Effect of Epoxy–Amine Stoichiometry on Cured Resin Material Properties

G. R. PALMESE and R. L. McCULLOUGH*

Center for Composite Materials and Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19716-3144

SYNOPSIS

Sizings and/or surface treatments are commonly employed to enhance the interaction of fiber reinforcements in polymer matrix composites. These modifications can induce physical and chemical interactions that cause local stoichiometric imbalances to occur that can affect the properties of the polymer matrix in the vicinity of the fiber surface. This work reports the results of an experimental study of the influence of stoichiometric imbalance on the thermoelastic properties of an epoxy–amine resin. It is shown that the modulus and glass transition temperature are significantly affected by relatively small variations in stoichiometry. These results suggest that a fiber-induced interphase region in thermosetting composites can exhibit material properties that are significantly different from those of the bulk resin. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Interfacial strength in fiber and polymer matrix composites is enhanced by the use of coupling agents or sizings[1] and/or surface treatments.[2] Surface treatments for carbon fibers are usually oxidation processes that tend to increase the specific area of the fibers and to add oxygen-containing functional groups to their surfaces.[3] These surface treatments and/or coupling agents are designed to alter the interactions of the fiber with the polymeric matrix and in so doing may alter the nature of the polymeric material in the vicinity of the fiber surface. The resulting interphase region may possess neither the properties of the reinforcement nor those of the homogeneous neat resin.

Two commonly accepted mechanisms for interphase formation in epoxy–amine/carbon fiber composite systems are: (i) the preferential adsorption of amine curing agent onto the graphite fiber surface and (ii) the diffusion into epoxy-rich sizings of amine from the bulk resin thus causing composition profiles to form. Both of these mechanisms can cause local stoichiometric imbalances to occur and structural inhomogeneities to develop that are frozen in place as the system vitrifies.

Recently, methods for predicting the local composition gradients in epoxy–amine/carbon fiber interphases have been developed.[4,5] Interphases possessing significant variations in local composition have been predicted for a variety of epoxy–amine systems in contact with carbon fibers.[5] Such compositional variations imply significant interphasial variations in epoxy–amine stoichiometry. Therefore, in order to understand the behavior characteristics of the interphase region, an understanding of the effects of stoichiometry on material properties is needed. The purpose of this work is to explore the sensitivity of material properties that affect thermoelastic behavior to variations in epoxy–amine stoichiometry.

Material Properties of Interest

Material properties that affect thermoelastic behavior are the coefficient of thermal expansion (α) and the elastic constants (C). For elastic materials the stress (σ) generated as a result of changes in temperature (T) and strain (ϵ) is given by

$$\sigma_{ij} = C_{ijkl}(\epsilon_{kl} - \sigma_{kl}\Delta T) \qquad (1)$$

where the elastic constants (C_{ijkl}) are related to Young's modulus (E), shear modulus (G), and Poisson's ratio (ν).

For amorphous polymeric systems the modulus and coefficient of thermal expansion (CTE) are strongly dependent on the test temperature relative to the glass transition temperature (T_g) of the material. The CTE for an amorphous polymer above the glass transition temperature is typically a factor of 2 or 3 greater than its value at temperatures below T_g. Above the glass transition temperature an amorphous polymeric material behaves as a liquid or rubber depending on the degree of crosslinking. For temperatures below T_g the material behaves as a glass. Hence, the elastic modulus for temperatures below the glass transition temperature is several orders of magnitude higher than that above T_g. Knowing the glass transition temperature of a material is essential for describing its mechanical behavior in relation to temperature.

Homogeneous epoxy–amine samples of varying stoichiometry have been prepared and characterized to determine the thermal expansion coefficient, modulus, and glass transition temperature.

EXPERIMENTAL

The glass transition temperature and the effects of temperature on modulus and CTE were evaluated for fully cured epoxy–amine samples of varying stoichiometries. A number of techniques commonly used for the characterization of polymers was used for this purpose. These techniques included differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), and dynamic mechanical analysis (DMA). The instruments employed for these characterizations are part of the DuPont 9800 thermal analysis system.

Materials

The Shell Epon-828 epoxy resin and Air Products PACM-20 (bis-p-aminocycloxexyl methane) amine curing agent was used for this investigation. The chemical structures of these compounds are shown in Figure 1. Epon-828 is a diglycidyl ether of bisphenol A resin with an average molecular weight of 377 g/mol. The reaction kinetics for this system have been investigated by Sanford,[6] Rhor,[7] and Enns.[8] All materials were used as received.

