Processing–Morphology–Property Relationships in Epoxy Resins Containing "Fortifiers"

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Synopsis

An investigation was carried out into the effect of an additive called "fortifier" on curing, morphology, and thermomechanical properties of epoxy resins. Differential scanning calorimetry, electron microscopy, and a series of mechanical measurements were performed on bifunctional and tetrafunctional formulations. It was found that the addition of fortifier resulted in an increase in the fracture surface roughness, the size of morphological inhomogeneities observed in the fractographs, and the ultimate tensile strength. At the same time, the glass transition temperature was found to decrease by at least 25°C in going from 0 to 15 phr of the fortifier in a formulation. The presence of fortifier had little effect on the rate of cure and on the strain energy release rate.

INTRODUCTION

In the last decade, a considerable amount of research has been done in the direction of toughening epoxies, while maintaining high modulus and thermal stability. Some researchers focused their attention on the introduction of a rubbery phase into epoxy networks,[1] while others studied the effects of blending a sterically hindered aliphatic amine with another amine curing agent, and then incorporating the blend into the network.[2,3] Still others sought to toughen epoxies by introduction of an organo-metallic cobalt complex into the network.[4,5]

Recently, it was reported that the addition of a class of chemical modifiers, termed "fortifiers," to epoxy resins, leads to improvements in strength and modulus of cured networks.[6,7] That interesting observation provided a direct incentive for the herein reported work which focuses on the addition of the reaction product of 1,2-epoxy-3-phenoxy propane and 4'-hydroxyacetanilide, hereafter referred to as "the fortifier," to bifunctional and, in some instances, tetrafunctional epoxy resins, and examines the ensuing effects on cure kinetics, morphology, and thermomechanical properties of cured networks.

The objectives of this study were:

1. To determine the effects incurred upon the addition of the fortifier on processing, morphology, and properties of the resin systems
2. To determine the effects of varying the cure schedule on processing, morphology, and properties of the resin systems
3. To determine the effects of varying the concentration of the amine curing agent on processing, morphology, and properties of the resin systems

EXPERIMENTAL

Materials

A bifunctional and a tetrafunctional epoxy resin formulations were prepared and investigated. Shell's Epon 826, a diglycidyl ether of bisphenol A (DGEBA), was the bifunctional epoxy resin used in this study. Ciba-Geigy Corporation's MY720, which consists primarily of 4,4'-tetraglycidyl diaminodiphenylmethane (TGDDM), was the tetrafunctional epoxy resin used. Both resins were characterized by IR and NMR spectroscopy, and by their epoxy-equivalent weights (EEW). The NMR spectra of resins were obtained on a Varian EM390 NMR spectrometer connected to a Varian EM-3930 spin decoupler. The IR spectra were produced on a Shimadzu infrared spectrophotometer IR-435, connected to a Shimadzu data recorder DR-1. The EEW of both epoxy resins was determined by a titration method described in ASTM D 1652-73.

Aldrich Chemical Company's diethylene triamine (DETA) was used to cure the DGEBA resin, and Ciba Geigy's HT976, which consists of 4,4'-diaminodiphenylsulfone (DDS), was used to cure the TGDDM resin.
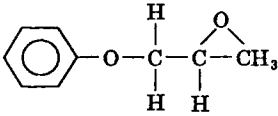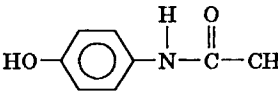
The structure and properties of the fortifier components are shown in Table I. The fortifier was also characterized by IR spectroscopy, and differential scanning calorimetry (DSC).

Sample Preparation

Fortifier

A mixture of 4'-hydroxyacetanilide (HAA) and diethylamine hydrochloride was prepared and added to 1,2-epoxy-3-phenoxypropane (EPP) in a 1000 mL round-bottom flask. EPP is continuously stirred while the powders are being added. The temperature of the oil bath is maintained below 100°C until the

TABLE I
Structure and Properties of Fortifier Components

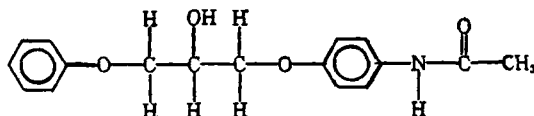| Chemical name	Acronym	Manufacturer	Properties
(±)1,2,Epoxy-3-phenoxypropane	EPP	Aldrich Chem. Co.	MWt = 150.18, bp = 245°C, d = 1.109 g/cc, clear liquid
4'-Hydroxyacetanilide	HAA	Eastman Kodak Co.	MWt = 151.17, mp = 171°C, white powder
Diethylamine hydrochloride	—	Aldrich Chem. Co.	MWt = 109.60, mp = 228°C, white crystals

Fig. 1.   Structure of EPPHAA fortifier.

mixture is completely added. After the mixture has been added the contents of the flask turn into a paste, at which point the heat is increased. When the temperature of the mixture reaches 120°C, the viscosity of the paste is low enough for efficient mixing. The reactants are continuously stirred to avoid hot spots in the flask. The reaction between EPP and HAA catalyzed by diethylamine hydrochloride is exothermic and hence the oil bath (at 170°C) is removed when the temperature in the flask exceeds 145°C. This minimizes the reaction temperature surpassing 160°C. Actually, the reaction mixture remains slightly above 160°C for approximately 10 min, but this does not cause any degradation or side reactions as seen from the FTIR spectra. Continuous stirring of the mixture ensures that the reaction takes place uniformly. Once the temperature of the flask stabilizes at 160°C, the oil bath is reintroduced and maintained at that temperature for 1 h. The chemical structure of the fortifier [the reaction product of EPP and HAA (EPPHAA)], and its FTIR spectrum are shown in Figures 1 and 2, respectively.

