Relationships between Stoichiometry, Microstructure, and Properties for Amine-Cured Epoxies

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ABSTRACT: Changes in microstructure and mechanical properties are investigated as a function of epoxy–amine stoichiometry. The epoxy–amine system studied exhibits a two-phase structure consisting of a hard microgel phase and a dispersed phase of soft, unreacted and/or partially reacted material. The size distribution of the microgel regions tends to increase with increasing amine content. Concurrently, the connectivity of the softer phase increases dramatically. This two-phase structure is inherently fractal, exhibiting a single glass transition temperature, T_g. The T_g and elevated-temperature properties of the epoxy are directly correlated with crosslink density and the percentage of microgel phase observed in microstructure studies. The fracture toughness at room temperature increases with increasing amine content, most likely due to the increased presence of the soft phase, which absorbs more energy during crack growth. Changes in modulus values at 30°C with stoichiometry are explained by considering the effective aspect ratio of the polymer structure in the determination of sample rigidity. Relationships between microgel sizes and the sizes of interphase regions that form in composite and adhesive systems are also discussed in terms of interphase properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 699–712, 1999

Key words: epoxy microstructure; epoxy–amine stoichiometry; thermomechanical properties; atomic force microscopy; interphase regions

INTRODUCTION

Epoxy resins have been extensively used in composite materials and as adhesives. In both of these applications, the resin cures in the presence of a solid surface. In several experimental studies of epoxies, certain reacting species have been shown to preferentially adsorb onto various surfaces using several techniques.[1–3] This preferential adsorption phenomenon has also been modeled for amine-cured epoxies.[4–9] From both the experimental and modeling results, the amine curing agent tends to migrate toward the solid surface, creating an amine-rich region adjacent to the surface. Generally, epoxy–amine systems are processed at the stoichiometric composition, for which the ratio of epoxide groups to amine hydrogens is 1:1. As will be discussed, the glass transition temperature and elevated temperature properties are often maximized by using a stoichiometric ratio. However, the preferential adsorption of amine molecules will create a localized region adjacent to the surface that is not at the stoichiometric point. The local microstructure and resulting properties that develop will likely be affected, thus creating an interphase region that has properties that differ from the bulk resin. The performance of composites and adhesives is dominated by the ability of the resin to transfer stress to the reinforcing fibers or to the adherand, and thus is controlled by the interphase region. Therefore, developing relationships between stoichiometry, microstructure, and prop-

Figure 1 Chemical reactions for a diepoxy–diamine system, such as the EPON 828-PACM 20 system: (a) epoxide ring-opening reaction with primary amine; (b) epoxide ring-opening reaction with secondary amine; and (c) etherification reaction between reacted and unreacted epoxy groups.

erties is necessary to understand the effects of interphase regions on the behavior of composite and adhesive systems.

Epoxy–Amine Reaction Chemistry

The resin system used in this work was EPON 828 epoxy cured with PACM 20 amine. The EPON 828 epoxy is based on the oligomeric prepolymer diglycidyl ether of bisphenol A (DGEBA), while the PACM 20 amine is a cycloaliphatic diamine with a chemical name of bis (*para*-amino cyclohexyl) methane. (See the Experimental section for further description of materials.) The crosslinking reactions between epoxy prepolymers and amine hardeners generally involve the opening of the epoxide ring by reaction with amine hydrogens, as shown in Figure 1.[4,10,11] Also shown in this figure is the etherification reaction between reacted and unreacted epoxy groups. For most epoxy–amine systems, the reaction rates for the epoxy–amine reactions are much higher than the etherification reaction, and often, the etherification reaction is only observed for excess-epoxy mixtures after the amine has been depleted.[10–12] Further, the reactions involving secondary amines proceed at a lower rate than those involving primary amines because of steric limitations.[7,13] Thus, the initial cure is largely dominated by primary amine reactions with some secondary amine reactions. As the glass transition temperature, T_g, approaches the cure temperature, T_c, the reactions become less kinetically controlled and more diffusion controlled. Eventually the reactions will stop without some of the secondary amine re-

actions occurring. Postcuring is then performed at a temperature greater than T_c to react remaining secondary amines with the remaining epoxide groups, thus increasing T_g closer to the postcuring temperature.[14] For epoxy-rich mixtures, postcuring can allow etherification reactions to occur. Because the rate of these reactions is low, the postcure time and temperature can significantly impact the final T_g of epoxy-rich samples.[10]