The ratio of PACM-20 curing agent to Epon-828 recommended by Shell[9] is 28 parts amine per hundred parts epoxy (28 pph PACM-20). Figure 2 is a plot of the heat evolved per unit weight of epoxy for varying amine–epoxy ratios. These values were obtained using DSC ramps from room temperature to 200°C at a rate of 10°C per minute. The plateau in the curve indicates the compositions for which complete reaction of epoxy functional groups has occurred, and the point at which the plateau begins identifies the composition known as the stoichiometric point for which the initial number of epoxy groups equals the initial number of amine hydrogens. At this composition all amine and epoxy functionalities may be reacted. This value is in good agree-

[A]

[B]
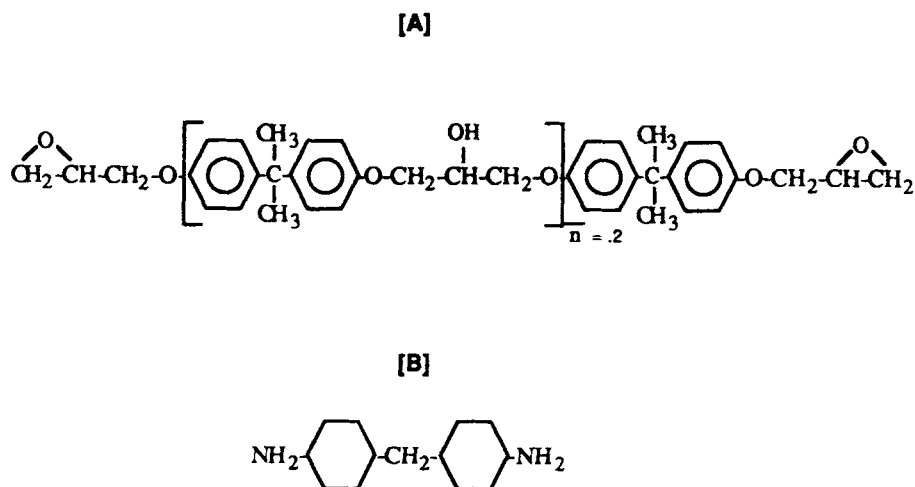
Figure 1 Chemical structure of the diglycidyl ether of (a) bisphenol A based Epon-828 and (b) PACM-20.
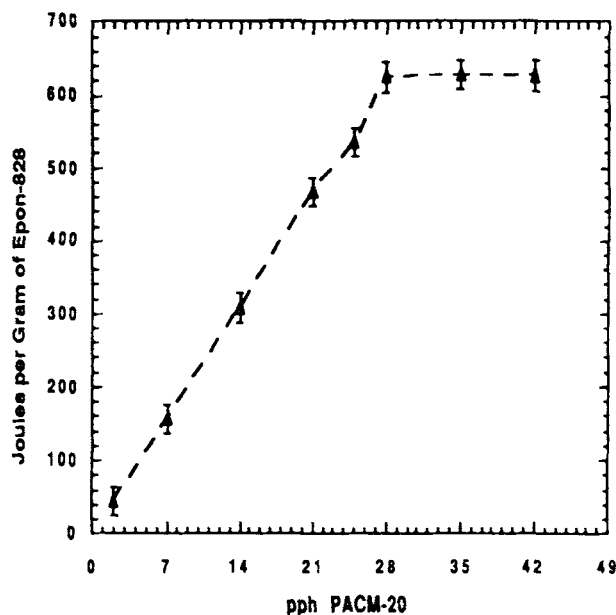
Figure 2   Total energy evolved measured using DSC per gram of epoxy as a function of stoichiometry for the Epon-828/PACM-20 resin system. Change of slope indicated 28 pph PACM-20 to be the stoichiometric composition.

ment with the ratio recommended by Shell. Thus 28 pph is considered the stoichiometric composition for the Epon-828/PACM-20 system.

Sample Preparation

Table I lists the Epon-828/PACM-20 samples of varying stoichiometry that were prepared for characterization. The materials include samples made with quantities of curing agent well in excess and in paucity of the stoichiometric composition. The two components were well mixed at room temperature. The efficacy of mixing was gauged by the amount of cloudiness visible during the procedure. Well-mixed samples appear clear, thus mixing was terminated when this condition was reached. The mixing process lasted between 10 and 15 min.

An aluminum mold was used to form slabs of cured resin from which samples were machined for characterization. Before filling with resin, the mold was coated with several layers of Freecote, a mold release agent. The top of the mold was left open to allow for the evolution upon cure of air bubbles trapped during the mixing process.

The slabs were cured in an oven controlled to within 1°C in two isothermal stages. All samples were held at 80°C for 2 h followed by 2 h at 160°C.

These conditions ensured complete conversion and allowed for evacuation of air bubbles from the sample. Following cure, samples were removed from the oven and were left to cool to room temperature. A typical slab measured $1 \times 10 \times 10$ cm and possessed a slightly curved upper surface. Samples for characterization were cut from the slabs using a diamond saw.

Determination of Material Properties

Modulus

Dynamic mechanical analysis has been used to measure the modulus of cured Epon-828/PACM-20 materials listed in Table I. The primary advantages of using DMA for the evaluation of moduli are twofold. First, modulus data over a large range of temperatures can quickly be obtained, and second, brittle samples can be characterized, which for practical purposes cannot be tested conveniently using a tensile testing apparatus such as an Instron. Values of the storage and loss moduli depend not only on temperature but also on the frequency of the deformations applied to determine these quantities. Our interest lies primarily in comparing the values of modulus for samples having different compositions. Therefore, all dynamic mechanical measurements were taken at a fixed frequency of 1 Hz. The amplitude of the oscillations was kept at 0.2 mm and Poisson's ratio was taken as 0.35 for all specimens.

