An Experimental Investigation of the Effect of Prepolymer Molecular Weight and Stoichiometry on Thermal and Tensile Properties of Epoxy Resins

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SYNOPSIS

An experimental study was undertaken to investigate the thermomechanical properties of a certain epoxy/amine configuration. The basic structure of all the epoxies was the same—DGEBA—and the curing agent used was PACM 20. By varying the epoxy prepolymer molecular weight and the stoichiometry between epoxy and amine, a range of different epoxy networks were produced. Glass transition temperatures were evaluated by using differential scanning calorimetry (DSC). Modulus values as well as an alternative T_g determination were provided by dynamic mechanical analysis (DMA). Coefficients of thermal expansion were obtained from thermomechanical analysis (TMA). The tensile tests conducted at room and elevated temperatures provided additional modulus data along with the yield point, tensile strength, and elongation at break data. Property vs. stoichiometry curves exhibited a maximum for the glass transition temperature and the over the T_g modulus at the stoichiometric point. On the other hand, the under T_g modulus showed a minimum at the stoichiometric point. The results of the yield strength show remarkable similarity with the results of the modulus. Strength and elongation at break do not show clear trends, but a much different behavior is exhibited between room and elevated temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Although crosslinked polymer networks have been widely used as adhesives and composite matrices, their processing–structure–property relationship has been investigated much less than has the case of thermoplastics. The practical difficulties of studying such polymers stem from the infinite network structure that they form upon crosslinking. An additional complication is that these networks are rarely regular; they usually contain imperfections such as free ends, intermolecular loops, and molecules trapped in the network but unattached to it.[1,2]

A particular network system that has found commercial success is the epoxy resin system.

Epoxy resins have been used as adhesives, high-performance coatings, and potting and encapsulating compounds. Since these thermosetting polymers are also used as matrices for composite materials, it is important from a composite material application point of view to examine the parameters that affect their mechanical properties. It has been shown in the literature that the region of the interphase between fiber and matrix is critical for composite mechanical properties. Two of the most commonly accepted mechanisms[3–5] for interphase formation are (a) the preferential absorption of curing agent on the fiber surface and (b) the diffusion of curing agent in epoxy-rich sizings. Both of these mechanisms lead to stoichiometric imbalances that are frozen in as the system vitrifies. It is important therefore to examine the effect of stoichiometry on material properties to gain insight into the behavior characteristics of the interfacial region.

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The mechanical properties of interest are the tensile properties and the coefficient of thermal expansion. Tensile properties include the Young's modulus, the yield point, and tensile strength. These properties are strongly dependent on the temperature at which the test is conducted relative to the glass transition temperature of the material. For temperatures above the glass transition temperature, the material behaves as a rubber and ideal rubber elasticity can be used to predict the modulus. Below the glass transition temperature, the material behaves as a glass and thermodynamic models are rarely employed to provide a relationship between structure and properties.

The glass transition temperature is an important characteristic parameter of the network structure. It is usually defined as the point of change of the slope on a volume vs. temperature graph; an increase in the thermal expansion coefficient threefold is usually observed between the glassy and the rubbery regions. Glass transition temperatures can also be defined on the storage modulus vs. temperature graph of dynamic mechanical analysis tests at a fixed frequency. At the transition point, the modulus of these polymers decreases by two or three orders of magnitude.

Another parameter that affects the network structure and properties is the epoxy prepolymer molecular weight. A range of prepolymer molecular weight is used in practice both as one component (together with the curing agent) of the matrix system and as fiber coatings or sizings. These coatings are applied to facilitate handling and processing of the fibers but are expected to locally change the interfacial structure. In commercial applications, high molecular weight epoxies, which are solid at room temperature, are used as fiber coatings. As the molecular weight of the epoxy prepolymer increases, its viscosity also increases, making processing of the polymer harder. On the other hand, as the prepolymer molecular weight increases, the resulting cross-linked structure from the curing becomes more rigid. It is important, therefore, to evaluate the effect of the epoxy prepolymer molecular weight on the cured epoxy material properties to optimize the fiber-coating selection that will lead to enhanced composite properties.

There are a number of experimental studies in the literature on epoxy resin amine-cured systems.[1,2,5-11] These studies indicate that as the distance between crosslink points decreases these glasses become more brittle. For a specific amine-cured epoxide system, the T_g is always highest for the fully reacted and higher crosslink density glass;

however, the modulus exhibits a local minimum at the same point. Palmese and McCullough[5] in their study of an epoxy/cyclo-aliphatic diamine system showed that the plot of the glassy modulus (at 50°C under the T_g) for each stoichiometry exhibits a global minimum at the stoichiometric point. The rubbery modulus for each stoichiometry (at 30°C over the T_g) behaves similar to the T_g itself, exhibiting a global maximum at the stoichiometric point.

In this work, an extensive experimental study was undertaken to investigate the thermomechanical properties of a certain epoxy/amine chemical configuration. The chemistry is the same for all the systems used here since the functionality between reactants is identical. To produce different epoxy networks, the epoxy prepolymer molecular weight and the epoxy amine stoichiometry were varied. Once these mixtures were produced and cured, several mechanical and thermal properties were experimentally determined. Differential scanning calorimetry, dynamic mechanical analysis, and thermomechanical analysis experiments were conducted on these samples. Tensile tests were conducted on dog-bone-shaped specimens of one epoxy amine combination at room and elevated temperatures.