Bifunctional Formulations

The DGEBA resin was mixed with 9.16, 11.0, and 13.7 phr (parts per hundred parts of resin) of DETA. These formulations correspond to epoxy-to-amine
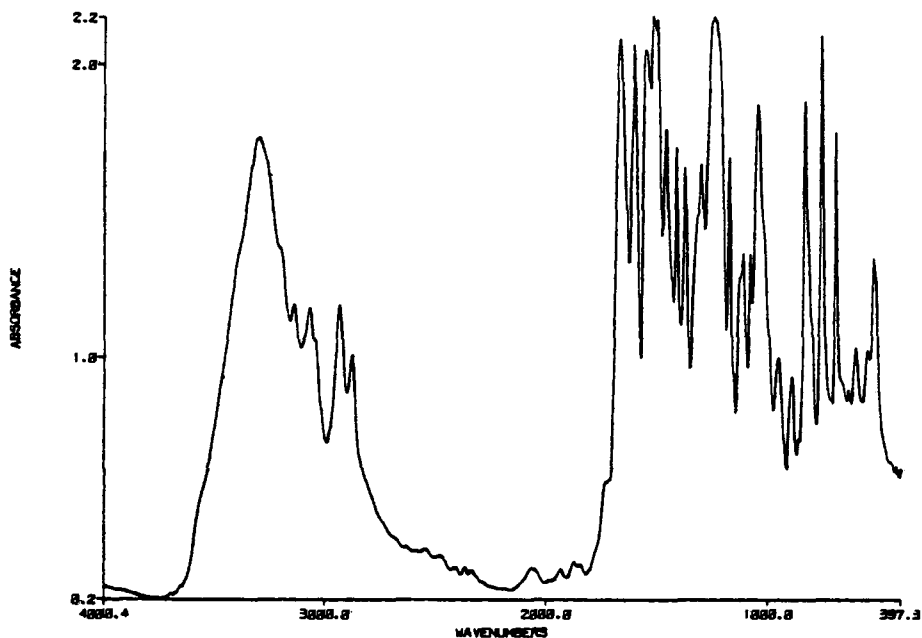

Fig. 2.   FTIR Spectrum of EPPHAA fortifier.

TABLE II
Fortified and Nonfortified Bifunctional Formulations

Stoichiometry (epoxy/amine)	DGEBA	DETA (phr)	EPPHAA (phr)
1.2	100	9.16	0; 8; 11.5; 15
1.0	100	11.0	0; 8; 11.5; 15
0.8	100	13.7	0; 8; 11.5; 15

ratios of 1.20, 1.00, and 0.80, respectively, based on the calculated value of the epoxy equivalent weight (EEW) of 182. Each DGEBA/DETA formulation was stirred for 5 min and then exposed to vacuum for 10 min; both operations were carried out at room temperature.

The various resin/curing agent/fortifier formulations are listed in Table II. The preparation of these formulations begins with the addition of EPPHAA to epoxy resin at 60°C. Thorough mixing is achieved by mechanical stirring, and the mixture is allowed to cool to room temperature before adding the curing agent. The following concentrations of fortifier, expressed in parts per hundred parts of resin (phr) by weight, were used in this study: 8, 11.5, and 15. Attempts to incorporate more than 15 phr of the fortifier were unsuccessful because formulations became unprocessable on the large scale, although small batches containing 20 phr of the fortifier were prepared for election microscopy.

A 0.16 cm thick casting was made of all formulations. The resin mixture was cast between two 35.6 × 35.6 × 0.16 cm aluminum plates clamped around three 35.6 × 2.54 × 0.16 cm aluminum strips. The procedure used to prepare the aluminum plates and strips was identical for all formulations. The aluminum plates were scraped clean of epoxy residue from the previous casting, washed with warm water to remove dust, and with acetone to remove organic residues. The plates were coated with Frekote 33 mold release agent (a product of Frekote Inc.), and allowed to dry overnight. The resin formulation was then poured onto the coated aluminum plates sealed and cured. Table II lists all fortified and nonfortified systems studied and Table III contains their cure schedules.

Tetrafunctional Formulation

The TGDDM resin was formulated with 28 phr of DDS. This corresponds to 0.56 ratio of epoxy to amine, using the EEW value for TGDDM of 125 g/

TABLE III
Cure Schedules[a] for Bifunctional Formulations

Cure cycle	25°C	60°C	90°C	130°C
Slow (S)	24	6	—	2
Intermediate (I)	12	4.5	1.5	2
Fast (F)	—	3	3	2
Fast (F')	3	—	3	2

[a] Numerical entries denote hours.

TABLE IV
Fortified and Nonfortified Tetrafunctional Formulations

Formulation	TGDDM	EPPHAA (phr)	DDS (phr)
100/0/28	100	0	28
100/6/28	100	6	28
100/8.5/28	100	8.5	28
100/11/28	100	11	28

eq. Each TGDDM/DDS formulation was stirred for 5 min and then exposed to full vacuum for 10 min; both operations were carried out at 110°C. In fortified systems, the ratio of amine to epoxy was kept at the same level as that in the nonfortified system—0.56. The TGDDM/DDS mixture was then formulated with 6, 8.5, and 11 phr of the fortifier. At these concentrations, the mole ratio of fortifier to resin is the same for bifunctional and tetrafunctional formulations, allowing for a direct comparison between the two systems.

For tetrafunctional formulations, the fortifier was first added to the TGDDM resin and the two were mixed at 80°C, at which temperature the mixture becomes homogeneous. DDS was added next and a clear amber-colored mixture was formed. The mixture was degassed at 80°C for 5 min and, while hot, poured between the aluminum plates kept at 60°C. The plates were then cooled to room temperature before putting them through the cure schedule. The cure schedule for the tetrafunctional formulation was: 1 h at 135°C followed by 2 h at 177°C, and a post-cure of 2 h at 200°C. All fortified and nonfortified TGDDM systems are listed in Table IV.

Techniques

Differential Scanning Calorimetry (DSC)

Samples for the analysis of reaction kinetics were prepared fresh the day of the run and kept on dry ice until needed. Small sample quantities of 5–15 mg

TABLE V
Heats of Reaction for Some Bifunctional Formulations

Formulation[a]	Isothermal reaction temperature (°C)	Heat of reaction (J/g)[b]
11/0/I	100	−530.74
11/0/I	80	−511.39
11/0/I	60	−471.76
11/8/I	100	−526.93
11/8/I	80	−498.02
11/8/I	60	−453.22
11/15/I	100	−420.69
11/15/I	80	−414.39
11/15/I	60	−368.20

[a] 11 is phr of DETA; 8 and 15 phr of EPPHAA; and I-intermediate cure cycle.
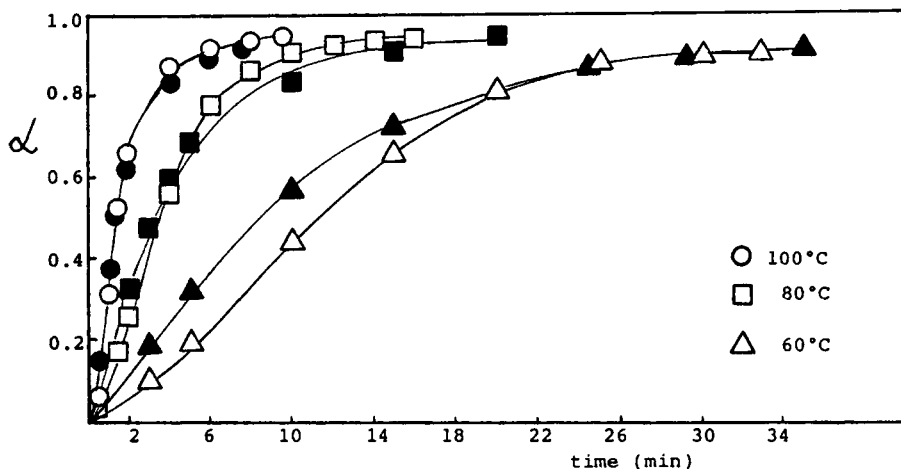[b] J/g of mixture.

