Processing-Morphology-Property Relationships in Epoxy Resins Containing an Organometallic Cobalt Complex

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Synopsis

An investigation was carried out into the effect of an organometallic complex, cobalt (III) acetylacetonate, on curing, morphology, and mechanical properties of several epoxy resins. Differential scanning calorimetry, electron microscopy, and a series of mechanical measurements were performed on bifunctional and tetrafunctional formulations. The addition of cobalt (III) acetylacetonate did not cause drastic changes in any of the systems investigated, although a slight effect on cure kinetics, Young's modulus, and fracture-surface morphology was noted. Also, there was no effect on the impact strength or the critical stress intensity factor of any of our formulations.

INTRODUCTION

In recent years, a considerable amount of research has been done in the direction of toughening epoxies. Some researchers focused their attention on the introduction of a rubbery phase into the epoxy network,[1] while others studied the effects of blending a sterically hindered aliphatic amine with a second amine curing agent and then incorporating the blend into the network.[2,3] Still others sought to toughen epoxies by introduction of a class of chemical modifiers, called "epoxy fortifiers," into the network.[4,5]

Most recently, it was reported that the addition of an organometallic cobalt complex to a tetrafunctional epoxy resin leads to improvements in flexural strength and fracture toughness of cured networks.[6,7] That interesting observation provided a direct incentive for the work here that focuses on the addition of cobalt (III) acetylacetonate (CoAcac) to bifunctional and 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 on the addition of cobalt (III) acetylacetonate (CoAcac) 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, and

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 formulation 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 diamino diphenylmethane (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 the ASTM D1652-73.

Aldrich Chemical Company's diethylene triamine (DETA) was used to cure the DGEBA resin, and Ciba Geigy's HT976, which consists of 4,4'-diamino diphenyl-sulfone (DDS), was used to cure the TGDDM resin.

Cobalt (III) acetylacetonate (CoAcac), obtained from Morton Thiokol Inc., was the organometallic modifier used. Its chemical structure and some of its properties are shown in Figure 1. CoAcac was also characterized by IR spectroscopy and differential scanning calorimetry (DSC).

Sample Preparation

Bifunctional Formulations

The DGEBA resin was mixed with 9.16, 11.0, and 13.7 parts per hundred parts of resin (phr) of DETA. These formulations correspond to epoxy-to-amine ratios of 1.20, 1.00, and 0.80, respectively, assuming an epoxide equivalent weight (EEW) for DGEBA 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.

To prepare successfully a homogeneous mixture, the CoAcac had to be dissolved before its introduction into the DGEBA/DETA formulation. Early in
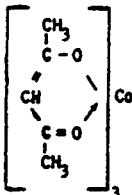
CHEMICAL NAME	ACRONYM	MANUFACTURER	PROPERTIES
cobalt (III)	CoAcac	Morton Thiokol, Inc.	MW = 356g/gmol
acetylacetonate			MP = 216°C
		BP = 340°C	
		green granules	

Fig. 1.   Structure and properties of cobalt (III) acetylacetonate (CoAcac).

the study, it was found that CoAcac dissolved only slightly in DETA at room temperature. At elevated temperatures, CoAcac dissolved fully in DETA with a change in color of the mixture from green to brown. Because previous researchers[6,7] had found that the reaction between CoAcac and their amine curing agent had favorably modified flexural properties of their epoxies, this method of modifier preparation was continued.

The various concentrations of DETA used in the DGEBA formulations were then reacted with 0.414, 2.07, and 4.14 phr of CoAcac. These phr of CoAcac correspond to 0.004, 0.02, and 0.04 mole ratio of CoAcac to DGEBA (assuming the DGEBA has a molecular weight of 344 g/gmol) in the formulation, respectively. The CoAcac/DETA mixture was reacted for 1.5 h at 100°C, and the product was characterized by IR spectroscopy. The DGEBA resin was then mixed with the CoAcac/DETA reaction product. Each DGEBA/CoAcac/DETA formulation was stirred for 5 min and then exposed to vacuum for 10 min; both operations were carried out at room temperature.

A 0.0625-in-thick casting was prepared of all formulations. The resin mixture was cast between two 14 in × 14 in × 0.0625-in aluminum plates clamped around three 14 × 1 × 0.0625-in 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 and 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 I lists all modified and nonmodified DGEBA systems studied, and Table II contains the cure schedules used.

Tetrafunctional Formulation

The TGDDM resin was formulated with 28 phr of DDS. This corresponds to a 0.56 ratio of epoxy to amine, assuming an EEW for TGDDM of 125 g per

TABLE I
Modified and Nonmodified DGEBA/DETA Systems

Batch	CoAcac (phr)	DETA (phr)	Cure schedule
Nonmodified systems			
0/11/S	0	11	Slow
0/11/I	0	11	Intermediate
0/11/F	0	11	Fast
0/9.16/I	0	9.16	Intermediate
0/13.7/I	0	13.7	Intermediate
Modified systems			
0.414/11/I	0.414	11	Intermediate
2.07/11/S	2.07	11	Slow
2.07/11/I	2.07	11	Intermediate
2.07/11/F	2.07	11	Fast
2.07/9.16/I	2.07	9.16	Intermediate
2.07/13.7/I	2.07	13.7	Intermediate
4.14/11/I	4.14	11	Intermediate

TABLE II
Cure Schedules for Modified and Nonmodified DGEBA/DETA Systems

	Temperature (°C)			
Cure schedules	25	60	90	130
Slow	24	6	—	2
Intermediate	12	4.5	1.5	2
Fast	—	3	3	2

Numerical entries denote time (h) at a certain temperature (°C).

TABLE III
Modified and Nonmodified TGDDM/DDS Systems

Batch	CoAcac (phr)	DDS (phr)
0/28	0	28
0/284/28	0.284	28
1.42/28	1.42	28
2.84/28	2.84	28

TABLE IV
Cure Schedule for Modified and Nonmodified TGDDM/DDS Systems

Temperature (°C)	Time (h)
135	1
177	2
200—postcure	2

equivalent. 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 modified systems, the ratio of amine to epoxy was kept at the same level as that in the nonmodified system—0.56. The TGDDM/DDS mixture was then formulated with 0.284, 1.42, and 2.84 phr of CoACac. These phr of CoAcac correspond to 0.004, 0.02, and 0.04 mole ratio of CoAcac to TGDDM (assuming that TGDDM has a molecular weight of 500 g/gmol). Each TGDDM/CoAcac/DDS formulation was mechanically stirred for 5 min and then exposed to vacuum for 10 min; both operations were carried out at 110°C. The aluminum plates were prepared in the same manner as for the DGEBA systems. All modified and nonmodified TGDDM systems are listed in Table III with their cure schedules described 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

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.