EXPERIMENTAL

Sample Materials and Preparation

Starting materials for the systems studied here consisted of four Shell epoxy resins, namely, Epon 825, 828, 834, and 1001F.[12] These resins range in molecular weight and, therefore, in viscosity from low-viscosity liquids to high-melting-point solids. The basic structure (diglycidyl ether of bisphenol-A, DGEBA) of all the epoxies is the same. The molecular structure of the epoxy prepolymer is given in Figure 1. The properties of these resins are deter-
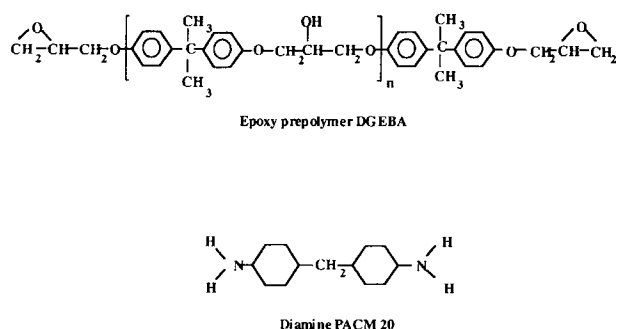

Epoxy prepolymer DGEBA

Diamine PACM 20

Figure 1   Molecular structure of epoxy prepolymer and diamine curing agent.

mined by the number of repeat units, n. Another important parameter directly related to n and molecular weight is the epoxy equivalent weight (EW). The latter parameter is defined as the mass of epoxy containing 1 g equivalent of epoxide. The properties of the prepolymers studied here are given in Table I. It is important to notice that all the resins, other than the 1001F, are in the liquid state at room temperature. The curing agent used throughout this work was PACM 20, a cyclo-aliphatic diamine with a molecular weight of 340. The molecular structure of the diamine curing is shown in Figure 1.

Samples were prepared by mixing a wide range of stoichiometries, i.e., between 10 and 50 pph of amine (parts amine per hundred parts of epoxy). The liquid epoxy prepolymers (Epon 825, 828, and 834) were set under a vacuum in an oven at 100°C to degas. The prepolymers were then mixed with the curing agent in cups for about 10 min. The amount of cloudiness of the sample indicated the quality of mixing, with perfectly mixed samples appearing clear.

An aluminum mold of dimensions 10 × 10 cm and depth of 1 cm was used to form slabs of resin. Before filling the mold with the resin, several layers of a mold-releasing agent were applied on the surface of the mold. The top of the mold was left open to allow for the evolution of air bubbles trapped during mixing.

The parts were cured in an oven controlled to within 1°C in two isothermal stages. The first isothermal segment consisted of 2 h curing at 80°C. The second was the postcuring segment, which was done after the slabs were released from the mold, at 160°C for 2 h. Following cure, samples were allowed to cool down to room temperature and were stored in a desiccator. Samples for testing were cut from the slabs using a diamond saw.

The solid prepolymer Epon 1001F had a T_g value of 80°C, making the above procedure impossible to follow. Increasing the temperatures to high enough temperatures above the T_g so that the resin would be in liquid form and mixable with the amine presented problems, since at such high temperatures, the curing started and accelerated before mixing was complete. On the other hand, differential scanning calorimetry samples were only 10 mg in weight and complete mixing for such small quantities could be achieved by impregnating very fine particles of epoxy with the liquid amine at room temperature. Curing in this case was done inside the DSC pan following the same curing schedule as that was used for the rest of the epoxies (using a suitable DSC temperature profile). For this reason, only T_g (and no me-

Table I   Epoxy Prepolymer Properties[12]

Resin	EW	EW (Mean)	MW	T_g
825	172–178	175	350	−18
828	185–192	187	375	−14
834	230–280	240	480	−5
1001F	350–550	375	750	80

chanical property) data are presented in this work for the epoxy resin based on the Epon 1001F prepolymer.

Thermal Analysis

Glass transition temperatures were evaluated using differential scanning calorimetry (DSC). Modulus values as well as an alternative T_g determination were provided by dynamic mechanical analysis (DMA). Finally, coefficients of thermal expansion were obtained from thermomechanical analysis (TMA).

DSC samples were prepared in the case of the Epon 825-, 828-, and 835-based epoxies by grinding a small quantity taken from the slab. After weighing, the sample was placed inside the DSC aluminum pan. In the case of Epon 1001F, curing of the system was conducted inside the pan. Temperature ramp profiles were set at 5°C from room temperature to 200°C. The absence of any residual reaction capacity was indicated by the absence of any exothermic peak above the T_g. Glass transition temperatures were obtained as the inflection point on the thermograph.

Modulus and glass transition temperatures were evaluated by the DMA technique. Values of storage and loss modulus depend not only on temperature but also on the frequency of the oscillation applied on the samples. In this work, a constant frequency of 1 Hz was used. The amplitude of oscillations was kept at 0.2 mm. DMA samples were prepared by cutting the cured resin slabs into specimens of dimensions 2 × 10 × 50 mm. After cutting, the specimens were mounted in the DMA clamps for testing. Specimens were temperature-ramped from room temperature to 200°C at a rate of 5°C/min.