Most samples for DMA evaluation were prepared by cutting the slabs of cured resin into rectangular

Table I   Epon-828/PACM-20 Sample Slabs Prepared for Testing

Slab ID[a]	Epon-828 (g)	PACM-20 (g)	pph PACM-20
100/10	207.60	21.43	10.30
100/14	73.37	10.27	14.00
100/18	112.54	20.26	18.00
100/21	93.93	20.04	21.34
100/25	87.21	21.36	24.49
100/28	97.21	27.31	28.09
100/32	89.32	28.32	31.71
100/35	102.52	36.32	35.43
100/42	107.85	50.3	46.64
100/49	174.90	88.04	50.34
100/56	175.90	100.40	57.08
100/63	49.87	31.60	63.36

[a] The identification number represents the desired weight ratio of Epon-828 to PACM-20.

specimens measuring roughly 3 × 10 × 50 mm using a diamond saw. The surfaces of these specimens were kept parallel to each other within 0.001 mm. Cured materials with compositions far from the stoichiometric point (100/10, 100/14, 100/56, 100/63) were difficult to cut with a diamond saw due to their brittle characteristics. These specimens were prepared by careful sanding. In all cases specimens with noticeable voids were rejected.

Dynamic mechanical characterizations were carried out by ramping the temperature at 10°C per minute from room temperature to 200°C. However, to obtain sufficient data above and below the glass transition temperature for the 100/10, 100/49, and 100/63 samples, the temperature had to be ramped from temperatures lower than room temperature. This was accomplished using a liquid nitrogen cooling accessory. Typical starting temperatures for such ramps were −60°C.

For isotropic materials the flexural modulus is equivalent to the Young's modulus. At room temperature, the flex storage modulus of a fully cured stoichiometrically formulated Epon-828/PACM-20 material measured by the DMA technique is 2.3 GPa. Shell[9] reports a tensile modulus of 2.5 GPa for the cured Epon-828/PACM-20 material of stoichiometric composition.

Values of modulus, which will be reported in sections to follow, represent the average over several runs taken of the sample; the error bars associated with these values indicate the spread of these measurements.

Glass Transition Temperature

The glass transition temperature for Epon-828/PACM-20 systems of varying composition were measured using TMA and DMA techniques. The TMA technique is discussed first.

A diamond saw was used to prepare samples measuring roughly 3 × 3 × 3 mm for the cured resins listed in Table I. These were characterized using the TMA apparatus to measure displacements as a function of temperature. The temperature was ramped from room temperature to 200°C at a rate of 5°C per minute.

The T_g for a sample was assigned to the temperature at which the displacement trace changes slope. Irregular displacement versus temperature behavior is often encountered upon first testing following cure. This is attributed to the relaxation of residual thermal stresses as the system passes the glass transition temperature for the first time following cure. Thus, temperature scans for each sample were taken

until the displacement behavior for consecutive runs did not appreciably change.

The glass transition temperatures were also evaluated using the DMA ramping experiments discussed in the previous section. The T_g is commonly defined as the temperature at which the loss modulus reaches a maximum. However, since often data is not collected at this point because the fixed frequency oscillation is lost, we assign the glass transition temperature as the temperature at which the storage modulus reaches a value half way between the initial and final values of the ramping range. Glass transition temperatures measured in this way are reported as the average of several measurements, and the associated error bars represent the spread of these data.

Thermal Expansion Coefficient

The TMA displacement versus temperature results used to evaluate T_g were employed to determine the thermal expansion coefficient by taking the derivative with respect to temperature of the displacement curves. Resulting CTE versus temperature plots will be reported.

RESULTS AND DISCUSSION

Glass transition temperature, modulus, and coefficient of thermal expansion data have been obtained using the techniques described for the samples listed in Table I. The data for each of these properties are summarized and analyzed in this section. Attention is given to pointing out the degree to which these properties are affected by stoichiometry and discussing possible mechanisms for explaining the observed behavior.

Glass Transition Temperature

Figure 3 is a plot of the glass transition temperatures measured by the DMA and TMA techniques as a function of the parts per hundred PACM-20 used for cure. The maximum value of T_g occurs at the stoichiometric point for both sets of data. However, the value measured using the DMA technique is higher than that using the TMA by roughly 10°C. Enns and Gillham[8] have reported a maximum T_g of 166°C for the same resin system. This discrepancy in T_g measurements using the two techniques does not occur for other epoxy–amine ratios tested; and, on the whole, the measurements of glass transition temperature using the two techniques are in close
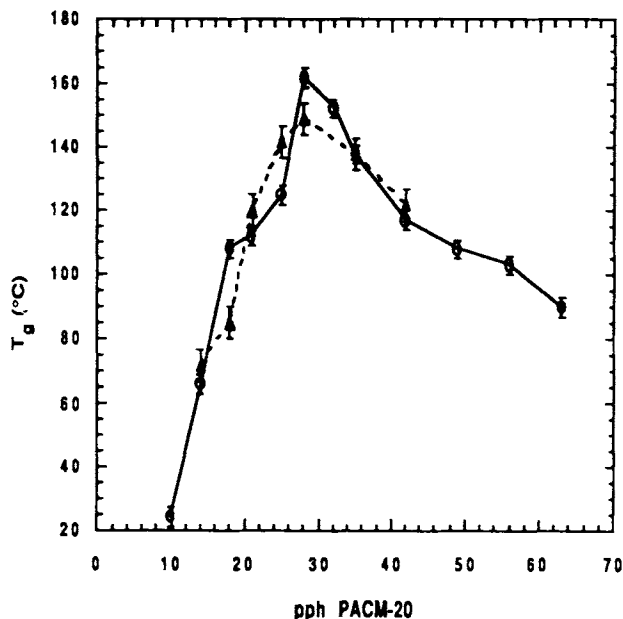
Figure 3 Glass transition temperature as a function of stoichiometry for the Epon-828/PACM-20 system. Glass transition temperature values obtained using TMA identified by (– –△– –) and DMA identified by (—⊖—).

agreement. The glass transition temperature depends strongly on the parts per hundred amine used. Amounts in excess or paucity of the stoichiometric composition result in drastically lower values of T_g.

