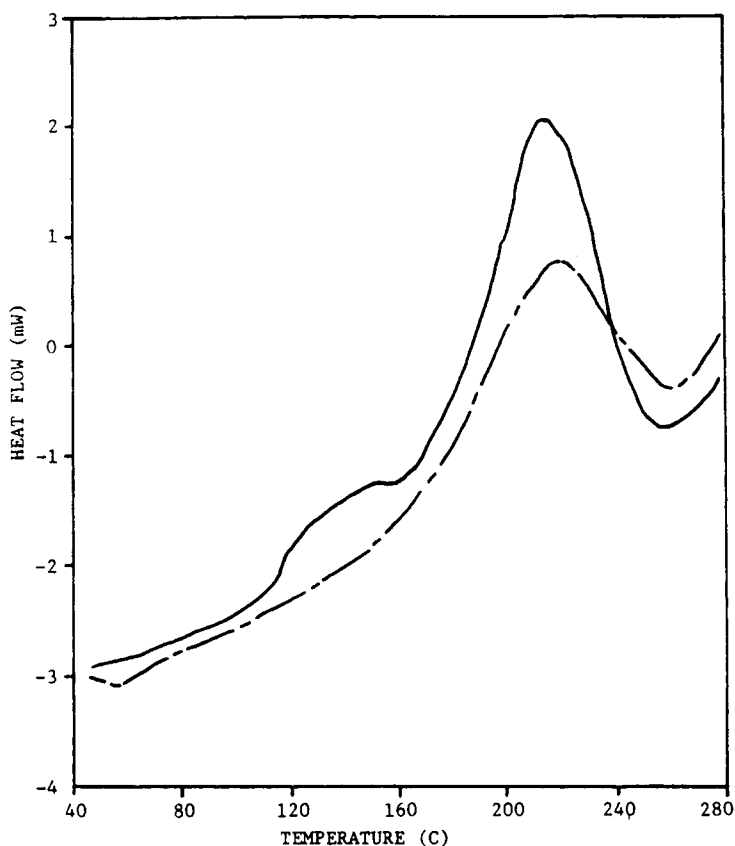


Fig. 9. DSC thermograms for as-received (—) and liquid-water exposed (---) Hercules 3501-6.

transition further supporting the conclusion that the extent of the cross-linking reaction was less for the moisture-treated sample and that a moisture-initiated etherification reaction is occurring.

### CONCLUSIONS

Moisture sorption studies indicate that the individual constituents of the TGDDM-*Novalac*-DDS- $\text{BF}_3$ :MEA epoxy system absorb a significant amount of moisture. *Novalac* epoxy absorbs a greater amount of water than TGDDM, possibly due to the greater surface area and greater number of diffusive sites in the *Novalac*. Because of their affinity for water, DDS, and  $\text{BF}_3$ :MEA increase the amount of moisture a system can absorb.

DSC results on the pure constituents and their mixtures indicate that DDS and  $\text{BF}_3$ :MEA are involved in complexes with the water. In particular, the water-sorbed DDS sample showed a characteristic, broad endothermic peak at 70°C. This may be due to the melting of a complex formed between DDS and water.  $\text{BF}_3$ :MEA thermograms show several exothermic peaks attributable to water reacting with complexes present in the catalyst. Epoxy resins, exposed to a moisture environment, had a greater extent of reaction

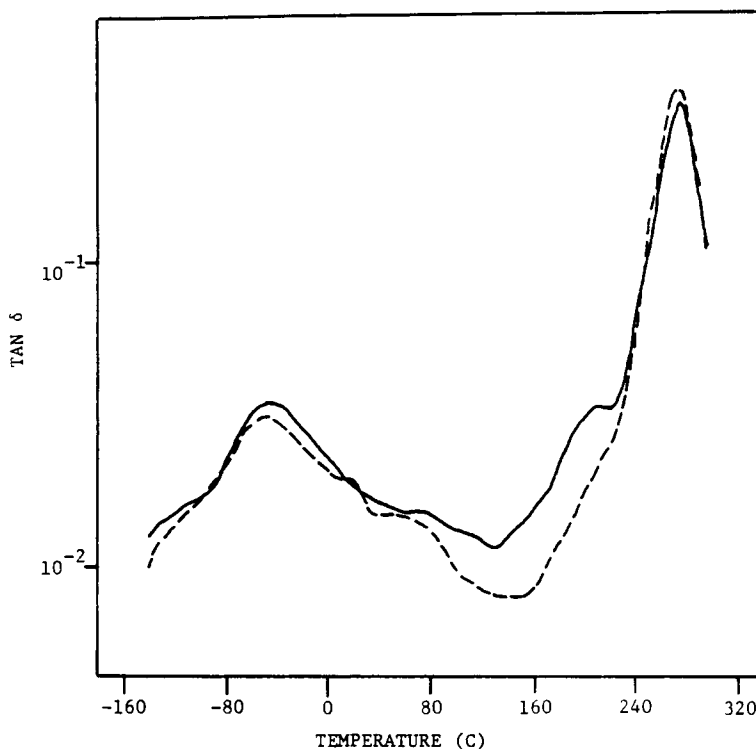


Fig. 10. Dynamic mechanical  $\tan \delta$  results as a function of temperature for as-mixed (—) and moisture-modified (- - -) TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA model system.

than "dry" samples. Moisture exposure decreased the extent of catalyzed reaction in the systems containing BF<sub>3</sub>:MEA, probably due to the reaction of the catalyst with water. Novalac-DDS and Novalac-DDS-BF<sub>3</sub> systems exhibited an endothermic peak similar to that observed for DDS alone. This indicates that the DDS complexes with water, even after being mixed with epoxies.