TMA specimen preparation involved the cutting of cubical specimens measuring roughly 3 × 3 × 3 mm. The temperature in the TMA cell was again ramped at 5°C/min from room temperature to 200°C. Noise due to thermal stresses developed during curing was often encountered, especially on the derivative of the displacement curve. This effect was diminished by heating the specimens first to their T_g and allowing for the stresses to relax. The T_g

Table II **Glass Transition Temperatures in °C for the Epon 828/PACM 20 System Obtained by Different Experimental Techniques**

Amine (pph)	DSC Results	DMA Results	TMA Results
15	45	53	40
20	78	90	88
25	96	105	105
30	161	165	163
35	143	150	155
40	153	135	140
45	119	127	122
50	79	90	70

reported in this work from TMA was defined as the point of change of slope on the displacement vs. temperature graph or, equivalently, by the discontinuity in the value of thermal expansion coefficient. The thermal expansion coefficients is defined as $\alpha = 1/L(\partial L/\partial T)_p$, where L is the length of the sample. Since TMA graphs give displacements or $\Delta L/L$, the derivative of this quantity yields the thermal expansion coefficient.

Tensile Testing

Tensile tests were conducted on dog-bone-shaped specimens of the Epon 828/PACM 20 epoxy/amine combination. After mixing the prepolymer and amine at varying stoichiometries, the mixture was poured into a dog-bone-shaped silicon mold. The specimens were allowed to cure and postcure in an oven according to the temperature profile followed for the epoxy plaques. The dog-bone specimens had a gauge length of 2 cm, a width of 4 mm, and a thickness of 2 mm. After polishing, the specimens were strain-gauged and stored in a desiccator.

Mechanical tests were carried out in an Instron 1125 series testing machine with a 2000 lb load cell. The machine was fitted with an environmental chamber between the grips. In addition to the control thermocouple for the chamber, a surface thermocouple was mounted on the sample and that temperature was monitored to assure thermal equilibrium in the chamber. After temperature in the chamber had equilibrated and the sample had reached the desired temperature level, tensile tests were conducted. At least five samples were tested for each stoichiometry and each temperature level. The crosshead speed of the Instron was kept at 0.5 cm/min for all the experiments. Load and strain

data were collected with an Optilog eight-channel multiplexing data acquisition system.

RESULTS AND DISCUSSION

Glass Transition Temperature

The effect of the evaluation technique on the glass transition temperature is examined first. The results for Epon 825/PACM 20 combination are presented in Table II. It is obvious that the T_g data obtained from different techniques follow the same trend with varying stoichiometry. Comparing the different techniques, DSC values are always lower than are DMA values by a difference that ranges between 3 and 13°C. TMA data, on the other hand, are generally closer to the DMA data than they are to the DSC data. This difference is less than 3°C for all cases other than the maximum and the minimum stoichiometry. Similar trends were obtained for Epon 828/PACM 20 and Epon 836/PACM 20.

These differences can be attributed to the relaxational, i.e., time-dependent, nature of the glass transition. T_g measurements can be affected by several factors including heating rate, thermal history, and frequency. Since heating rate and thermal history are kept constant among the methods, it is likely that the frequency difference is the origin of the discrepancies. The measurement frequency in the DSC is 0 Hz, as compared to the frequency of the DMA, which is 1 Hz. The relationship between frequencies and temperatures is an Arrhenius type of equation with T_g decreasing as frequency decreases. TMA frequencies are a function of the testing time scale, but the results are expected to be closer to the DMA data than they are to the DSC data.

Data for epoxies based on Epon 825 and 828 and 835 from DMA and for the epoxy based on Epon 1001F from DSC are shown in Figures 2 and 3. The results for the Epon 828/PACM 20 system agree very well with the results of Palmese et al.[5] All the curves show maxima at the stoichiometric point for each resin (the mixing ratio that leads to one epoxy group per amine N—H bond). Obviously, the stoichiometric point varies with the molecular weight of the epoxy. The slope of the T_g decrease is more pronounced for the epoxy-rich region than for the amine-rich region. The same trend has been identified in the literature for similar systems.[1,5,6,8,11]

The effect of the stoichiometry can be better explained by introducing the epoxy-to-amine ratio r, defined by the following equation:
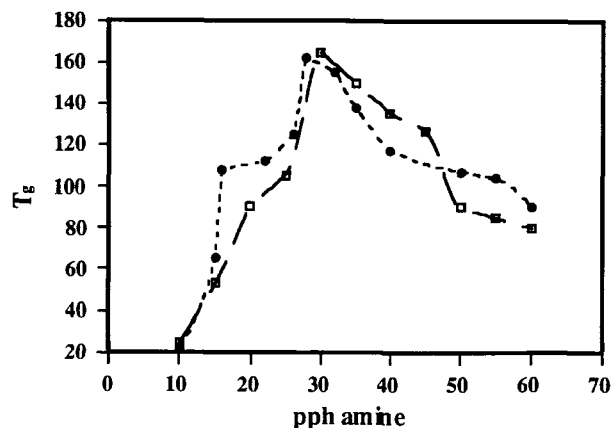
Figure 2 T_g variation with stoichiometry for (— □ —) Epon 825- and (- - ● - -) Epon 828-based systems.

$$r = \frac{2\,MW_e}{MW_a}\left(\frac{w_a}{w_e}\right) \tag{1}$$

where MW_e and MW_a are the molecular weights of epoxy and amine, respectively, and w_a/w_e is the weight ratio of the two components (pph amine). To explain the prepolymer MW effect on the stoichiometric point, the data are plotted again but with respect to r with the results shown in Figure 4. The similarity between all the systems is more pronounced than in Figures 2 and 3 due to the existence of a common maximum at the same point r.

Glass transition dependence on stoichiometry and epoxy MW can be explained by examining the crosslink density and the molecular weight between crosslinks, M_c, which is inversely proportional to the crosslink density but also depends on the MW of the monomers. It is pointed out in the literature that the higher the crosslink density, the more rigid or constrained the structure becomes.[1,6,8,11] Therefore, higher temperatures are needed for the molecular motions characteristic of the transition temperature. Among systems made out of the same monomers, the stoichiometrically balanced system having the highest crosslink density will also exhibit the maximum T_g.