Fig. 3.   Degree of conversion (α) as a function of time with temperature as a parameter: (O) no fortifier; (●) 11.5 phr fortifier.

were then placed in hermetically sealed aluminum pans. The measurements of heat of reaction were taken with a Perkin-Elmer DSC7 and the data were stored and analyzed on a Perkin-Elmer 7500 computer.
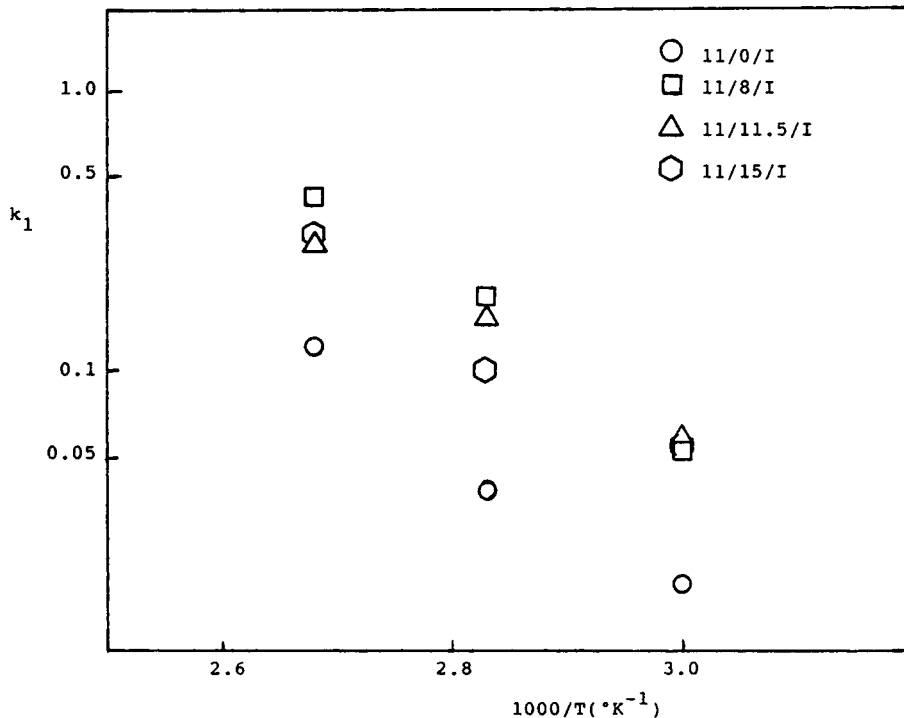

Fig. 4.   Reaction rate constant k_1 as a function of temperature with fortifier concentration as a parameter.
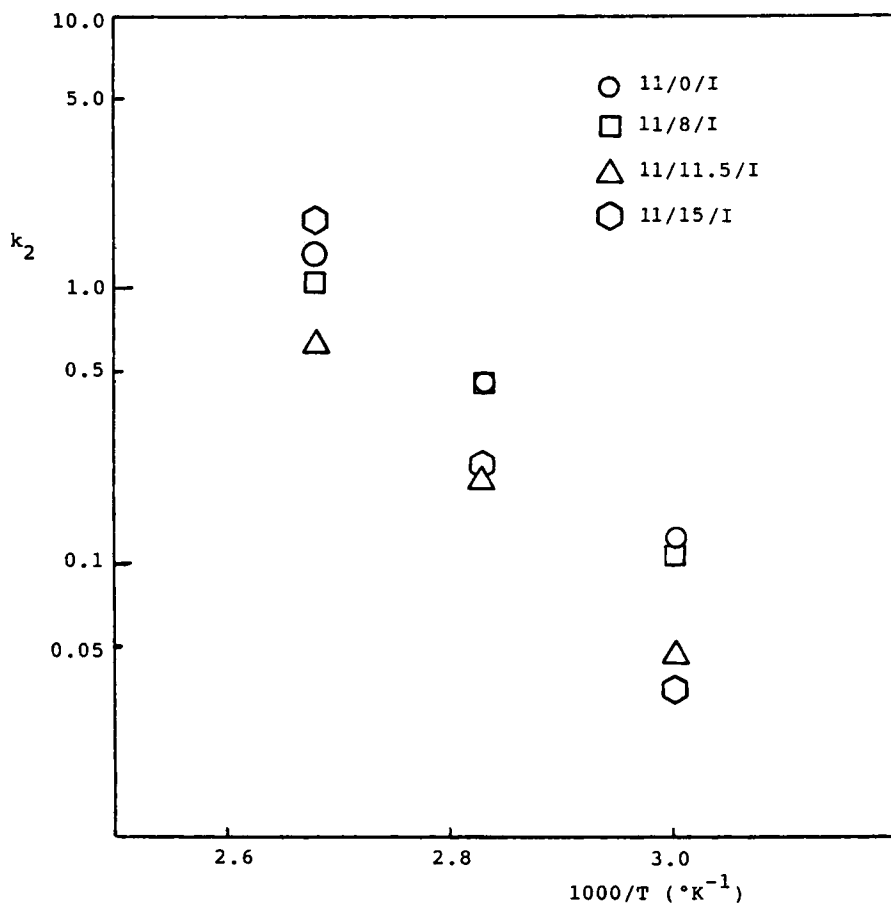
Fig. 5. Reaction rate constant k_2 as a function of temperature with fortifier concentration as a parameter.

Samples for the measurement of glass transition temperature were cut from cured resin panels and run at 10°C/min. A minimum of three samples were tested per datum point. Samples for all thermal and mechanical property measurements were conditioned in a desiccator for 2 weeks at room temperature prior to testing.

Dynamic Mechanical Analysis (DMA)

Specimens for dynamic mechanical measurements were cut from cured resin panels to 3 × 1.15 cm size. Measurements were performed in a DuPont DMA982 module connected to a 1090 thermal analyzer. All tests were run at an oscillation amplitude of 0.2 mm peak-to-peak. A heating rate of 5°C/min was used for the DGEBA, and a heating rate of 10°C/min was used for the TGDDM systems. A minimum of two specimens were tested per datum point.