The glass transition temperature of a material is affected by the rigidity of the molecule. For rigid or constrained molecules, higher temperatures are needed to allow for the molecular motions associated with the deformation of the material. During the cure of a stoichiometrically balanced epoxy–amine, following gelation, the crosslink density of the resin increases with increasing conversion and reaches a maximum at full conversion. The epoxy–amine network that forms becomes stiffer as the crosslink density increases and a corresponding increase in T_g is observed. This behavior has been investigated by Enns and Gillham[8] for a stoichiometric mixture of Epon-828/PACM-20 at various stages of cure. These workers quantified their results using the Di Benedetto equation.

The crosslinking density of epoxy–amine thermosetting systems is affected by the amount of curing agent used. The use of more or less than the stoichiometric quantity of curing agent required for stoichiometrically balanced cure, leads to final structures having lower crosslink densities and therefore lower glass transition temperatures than

the resin cured at the stoichiometric point. If amounts of curing agent greatly in excess or paucity of the stoichiometric composition are used, gelled networks will not form. Such limits can be predicted using Flory's theory of gelation.[10] For the Epon-828/PACM-20 system these are 14 and 56 pph PACM-20. Under such conditions the concept of network stiffening crosslinks is not applicable. The decrease in glass transition temperatures in this regime can be attributed to increasing numbers of chain ends. The reasoning for this is based on the free volume argument that chain ends have excess free volume associated with them that can ease the movement of molecules and therefore lower values of T_g.

Our purpose for investigating the effects of stoichiometry on material properties of epoxy–amine systems is to eventually relate these properties to predicted interphase composition profiles. Methods that exist for the prediction of glass transition temperatures for crosslinked epoxy systems are based on empirical and theoretical considerations. Recently Bellenger et al.[11] have developed a method for the prediction of T_g for epoxy–amine networks formed from off-stoichiometry compositions. However, to date, to obtain reliable T_g values for epoxy–amine systems cured with varying amounts of curing agent, direct measurement is advisable.

Modulus

Figure 4 shows the flex modulus at 30, 105, and 135°C as a function of amine used for cure. For the 30°C plot two maxima are apparent: one at 18 pph amine with a value of 3.2 GPa, and the other between 48 and 56 pph amine having a value of 2.4 GPa. Between these maxima, near the 42-pph amine mark, the value of modulus attains a local minimum of 2.0 GPa. The modulus has a value of 2.3 GPa at the stoichiometric point (28 pph PACM-20). For compositions varying between 18 and 56 pph the value of the modulus varies roughly 60%. On either side of the maxima (parts per hundred amine greater than 56 and less than 18), the modulus drops sharply to significantly lower values.
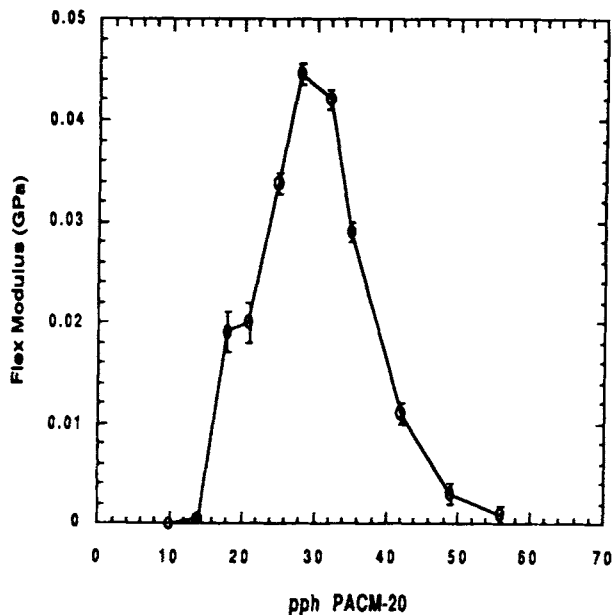
The sharp drops in moduli for these compositions are due to the fact that the testing temperature is nearing the glass transition temperature of the samples. This effect is more pronounced for the modulus curves at 105 and 135°C. Values of modulus several orders of magnitude less than the value of the stoichiometric point are evident. These are characteristic of the rubbery state above T_g. The range of compositions for which the modulus corresponds to the glassy state decreases with increasing temper-
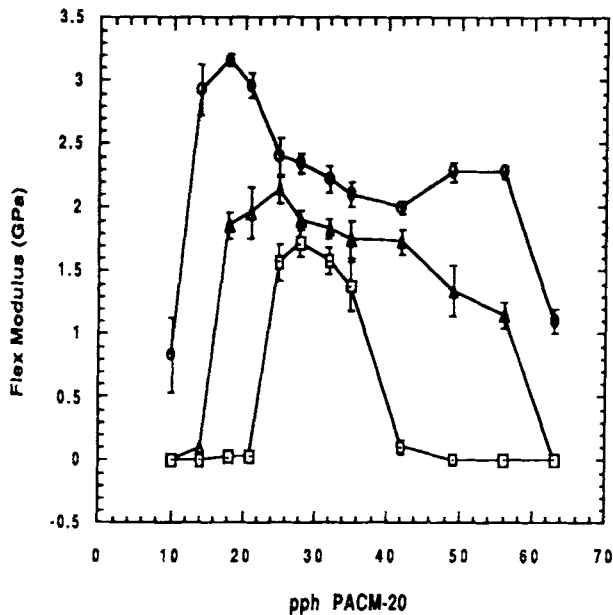
Figure 4 Flexural modulus measured for several temperatures as a function of stoichiometry for the Epon-828/PACM-20 system. Measurements obtained using DMA at 1 Hz [(——⊖——) 30°C; (——△——) 105°C; (⊡) 135°C].
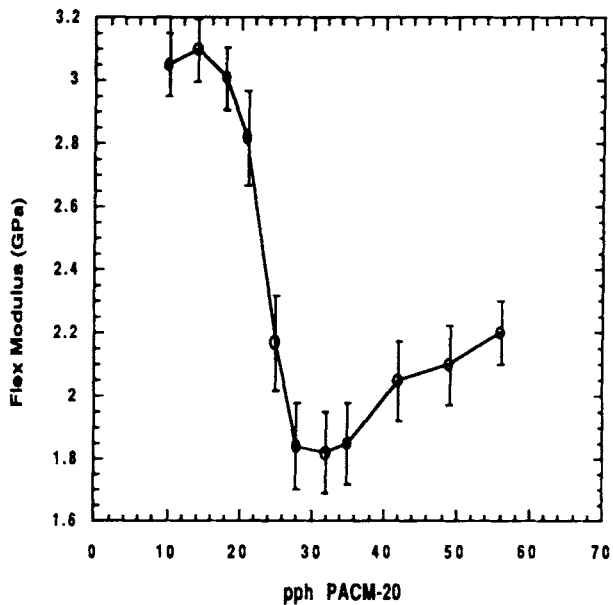