As epoxy–amine stoichiometry changes, the reaction rates will change. Epoxy–amine reaction rates generally increase with increasing amine content.[7,10,12] Also, for EPON 828-PACM 20, the percent conversion of epoxy groups reaches 100% for 35 parts amine per 100 parts epoxy or greater during a 2-h cure at 80°C.[7] For the same curing procedure, the stoichiometric mixture yields approximately 80% conversion, while conversion in epoxy-rich mixtures is considerably lower.[7] In epoxy-rich mixtures, etherification, illustrated in Figure 1(c), can take place after the amines have been completely reacted and increase the crosslink density of the epoxy.[10,12] Also, several types of degradation reactions, such as oxidation, can occur, particularly at curing or postcuring temperatures higher than the highest possible resin glass transition temperature, $T_{g\infty}$.

Microstructure of Epoxy Resins

Several investigations of epoxy microstructure have been made in which techniques such as optical and electron microscopies were used to observe polymer surfaces that had been etched,[15–18] strained,[19] or fractured at low temperatures.[18] In each of these studies, a two-phase structure, consisting of a high-density nodular phase surrounded by a low-density dispersed phase was observed. The nodular structures observed in these studies varied in size from 6 nm up to 70 μm. In general, small, highly crosslinked microgel particles with diameters on the order of 10 nm are the main microstructural features with larger structures consisting of aggregates of these gel particles.[15,19] In one study,[15] the nodule size increased in size with increasing amine content for the EPON 828-MPD system. Within larger nodular structures, smaller nodular structures, referred to as microgels, with sizes ranging from 20–200 nm were observed. The average size and the distribution of sizes of microgels and nodules increased with increasing amine content.[15] Based on these and other observations, a model for the formation of these structures was proposed:[15] (1) microgel particles, consisting of uniformly coherent network structures, nucleate and grow; (2)

these microgel particles begin to interact, joining to form less coherent clusters or microgels, which continue to interact with nearby microgel particles and other microgels; and (3) at gelation, the microgels pack together to form the gel network, which is continuous but not uniformly coherent. Unreacted or partially reacted prepolymers form the dispersed phase, which becomes a second continuous network as the reactions proceed to completion.

This model has definite implications for structural formation as a function of stoichiometry. As the composition moves away from the stoichiometric point, the tendency towards the formation of linear structures increases, and the time to the onset of the formation of microgel particles will increase. For increasing amine content, reaction rates tend to increase and the extent of epoxy conversion increases. The interaction of these processes could provide an explanation for the increase in average size and size distribution of microgels with increasing amine content. In the case of excess epoxy, reaction rates are lower, and the extent of epoxy conversion is also low. At gelation, the size of the microgel particles will be significantly smaller than for stoichiometric or amine-rich samples, and the interactions between microgel particles will be limited, thus limiting the microgel sizes.

The effects of stoichiometry on the properties and behavior of epoxy polymers have been studied extensively.[4–7,20] In each of these studies, the EPON 828-PACM 20 system was used. While trends between epoxy properties and stoichiometry were observed, no studies were performed relating stoichiometry to the resulting microstructure, which ultimately controls the properties. In this article, epoxy microstructure will be studied with respect to stoichiometry, and stoichiometry–microstructure–property relationships will be developed. First, the materials and experimental techniques are described. Investigations of epoxy microstructure are then discussed, followed by studies of the effects of stoichiometry and microstructure on the properties of the epoxy system.