Among all the structure–T_g correlations, the one used most often is the semiempirical approach followed by Nielsen,[2] which can be directly applied to nonstoichiometric mixtures. Nielsen showed that for low concentrations of curing agents the glass transition temperature can be given by an equation of the form
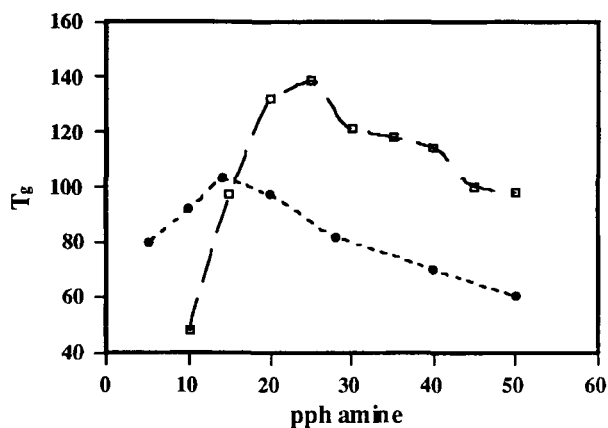
$$T_g - T_{gu} = \frac{C}{M_c} \tag{2}$$

Figure 3 T_g variation with stoichiometry for the (— □ —) Epon 834- and (- - ● - -) Epon 1001F-based systems.

In the above equation $1/M_c$ is an expression of the degree of crosslinking for a system based on the same monomers but varying stoichiometry. Nielsen averaged the results from different studies and gave a number for C equal to 3.9×10^4 g K/mol. Usually, M_c is experimentally evaluated from rubbery phase (over the T_g) modulus data, a method that can be highly inaccurate. Therefore, Nielsen's original approach gave slopes that varied between 2 and 4 $\times 10^4$. Bellenger et al.[6] and Vallo et al.[11] used statistical approaches to predict crosslinking density based on stoichiometry. The shape of the crosslink density curves was identical to the shape of each of the curves in Figures 2 and 3. Nielsen's equation seems to give good predictions for any single DGEBA-based system with the maximum being at the stoichiometric point and a faster drop of the
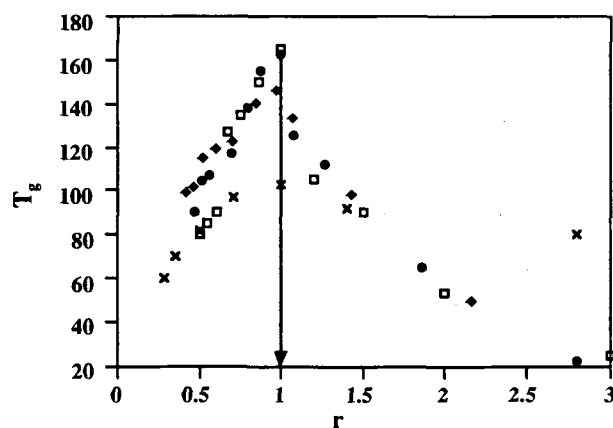

Figure 4 Glass transition temperature vs. epoxy-to-amine group ratio r: (□) Epon 825-, (●) Epon 828-, (♦) Epon 834-, and (x) Epon 1001F-based systems.
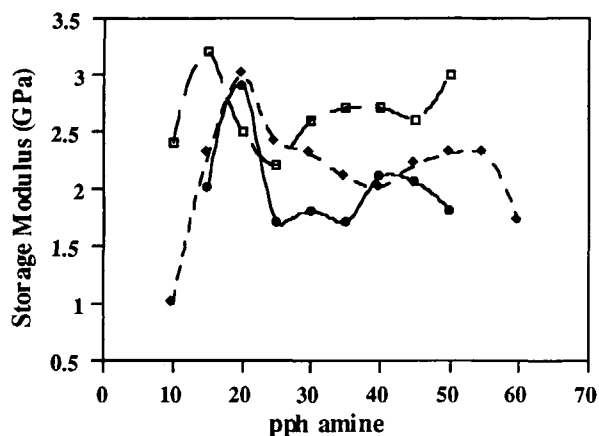
Figure 5   Room-temperature storage modulus variation with stoichiometry: (-●-) Epon 825, (— ♦ —) Epon 828-, and (— □ —) Epon 834-based systems.

curve for the epoxy-rich side and a slower drop for the amine-rich side.

The proportionality dependence of T_g on crosslink density and, therefore, on $1/M_c$, cannot only explain the shape of each individual curve but also the relationship between curves based on different prepolymers. In this work, M_c was varied not only by changing the crosslink density through stoichiometry but also through the monomer MW. Figure 4 shows that as the prepolymer MW increases from 825 to 1001F the overall level of T_g (the maximum along with both sides of the curve) decreases. This behavior is consistent with eq. (2) with an equal value T_{gu} for all systems. Since the prepolymer MW and M_c are proportional to each other for constant degree of crosslinking (and, therefore, stoichiometry), the M_c for the high MW-based systems increases and, therefore, T_g decreases. As a result, the T_g of these systems can be controlled either by a variation in prepolymer MW or by a variation in stoichiometry.

Modulus Evaluation and Temperature Dependence

The DMA technique offers the advantage of providing modulus values over a wide temperature range. For a high enough span-to-thickness ratio (over 30 in our experiments) and for isotropic materials, the storage modulus obtained from DMA measurements is equivalent to the Young's modulus of the material.