Figure 5 Flexural modulus at temperatures 30°C above T_g as function of stoichiometry for the Epon-828/PACM-20 system. Measurements obtained using DMA at 1 Hz.

ature. For higher temperatures (105 and 135°C), there exist no minima near the stoichiometric point; rather, the modulus reaches a maximum value near this composition (105°C, 2 GPa, 25 pph amine; 135°C, 1.65 GPa, 28 pph amine). Furthermore, even at the stoichiometric point below T_g the values of modulis decrease with increasing temperature. Therefore, the behavior of modulus as a function of amine used for crosslinking is greatly affected by temperature.

The effect of the glass transition temperature on the modulus of the series of Epon-828/PACM-20 systems can be minimized by plotting the modulus as a function of composition for temperatures that differ from the glass transition temperature of each material by the same amount. Two regimes of interest are identified: (a) the modulus of the series of materials above T_g and (b) the modulus of the series below T_g. Figure 5 is a plot of the flex modulus as a function of Epon-828/PACM-20 composition above the glass transition temperature. Each value has been taken 30°C above the glass transition temperature of the material tested. Figure 6 is a plot of the flexural modulus as a function of composition below the glass transition temperature. In this case each value has been taken 50°C below the glass transition temperature.

The salient features of these figures are that in the rubbery state above T_g, the modulus is greatest at the stoichiometric composition while in the glassy

Figure 6 Flexural modulus at temperatures 50°C below T_g as function of stoichiometry for the Epon-828/PACM-20 system. Measurements obtained using DMA at 1 Hz.

state below T_g the modulus reaches a minimum at the stoichiometric point. This suggests that the material structure affects the modulus by competing mechanisms. The Young's modulus (E) can be related to the second derivative with respect to strain (ϵ) of the Helmholtz free energy (A).

$$E = \left(\frac{\partial A^2}{\partial \epsilon^2}\right)_T \tag{2}$$

Thus, in terms of the internal energy (U) and the entropy (S), the elastic modulus is given by

$$E = \left(\frac{\partial U^2}{\partial \epsilon^2}\right)_T - T\left(\frac{\partial S^2}{\partial \epsilon^2}\right)_T \tag{3}$$

The elastic behavior of amorphous polymers above the glass transition temperature has been successfully modeled by assuming that the internal energy is not affected by displacement. This theory, known as the theory of rubberlike elasticity, presumes the modulus is affected only by changes in entropy upon deformation. The change in entropy is related to conformational changes caused by deformations. The magnitude of these changes is affected by the structure of the material and has been related to average molecular weight between crosslinks. Equa-

tion (4) is a commonly used expression derived from rubberlike elasticity theory,[12] which relates the elastic modulus to the molecular weight between crosslinks (M_c) and density (ρ) for small deformations.

$$E = \frac{3RT\rho}{M_c} \tag{4}$$

For the set of stoichiometrically varied Epon-828/PACM-20 systems tested, the average molecular weight between crosslinks is inversely proportional to the glass transition temperature. Therefore, for the rubberlike elasticity theory to describe the modulus behavior of the Epon-828/PACM-20 system, the measured values of modulus above the glass transition temperature should vary proportionally with the quantity $T\rho T_g$. In fact, this is the case. Figure 7 is a plot of the modulus above the glass transition temperature as a function of $T\rho T_g$, which demonstrates this proportionality. Statistical models exist for predicting M_c as a function of composition,[13,14] however, this analysis is sufficient to point out that for temperatures above T_g entropic mechanisms control modulus, and that a theory is available to predict observed behavior in this regime.