Thermogravimetric Analysis (TGA)

The oxidative degradation measurements were performed in a DuPont 951 TGA connected to a DuPont 1090 thermal analyzer. All samples were heated

TABLE VI
Glass Transition Temperatures of Bifunctional Formulations

Formulation	DSC (T_g)	DMA $(T_g = T_\alpha)$	DMA (T_β)
11/0/I	113.3	131.3	−14.0
11/8/I	99.6	116.2	−17.0
11/11.5/I	89.2	109.7	−27.2
11/15/I	89.8	107.2	−25.5
13.7/0/I	125.8	139.8	−6.0
13.7/8/I	94.0	109.0	−27.2
13.7/11.5/I	93.8	101.2	−27.0
13.7/15/I	86.1	99.5	−30.5
9.16/0/I	103.5	123.0	−10.7
9.16/8/I	89.0	104.0	−44.0
9.16/11.5/I	80.0	97.2	−40.0
9.16/15/I	79.7	96.2	−39.0
11/0/S	108.6	130.5	−18.0
11/8/S	104.3	128.2	−15.0
11/11.5/S	96.5	115.0	−14.5
11/15/S	89.8	107.7	−35.0
11/0/F'	123.7	131.7	−22.2
11/8/F'	111.7	123.0	−25.0
11/11.5/F'	111.0	114.7	−24.2
11/15/F'	100.6	108.0	−28.5
11/0/F'	127.1	137.5	−13.3

at a rate of 10°C/min from 100 to 450°C, and a minimum of two samples were tested per datum point.

Impact Strength Measurements

Izod impact tests were conducted on specimens cut from 0.635 cm thick cured resin panels, uniform in thickness and free from defects. The panels were

TABLE VII
Glass Transition Temperatures of Bifunctional Formulations for Various Curing Agent and Fortifier Concentrations

Formulation[a]	DMA [T_g (°C)]
1.2/0/I	123.0
1.2/8/I	104.0
1.2/11.5/I	97.2
1.2/15/I	96.2
1/0/I	131.3
1/8/I	116.2
1/11.5/I	109.7
1/15/I	107.2
0.8/0/I	139.8
0.8/8/I	109.0
0.8/11.5/I	101.2
0.8/15/I	99.5

[a] Each formulation is given as phr curing agent/phr fortifier/cure cycle.

TABLE VIII
Glass Transition Temperature of Control Bifunctional Formulation for Various Cure Cycles

Formulation	DMA [T_g (°C)]
11/0/I	131.3
11/0/S	130.5
11/0/F'	131.7
11/0/F	137.5

cast and cured as described earlier, and specimens were cut to size (6.35 × 1.27 × 0.635 cm as recommended by ASTM) using a Felker Bay State/Dresser 41-AR diamond blade bench saw. A sharp 22′ notch was machined into the specimen with a single tooth cutting tool. A minimum of nine specimens were tested per datum point. Tests were conducted on a Wiedemann-Baldwin impact tester (Wiedemann Machine Co.) following the procedure outlined in ASTM D256-81.

Tensile Property Measurements

Tensile tests were conducted in an Instron tester at a crosshead speed of 0.13 cm/min, on specimens cut from 0.16-cm-thick cured resin panels, uniform in thickness and free from defects. Specimens were machined to the size of type IV dogbones, as described in ASTM D 3039-76. A minimum of six specimens were tested per datum point. The low and high temperature tests were conducted with the aid of an insulated stainless-steel jacket which was heated to 60°C for high temperature tests and cooled by liquid nitrogen to −55°C for low temperature tests.

TABLE IX
Glass Transition Temperature of Bifunctional Formulations for Various Cure Cycles
and Fortifier Concentrations

Formulation	DMA (T_g)
11/0/I	131.3
11/8/I	116.2
11/11.5/I	109.7
11/15/I	107.2
11/0/S	130.5
11/8/S	128.2
11/11.5/S	115.0
11/15/S	107.7
11/0/F'	131.7
11/8/F'	123.0
11/11.5/F'	114.7
11/15/F'	108.0
11/0/F	137.5

TABLE X
Glass Transition Temperatures for Various Bifunctional Formulations
Obtained from Dynamic Mechanical Analysis

Formulation	T_g (°C)
11/0/I	131.3
11/8/I	116.3
11/11.5/I	109.7
11/15/I	107.2
13.7/0/I	139.8
13.7/8/I	109.0
13.7/11.5/I	101.2
13.7/15/I	99.5
9.16/0/I	123.0
9.16/8/I	104.0
9.16/11.5/I	97.2
9.16/15/I	96.2
11/0/S	130.5
11/8/S	128.2
11/11.5/S	115.0
11/15/S	107.7
11/0/F′	131.7
11/8/F′	123.0
11/11.5/F′	114.7
11/15/F′	108.0

Fracture Toughness

Linear elastic fracture mechanics analysis was applied to calculate the fracture energy of samples prepared in the form of adhesive joints. Height-tapered double cantilever (HTDCB) specimens were used for fracture energy measurements. By tapering the specimen height, the strain energy release rate in mode I (G_{Ic}) becomes independent of the crack length. The preparation of the surfaces of HTDCB specimens is described elsewhere.[3] Upon priming, the bonding surfaces were ready for the application of adhesive. Resin, curing agent, and fortifier were then mixed, applied onto the beams, and cured according to the schedule outlined in Table III. The HTDCB samples were fractured in an Instron tensile tester Model TM-L at room temperature at a crosshead speed of 0.13 cm/min. The calculation of the critical strain energy release rate was performed as described in our previous communication.[3]

TABLE XI
Glass Transition Temperatures for Tetrafunctional Formulations
Obtained from Dynamic Mechanical Analysis

Formulation	T_g (°C)
100/0/28	262.0
100/6/28	242.7
100/8.5/28	225.0
100/11/28	218.0

TABLE XII
Ultimate Tensile Strength (UTS) and Tensile Modulus (E)
for Various Bifunctional Formulations

Formulation	UTS $\times 10^{-8}$ (Pa)	E (GPa)
11/0/I	4.34	6.47
11/8/I	4.35	5.63
11/11.5/I	5.76	5.38
11/15/I	6.21	5.80
13.7/0/I	4.03	3.57
13.7/8/I	4.61	3.83
13.7/11.5/I	6.41	6.14
13.7/15/I	7.06	6.56
9.16/0/I	4.88	6.15
9.16/8/I	4.75	5.95
9.16/11.5/I	5.90	5.78
11.2/15/I	6.96	5.71
11/0/S	4.53	5.18
11/8/S	4.55	5.51
11/11.5/S	5.16	5.83
11/15/S	6.07	7.28
11/0/F'	3.86	4.38
11/8/F'	4.59	5.26
11/11.5/F'	5.61	7.22
11/15/F'	7.08	8.99
11/0/F'	4.69	4.29

Transmission Electron Microscopy (TEM)

A Varian vacuum evaporator VE-10 was used for the carbon–platinum shadowing of fracture surfaces of bifunctional resin formulations. Samples were shadowed at a pressure of less than 10^{-4} torr and the details of our microscopic investigation have been reported elsewhere.[3] A Philips Model EM200 transmission electron microscope was used in this study.