In Figure 5, the results for the room-temperature storage modulus are plotted with respect to the stoichiometry for the three epoxy resin systems tested by DMA. The resin based on high molecular weight

epoxy prepolymer Epon 834 generally shows higher moduli than do the resins based on lower MW, i.e., Epon 825 and 828. There are, however, some features common for all the resins tested here. First, it is important to point out that in contrast to the glass transition behavior there exists a broad local minimum at the optimum stoichiometric point. Generally, there are two local maxima in all the curves: one at a point lower and one at a point higher than the stoichiometric ratio for each of these resins. In particular, for the Epon 825-based system, there are two maxima at 20 and 45 pph amine with the optimum stoichiometry at 30 pph. For the Epon 828-based system, the maxima appear at 20 and 55 pph with the optimum stoichiometry at 28 pph. Finally, following a similar trend, maxima for the Epon 834-based system appear at 15 and 50 pph with the optimum stoichiometry at 25 pph. On the extreme points further than the two maxima, the modulus decreases significantly, due to the test temperature approaching the glass transition temperatures at those areas.

In Figure 6, the storage modulus for each one of the systems is plotted at an elevated temperature level of 100°C. As the temperature increases, two phenomena become evident: First, the modulus values are reduced by as much as 50% for the middle region of the graph, where specimens are below T_g. Second, as T_g is approached for each stoichiometry, the two local maxima diminish and a very broad maximum around optimum stoichiometry is observed.

To minimize the effect of glass transition temperature on the modulus results, the modulus can be plotted at temperatures that differ from the glass
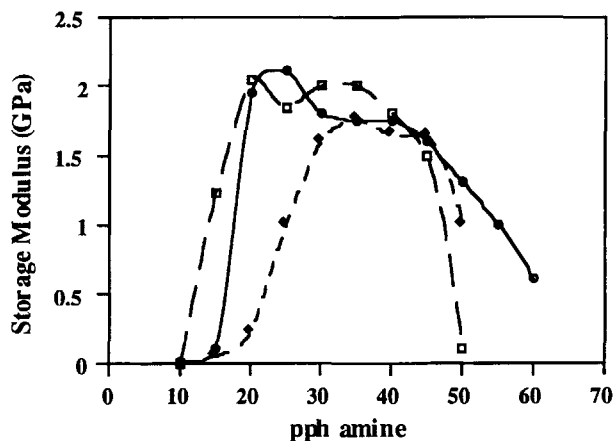

Figure 6   Storage modulus plot vs. stoichiometry at 100°C: (— ● —) Epon 825-, (-●-) Epon 828-, and (—□—) Epon 834-based systems.

transition temperature by a specified amount.[5] The modulus is plotted separately for two regions: the region under T_g where data correspond to temperatures 50°C under the glass transition temperature of each stoichiometry and the region over the T_g where the data correspond to 30°C above the glass transition temperature of each stoichiometry.

The under-T_g behavior displays very similar features for all three epoxies, as indicated by Figure 7. High values of the storage modulus are obtained at the epoxy resin-rich part of the curves with an abrupt drop at the respective stoichiometric points of each epoxy. The modulus data reach a low plateau at the amine-rich part of the curve. This modulus plateau seems to increase as the molecular weight of the epoxy prepolymer increases. The minimum of the modulus at the stoichiometric point has been identified in the literature as the antiplasticization effect.[1,5,7,10,13] According to this theory, a small amount of nonreacting additives can increase the glassy state modulus of the epoxy material, due to a decrease in free volume available for segmental mobility. In nonstoichiometric epoxy/amine reactive mixtures, there exists an amount of unreacted monomers or oligomers (sol phase) that are not incorporated in the network structure. Away from the stoichiometric point on either side (epoxy- or amine-rich), these amounts keep increasing and the free volume is further reduced. This leads to a loss of segmental mobility and, therefore, to an increase of the glassy modulus.

A very different behavior is exhibited in the over-T_g behavior of the resins, depicted in Figure 8. Here, a very distinctive maximum is reached at the stoichiometric point of every resin. The maximum value decreases with increasing molecular weight of the
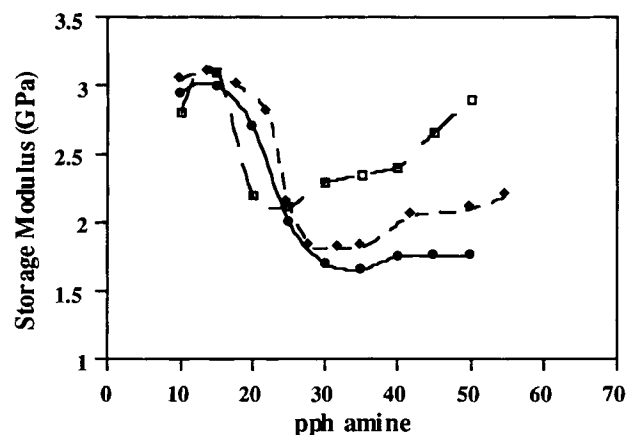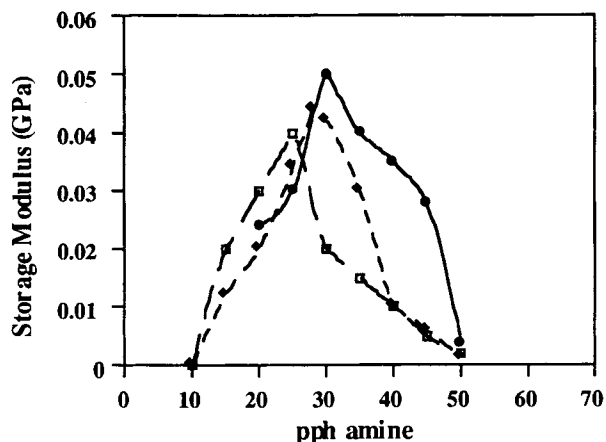

Figure 8 Storage modulus vs. stoichiometry at $T = T_g$ + 30°C: (-●-) Epon 825-, (— ♦ —) Epon 828-, and (— □ —) Epon 834-based systems.

epoxy prepolymer. A comparison of this plot with the T_g vs. stoichiometry data (Fig. 2) shows a similar dependence on stoichiometry for the two properties.