Figure 6 clearly indicates that the entropic elasticity theory cannot be used to model the behavior
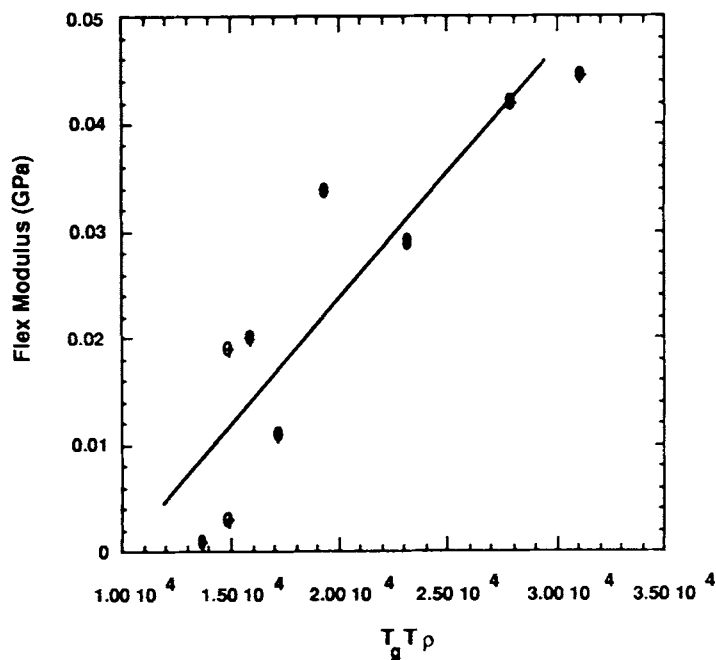
Figure 7 Correlation between flexural modulus and the parameter $T_g T\rho$, which shows rubberlike elasticity theory adequately describes the modulus behavior as a function stoichiometry for temperatures above T_g.

Table II Epoxy–Amine Systems That Exhibit Inverse Dependence of Modulus with Respect to Crosslink Density

Authors	System	% Variation from Minimum
Bellenger et al.[16]	DGEBA-DDM	23
Kim et al.[18]	DGEBA-MDA	38
Madsen et al.[19]	Epoxy Novolac imidazole	11
Current	Epon-828/PACM-20	>100

of modulus as a function of composition below T_g for the series of Epon-828/PACM-20 resins. Several workers report similar behavior of modulus as a function of composition for a variety of epoxy–amine systems below T_g. These are summarized in Table II. In all cases the variations of modulus as a function of composition are significant. Evidently, the change in internal energy with respect to strain contributes strongly to the determination of modulus in the glassy state. Hence, the molecular interactions must play an important role in determining the modulus below T_g. The inverse dependence of modulus on the degree of conversion has been described as internal "antiplasticization."[15,16]

Similar antiplasticization has been observed for a range of additives that can be used to enhance the behavior characteristics of epoxy systems. Garton et al.[15] and Daly et al.[17] report that the use of small amounts of nonreacting additives can increase the glassy state modulus of the epoxy material substantially. This change was attributed to a decrease in free volume available for segmental mobility; the reduction in free volume could be attributed to the smaller "holes" not accessible to the polymer being filled by the additives.

A similar argument can be made to explain the antiplasticization behavior of epoxy resins cured with nonstoichiometric amounts of curing agent. The unreacted monomers reduce the free volume available for segmental motion of the polymeric molecules. These segmental motions are associated with the β transitions identified by the dynamic loss spectrum of a polymer. Bellenger et al.[16] have reported a decrease in the intensity of the loss peak associated with the β transition for the DGEBA-DDM system cured with nonstoichiometric quantities of amine compared to the system cured at the stoichiometric point. This corroborates the view that a decrease in segmental mobility causes an increase in modulus.

It is apparent that the glassy state modulus of epoxy–amine systems is very sensitive to the amount of amine used for cure. While explanations exist for the antiplasticization behavior, a theory capable of predicting the modulus of polymeric materials in the glassy state as a function of composition or structural attributes is not available. It appears that the approach to be taken is one where the internal energy of the system is predicted on the basis of network structure and composition. Ideas based on free volume can then be used to help describe the structure of the material.
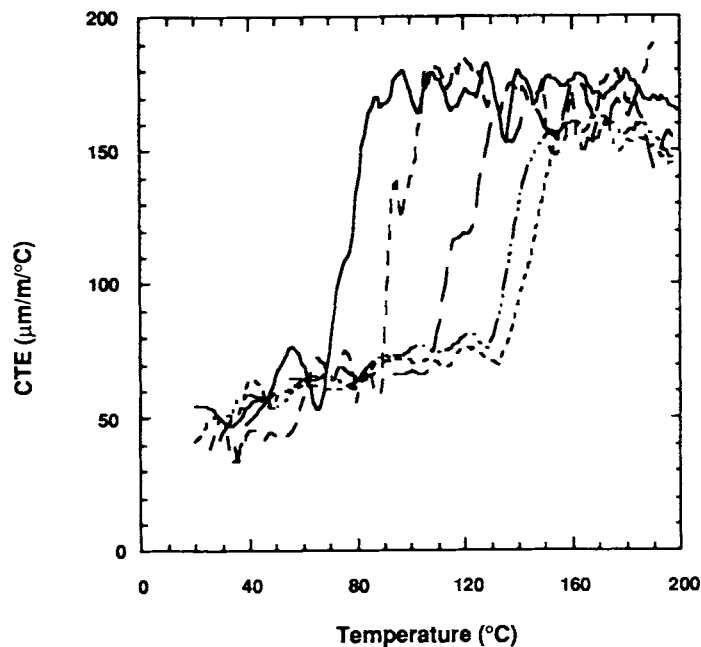
Thermal Expansion Coefficient

