

High Performance Epoxy Resins Cured in the Presence of BF_3 Catalyst*

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Synopsis

Dynamic mechanical experiments have been conducted on an epoxy system made with tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) and polyglycidyl ether of Bisphenol A Novalac that were cured with 4,4'-diaminodiphenyl sulfone (DDS) in the presence of Boron trifluoride monoethylamine catalyst ($\text{BF}_3\cdot\text{EtNH}_2$). As the concentration of $\text{BF}_3\cdot\text{EtNH}_2$ increased, the low temperature β -transition magnitude increased slightly. The α_1 -transition observed in the uncatalyzed system decreased significantly with the addition of $\text{BF}_3\cdot\text{EtNH}_2$ catalyst. The α_2 or glass transition temperature of this system increased with increasing catalyst concentration. Both the catalyzed and uncatalyzed epoxy formulations studied in this work are important due to their similarity to systems used commercially in epoxy matrix composites.

INTRODUCTION

High-performance, amine-cured epoxies have found increased usage as the matrix material in carbon fiber reinforced composites for load-bearing structural applications. Dynamic mechanical experiments are extensively applied to gain information not only about mechanical properties, but also to gain some morphological information about these epoxy matrix systems.

Our previous studies have focused on the commercially important resin system consisting of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) and polyglycidyl ether of Bisphenol A Novalac cured with 4,4'-diaminodiphenyl sulfone (DDS).^{1,2} Dynamic mechanical experiments have been used to determine the effect of amine concentration and the influence of processing conditions and stoichiometry of the various constituents on the network structure and the viscoelastic properties of the TGDDM–Novalac–DDS system.^{1,2}

In general, Lewis acid catalysts are used to reduce the cure time in manufacturing composite parts. Boron trifluoride (BF_3) compounds are commercially important Lewis acid catalysts used in epoxy resin systems. Accordingly, this study is focused on the catalytic effect of $\text{BF}_3\cdot\text{EtNH}_2$ on the structure and properties of the TGDDM–Novalac–DDS system as can be observed by dynamic mechanical experiments.

EXPERIMENTAL

Four resin batches were prepared containing 88.5% by weight TGDDM (Ciba-Geigy MY720), 11.5% by weight Novalac (Celanese EPI-REZ-SU-8) and

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25 phr DDS (Ciba-Geigy Eporal) with 0, 1, 2, and 3 phr boron trifluoride monoethylamine ($\text{BF}_3 \cdot \text{EtNH}_2$). The phr is based on 100 total parts by weight of both epoxy resins. MY720, although not a pure form of the TGDDM, was chosen due to its commercial significance. The uncatalyzed system is similar to several commercial epoxies, including NARMCO 5208,³ and has been extensively characterized^{1,2} in our previous studies. The addition of $\text{BF}_3 \cdot \text{EtNH}_2$ catalyst to our basic formulation allows us to extend comparison of our data to additional important epoxy systems, including Hercules 3501.⁴

The TGDDM, Novalac, and DDS components were mixed at a temperature of 135°C and a stirring speed of 575 rpm according to our earlier described procedure outlined in Ref. 2. After the resin was cooled for 5 min to approximately 120°C , the $\text{BF}_3 \cdot \text{EtNH}_2$ was added and stirred for 2 min. The mixture was frozen to stop the reaction and stored at 0°C until needed.

When a film was needed the mixed resin was heated to 121°C and degassed in a vacuum for 30 min. The mixture was molded between smooth machined steel plates. Spacers, of sufficient thickness to yield films approximately 0.01 cm thick, were placed between the plates. The mold was bolted together and placed in an oven at 177°C . Films were cured for 2 h and cooled slowly. Cure times and temperatures were selected close to those used in commercial production of epoxy matrix composites with this system.¹ Samples measuring 0.4