EXPERIMENTAL

Materials

The resin system used throughout this work is a thermally cured epoxy consisting of EPON 828 epoxy, manufactured by Shell Corp., and PACM 20 amine curing agent, manufactured by Air Products, Inc. The chemical structure of the two

Figure 2   Chemical structures of (a) EPON 828 epoxy, where $n = 0.2$, and (b) PACM 20 amine.

components are shown schematically in Figure 2, where $n = 0.2$ for EPON 828. This particular polymer system was chosen because it is easy to process, relatively safe to handle, and its thermal and mechanical properties, reaction characteristics, and interaction with fiber surfaces have been studied extensively.[4–9,21,22] For this system, a ratio of 28 parts of amine per 100 parts epoxy yields one epoxide group for every amine hydrogen, and thus is the stoichiometric composition.[4,6,7,21,22]

Microstructure Studies

To investigate the effects of stoichiometry on the microstructure of EPON 828-PACM 20, samples with epoxy–amine compositions of 14, 20, 28, 50, and 70 parts amine per 100 parts epoxy were used. (Herein, parts amine per 100 parts epoxy will be abbreviated as pph amine, and samples will be designated by stoichiometry in the following manner: 14 pph amine samples are designated 100–14, 28 pph amine samples are designated 100–28, etc.) One sample at each of these compositions was processed at 80°C for 2 h. As will be discussed, the microstructures of the epoxy samples are not expected to change significantly during postcuring. Therefore, the observed trends in microstructure are valid for both standard cure and postcured samples. After processing, these samples were imaged using an atomic force microscope (AFM) in TappingMode™. Topographic and phase images, corresponding to changes in the amplitude and the phase, respectively, of the oscillating AFM cantilever probe, were recorded using a Digital Instruments Multimode Scanning Probe Microscope.

Phase images were obtained using as-processed samples without any sample preparation. A silicon probe with dimensions of $125 \times 3 \times 1$ μm and a tip radius of 5–10 μm was oscillated at its mode-1 resonance frequency and a set-point voltage between 50 and 55% of the free vibrational amplitude in air. The difference between the set point and the free amplitude is directly

related to the amount of force applied to the surface during imaging. Although lower forces are recommended for imaging topography, higher forces tend to enhance the phase contrast, which is a function of elastic and viscoelastic properties of the sample.[23] Harder, less viscoelastic phases will be brighter than softer, more viscoelastic phases. Thus, the phase image reveals differences in properties of topographic features and often shows the underlying microstructure that might not be evident in the topographic image.

To verify structures observed in phase images, samples were etched and the resulting topography was imaged using the AFM. In an attempt to etch away the low-density phase, the samples were immersed in a solution of chromic and sulfuric acid at 50°C for 10–30 s. (The chromic–sulfuric acid solution is a commercially available cleaning solution composed of 93.87% sulfuric acid, 0.50% chromium trioxide, and 5.63% water by volume.) Short durations of acid immersion were used because of the propensity for the acid to react with unreacted amine in the amine-rich samples. Besides reactions of acid and amine, this treatment should cause oxidation of hydroxyl groups, rendering the lower molecular weight species more soluble in water without significantly affecting the solubility of the high molecular weight constituents.[16,18] After acid immersion, the samples were cleaned ultrasonically in distilled water for 20 min and rinsed with distilled water to remove the more soluble phase. The etched samples were then imaged with the AFM using setpoint voltage values that were 80–90% of the free amplitude; i.e., the settings were more appropriate for producing topographic images as opposed to phase images.

Studies of Epoxy Properties

The recommended processing cycle for the EPON 828-PACM 20 polymer system is a 2-h cure at 80°C, referred to herein as the standard cure, followed by a two hour postcure at 160°C.[4,7] This processing cycle is for a stoichiometric mixture, however, and might not be appropriate for any other epoxy–amine ratio. Therefore, the effects of postcuring on samples processed with a variety of epoxy–amine ratios were studied. The epoxy–amine ratios used included all of those listed in Table I. One sample of each stoichiometry was processed using the standard cure, tested using dynamic mechanical analysis (DMA), postcured, and retested using DMA. For the DMA testing, a Rheometrics

Table I Sample Designation and Corresponding Amounts of Epoxy and Amine Used to Make Samples for the Study of Microstructure and the Measurement of Density, and Thermomechanical Properties

Sample Designation	Mass (g) EPON 828	Mass (g) PACM 20	pph Amine
100-14	48.9	7.0	14.3
100-20	32.3	6.4	19.8
100-28	33.5	9.5	28.4
100-40	29.8	12.1	40.6
100-50	31.9	16.0	50.2
100-60	35.0	21.2	60.6
100-70	21.2	14.9	70.3

Solids Analyzer (model RSA 2) was used, and samples were processed with the following approximate dimensions: length = 52–56 mm, width = 8–13 mm, and thickness = 1.2–2.5 mm. Each sample was tested using a three-point bend loading configuration (i.e., flexural oscillation), a temperature ramp rate of 2°C/min, and a loading frequency of 1 Hz. The storage modulus, E'', the loss modulus, E'', and tan δ were recorded as a function of temperature, T. The glass transition temperature, T_g, was taken as the peak in E'' as recommended in ASTM D 4065, Standard Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics.