Samples for the analysis of the glass transition temperature were cut from the 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 measurements were conditioned for 2 weeks at room temperature prior to testing.

Dynamic Mechanical Analysis (DMA)

Specimens for dynamic mechanical measurements were cut from the cured resin panels to 30 mm × 11.5 mm size. Measurements were performed in a Du Pont 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. Samples were continuously purged with compressed air at 200 cc/min in order to compare the results obtained in our study with those of previous researchers.[6,7] All samples were heated at a rate of 10°C/min from 100°C 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 $\frac{1}{4}$-in-thick cured resin panels, uniform in thickness and free from defects. Specimens were cut to size (2.5 in × 0.5 in × 0.25 in) using a Felker Bay State/Dresser 41-AR diamond blade bench saw. A sharp 22-foot 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 (Widemann Machine Company) following the procedure outlined in ASTM D256-81.

Tensile Property Measurements

Tensile tests were conducted in an Instron tester at a crosshead speed of 0.05 in/min, on specimens cut from $\frac{1}{16}$-in-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 D3039-76. 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 whereby the temperature was controlled with liquid nitrogen and a solid-state relay, respectively.

Single-edge Notched (SEN) Measurements

SEN tests were conducted on specimens cut from $\frac{1}{16}$-in cured resin panels, uniform in thickness and free from defects and cut to size (2.9 in × 0.5 in)

using a Felker Bay State/Dresser 41-Ar diamond blade bench saw. A sharp crack was introduced in the specimen, resulting in high-stress concentration at the crack tip, which provides a lower limiting value of the critical stress intensity factor in tensile mode (K_{IC}). A minimum of six specimens were tested per datum point. The SEN specimens were fractured in an Instron tensile tester at room temperature and at a crosshead speed of 0.05 in/min. The calculation of K_{IC} was performed as described in ASTM STP 410.

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 EM200 model 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 modified and nonmodified DGEBA/DETA formulations. We reiterate that the details of our kinetic analysis have been reported at length in several recent publications by our group,[11,12] and will not be restated here. Suffice it to say that the following autocatalytic reaction rate equation was found to describe the kinetics well:

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

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.[8-10] 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 CoAcac concentration. When the amount of CoAcac introduced into the DGEBA/DETA system is increased from 0 to 2.07 phr, the ultimate heat of reaction remains essentially constant, whereas a further increase from 2.07 phr to 4.14 phr causes the ultimate heat of reaction to decrease. Although

TABLE V
Ultimate Heat of Reaction (H_{ult}) as a Function of CoAcac
Concentration for Formulations with 11 phr DETA

Batch	H_{ult} (J/g)	Standard deviation (J/g)
0/11	554.5	23.3
0.414/11	559.6	14.9
2.07/11	557.6	1.3
4.14/11	507.3	6.0

it is conceivable that CoAcac may cause the formation of a sterically hindered complex with the amine curing agent at higher CoAcac phr,[7] further work using reactive-group distinguishing methods (such as Fourier transform infrared spectroscopy) would be necessary to confirm that possibility. If, indeed, a complex forms, the amount of amine curing agent available for crosslinking would decrease, resulting in a decrease in the ultimate heat of reaction.

A series of isothermal degree of conversion curves as a function of time for the nonmodified DGEBA/DETA batch (0/11) are shown in Figure 2. With an increase in cure temperature, an increase in the slope of the sigmoidal curve is noted. Plots of the isothermal degree of conversion as a function of time for the modified batches are analogous in characteristics and are not shown here. The peak in reaction rate as a function of temperature is shown in Figure 3. As expected, the peak in reaction rate increases with increasing temperature. A linear relationship was observed for all batches, with the nonmodified batch having a somewhat lesser slope than the modified batches. Figure 4 shows the time required to reach the peak (t_p) in reaction rate as a function of temperature. Again, as expected, that time was found to decrease with increasing temperature, but no clear trend was observed as a function of the concentration of CoAcac.

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. k_1 was found to increase with increasing temperature, and, interestingly, the values obtained for the batch modified with 4.14 phr of CoAcac were lower than those of the other batches. The reaction rate constant k_2 was also found to increase with increasing temperature, but no trend was observed in k_2 with varying concentration of CoAcac. The energies of activation for both k_1 and k_2
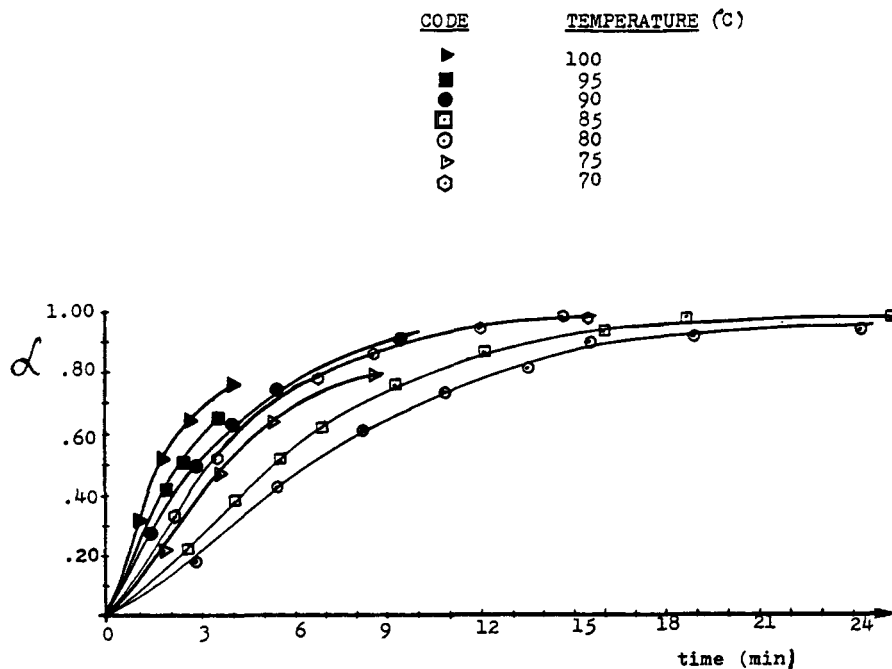