RESULTS AND DISCUSSION

Cure Kinetics

We begin our discussion by presenting the results of kinetic analysis of fortified and nonfortified DGEBA/DETA formulations. We reiterate that the

TABLE XIII
Impact Strength of Stoichiometric Bifunctional Formulation
for Various Concentrations of Fortifier

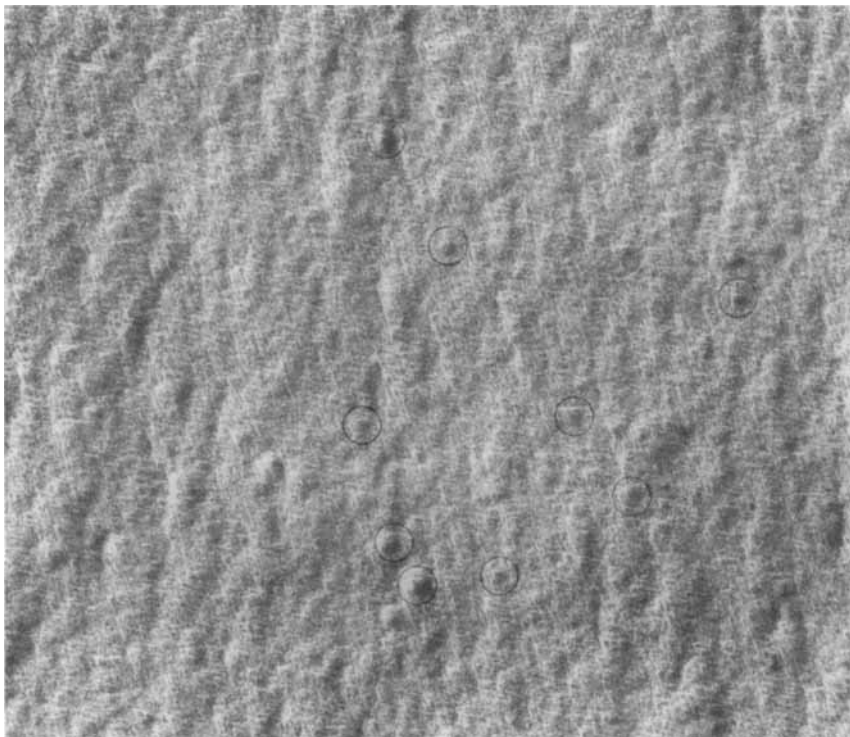| Formulation	T_g (°C)	Impact strength (J/m)
11/0/I	131.3	15.4
11/8/I	116.25	28.9
11/11.5/I	109.75	29.9
11/15/I	107.25	30.9

Fig. 6.   TEM micrograph of a C-Pt replica of fracture surface at 135,000 × magnification. Formulation: 13.7/20/I.

details of the kinetic analysis employed in this study have been reported at length in several recent publications by various researchers[8-10] and by our group,[11,12] and will not be restated here. Suffice it to say that the following phenomenological autocatalytic reaction rate equation was found to describe the kinetics well:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{1}$$

where α is the degree of conversion, k_1 and k_2 are the reaction rate constants, and $(m + n)$ is the overall reaction order. The sum of kinetic exponents $m + n$ was assumed to be equal to 2.[8-12] The highlights of our kinetic study are presented below.

In Table V the values of the ultimate heat of reaction (H_{ult}) are listed as a function of fortifier concentration. The values for nonfortified (control) samples compare well with the literature values.[8-13] Two general observations were made. First, for each formulation, the heat of reaction was found to decrease with decreasing cure temperature, which is quite natural. And second, the heat of reaction was lower in all fortified formulations, indicating that the presence of fortifier slows down the cure process. However, if fortifier is assumed to be completely nonreactive, as suggested by Daly et al.,[7] the observed decrease in
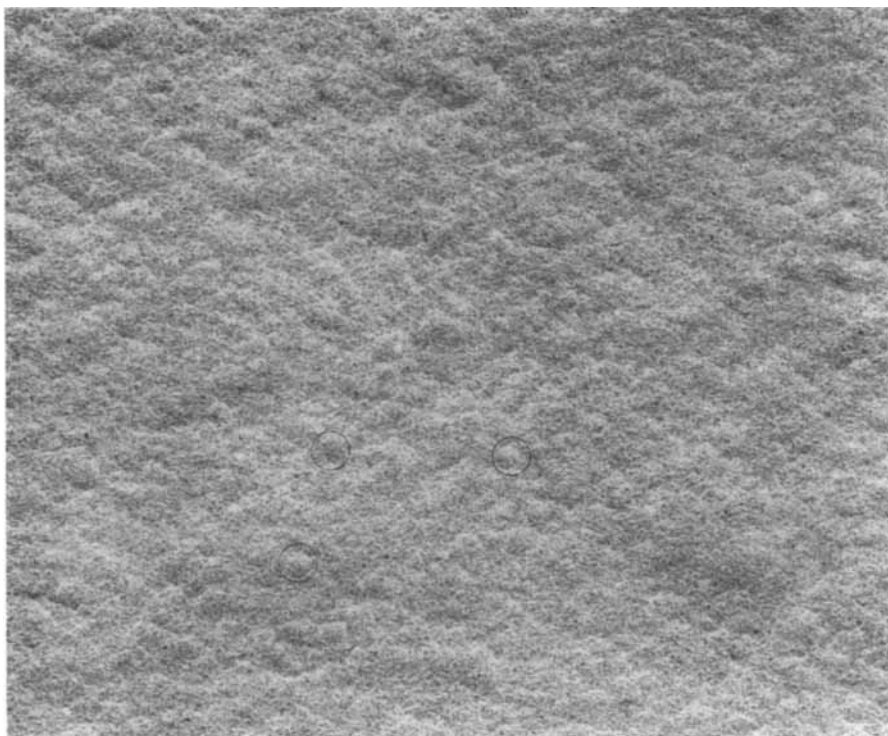
Fig. 7.   Same as Figure 5. Formulation: 11/20/I.

the heat of reaction becomes less pronounced upon normalization of the reaction exotherm with respect to the weight of mixture excluding the fortifier. Further work, using a reactive group distinguishing technique, such as FTIR, would be necessary to clarify the underlying molecular mechanism of cure.

A series of isothermal degree of conversion curves as a function of time for the nonfortified (control) DGEBA/11 phr DETA batch and one fortified formulation (containing 11 phr DETA and 11.5 phr EPPHAA) is shown in Figure 3. With an increase in cure temperature, an increase in the slope of the sigmoidal curve is noted, but the difference between fortified and nonfortified formulation is very small. Plots of the isothermal degree of conversion as a function of time for other fortified batches have analogous characteristics and are not shown here.