To develop relationships between microstructure and properties, density and dynamic mechanical properties were measured on samples with the same epoxy–amine compositions that were used for the microstructure studies. These samples were also processed at 80°C for 2 h, as were the microstructure samples. Themomechanical properties were measured for these samples using DMA, as previously described. Density measurements were also made using the density gradient column technique. For this study, a mixture of deionized water and calcium nitrate at 30°C was used which produced a linear variation in density with column height, as described in ASTM D 1505, Standard Test Method for Density of Plastics by the Density–Gradient Technique. The density variation in the column was evaluated by measuring the heights of six standard floats of known density. Two samples of each stoichiometry, which had approximate dimensions of 10 mm × 10 mm × 1.5 mm, were dropped into the fluid column. The heights of the samples and the standard floats were measured periodically until

Figure 3 Phase image of an unetched 100-14 sample. The difference between white and black regions represents a phase difference of 90°.

Figure 4 Phase image of an unetched 100-20 sample. The difference between white and black regions represents a phase difference of 90°.

equilibrium heights were reached. The densities of the samples were then calculated using the measured heights and the linear relation between density and height for the column. The sensitivity of the density gradient was determined to be 0.00035 g/cm^3/mm.

RESULTS AND DISCUSSION

Phase Images of Unetched Samples

AFM phase images are currently only qualitative in nature, and for that reason, scanning conditions must be very similar for meaningful comparisons to be drawn between images. Thus, phase images of unetched 100–14, 100–20, 100–28, 100–50, and 100–70 samples were produced using the following settings: a set-point voltage equal to 50–55% of the free vibrational amplitude, which ranged from 2.5–3.0 V; a scan rate of 1.5 Hz; and integral and proportional gains of 0.2 and 2.0, respectively. Scan sizes of 1, 8, and 40 mm were used to investigate microstructure on several different size scales for each sample. A two-phase structure, distinguished by light and dark regions on the phase image, was observed for each sample, but only on length scales less than 1 μm. Large nodular regions 10–70 μm in diameter were not observed, as had been reported in several other studies.[15,17,18]

Representative phase images of the 100–14, 100–20, 100–28, 100–50, and 100–70 samples are shown in Figures 3–7, respectively. For all of these 1 μm-square scans, the region of the sample that was imaged was very flat, with topographic changes of less than 30 nm over the scanned

Figure 5 Phase image of an unetched 100-28 sample. The difference between white and black regions represents a phase difference of 90°.

Figure 6 Phase image of an unetched 100-50 sample. The difference between white and black regions represents a phase difference of 90°.

region. Thus, the phase contrast should not be influenced significantly by differences in sample topography. Also, the phase contrast between white and black for each of these images is 90°, which is an extremely large range. Therefore, the property differences between the two phases is quite significant.

For the epoxy-rich samples, the sizes of the light (hard) regions tend to be much smaller than for the stoichiometric and amine-rich samples. This observation tends to correlate with reported trends of increasing microgel sizes with increasing amine content. Also, the size distribution of the harder microgel phase appears to increase with increasing amine content, as has been reported elsewhere.[15] The connectivity of the microgel regions is quite high for the stoichiometric sample, while the soft dispersed phase has poor connectivity. For off-stoichiometry samples, the soft phase retains a large degree of connectivity, particularly for amine-rich samples. In fact, for epoxy-rich and stoichiometric samples, the low-density phase tends to be dispersed within a high density matrix, whereas for the amine-rich samples, both low-density and high-density phases exist as distinct matrices.