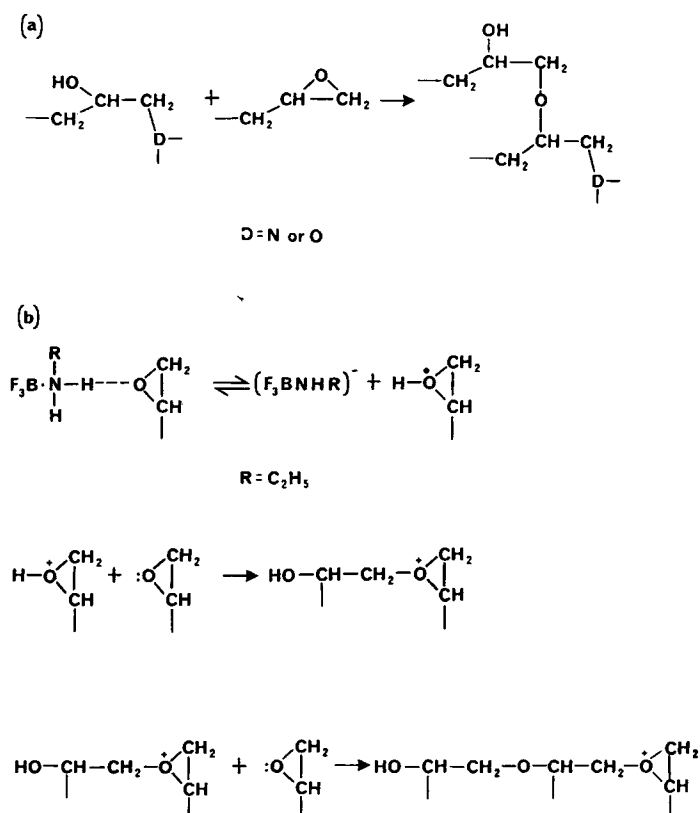


Fig. 1. (a) Hydroxyl polymerization of epoxy. (b) $\text{BF}_3 \cdot \text{EtNH}_2$ catalyzed epoxy homopolymerization.^{7,8}

cm \times 5 cm were cut using a scratch and break technique. Sample edges were sanded smooth to produce an edge of high quality for dynamic mechanical experiments.

Dynamic mechanical experiments and error analysis of the data were conducted on a Rheovibron DDV II according to our well-established procedures.⁵ Corrected data are reported here in the traditional $\tan \delta$ and dynamic modulus quantities.

RESULTS AND DISCUSSION

Polymerization mechanisms and resulting network structures for high-performance amine-cured epoxy systems have been extensively studied, assuming that the epoxide groups react in a stepwise manner with primary and secondary amino hydrogens.² Homopolymerization of the epoxide groups and hydroxyl reactions were assumed negligible compared to the amino hydrogen reactions.^{2,6}

Hydroxyl and homopolymerization reactions, in addition to primary and secondary amino hydrogen reactions, may be significant in the cure of the TGDDM–Novalac–DDS system in the presence of $\text{BF}_3\text{:EtNH}_2$. The hydroxyl reaction is shown in Figure 1(a). Reaction mechanisms involving epoxy homopolymerization, as shown in Figure 1(b), have been described for systems catalyzed by BF_3 compounds.^{7,8} Therefore, homopolymerization reactions can be expected to occur to a more significant extent for the TGDDM–Novalac–DDS system reacted in the presence of $\text{BF}_3\text{:EtNH}_2$ than for uncatalyzed systems. Crosslinks result from all secondary amino–hydrogen reactions or whenever three or more epoxide groups from a monomer molecule have participated in amino–hydrogen, hydroxyl, or homopolymerization reactions.²

Two main viscoelastic transitions were observed in the dynamic mechanical data as shown in Figure 2(a) for $\tan \delta$. The β transition, centered at approximately -50°C , is a complex transition, primarily attributable to crankshaft rotation about hydroxy–ether groups that are a result of epoxy–amine reactions,^{1,2} but also consisting of the contributions due to segmental motion of other structural groups that are a result of homopolymerization.⁹ The magnitude of the β -transition is insensitive to the extent of homopolymerization reaction.⁹ However, both breadth and magnitude of the β -transition are quite sensitive to the extent of amino–hydrogen reaction, and are, therefore, useful in determining the relative extent of this reaction.^{2,9}