Fig. 2. Degree of conversion (α) as a function of time with temperature as a parameter.
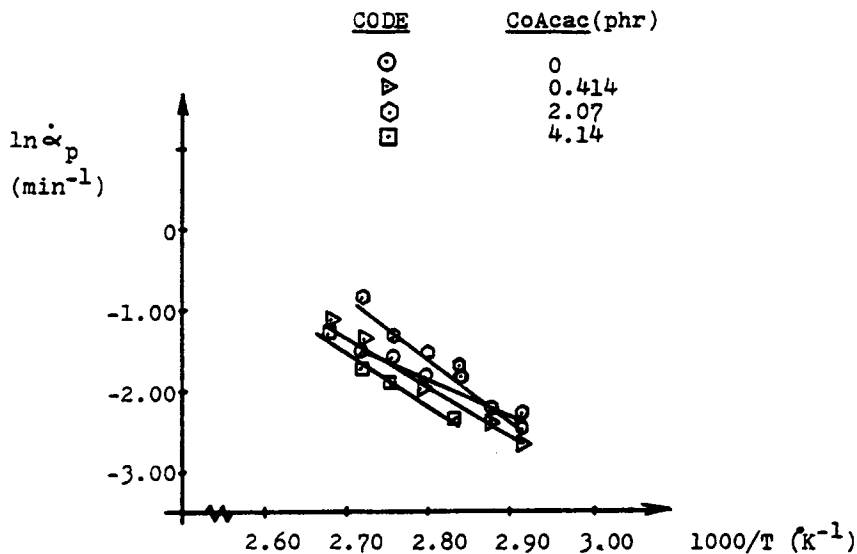
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Fig. 3.   Reaction rate at peak (α_p) as a function of temperature with CoAcac concentration as a parameter.

were within the range reported in the literature for different epoxy formulations.[11-14]

In summary, an autocatalytic reaction model was found to describe adequately the kinetics of cure of nonmodified and CoAcac-modified DGEBA/DETA systems. The model did account for various characteristics of autocatalytic reaction, including the maximum in reaction rate, sigmoidal shape of degree of cure vs.
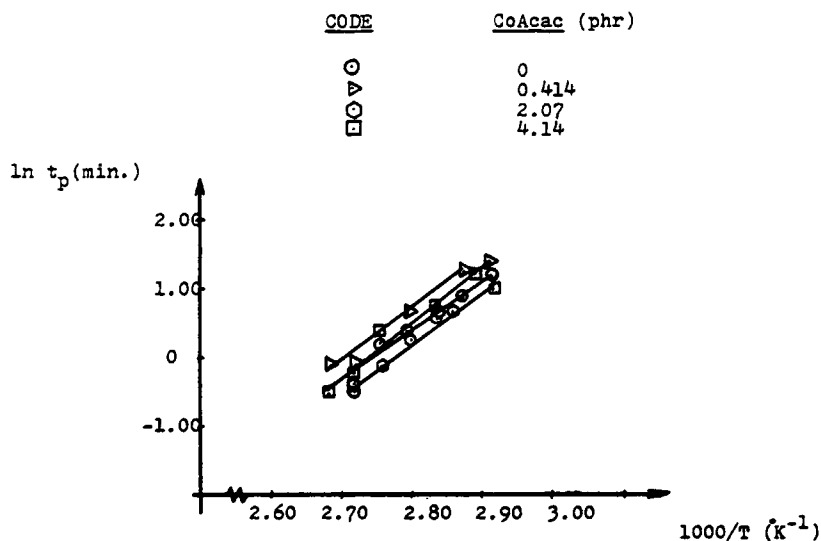
Fig. 4.   Time to reach the peak reaction rate (t_p) as a function of temperature with CoAcac concentration as a parameter.

TABLE VI
Effect of Cure Schedule on Glass Transition Temperature

Batch	T_g (°C)
0/11-F	127
0/11-I	116
0/11-S	109
2.07/11-F	116
2.07/11-I	114
2.07/11-S	113

time curves, and the observed decrease in t_p with temperature. Moreover, despite data scatter, certain trends were observed with varying concentration of CoAcac. First, the ultimate heat of reaction significantly decreased in the batch modified with 4.14 phr of CoAcac as compared with the other batches; previous work[7] suggests that CoAcac may cause the formation of a sterically hindered complex with the amine curing agent, which would effectively reduce the available curing agent for crosslinking. Second, the batch modified with 4.14 phr of CoAcac had a lower degree of conversion at the peak of the reaction rate than did all other batches; the concept of a lower amount of available curing agent for crosslinking may again apply. Third, the nonmodified batch had a lesser slope in the plot of the peak in the reaction rate than did the modified batches. Fourth, the values for the kinetic rate constant k_1 of the batch modified with 4.14 phr of CoAcac were lower than for the other batches.

The Glass Transition Temperature

The effect of cure schedule on the glass transition temperature, as determined by DSC, is shown in Table VI. In varying the cure schedule from fast to slow, the T_g decreases for both modified and nonmodified batches. Previous researchers,[15] working with TGDDM/DDS systems and using a dynamic mechanical analyzer to measure the glass transition, found similar trends with varying cure schedule.

The effect of DETA concentration on the T_g of six modified and nonmodified formulations is shown in Table VII. In varying the DETA concentration from 9.16 to 13.7 phr, the T_g increases. Similar results were reported earlier for

TABLE VII
Effect of DETA Concentration on Glass Transition Temperature

Batch	T_g (°C)
0/9.16-I	103
0/11-I	116
0/13.7-I	126
2.07/9.16-I	95
2.07/11-I	114
2.07/13.7-I	123

TABLE VIII
Effect of CoAcac Concentration on Glass Transition Temperature

Batch	T_g (°C)
0/11-I	116
0.414/11-I	133
2.07/11-I	114
4.14/11-I	105

systems in which DGEBA was cured with 2,5-dimethyl 2,5-hexane diamine[3] and DETA.[15] According to the authors, such a trend should be expected because curing agent-rich formulations would lead to the formation of a higher crosslink density network and thus to a higher glass transition temperature.

The data in Table VIII illustrate the effect of concentration of CoAcac on T_g. In varying the phr of CoAcac from 0 to 4.14, the T_g first increases and then decreases. The changes are dramatic in that with the first introduction of CoAcac (a change of CoAcac from 0 to only 0.37 wt % CoAcac in the resin system) the T_g increases by 17°C. With the next increase of CoAcac, five times the previous amount, the T_g decreases to about the same value as in the nonmodified sample. Any further increase in the amount of CoAcac incorporated in the DGEBA/DETA system causes a decrease in T_g.