Another observable trend is the increase in the relative amount of the softer phase for increasingly epoxy-rich and amine-rich samples. To quantify these differences, 1-μm images from

three different regions of each sample were analyzed using a bearing analysis. This type of analysis is used to compute the percentage of the surface that lies above or below a chosen height or, in this case, phase angle. For all of the phase images used for these calculations, the bearing distributions for the dark-colored regions fell between 70 and 90°, while those for the light-colored regions were between 0 and 45° with a significant break between the two distributions. For consistency, the hard phase was defined by phase contrast values less than 60°.

The results of these analyses are shown in Figure 8 as a plot of relative area of the hard phase with respect to the total area as a function of amine content. The stoichiometric sample contains the highest percentage of the harder phase as would be expected, because the stoichiometric sample should have the highest crosslink density. The epoxy-rich and amine-rich samples contain a significant amount of unreacted species and thus a larger percentage of the softer phase. Postcuring a stoichiometric sample would increase the extent of conversion to close to 100%, possibly resulting in the much larger nodular structures observed in other studies.[15,17,18] Epoxy-rich samples could also reach high degrees of conversion through etherification reactions, leading to more homogeneous microstructures. However, amine-rich samples will always contain unreacted amine and thus will exhibit a two-phase microstructure.

Figure 7 Phase image of an unetched 100-70 sample. The difference between white and black regions represents a phase difference of 90°.

Figure 8 Percentage of area of the hard phase, calculated using a bearing analysis, as a function of amine content. The data plotted are averages and standard deviations of values calculated from three different 1-μm images for each sample.

For a composite or adhesive system in which the interphase region is predicted to be amine rich, this two phase microstructure could form next to the solid surface. In fact, the preferential adsorption of reacting species might cause the interphase microstructure to contain a large amount of the soft phase. The properties of the interphase region would then be highly dependent on the low-density phase, which contains unreacted and partially reacted species. Also, because the microstructural features are significantly larger than the predicted interphase sizes, the interphase microstructure might not be characteristic of any particular stoichiometry. Thus, mapping properties of bulk epoxy samples to predicted interphase stoichiometries, as has been done in previous studies,[4–9,20] will only be valid for systems in which the interphase size is much larger than the sizes of microstructural features.

Topographic Images of Etched Samples

Portions of the samples used for the phase imaging studies were etched by brief immersion in a chromic acid-sulfuric acid solution. Because sulfuric acid will react with amine groups, the amine-rich samples were significantly more affected by the etching process than the epoxy-rich and stoichiometric samples. In fact, etching of the amine-rich samples resulted in a visible whitening of the surfaces, while only slight discolorations were noticed for the etched 100–14, 100–20, and 100–28 samples. After etching, the samples were cleaned in an ultrasonic bath of distilled water for 20 min to remove the soluble phase, and then rinsed with distilled water and dried with a pressurized air stream to remove any precipitated

material. Thus, the remaining topographic features are assumed to be the hard microgel phase.

Topographic AFM images for the etched 100–20, 100–28, and 100–70 samples are shown in Figures 9–11, respectively. From these topographic AFM images, varying degrees of roughness were observed for the etched samples. Large topographic variations were observed in the amine-rich samples due to the formation of large pits during the etching process. The topographic variations in the 100–14, 100–20, and 100–28 samples were much less than for amine-rich samples. In general, the topographic features were observed to change from small nodular or gel-like features to progressively larger nodular features as amine content increased from 14 to 70 pph. As shown in Figure 9, small nodular features ranging from 40–150 nm in diameter predominate the microstructure of the etched 100–20 sample (also see Table II). Similar nodular features are observable throughout the microstructure of the 100–28 sample, as shown in Figure 10. However, the size of the features are significantly larger, ranging from 80–200 nm in diameter. The microstructure of the 100–70 sample, shown in Figure 11, is significantly different than that of the 100–20 and 100–28 samples. The structures tend to be more coarse and contain a much wider range of sizes. Some smaller features of similar sizes to the features in Figures 10 and 11 can be observed. However, features that are 500 nm or larger in diameter are also observed, some of which appear to be composed of smaller microgels, while others have a less discernible structure.