The high temperature, α -transition has been observed to separate into two transitions, α_1 and α_2 , depending on the extent of cure of the sample.¹ For a partially cured sample, $\tan \delta$ increases with temperature until approximately 190°C due to the increased mobility of the polymer chains attributed to the glass transition of the original sample. As the sample temperature is increased above 190°C , the increased mobility of the polymer chains overcome steric and diffusional limitations of the network allowing further curing reaction. The greater extent of reaction resulting in crosslinking decreases the molecular mobility, causing a decrease in $\tan \delta$ and an increase in the dynamic modulus. The α_2 peak is attributable to the glass transition of the sample when it has gone through additional cure during the dynamic mechanical experiment.¹

The dynamic mechanical properties, presented in Figure 2, reflect the changes

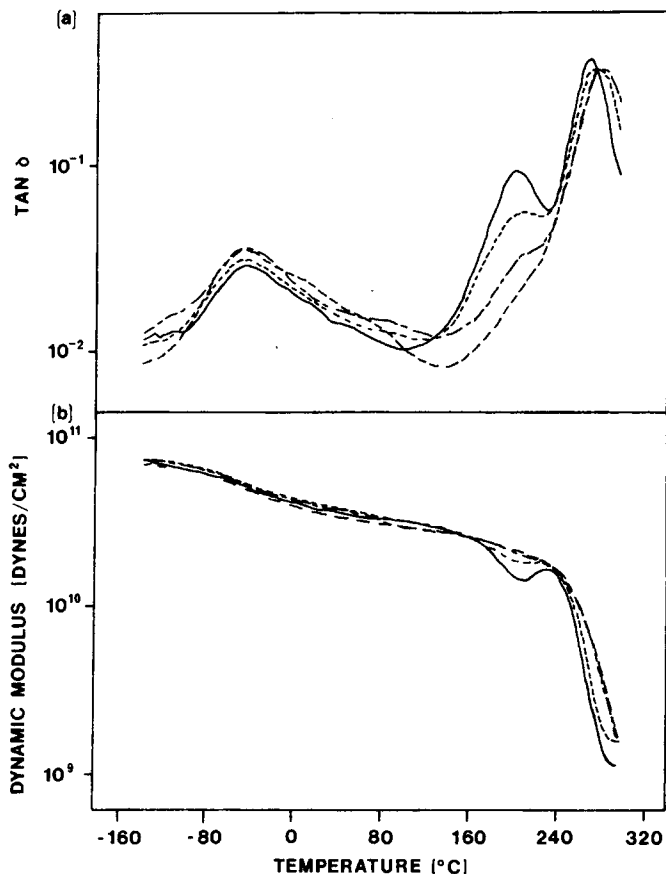


Fig. 2. Dynamic mechanical properties for TGDDM-Novalac-DDS with different 3 phr of $\text{BF}_3:\text{EtNH}_2$. (a) $\text{Tan } \delta$ as a function of temperature. (b) Dynamic modulus as a function of temperature. (—) 0 phr BF_3 ; (---) 1 phr BF_3 ; (- - -) 2 phr BF_3 ; (- - -) 3 phr BF_3 .

of the network structure due to the presence of $\text{BF}_3:\text{EtNH}_2$ catalyst. The magnitude and breadth of the β -transition increased slightly with $\text{BF}_3:\text{EtNH}_2$ content. The exothermic nature of the $\text{BF}_3:\text{EtNH}_2$ -catalyzed reaction provides enough heat to allow additional amine-epoxy reaction. The additional amine-epoxy reaction results in more hydroxyether groups and, therefore, a more pronounced β -transition. As shown in Figure 3, the effect of increasing $\text{BF}_3:\text{EtNH}_2$ concentration diminishes between 2 phr and 3 phr $\text{BF}_3:\text{EtNH}_2$. This may be due to steric and diffusional hindrance and to the depletion of available amine for further reaction to occur. The amount of $\text{BF}_3:\text{EtNH}_2$ catalyst used exhibits no discernible effect on the temperature location of the β -transition maximum.