The rubbery modulus dependence on stoichiometry can be explained by the theory of rubber elasticity.[2,5] This theory is based on the premise that the internal energy is not affected by changes in displacement. In addition, for a small deformation, Gaussian or random coil behavior for the chain segments can be assumed. The changes in entropy are related to conformational changes caused by the deformations. The shear modulus of an ideal rubber is then given by the following equation:

$$G = \nu'RT = \frac{\rho RT}{M_c} \qquad (3)$$

where ν' is the effective concentration of network chains per volume; R, the ideal gas constant; and ρ, the density. By comparing eqs. (2) and (3), the same inversely proportional dependence of the glassy modulus and the glass transition temperature is obtained. This can explain the similarity of the glass transition temperature and the rubbery modulus dependence on the stoichiometry.

Thermal Expansion Coefficient

In Figures 9 and 10, the temperature dependence of thermal expansion coefficients for the systems based on Epon 825 and the 836 is displayed. As was the case with the modulus, the thermal expansion coefficient shows a steplike change at the glass transition temperature. Other than the effect of stoichiometry on the glass transition temperatures, which has al-
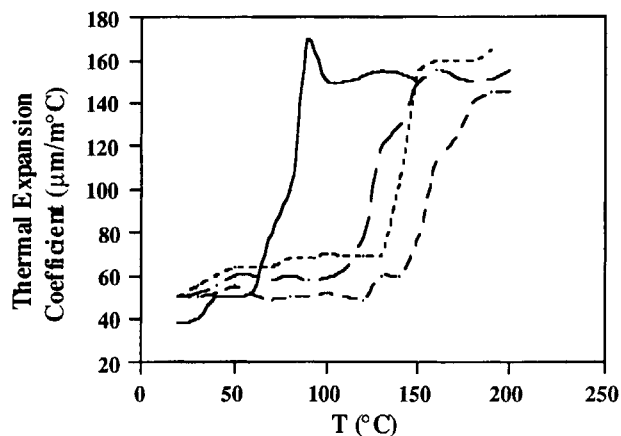

Figure 7 Storage modulus plot vs. stoichiometry at $T = T_g - 50$°C: (-●-) Epon 825-, (— ♦ —) Epon 828-, and (— □ —) Epon 834-based systems.

Figure 9 Thermal expansion coefficient for Epon 825: (———) 20 pph, (— · –) 25 pph, (———) 30 pph, and (- - - - -) 35 pph of diamine stoichiometry in the mixture.

Figure 11 Stress–strain behavior for 28 pph Epon 828/ PACM 20 epoxy system: (-⊖-) room temperature; (- - ▲ - -) $T = 70°C$; (- - + - -) $T = 110°C$.

ready been identified, the three epoxy systems investigated here show similar thermal expansion coefficient values within experimental error.

The behavior can again be analyzed in two regimes: Under the T_g, there is a slight increase of the thermal expansion coefficient with temperature, ranging from 50 to 70 mm/m°C. Above the T_g, the thermal expansion coefficients are essentially constant with temperature, ranging between 140 and 170 mm/m°C.

Tensile Results

A typical set of stress–strain curves (at the stoichiometric point) is shown in Figure 11. The effect of temperature on the stress–strain curve is to increase the ductility of the material. The yielding be-
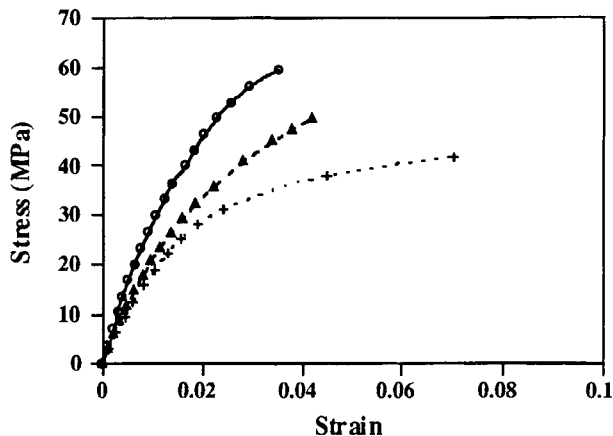
havior was more pronounced for the off-stoichiometry mixtures.