In the next set of experiments, the effects of cure schedule, DETA concentration, and CoAcac concentration on the glass transition were investigated by dynamic mechanical analysis (DMA). In varying the cure schedule from fast to slow, the T_g decreases in both nonmodified and modified DGEBA/DETA batches, as shown in Table IX. In varying the DETA phr from 9.16 to 13.7, the T_g increases for both nonmodified and modified batches as seen in Table X. Again, similar results were obtained with systems containing DGEBA cured with 2,5-dimethyl 2,5-hexane diamine,[3] and DGEBA cured with DETA.[15]

Table XI presents DMA data obtained from four modified and nonmodified DGEBA/DETA batches and four modified and nonmodified TGDOM/DDS batches. The data show the effect of varying the concentration of CoAcac on the T_g. With increasing concentration of CoAcac, the T_g of DGEBA/DETA systems passes through a maximum and then decreases. Similarly to the results of the DSC study, the changes in T_g are dramatic. In the same table, we also

TABLE IX
Effect of Cure Schedule on Glass Transition Temperature

Batch	T_g (°C)
0/11-F	137
0/11-I	131
0/11-S	130
2.07/11-F	133
2.07/11-I	130
2.07/11-S	128

TABLE X
Effect on DETA Concentration on Glass Transition Temperature

Batch	T_g (°C)
0/9.16-I	123
0/11-I	131
0/13.7-I	140
2.07/9.16-I	107
2.07/11-I	130
2.07/13.7-I	134

TABLE XI
Effect on CoAcac Concentration on Glass Transition Temperature

Formulation	Batch	T_g (°C)
DGEBA/DETA	0/11-I	131
	0.414/11-I	144
	2.07/11-I	130
	4.14/11-I	112
TGDDM/DDS	0/28	262
	0.284/28	260
	1.42/28	250
	2.84/28	238

TABLE XII
Effect of CoAcac Concentration on T_{ox}

Formulation	Batch	T_{ox} (°C)
DGEBA/DETA	0/11-I	341.7
	0.414/11-I	348.0
	2.07/11-I	350.5
	4.14/11-I	356.1
TGDDM/DDS	0/28	340.2
	0.284/28	350.8
	1.42/28	357.7
	2.84/28	359.0

present the data for the TGDDM/DDS systems. With increasing concentration of CoAcac, the T_g for the TGDDM/DDS systems shows only a decreasing trend. Others studied a similar system (TGDDM/DDS modified with CoAcac and containing small amounts of novolac) and found analogous results.[7] Finally, we note that the secondary relaxation T obtained from DMA spectra did not show any distinct trends as a function of the type of formulation.

Thermogravimetric Properties

Table XII describes the effect of CoAcac concentration on T_{ox} of four modified and nonmodified DGEBA/DETA batches and four modified and nonmodified

TGDDM/DDS batches. In both resin systems, an increase in CoAcac concentration produced an increase in T_{ox}. A previous study with a tetrafunctional formulation[6,7] found the opposite trend, the only difference being that their TGDDM/DDS system contained a small amount (ca. 6%) of a novolac-type resin. It is not clear, however, why a small amount of novolac would reverse the trend of increasing T_{ox} with increasing CoAcac. No effect of cure schedule on T_{ox} was noted.

Mechanical Properties

Before presenting the data on ultimate mechanical properties, we would like to underline the fact that most fracture tests give scattered readings, and, therefore, statistical manipulation of the data is often necessary. In this study, we chose the method of confidence intervals to describe the statistical significance of data. The theory of confidence intervals is based on the fact that the true mean value of a measurement is a constant that will always remain unknown. However, limits may be set about the experimentally determined mean within that one may expect to find the true mean, with a given degree of probability. The interval defined by these limits is called the confidence interval. In this study, the 68% confidence interval was arbitrarily chosen as the basis for the comparison. At the 68% confidence interval, there exists a 68% probability that the true mean is within the given interval.

Table XIII presents the data obtained from Izod impact tests on four DGEBA/DETA batches. The table shows an overlap of the 68% confidence interval for the impact strength of modified and nonmodified batches, suggesting that the introduction of CoAcac did not affect the impact strength at the 68% confidence interval.

Table XIV presents tensile data on six modified and nonmodified DGEBA/DETA batches. The data illustrate the effect of varying the concentration of DETA on tensile properties of the resin system at room temperature. Young's modulus increased significantly at the 68% confidence interval in going from the batch with 13.7 phr to that with 11 phr DETA for both modified and nonmodified batches. Other researchers[15] found that the modulus obtained from DMA studies on DGEBA/DETA systems increases with decreasing curing agent concentration. Invoking the concept of inhomogeneous morphology, they argued that the higher curing agent concentration led to more excessive intranodular reactions at the expense of the internodular matrix. If that were the

TABLE XIII
Effect on CoAcac Concentration on Impact Strength of Modified
and Nonmodified DGEBA/DETA Systems

Batch	Impact strength (ft-lb/in)
0/11-I	0.2510–0.3240
0.414/11-I	0.2745–0.5027
2.07/11-I	0.2805–0.3597
4.14/11-I	0.2884–0.5196