The presence of $\text{BF}_3:\text{EtNH}_2$ significantly altered the α_1 -transition observed for this epoxy system. The α_1 -transition as described by $\text{tan } \delta$ has been shown to decrease with increasing crosslink density.² As the $\text{BF}_3:\text{EtNH}_2$ concentration was increased, the $\text{tan } \delta$ magnitude of the α_1 -transition decreased until, at 3 phr $\text{BF}_3:\text{EtNH}_2$, the peak was virtually eliminated. Since the amount of DDS remained constant at 25 phr, the additional crosslinking indicated by the reduction

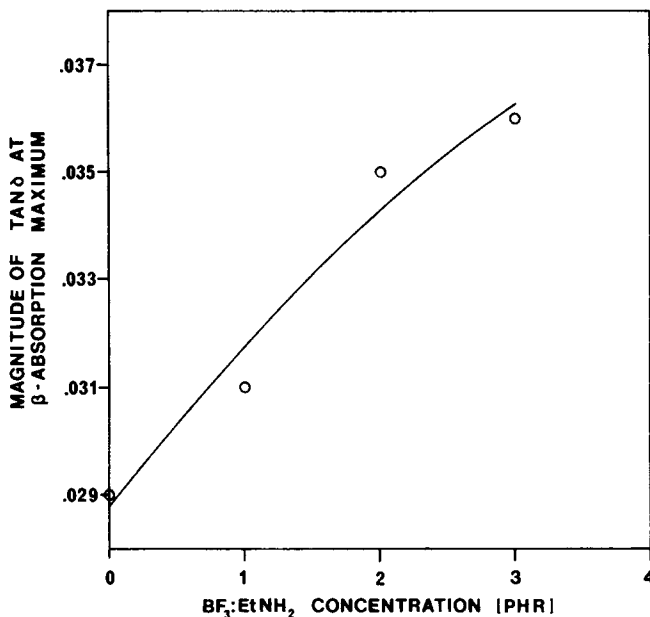


Fig. 3. Magnitude of $\tan \delta$ at β absorption maximum for TGDDM-NOVALAC-DDS epoxy system as a function of $\text{BF}_3:\text{EtNH}_2$ concentration used in the sample formulation.

in α_1 magnitude can be attributed primarily to $\text{BF}_3:\text{EtNH}_2$ -catalyzed homopolymerization. The extent of the increased amine reaction, as is evident from β -transitions, due to the exothermal $\text{BF}_3:\text{EtNH}_2$ reaction is not significant enough to cause the large changes in the α_1 peak observed.

The temperature of the α_2 peak $\tan \delta$ maximum increased from 268°C for the uncatalyzed resin to 277°C for the resin reacted with 3 phr $\text{BF}_3:\text{EtNH}_2$. Network stability to higher temperatures for increasing $\text{BF}_3:\text{EtNH}_2$ concentration can be attributed to hindered chain mobility caused by a higher extent of epoxide reaction. The effect of increasing $\text{BF}_3:\text{EtNH}_2$ concentration diminishes above 2 phr BF_3 .

Little change in the dynamic modulus was observed below 120°C due to the $\text{BF}_3:\text{EtNH}_2$ catalyst. Above 120°C , the dynamic modulus deviates, as shown in Figure 2(b), due to increases in the degree of initial epoxide reaction with increasing $\text{BF}_3:\text{EtNH}_2$ concentration. For ease of comparison with previous results, the glass transition temperature (T_g) can be defined as the temperature where the dynamic modulus is equal to one half the dynamic modulus at room temperature ($T_g = T_{g\text{ERT}/2}$).^{1,10} This glass transition temperature increased with BF_3 content as shown in Figure 4. This effect is indicative of the greater extent of epoxide reaction due to the presence of $\text{BF}_3:\text{EtNH}_2$ catalyst.

CONCLUSIONS

Dynamic mechanical experiments indicate that catalysis of TGDDM-NOVALAC-DDS epoxy with $\text{BF}_3:\text{EtNH}_2$ significantly affects the network structure of the system.