The kinetic rate constant k_1 describes the initial reaction rate and was determined directly from the isothermal reaction rate vs. time curves for each batch. As shown in Figure 4, k_1 was found to increase with increasing temperature and, interestingly, the values obtained for the fortified batches were higher than those of the control samples. The reaction rate constant k_2 was also found to increase with increasing temperature, but no distinct trend was observed in k_2 with varying concentration of the fortifier, as shown in Figure 5. The energies of activation for k_1 fell between 10 and 13 kcal/mol and those for k_2 between 16 and 22 kcal/mol, both within the range reported in the literature for different epoxy formulations.[8-14]

Fig. 8.   Same as Figure 5. Formulation: 9.16/20/I.

In summary, an autocatalytic reaction model was found to describe adequately the kinetics of cure of both nonfortified and fortified DGEBA/DETA systems. The model did account for various characteristics of autocatalytic reaction, including the maximum in reaction rate observed in DSC thermograms, sigmoidal shape of degree of cure vs. time curves (shown in Fig. 3) and the observed decrease in the time to reach the peak in reaction rate (t_p) with temperature. However, apart from higher initial reactivity and lower total heat of reaction in fortified formulations, differences between kinetics of fortified and nonfortified formulations were small.

Glass Transition Temperature

The effect of cure schedule and composition on the glass transition temperature of bifunctional formulations, as determined by DSC and DMA, is summarized in Table VI. The glass transition temperature (T_g) shows distinct trends with changes in epoxy/amine ratio, fortifier concentrations, and cure cycles. The data analysis presented here will be based on the values of α-transition in DMA spectra because the trends in T_g as measured by DMA and DSC are the same, as can be seen from Table VI, and because T_g values for tetrafunctional formulations were obtained only from DMA. Our observations are summarized below.
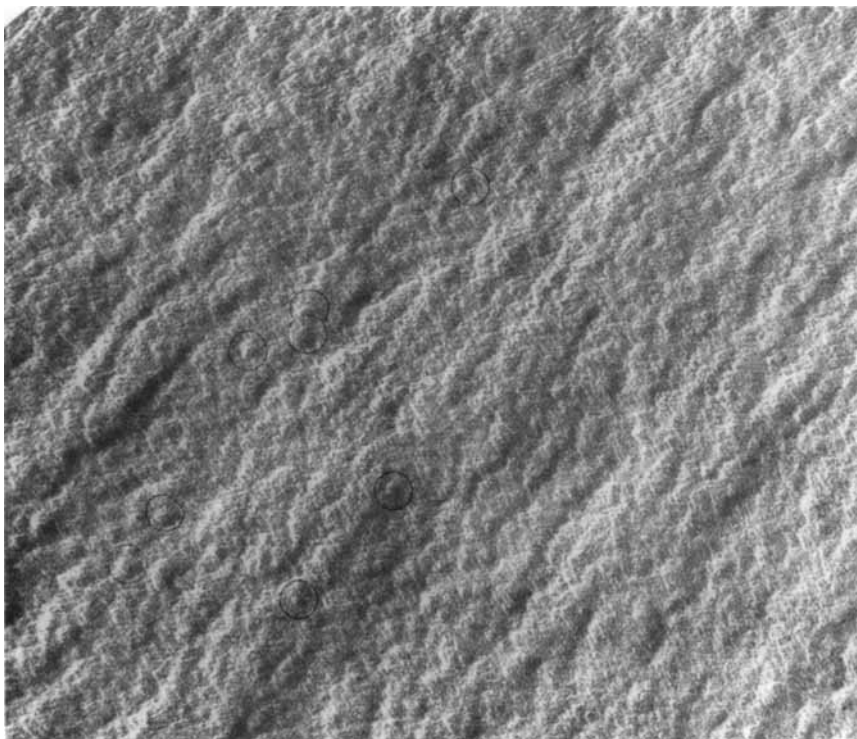
Fig. 9. Same as Figure 5. Formulation: 11/20/S.

Bifunctional Formulation

Change in T_g with Change in Curing Agent Concentration. Increasing the curing agent concentration from 9.16 to 13.7 phr leads to an increase in glass transition temperature for the control formulation while in the fortified formulations the curing agent concentration of 11 phr (stoichiometric ratio of epoxy/amine) gives the highest value for glass transition temperature, as shown in Table VII, for intermediate cure cycle. In fortified formulations containing 13.7 phr of curing agent, the values of glass transition temperature are higher then for fortified formulations containing 9.16 phr of curing agent. We emphasize that the addition of fortifier decreases the glass transition temperature for all concentrations of curing agent by at least 25°C, in going from the control formulation to that containing 15 phr of the fortifier.

Change in T_g with Change in Cure Schedule. The analysis of the effect of cure cycles on T_g for nonfortified formulations showed interesting results. As seen in Table VIII, the three cure cycles with an initial room temperature curing period have T_g's within a very narrow range with a deviation of 0.633 (this lies within the standard deviation of the average values for the T_g's). On the other hand, the fast cure cycle (F), which has an initial curing period at an elevated temperature (60°C), has a slightly higher T_g for the control formulation. Unfortunately, attempts to cure fortified formulations in the fast cure cycle were met with runaway reactions leading to unprocessability of the system.
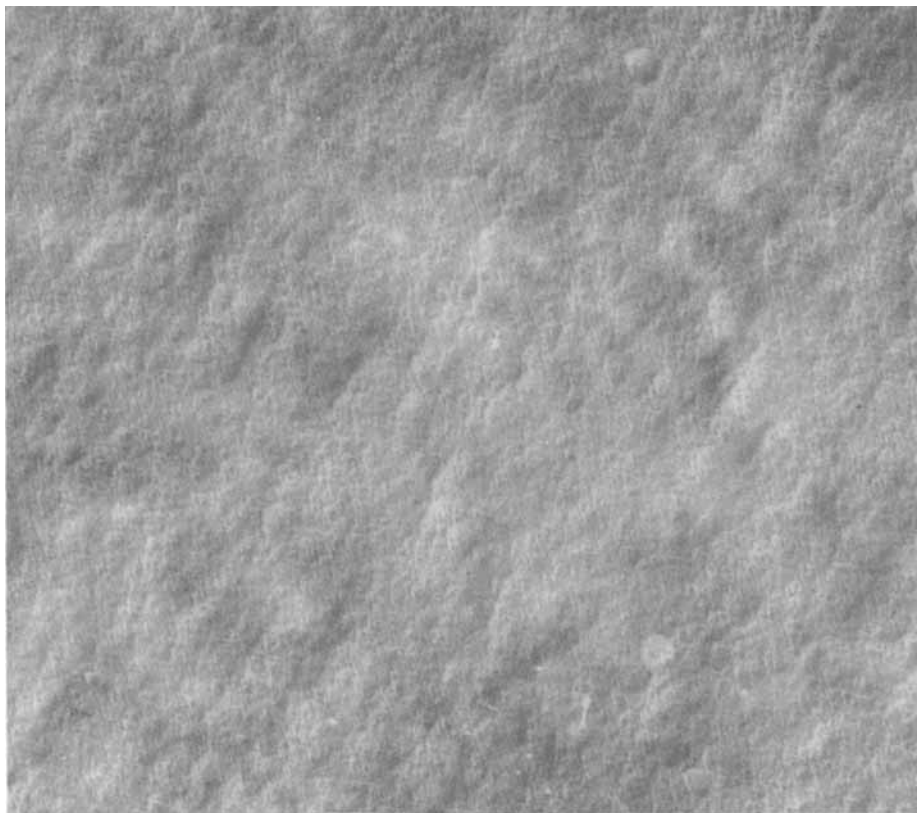
Fig. 10.   Same as Figure 5. Formulation: 11/0/S.