The range of values in this and subsequent tables indicates the 68% confidence interval.
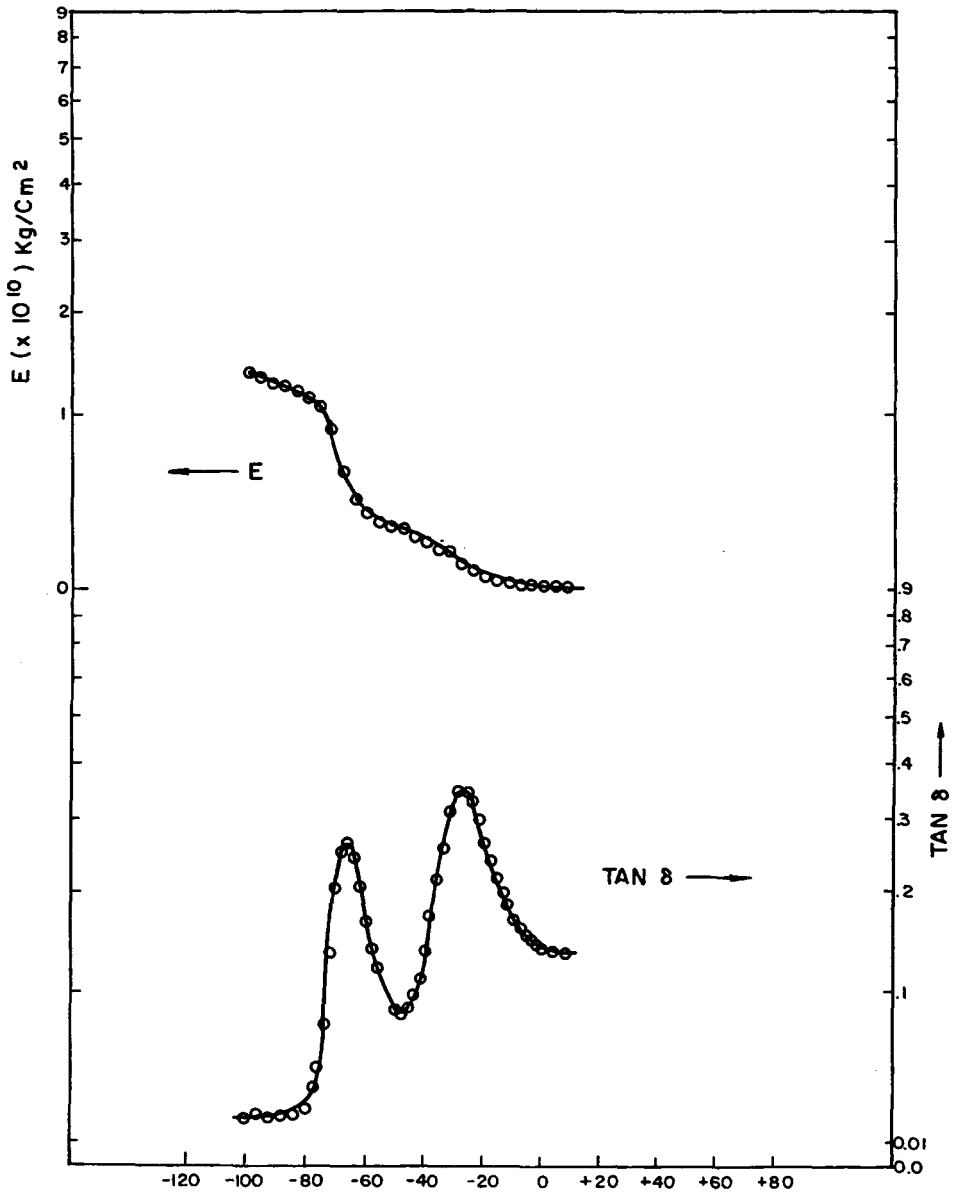
Fig. 4. Elastic modulus tan δ dip, film D.

amount of F/R resin in the dip, the F/R ratio in the dip and presence of special additives such as wax and silanes, all play a very important role in controlling the elastic moduli and the damping properties (tan δ) of the tire cord dip films. It is also concluded from the data presented in this publication that if fiber glass tire cord yarns had flexible size, then a good directive indication of the cord's fatigue properties can be obtained from the dynamic mechanical properties of the dip films. The fact that a correlation between the dynamic me-

TABLE XVII
Effect of CoAcac Concentration on K_{IC}

Batch	K_{IC} (lb-in$^{-3/2}$)
0/11-I	867.4–1531.8
0.414/11-I	909.7–1193.3
2.07/11-I	884.8–1088.2
4.14/11-I	948.8–1270.4

Young's modulus decreased with the addition of small amounts of CoAcac to the DGEBA/DETA system. The first addition of CoAcac (only 0.37% CoAcac in the formulation) produced the greatest decrease in Young's modulus. Increasing the concentration of CoAcac from 0.414 to 2.07 phr did not significantly change Young's modulus. When the concentration of CoAcac was increased further to 4.14 phr, Young's modulus increased, but its value remained below that of the nonmodified batch. The effect of CoAcac concentration on tensile properties at higher (60°C) and lower temperature (−55°C) was also investigated. At lower temperature, Young's modulus was found to decrease with the addition of CoAcac, following the trend observed at room temperature, whereas changes in CoAcac concentration had no effect on the modulus at 60°C.