The β -transition magnitude and width increased slightly with increasing

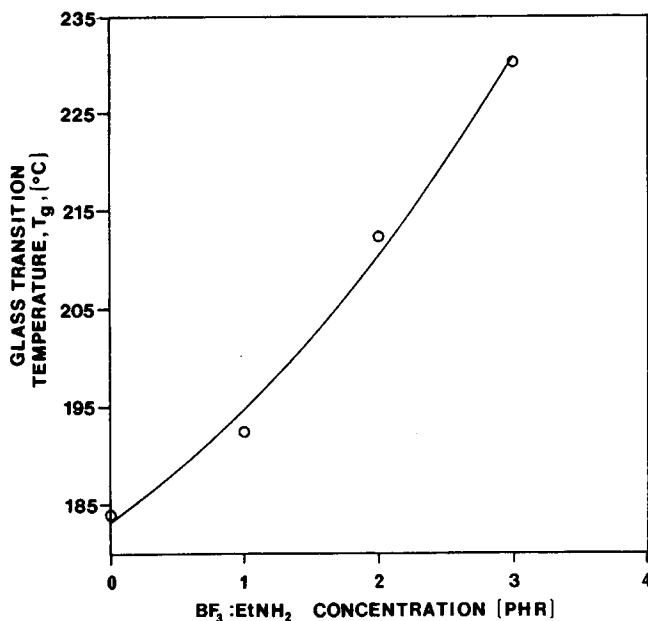


Fig. 4. Glass transition temperature (T_g) of the TGDDM–Novalac–DDS epoxy as a function of $\text{BF}_3\text{:EtNH}_2$ concentration. T_g is defined as the temperature where the sample's dynamic modulus equals half of its dynamic modulus at room temperature ($E = E_{RT}/2$).

$\text{BF}_3\text{:EtNH}_2$ concentration. The β -transition is due mainly to rotation about hydroxyether groups resulting from amine–epoxy reactions. One may postulate that the observed increase in the β -transition may be attributed to the additional amine reaction driven by the heat from the exothermal $\text{BF}_3\text{:EtNH}_2$ -catalyzed polymerization.

The α -transition split into two distinct peaks, the α_1 and α_2 . The α_1 peak is the result of the glass transition of the original network with the superposition of additional epoxide reaction above 190°C. The α_1 peak vanishes as $\text{BF}_3\text{:EtNH}_2$ content increases due to the increasing extent of reaction. Less significant changes in the β -transition, compared to α_1 changes, indicate that the disappearance of the α_1 transition may be due primarily to additional homopolymerization, rather than epoxy–amine reaction. The α_2 peak is attributable to the glass transition of the final network. The glass transition temperature increases with increasing $\text{BF}_3\text{:EtNH}_2$ concentration as a result of the higher degree of crosslinking present.

In summary, this work has elucidated the effect of the addition of $\text{BF}_3\text{:EtNH}_2$ catalyst on a commercially important mixture of epoxies as can be observed with dynamic mechanical experiments. Studies are continuing to determine how each constituent epoxy is affected by $\text{BF}_3\text{:EtNH}_2$ catalysis. Preliminary results indicate that the reduction of the α_1 -transition is quite complex and may be due to homopolymerization as well as secondary amino–hydrogen epoxide group reactions.

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References

1. J. D. Keenan, J. C. Seferis, and J. T. Quinlivan, *J. Appl. Polym. Sci.*, **24**, 2375 (1979).
2. H. S. Chu, M. S. thesis, Department of Chemical Engineering, University of Washington, 1980; H. S. Chu and J. C. Seferis, in *The Role of the Polymeric Matrix on the Processing and Properties of Composite Materials*, J. C. Seferis and L. Nicolais, Eds., Plenum, New York, to appear.
3. C. A. May, J. S. Fritzen, and D. K. Whearty, AFML-TR-76-112, June 1976.
4. J. F. Carpenter, N00019-77-C-0155, May 1978.
5. A. R. Wedgewood and J. C. Seferis, *Polymer*, **22**, 966 (1981).
6. J. P. Bell, *J. Polym. Sci., A-2*, **8**, 417 (1970).
7. W. G. Potter, *Epoxy Resins*, Iliffe, London, 1970.
8. J. J. Harris and S. C. Temin, *J. Appl. Polym. Sci.*, **10**, 523 (1966).
9. M. Ochi, M. Okazaki, and M. Shimbo, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 689 (1982).
10. R. J. Morgan and J. E. O'Neal, *Polym. Plast. Technol. Eng.*, **10**(1), 49 (1978).

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