The elastic modulus was calculated from the initial slope of the stress–strain curves. The modulus calculated from this test is plotted in Figure 12 with respect to stoichiometry at three temperature levels, i.e., room temperature, 70°C, and 110°C. The values obtained here are about 30% higher as compared to the storage flexural moduli obtained from DMA experiments, but the trends with stoichiometry and temperature are the same. The discrepancies can be explained by the difference between tensile and bending modes and agree well with similar flexural and tensile data reported in the literature.[1,14] The modulus shows again a minimum at the optimum stoichiometric point due to the antiplasticization effect. As temperature in-
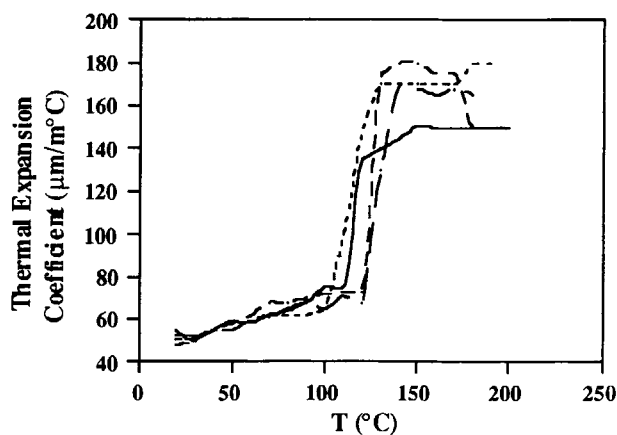

Figure 10 Thermal expansion coefficient for Epon 836: (———) 20 pph, (— · –) 25 pph, (———) 30 pph, and (- - - - -) 35 pph of diamine stoichiometry in the mixture.
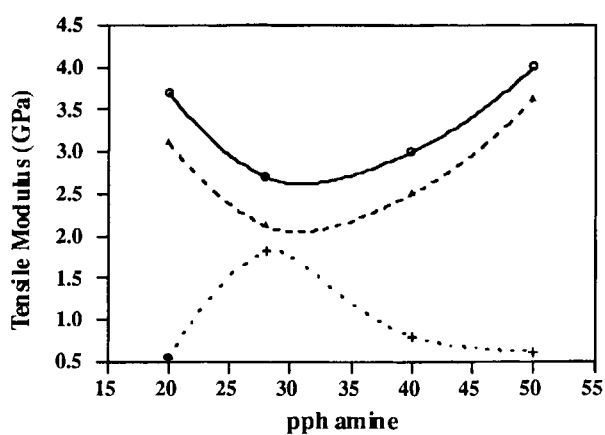

Figure 12 Elastic modulus as a function of stoichiometry: (-⊖-) room temperature; (- - ▲ - -) $T = 70°C$; (- - + - -) $T = 110°C$.

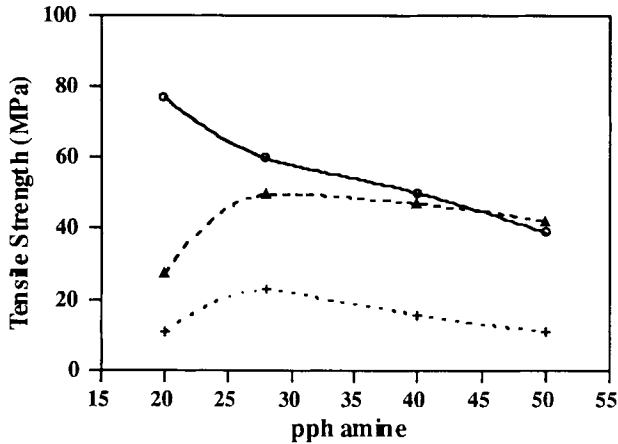**Figure 13** Tensile strength as a function of stoichiometry: (-⊖-) room temperature; (- - ▲ - -) T = 70°C; (- - + - -) T = 110°C.

Figure 14 Failure strain as a function of stoichiometry: (-⊖-) room temperature; (- - ▲ - -) T = 70°C; (- - + - -) T = 110°C.

creases closer to the glass transition temperatures of the specimens or the rubber elasticity region, this effect is reversed. A maximum appears to be forming at the stoichiometric point, where crosslinking density is maximum.

Tensile strength, strain at failure, and yield stress were evaluated from the stress/strain plots and the results are displayed in Figures 13, 14, and 15, respectively. At room temperature, the tensile strength decreases with increasing amine concentration in the mixture. As temperatures increase, the strength decreases and a maximum forms at the stoichiometric point. Therefore, close to—or in—the rubberlike elastic region, all properties, including the tensile strength, appear to be dominated by the crosslink density. The curve at this region follows the behavior of the modulus and the strain at failure. These observations suggest that at high strains' strength is sensitive to intermolecular packing and free volume as well as to crosslinking density. In addition, molecular architecture becomes a factor.[1,10,14]

The ultimate strain shows a maximum at the stoichiometric point, with a range between 1.2 and 3%. This range increases dramatically with temperature to between 0.5 and 8% at 110°C. These results qualitatively agree with those of Morgan et al.,[1] Kim et al.,[10] and Gupta et al.[14] The stoichiometric samples have a regular network and, therefore, the stress field is expected to be uniform, leading to high elongation at break. For different stoichiometries, the irregularity of the network may lead to stress concentrations and, therefore, to lower elongations at break. The yield point behavior of these systems is important from a fracture point of
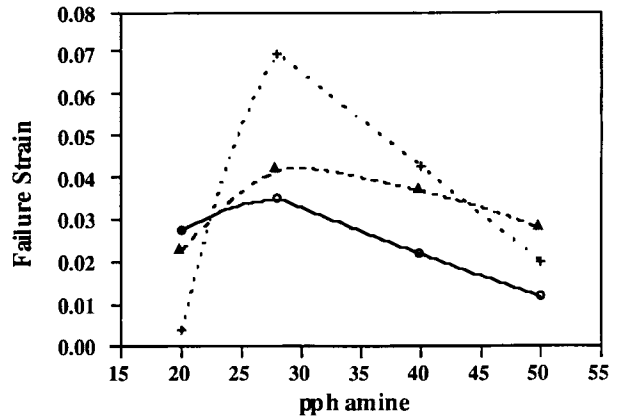
view according to Gupta et al.,[14] who observed similarities between fracture toughness and elongation at break curves with varying stoichiometry.