In the fortified formulations, varying the cure cycle does change the T_g. For the lowest concentration (8 phr) of fortifier, the slow (S) cure cycle leads to the highest T_g with the fast (F') cycle giving a slightly lower T_g and the intermediate (I) cycle giving the lowest T_g (Table IX). The same trend was also observed for the next higher fortifier concentration (11.5 phr). However, the highest fortifier concentration (15 phr) does not show any discernible change in T_g with change in cure cycle; the deviation between the T_g's is 0.38°C, which lies within the standard deviation of averaged values.

Change in T_g with Change in Fortifier Concentration. The addition of fortifier leads to a decrease in glass transition temperature of all formulation. Also, the more fortifier in the formulation, the lower its T_g, as seen in Table X.

Tetrafunctional Formulation

In the tetrafunctional system similar trends were observed. The most interesting results are summarized in Table XI, which shows that increasing the fortifier concentration leads to a decrease in the T_g of the system.

Thermogravimetric Properties

Thermogravimetric data, obtained using DuPont's 951 TGA at 10°C/min in nitrogen atmosphere, showed no particular trend. The extrapolated onset of

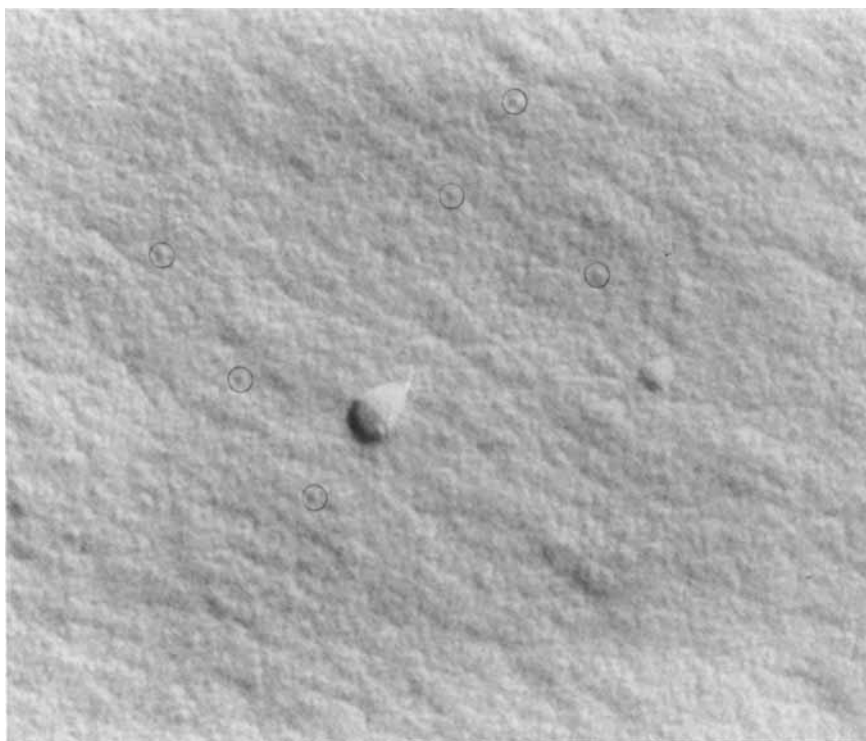Fig. 11.   Same as Figure 5. Formulation: 11/8/S.

the rapid weight loss was within ± 5°C (340 ± 5°C) for all formulations, irrespective of cure schedule or fortifier concentration.

Mechanical Properties

Tensile Properties

The following major observations were made upon analysis of tensile data of all formulations as a function of cure schedule and concentration of fortifier. An increase in the concentration of fortifier resulted in an increase in the ultimate tensile strength (UTS) of all samples as shown in Table XII. Typically, initial addition of 8 phr of fortifier gave rise to a small increase in the UTS, whereas the subsequent increase in the fortifier concentration (to 11.5 and to 15 phr) led to a large increase in the UTS.

The UTS for the control formulation increased with an increase in cure time in going from fast to slow cure cycle. In the fortified formulations, however, the fast cure cycle generally yielded the highest UTS and the slow cycle the lowest.

Tensile (or Young's) modulus data are also listed in Table XII. Modulus of the stoichiometric formulation increased as a function of fortifier concentration in both slow and fast cure cycle but it showed no trend for the intermediate cycle.
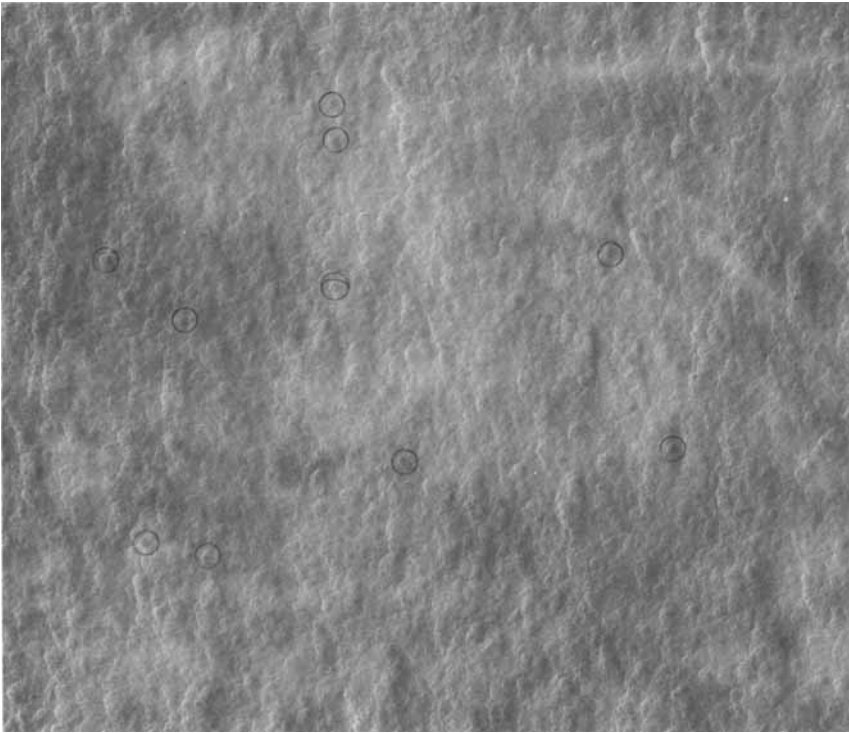
Fig. 12.   Same as Figure 5. Formulation: 11/15/S.