In the next set of experiments, the critical stress intensity factor in mode I, K_{IC}, was determined from the single-edge notch test. According to the results
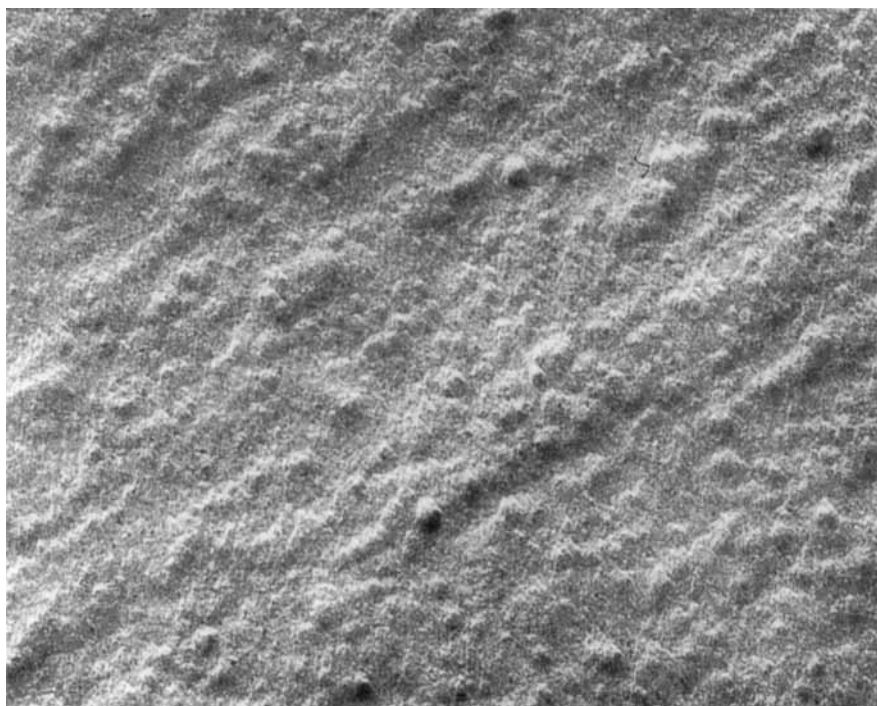
Fig. 5.　TEM micrograph of a C—Pt replica of fracture surface at 135,000× magnification. Formulation: 4.14/13.7-I.
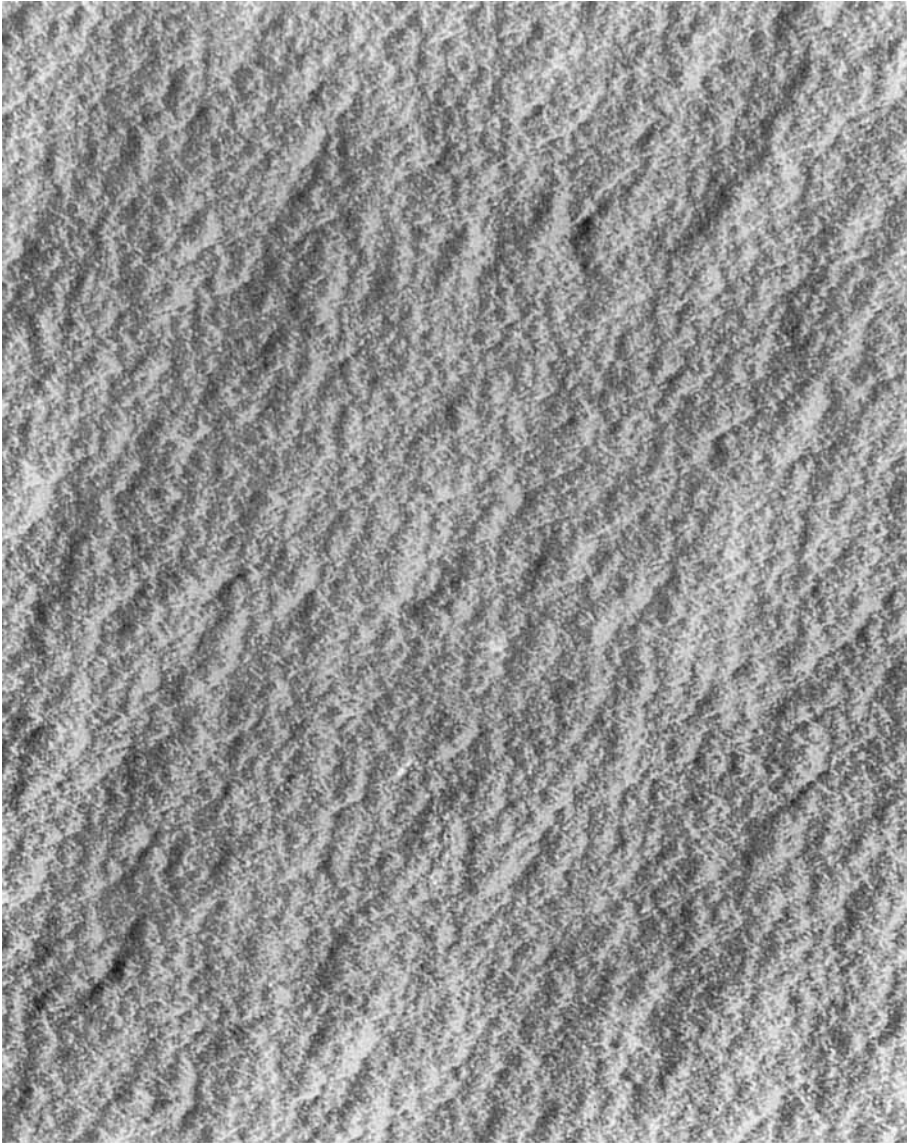
Fig. 6.   Same as Figure 5. Formulation: 4.14/11-I.

listed in Table XVII, there is no difference in K_{IC} values between modified and nonmodified DGEBA/DETA batches at the 68% confidence interval. Analogous observation was recorded for TGDDM/DDS systems.