The microscopic yield stress is defined as the stress at the onset of nonlinear behavior on the stress/strain plot. The yield strength results show similarity with the modulus results with values decreasing as the temperature increases. Gupta et al.[14] proposed that yield occurs at a critical shear stress that is a constant fraction of the modulus of rigidity. The same authors conducted volumetric studies on tensile specimens. Their analysis showed that an increase in free volume with tensile deformation is a likely mechanism for yield in these materials.

In summary, all properties at high temperatures show maxima at the stoichiometric point, because they are close to—or in—the rubber elasticity region and properties are only affected by the crosslink
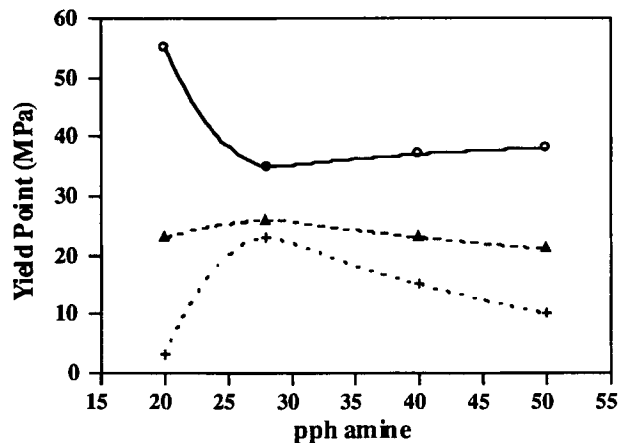

Figure 15 Yield stress as a function of stoichiometry: (-⊖-) room temperature; (- - ▲ - -) T = 70°C; (- - + - -) T = 110°C.

density. At these temperature levels, materials behave roughly as fluids with crosslinks acting as pinpoints. At temperatures under T_g, the tensile properties do not show such clear trends.

CONCLUSIONS

An experimental investigation was undertaken to evaluate the effect of epoxy prepolymer molecular weight and epoxy/amine stoichiometry on material properties. Glass transition temperature, modulus, thermal expansion coefficient, and ultimate tensile properties were shown to vary with stoichiometry. Although T_g showed a maximum at the optimum stoichiometry, the modulus exhibited a minimum at the same point. The glass transition dependence on stoichiometry and epoxy MW can be explained in terms of the crosslink density and the molecular weight between crosslinks. The higher the crosslink density, the more rigid or constrained the structure becomes. The stoichiometrically balanced system having the highest crosslink density will also exhibit the maximum T_g. On the other hand, increasing the molecular weight of the prepolymer and keeping stoichiometry constant leads to an increase in M_c and, therefore, to a decrease in T_g.

The minimum of the modulus at the stoichiometric point is associated with the anti-plasticization effect. This effect, which has been identified in similar systems by other workers, can be attributed to an increasing amount of unreacted oligomers not incorporated in the network structure as the system moves away from the stoichiometric point. The rubbery (over T_g) modulus follows the T_g trends with stoichiometry and shows a maximum according to the principles of rubber elasticity. The results of the yield strength show remarkable similarity with the results of the modulus. Strength and elongation at break do not show clear trends but a much different behavior is exhibited between room and elevated temperatures.

REFERENCES

1. R. J. Morgan, F.-M. Kong, and C. M. Walkup, *Polymer*, **25**, 375–386 (1984).
2. L. E. Nielsen, *J. Macromol. Sci.-Rev. Macromol. Chem. C*, **3**, 69–103 (1969).
3. T. P. Skourlis and R. L. McCullough, *Compos. Sci. Technol.*, **49**, 363–368 (1993).
4. L. T. Drzal, M. J. Rich, M. F. Koenig, and P. F. Lloyd, *J. Adhes.*, **16**, 133–152 (1983).
5. G. R. Palmese and R. L. McCullough, *J. Appl. Polym. Sci.*, **46**, 1863–1873 (1992).
6. V. Bellenger, W. Dhaoui, J. Verdu, J. Galy, Y. G. Won, and J. P. Pascault, *Polymer*, **20**, 2013–2018 (1989).
7. V. Bellenger, W. Dhaoui, J. Verdu, J. Boye, and C. Lacabanne, *Polym. Eng. Sci.*, **30**, 321–325 (1990).
8. J. Galy, A. Sabra, and J. P. Pascault, *Polym. Eng. Sci.*, **26**, 1514–1523 (1986).
9. A. Hale, C. W. Macosko, and H. E. Bair, *Macromolecules*, **24**, 2610–26221 (1991).
10. S. L. Kim, M. D. Skibo, J. A. Manson, R. W. Hertzberg, and J. Janiszewski, *Polym. Eng. Sci.*, **18**, 1093–1099 (1978).
11. C. I. Vallo, P. M. Frontini, and R. J. Williams, *J. Polym. Sci. Part B Polym. Phys.*, **29**, 1503–1511 (1991).
12. Shell Inc., *EPON Resin Structural Reference Manual*, 1981.
13. M. S. Vratsanos and R. J. Farris, *Polym. Eng. Sci.*, **29**, 806–816 (1989).
14. V. B. Gupta, L. T. Drzal, C. Y.-C. Lee, and M. J. Rich, *Polym. Eng. Sci.*, **25**, 812–823 (1985).