The dynamic mechanical results on cured samples indicate that the properties of the TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA system may be slightly affected by the presence of water during cure. Water was added to this epoxy system prior to B-staging. The  $\beta$ -transition magnitude decreased for the water-modified system, indicating a decrease in the extent of amine-epoxide reaction. The  $\alpha_1$  peak disappeared when water was added, which indicates a higher extent of reaction due to water-initiated etherification reaction. The  $\alpha_2$  peak temperature decreased, indicating a lower extent of crosslinking for the moisture-modified system. The emergence of the  $\omega$  peak in the moisture-modified system is directly attributable to the retained moisture and/or heterogeneities produced in the epoxy network. The presence of moisture in the TGDDM-Novalac-DDS-BF<sub>3</sub>:MEA epoxy system could have an impact on the processability of the resin. The resulting bulk properties of the cured system, however, should not be greatly affected by the presence of moisture during cure as can be seen by the slight depression of the glass transition.

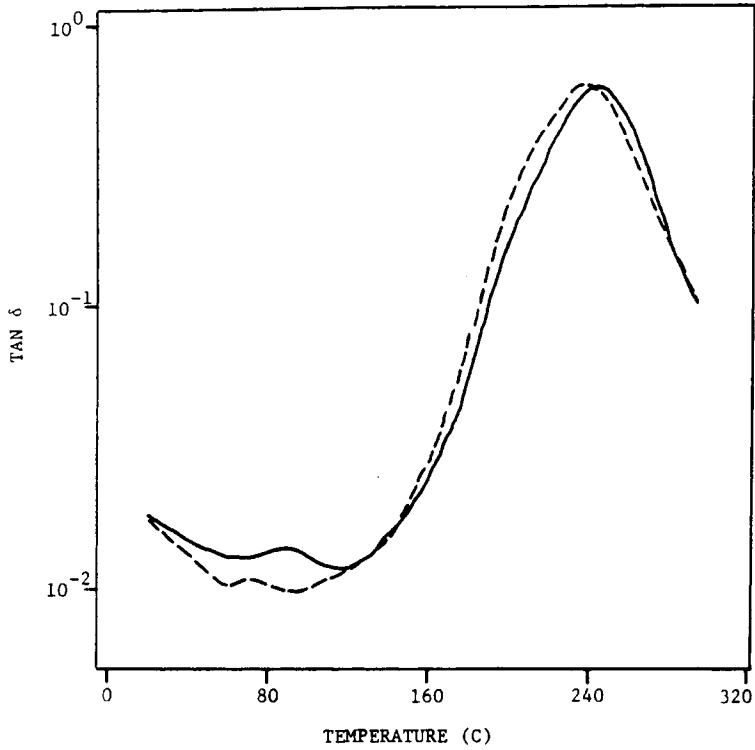


Fig. 11. Tan  $\delta$  plots of dynamic mechanical results for as-received (—) and moisture-modified (- - -) Hercules 3501-6 commercial resin formulations.

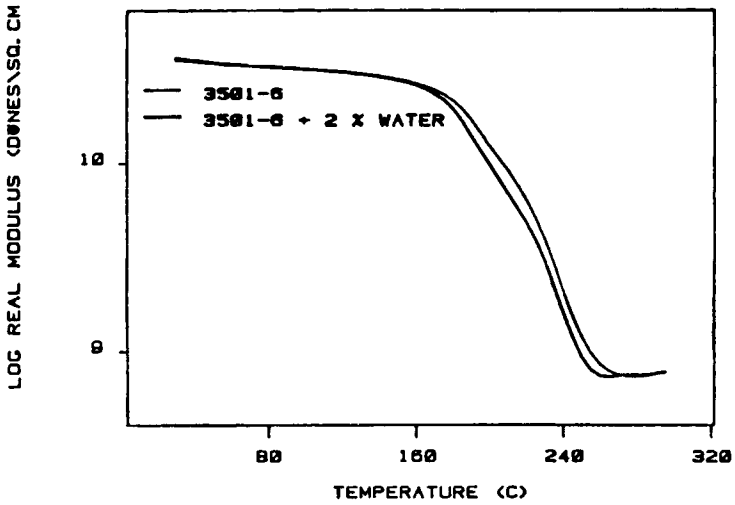


Fig. 12. Modulus plots of dynamic mechanical results for as-received (—) and moisture-modified (- - -) (2%  $H_2O$ ) Hercules 3501-6 commercial resin formulations.

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