Morphology

The final objective of this study was to relate the processing and property characteristics of modified and nonmodified epoxy systems to their morphology. It is now generally agreed on that cured epoxy systems are characterized by an
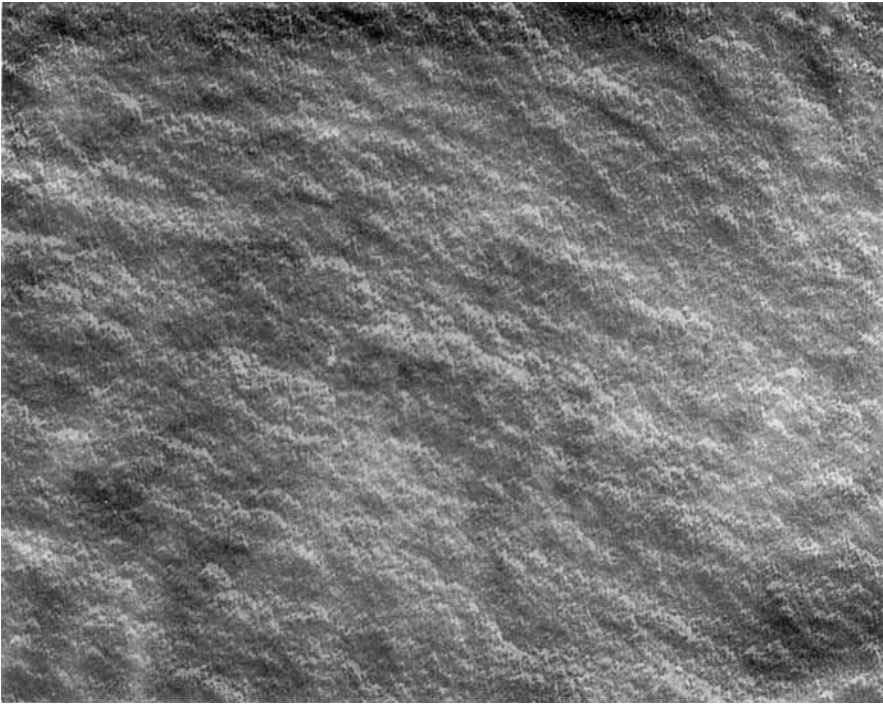
Fig. 7.   Same as Figure 5. Formulation: 2.07/11-S.
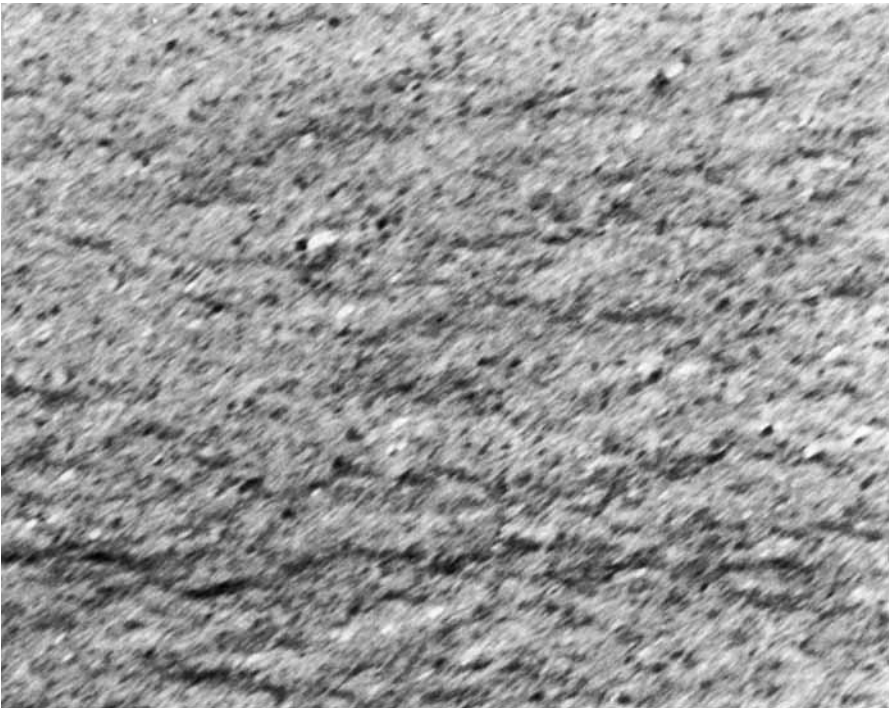
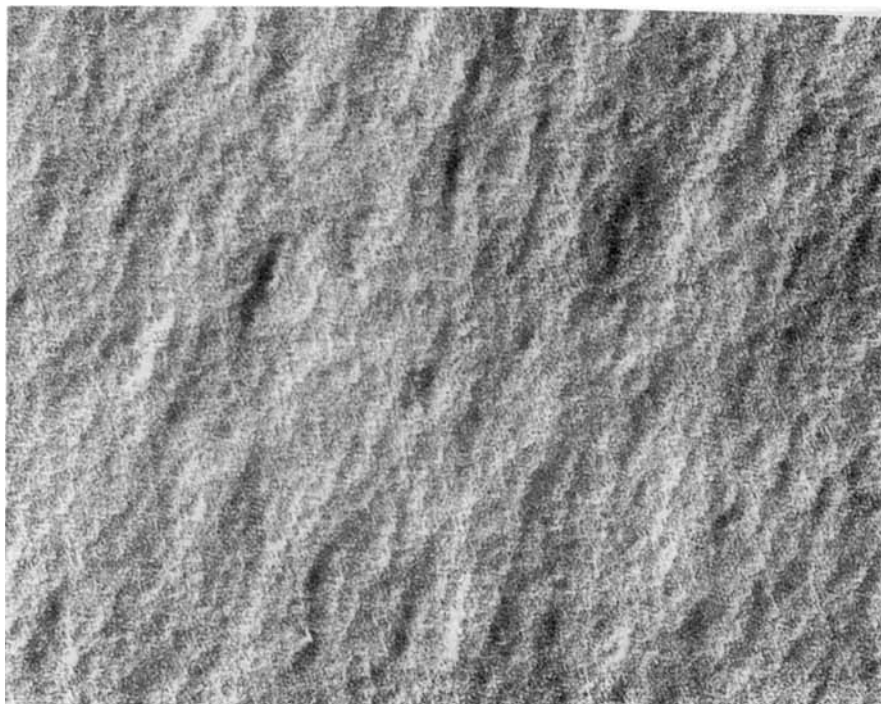Fig. 8.   Same as Figure 5. Formulation: 2.07/11-I.

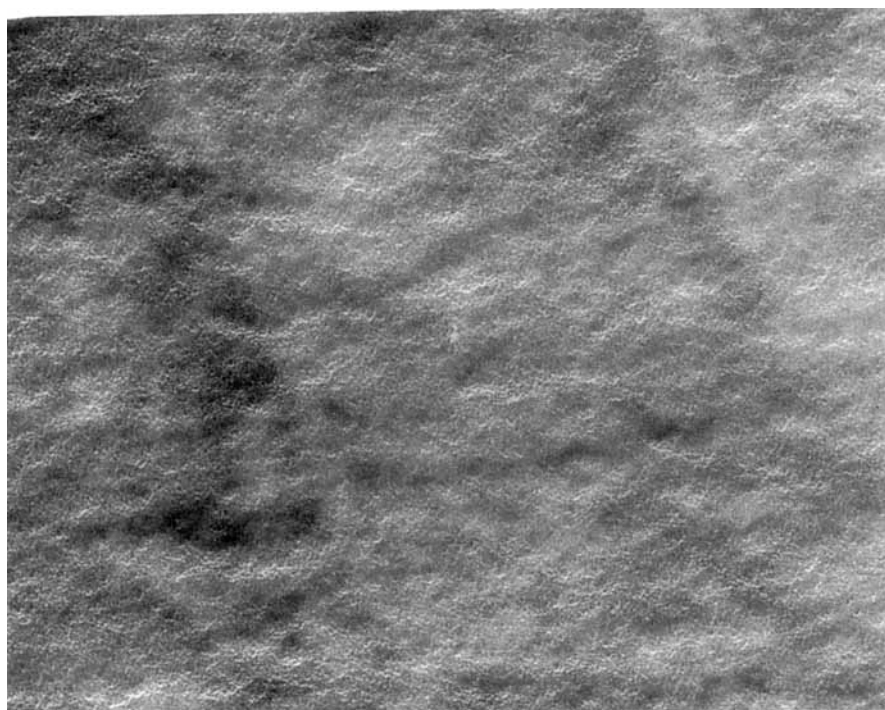Fig. 9.   Same as Figure 5. Formulation: 2.07/11-F.