Figure 8 shows plots of the thermal expansion coefficient as a function of temperature for a series of Epon-828/PACM-20 resins of varying composition. As with the modulus, the greatest difference in thermal expansion coefficient can be found when comparing values corresponding to temperatures above and below T_g. The CTE above T_g is typically two to three times greater than the value below T_g for all the samples tested. It is convenient, therefore, to discuss the effect of initial amine concentration on CTE in terms of two regimes: one above T_g and the other below T_g.

The coefficient of thermal expansion for the Epon-828/PACM-20 systems tested shows no apparent systematic variation with temperature above the glass transition temperature. Thus, for a given sample, the CTE is essentially constant for temperatures greater than T_g. However, the value of CTE above T_g does depend on the amount of amine used for cure. The coefficient of thermal expansion displays a minimum near the stoichiometric point. This is illustrated by the plot given in Figure 9 of CTE as a function of amine concentration for temperatures above T_g. The variation in CTE is only about 10% for the given range of composition. This is a much smaller change than that observed for the modulus above the glass transition temperature.

Figure 8 shows that below the glass transition temperature the CTE traces for all materials essentially superpose each other. At a given temperature below T_g, the CTE is independent of stoichiometry
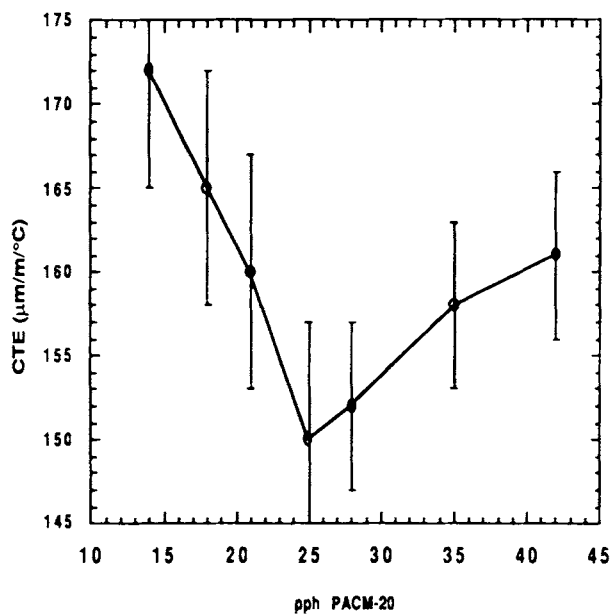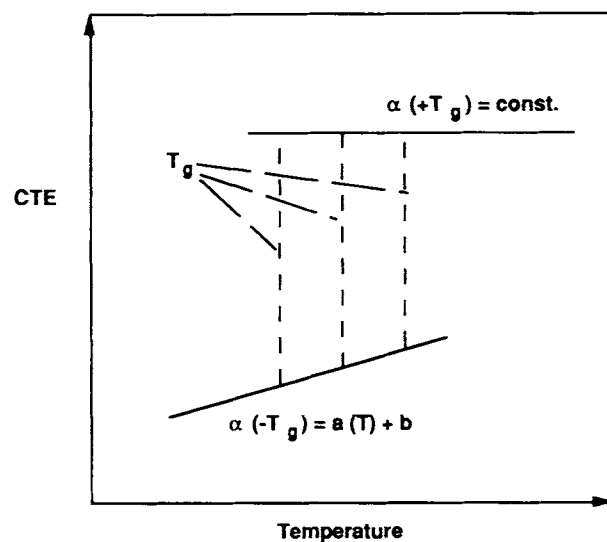
Figure 8 Coefficient of thermal expansion (CTE), obtained using TMA (5°C/min) as a function of temperature for Epon-828/PACM-20 systems of varied compositions. [(———) 14 pph; (— — —) 18 pph; (- - - - -) 28; (—-—-—) 35; (—-—) 42].

within the noise levels of the measurements. Below T_g, however, the thermal expansion coefficient is a monotonically increasing function of temperature

that may be fitted by a straight line. In the range of temperatures between 20 and 140°C the thermal expansion coefficient varies from 40 to 70 μm/m °C. Therefore, although the CTE below T_g is constant

Figure 9 Coefficient of thermal expansion (CTE) above T_g for the Epon-828/PACM-20 system as a function of stoichiometry measured using the TMA technique.