The roughness of the etched samples was evaluated using the AFM analysis software. The root-mean-square roughness value, defined as the standard deviation of height values about an average height, was calculated for topographic images from three different regions of each sample, as listed in Table II. This roughness value was smallest for images of the etched stoichiometric sample, ranging from 42–44 nm, and was only slightly higher for epoxy-rich samples, ranging from 45–49 nm. For the 100–50 and 100–70 samples, roughness values were significantly higher, ranging from 65–75 nm. These roughness differences seem to correlate with observations of the connectivity of the remaining microgel phase. For the 100–20 and 100–28 samples (see Figs. 9 and 10, respectively), the microgel structure is significantly more connective than that of the 100–70 sample (see Fig. 11), and slightly more pitting is observed for the 100–20 sample compared to the 100–28 sample. Thus, comparing the observa-

Figure 9   Topographic AFM image of an etched 100-20 sample. Height range from black to white is 500 nm.

tions of topographic features in etched samples with the observations from the phase images, the sizes, size distributions, and connectivity of struc- tural features are fairly consistent. These corre- lations are summarized in Table II. In this table, the average microgel size has been estimated

Figure 10   Topographic AFM image of an etched 100-28 sample. Height range from black to white is 500 nm.

Figure 11   Topographic AFM image of an etched 100-70 sample. Height range from black to white is 500 nm.

from measurements of at least 20 microgel diameters per sample, and the size distribution is characterized by ± 1 standard deviation about this average value.

Effect of Stoichiometry and Microstructure on Density

The results of the density measurements are shown in Figure 12 as a plot of density vs. amine content. Both data points for each stoichiometry are shown in Figure 12, although for all stoichio-

metries except 14 pph amine, the samples equilibrated at the same height within experimental error. A clear trend of decreasing density with increasing amine content is observed. If the polymer density correlated to the crosslink density, the 100–28 samples would have the highest density, which is clearly not the case. However, a higher degree of crosslinking is often linked to an increase in free volume. For a macroscopic measurement such as density, differences in free volume are likely more important than differences in

Table II   Comparison of Microstructure Results between the Phase Imaging Studies and the Topography Studies

Sample	Average Microgel Size (nm)		Connectivity	
	Phase	Topography	% Microgel	Roughness
100-14	30 ± 20	70 ± 40	69 ± 5	48 ± 1nm
100-20	50 ± 30	100 ± 60	80 ± 3	47 ± 2nm
100-28	60 ± 40	130 ± 50	91 ± 2	43 ± 1nm
100-50	80 ± 70	250 ± 160	56 ± 5	69 ± 4nm
100-70	100 ± 90	300 ± 220	49 ± 9	71 ± 4nm

Connectivity is quantified by the percentage of microgel phase for the phase images (see Fig. 8) and by roughness for the topographic images. Average values are given along with $\pm$ one standard deviation.

Figure 12   Density as a function of epoxy–amine stoichiometry.

crosslink density. Thus, the variation in density might be indicative of an increase in free volume with increasing amine content.

Observations from the microstructure studies indicate that the stoichiometric sample has the highest percentage of the hard, high density phase, and the soft phase is dispersed within the microgels. In comparison, the hard-phase regions in the amine-rich samples have a much broader size distribution (see Table II), and these regions are generally surrounded by a much larger pool of the soft phase. From these microstructural observations, the density of the amine-rich samples should be less than that of epoxy-rich and stoichiometric samples, as is observed. Further, as amine content increase above 28 pph, the packing of the microgel phase becomes looser as the percentage of the softer phase increases, resulting in the observed decrease in density. As amine content decreases below 28 pph, the size of the microgel regions decreases, but the T_g also decreases. This decrease in T_g is indicative of a decrease in room-temperature free volume, resulting in the measured increase in density for increasingly epoxy-rich samples. In any case, the measured density variations do not correspond to expected variations in crosslink density but appear to depend on larger scale variations in microstructure and free volume.

Effect of Stoichiometry and Microstructure on Thermomechanical Properties

Standard Cure vs. Postcure

As discussed previously, initial studies were conducted to evaluate the effect of postcuring on off-stoichiometry samples. After the standard cure, all the samples were mainly transparent with a slight translucency characterized by a white color. However, noticeable color changes were observed in all the nonstoichiometric samples after postcuring. Amine-rich samples had turned a yellowish-brown color and had lost some of their translucency. This change in appearance was worse for specimens that were farther away from the stoichiometric point. Also, upon sectioning the samples, the color change was observed to be worse near the edges of the sample than in the center of the sample. These observations indicate that ambient oxygen is diffusing into the samples at 160°C (the postcure temperature) and oxidizing the unreacted amine groups. The greater the excess amine, the worse the color change. Also, the concentration of oxygen that diffuses into the sample will decrease with penetration depth, resulting in less color change in the center compared to the surface.