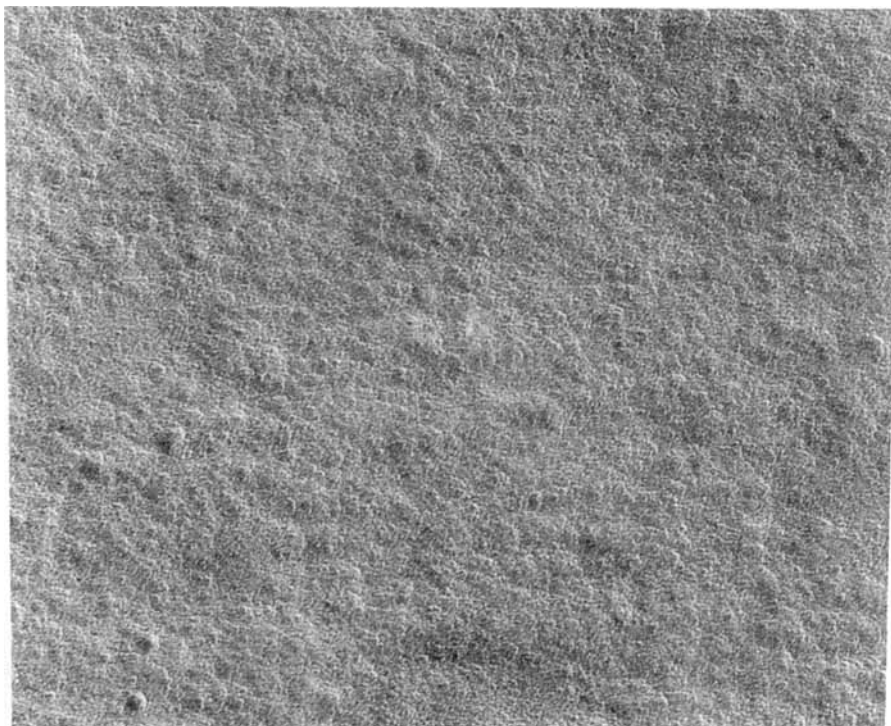Fig. 10.   Same as Figure 5. Formulation: 0/13.7-I.

Fig. 11. Same as Figure 5. Formulation: 0.414/13.7-I.

imhomogeneous morphology composed of more highly crosslinked regions dispersed in a lower crosslink density matrix. In this study, the extent of inhomogeneity was found to vary as a function of sample formulation and cure conditions.

Figures 5 and 6 show the effect of decreasing DETA concentration from 13.7 to 11 phr on the fracture surface morphology of DGEBA/DETA systems modified with 4.14 phr of CoAcac. In samples with DETA concentration of 13.7 phr (Fig. 5), roughly spherical inhomogeneities (nodules), ranging in size from 300 to 350 Å, were clearly evident. At DETA concentration of 11 phr, the nodular structure was also pronounced with the size ranging from 200 to 270 Å. Hence, as the concentration of DETA decreased from 13.7 to the stoichiometric value of 11 phr, the nodular size decreased.

As established above, the T_g of these systems was also found to decrease with decreasing concentration of DETA, whereas the Young's modulus increased significantly at the 68% confidence interval. An explanation for the observed phenomenon has been put forward earlier,[15] whereby an increase in the concentration of curing agent produces an increasingly inhomogeneous surface because the higher curing agent concentration leads to more excessive intranodular (as opposed to internodular) reactions.

Figures 7–9 show the effect of varying the cure schedule from fast to slow on the morphology of fracture surfaces of the DGEBA/DETA system modified with 2.07 phr of CoAcac. The slow cure schedule (Fig. 7) did not yield a very pronounced nodular structure. The nodules appear to align themselves in rows and are small in size, averaging 200 Å. Increasing the rate of cure from slow to intermediate (Fig. 8) led to a slightly more pronounced nodular structure; the

Fig. 12. Same as Figure 5. Formulation: 2.07/13.7-I.

average size was again 200 Å, and nodular alignment was visible. A further increase in the rate of cure from intermediate to fast (Fig. 9) resulted in still more pronounced nodules. Again, some alignment of nodules was observed, with a typical row containing four to 10 nodules. A slight increase in the nodular size was also observed; the average size was now about 250 Å. Thus, we conclude that in DGEBA/DETA systems containing 2.07 phr of CoAcac, a slight increase in the nodular size was observed with increasing rate of cure. Recalling the results of our thermomechanical tests, the T_g was also found to increase with the variation in cure schedule from slow to fast.

By comparing Figures 5, 7, 11, and 12, one can deduce the effect of increasing concentration of CoAcac on the morphology of fracture surfaces of DGEBA/DETA systems containing 13.7 phr of DETA and cured using an "intermediate" cure schedule. With 0 phr of CoAcac (Fig. 10), individual nodules were difficult to discern, but an inhomogeneous surface with some aligned features was apparent. An increase in the concentration of CoAcac from 0 to 0.414 phr (Fig. 11) produced a rougher fracture surface. The surface gave the appearance of an increased quantity of inhomogeneities, although individual nodules were difficult to discern. The average nodular size ranged from 200 to 250 Å. Further increase in the CoAcac concentration to 2.07 phr (Fig. 12) yielded a nodular structure comparable to that of the formulation containing 0.414 phr of CoAcac. Again, individual nodules were not clearly discernible. An increase in the CoAcac concentration to 4.14 phr produced a clearer and more pronounced nodular structure as seen in Figure 5, with an average nodular size between 300 and 350 Å. Thus, we conclude that in DGEBA/DETA systems containing 13.7 phr

of DETA and cured using the "intermediate" cure schedule surface roughness along with nodular size increased with increasing concentration of CoAcac.

CONCLUSIONS

The main objective of this study was to obtain processing-property-morphology correlations for CoAcac modified and nonmodified epoxy systems, and the following observations were made:

1. An autocatalytic kinetic model was used to describe the cure of modified and nonmodified DGEBA/DETA systems.
2. As the concentration of DETA was decreased from 13.7 to 9.16 phr, the T_g decreased, the Young's modulus increased, and the nodular size decreased.
3. With a decrease in the rate of cure for DGEBA/DETA systems containing 2.07 phr of CoAcac, the T_g decreased, no clear trend was seen in the Young's modulus, and the nodular size decreased.
4. In DGEBA/DETA systems containing 13.7 phr of DETA and cured in the "intermediate" cure schedule, the surface roughness along with the nodular size increased with increasing concentration of CoAcac.
5. It was generally observed that with increasing concentration of CoAcac, the T_g for the DGEBA/DETA system peaked and then decreased, the T_g for the TGDDM/DDS system decreased continuously, and the T_{ox} increased slightly for both resin systems. Also, the introduction of CoAcac in DGEBA/DETA and TGDDM/DDS systems did not significantly affect the impact strength or the critical stress intensity factor.

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