The effect of fortifier concentration on tensile properties at higher (60°C) and lower temperature (−55°C) was also investigated. At lower temperature, Young's modulus was generally found to increase and then level off with the addition of fortifier. Similar but less pronounced response was noted at 60°C. The UTS of samples cured in intermediate cycle increased upon the addition of 8 phr of fortifier and then leveled off.

Fracture Properties

Almost all fracture specimens exhibited an apparent cohesive [center of bond (CoB)] failure. Occasionally, a crack was found to propagate (over a short distance) along the resin–metal interface, but such points were not considered for the calculations of strain energy release rate. The values of G_{Ic} for several formulations with different fortifier concentration were obtained by averaging at least three HTDCB specimens. Generally, eight points were recorded for each specimen of which six points with the lowest standard deviation were used to calculate G_{Ic}. The values so obtained compare well with those reported in the literature, which typically range from 140 to 250 J/m^2 for various bifunctional epoxies.[15] Our fracture study shows an initial increase in G_{Ic} with the addition of 8 phr of fortifier from the control value of 190 to 250 J/m^2. But a further increase in fortifier concentration to 11.5 and 15 phr causes the fracture toughness to drop below the value of the control sample to about 140 J/m^2.

Impact Properties

A somewhat surprising result was obtained from the impact test at room temperature. Table XIII lists the values of impact strength as a function of fortifier concentration for intermediate cure cycle. A twofold increase in impact strength was noted in samples with 8 phr of fortifier, with only a slight change upon further increase in fortifier concentration.

Morphology

Our final objective was to attempt to relate the processing and property characteristics of fortified and nonfortified epoxy systems to their morphology. In this study, the extent of morphological inhomogeneity, as determined from transmission electron micrographs of fracture surfaces, was found to vary as a function of sample formulation and cure conditions.

Figures 6–8 show the effect of decreasing DETA concentration from 13.7 to 11 to 9.16 phr, on the fracture surface morphology of DGEBA/DETA systems containing 20 phr of the fortifier. In samples with DETA concentration of 13.7 phr (Fig. 6) roughly spherical inhomegeneities (nodules), ranging in size from 300 to 350 Å, were clearly evident. At DETA concentration of 11 phr, the nodular structure was less pronounced, with average size of about 250 Å. Further decrease in DETA concentration led to even smaller nodules, ranging in size from 200 to 250 Å. Hence, as the concentration of DETA decreased, the nodular size decreased.

As established earlier, the T_g of the control system was also found to decrease with decreasing concentration of DETA, while the Young's modulus increased significantly in going from 13.7 to 11 phr and then decreased slightly at 9.16 phr of DETA. An explanation for the observed phenomenon has been put forward earlier,[16] whereby an increase in the concentration of curing agent produces an increasingly inhomogeneous epoxy network because the higher curing agent concentration leads to more excessive intranodular (as opposed to internodular) reactions, causing a decrease in the modulus.

Figures 6 and 9 show the effect of varying the cure schedule from intermediate to slow on the morphology of fracture surfaces of the DGEBA/DETA system with 20 phr of fortifier. The intermediate cure schedule did not yield a very pronounced nodular structure as shown in Figure 7. Decreasing the rate of cure from intermediate to slow (Fig. 9) led to a more pronounced nodular structure; the average size was about 300 Å, and nodular alignment was visible. Thus we conclude that in DGEBA/DETA systems containing 20 phr of fortifier, a decrease in the rate of cure was accompanied by a slight increase in the nodular size.

By comparing Figures 10 and 11 one can deduce the effect of increasing concentration of fortifier on the morphology of fracture surfaces of DGEBA/DETA systems containing the stoichiometric amount of DETA and cured in the slow cure schedule. In the control systems (Fig. 10), individual nodules were difficult to discern, but a global inhomogeneous surface with some aligned features was noted. An increase in the concentration of fortifier from 0 to 8 phr (Fig. 11) produced a rougher fracture surface. The surface gave the appearance of an increased quantity of inhomogeneities and, although individual nodules were still difficult to discern, the average nodular size was estimated

to range from 200 to 250 Å. Further increase in the fortifier concentration to 15 phr (Fig. 12) yielded a nodular structure similar to that of the formulation containing 8 phr of the fortifier (Fig. 11). Again, individual nodules were not readily discernible. Still further increase in the fortifier concentration to 20 phr produced a clearer and more pronounced nodular structure as seen in Figure 9, with an average nodular size between 300 and 350 Å. Thus we conclude that in DGEBA/DETA systems containing 11 phr of DETA and cured in the intermediate cure schedule, surface roughness along with nodular size increased with increasing concentration of fortifier. This supports an earlier argument by Daly et al.,[7] who speculated that the observed broadening of the α-transition (T_g) in fortified samples might have been caused by the presence of small (hundreds of angströms) inhomogeneities.

CONCLUSIONS

The main objective of this study was to obtain processing–property–morphology correlations for fortified and nonfortified epoxy systems, and the following observations were made:

1. A phenomenological autocatalytic kinetic model describes cure of both fortified and nonfortified DGEBA/DETA systems with little difference between them.

2. As the concentration of curing agent (DETA) was decreased, the T_g decreased in control formulations and peaked at 11 phr in fortified formulations, the ultimate tensile strength increased, and the size of morphological inhomogeneities (nodules) decreased.

3. With a decrease in the rate of cure for fortified DGEBA/DETA systems, the T_g generally increased, the nodules became more pronounced and the UTS decreased, but no clear trend was seen in the Young's modulus.

4. In DGEBA/DETA systems containing 11 phr of DETA and cured in intermediate cure schedule, the fracture surface roughness along with the nodular size increased with increasing concentration of the fortifier.

5. It was generally observed that with increasing concentration of the fortifier, the T_g for the DGEBA/DETA systems peaked and then decreased, the T_g for the TGDDM/DDS systems decreased continuously, and the T_{ox} changed only slightly for both resin systems. Finally, the introduction of the fortifier in DGEBA/DETA systems did not affect the strain energy release rate but did increase the impact strength.

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