Only slight discolorations were observed in the epoxy-rich and on-stoichiometry samples after postcuring, most likely because the number of unreacted amine groups was much less than for the amine-rich samples. However, the 100–14 samples did exhibit more of a color change than the 100–20 or 100–28 samples. This observation could be due to etherification reactions, which would be more prevalent as the relative amount of epoxy increases. Also, oxidation or other degradative reactions could also be responsible for the color changes of epoxy-rich specimens.

Dynamic mechanical analysis (DMA) was used to study changes in thermomechanical response caused by postcuring. Changes in the room-temperature storage modulus, E', and glass transition temperature, T_g, taken as the peak in the loss modulus, E'', are reported in Table III. The T_g of the 100–28 (stoichiometric) sample increased by 60°C, up to the postcuring temperature, as expected. For the nonstoichiometric samples, postcuring increased T_g values by only 2–7°C. This result indicates that for many of the nonstoichiometric samples, most of the possible epoxy–amine crosslinking reactions occurred during the standard cure. For amine-rich samples, this result is expected because conversion of epoxy groups during the standard cure reaches 100% for amine concentrations greater than or equal to 35 pph.[7] Thus, because the epoxy–amine reactions had been completed during the standard cure, the unreacted amine groups were free to oxidize during the postcure. This oxidation process might not be realistic of nonstoichiometric interphase regions near surfaces embedded within a stoichiometric epoxy–amine mixture.

Table III Glass Transition Temperature and Flexural Storage Modulus Measured Using DMA after Processing with a Standard Cure at 80°C and after a Subsequent Postcure at 160°C

	After Standard Cure		After Postcure	
Sample	T_g (°C)	E′(30°C) (GPa)	T_g (°C)	E′(30°C) (GPa)
100-14	58	1.2	65	1.2
100-20	81	2.2	88	2.3
100-28	107	1.7	161	1.7
100-40	116	1.5	120	1.6
100-50	101	1.7	106	1.7
100-60	88	2.4	91	2.4
100-70	76	2.5	78	2.5

Values are representative of a single sample for each stoichiometry.

Besides the stoichiometric sample, the largest increase in T_g values occurred for the epoxy-rich samples, indicating that some etherification reactions took place during postcure. Thus, the observed color changes in these samples, discussed previously, are most likely related to etherification. Degradative reactions could also be involved because the postcure temperature is much greater than the T_g values of these specimens. However, the slow etherification process can eventually lead to T_g values of epoxy-rich samples that are higher than that of stoichiometric samples.[10,21] Because degradation reactions generally take place at temperatures higher than $T_{g\infty}$, they might not be active in epoxy-rich samples during postcuring.

Postcuring had no effect on the flexural storage modulus values, E′, at 30°C as listed in Table III. This observation is consistent with results of other studies for which no significant changes in modulus were observed after postcuring.[16,24] Because only small changes in T_g occurred for nonstoichiometric samples, no significant changes in crosslink density or microstructure due to postcuring would be expected. For the stoichiometric sample, the microstructure is already dominated by the microgel phase. The presence of a small amount of softer, unreacted or partially reacted material dispersed between the microgels apparently is sufficient to suppress the T_g. Postcuring causes virtually complete conversion of any unreacted species, such that the remaining soft phase disappears and the T_g increases considerably. However, the change in microstructure would be slight, and apparently has a negligible effect on the modulus at temperatures below T_g.