Figure 10 Schematic representation for a model that can be used to describe the behavior of the thermal expansion coefficient as a function of temperature and stoichiometry.

**Table III Summary of the Dependence of Material Properties on Stoichiometry for the Epon-828/
PACM-20 Epoxy–Amine Thermosetting System**

Property	Dependence on Amine Concentration	Property Variation
T_g	Maximum at stoichiometric composition	Very strong
Flex modulus above T_g ($T_g + 30°C$)	Maximum at stoichiometric composition	Strong
Flex modulus below T_g ($T_g - 50°C$)	Minimum at stoichiometric composition	Strong
Thermal expansion (CTE) above T_g	Minimum at stoichiometric composition	Weak
Thermal expansion (CTE) below T_g	No effect	—

for the range of compositions, it varies substantially with temperature.

The measurements of CTE for the Epon-828/ PACM-20 systems of varying stoichiometry have shown that, within 10%, the values of CTE are constant at a given temperature for a wide range of compositions as long as the materials being compared are in the same state. This provides the basis for a simple empirical model that can be used to predict the CTE as a function of stoichiometry and temperature. The variations in thermal expansion as a function of temperature are described by two lines for all stoichiometric compositions. One line assigns the value of thermal expansion coefficient above T_g, and the other, the linear dependence of CTE on temperature below T_g. The glass transition temperature marks the temperature at which a step occurs from one line to the other. Figure 10 illustrates this procedure schematically. The information required to construct these curves are the general value of CTE above T_g, the parameters that describe the line below T_g, and the relationship between stoichiometry and T_g. Under this model all CTE data can be obtained by characterizing one sample.

SUMMARY AND CONCLUSIONS

The primary objective of this work was to determine whether local variations in interphase composition can significantly affect interphasial material properties. Accordingly, the effect of stoichiometry on the material properties of epoxy–amine thermosetting systems has been investigated. The material properties, including the glass transition temperature, modulus, and thermal expansion coefficient, of the Epon-828/PACM-20 system have been measured as a function of stoichiometry and temperature. Table III summarizes resulting trends qualitatively. The results of this study show that the material properties are significantly affected even by relatively small variations in stoichiometry. It is

therefore expected that interphases should possess material properties significantly different than those of the bulk material. In particular, the strong dependence of the glass transition temperature on composition suggests that the modulus of the interphase material could be dramatically reduced at elevated temperatures. The results reported here can be used in conjunction with predicted concentration profiles to map material property variations throughout the interphase region. This mapping will be treated in a separate communication.

This work has also shown that there is a significant lack of understanding regarding the variations of material properties with respect to stoichiometry. Currently there exists no theory for predicting the behavior of glassy state modulus as a function of composition. The existence of viable structure–property models would enable fewer experiments to be performed in order to characterize the stoichiometrically dependent behavior of a given thermosetting resin system.

REFERENCES

1. E. P. Pleuddemann, *Composite Materials*, R. H. Kroch and L. J. Broutman, Eds., Academic Press, New York, 1974, Volume 6.
2. D. J. Johnson, *Chemistry and Physics of Carbon*, P. A. Thrower, Ed., Marcel Dekker, New York, 1983, Volume 20, p. 1.
3. E. Fitzer and R. Weiss, *Carbon*, **25**, 455 (1987).
4. G. R. Palmese and R. L. McCullough, *J. Adhesion*, to appear.
5. G. R. Palmese, Origin and Influence of Interphase Material Property Gradients in Thermosetting Com-

posites, Ph.D. Dissertation, University of Delaware, Newark Delaware (December 1991).

6. W. M. Sanford and R. L. McCullough, *J. Polym. Sci. Polym. Phys.*, **28**, 973 (1990).

7. D. F. Rhor, Modeling Reaction and Diffusion in Epoxy-Amine Polymerization Kinetics, Ph.D. Dissertation, University of Delaware, Newark, Delaware (1987).

8. J. B. Enns and J. K. Gillham, *J. Appl. Polym. Sci.*, **28**, 2567 (1983).

9. Shell EPON Resin Structural Reference Manual.

10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.

11. V. Bellenger, W. Dhaoui, J. Verdu, J. Galy, Y. G. Won, and J. P. Pascault, *Polymer*, **30**, 2013 (1989).

12. P. C. Hiemenz, *Polymer Chemistry*, Marcel Dekker, New York, 1984.

13. D. R. Miller and C. W. Macosko, *Macromolecules*, **9**, 206 (1976).

14. D. R. Miller and C. W. Macosko, *Macromolecules*, **11**, 656 (1978).

15. A. Garton, P. D. McLean, W. T. K. Stevenson, J. N. Clark, and J. H. Daly, *Polym. Eng. Sci.*, **27**, 1620 (1987).

16. V. Bellenger, W. Dhaoui, and J. Verdu, *Polym. Eng. Sci.*, **30**, 321 (1990).

17. J. Daly, A. Britten, and A. Garton, *J. Appl. Polym. Sci.*, **29**, 1403 (1984).

18. S. L. Kim, M. D. Skibo, J. A. Manson, R. W. Hertzberg, and J. Janiszewski, *Polym. Engr. Sci.*, **18**, 1093 (1978).

19. P. A. Madsen and R. T. Foister, *J. Appl. Polym. Sci.*, **37**, 1931 (1989).