Effects of Stoichiometry and Microstructure on Resin Properties

The effects of epoxy–amine stoichiometry on T_g, E′, fracture toughness G_{Ic}, and tensile properties, such as tensile strength, yield stress, and failure strain, of the EPON 828-PACM 20 system have been previously investigated.[4,6,7,20] In Figure 13, T_g values measured using DMA are plotted as a function of amine content. The results for the postcured samples of the present work agree with results of two previous studies. As discussed previously, T_g is highest for the stoichiometric composition. Generally, T_g increases with increasing degree of conversion and, thus, with increasing crosslink density.[12] Because samples processed at the stoichiometric composition possess the highest crosslink density,[25] they also have the highest T_g. However, for the standard cure samples, the 100–40 samples that are slightly amine-rich actually have a higher T_g than the 100–28 samples (see Table III). Assuming the high density microgel structures are formed at gelation, further curing would act to increase the crosslink density and decrease the amount of the low-density phase. Because a higher degree of conversion is reached during the standard cure for the 100–40 samples compared to the 100–28 samples, a similar ratio of hard phase to the soft phase is probably achieved. Upon postcuring, the soft phase disappears in the 100–28 sample, leading to a substantial increase in T_g, while the microstructure, and hence, T_g for the 100–40 sample remains virtually unchanged.

Figure 13 Glass transition temperature as a function of amine content for EPON 828-PACM 20. Data from Palmese and Skourlis can be found in refs. 4 and 7, respectively.

Figure 14 Flexural storage modulus at 100°C, measured using DMA, as a function of amine content for EPON 828-PACM 20. Data points are representative of data from the present study and from refs. 4 and 7.

Figure 16 Flexural storage modulus at 30°C, measured using DMA, as a function of amine content for EPON 828-PACM 20. Data from Palmese and Skourlis can be found in refs. 4 and 7, respectively.

Other elevated-temperature properties, such as modulus and fracture toughness, also tend to be maximum for stoichiometric compositions, as shown in Figures 14 and 15, respectively. Besides modulus and fracture toughness, elevated-temperature tensile strength and tensile yield stress also exhibit maximums for stoichiometric compositions for both EPON 828-PACM 20[7] and EPON 828-mPDA.[25] Considering these epoxies to be composite materials, their properties might follow a weakest-link argument. Based on the microstructure results, the microgel phase of the stoichiometric sample should have the highest connectivity compared to that of off-stoichiometry samples. At elevated temperatures, the low density phase is apparently the weak link of the material, and the higher percentage of the microgel phase for stoichiometric samples translates into higher strength, rigidity, and toughness compared to off-stoichiometry samples.

Room-temperature properties, however, do not generally reach a maximum for the stoichiometric

Figure 15 Fracture toughness at 25 and 110°C as a function of amine content (data from ref. 20).

composition. For example, flexural modulus values at 30°C, measured using DMA, reach a minimum at or near the stoichiometric composition, as shown in Figure 16. Similar observations have been made for a variety of other epoxy-amine systems.[16,25,26] One possible explanation could be related to the effective aspect ratio, α, defined as the ratio of length to effective diameter of the polymer chains.[27] Reactions involving secondary amines proceed at a lower rate than those involving primary amines because of steric limitations.[7,13] Because of this effect, the tendency towards the formation of linear structures increases as the composition moves away from the stoichiometric point.[11] Thus, the microgel structures in the off-stoichiometry samples are likely to have a less dense network structure with more linear chains, while the microgel structures in the stoichiometric samples contain a much tighter network. However, higher amounts of branching and crosslinking decrease the effective aspect ratio, α, of the structure, thus decreasing the efficiency of load transfer. Therefore, as the amount of amine increases up to around 20 pph, the volume fraction of microgel regions, v, and α both increase, resulting in an increase in modulus (see Fig. 16). Further increasing the amine content up to the stoichiometric point results in an increase in v, but produces a higher crosslink density structure with a lower aspect ratio. Thus, the modulus actually decreases due to the decrease in load-bearing efficiency. Increasing the amine content above 28 pph leads to a decrease in v and an increase in α. Thus, modulus increases again. Above a certain amine–epoxy ratio, however, both v and α will decrease, causing the modulus to decrease dramatically.

The increase in room-temperature fracture toughness with increasing amine content (see Fig. 15) is also not easily explained. Although the hard microgel regions could act as internal flaws,[15] the soft phase could absorb more energy during crack growth than the hard phase. The fracture process of glassy polymers generally involves a combination of craze and crack propagation. Crazes are more likely to form in the low-density regions, because the fibrillation process, i.e., the drawing of material across the craze, will be inhibited by aggregates of microgels.[19] The formation and propagation of thick, well-developed crazes is more likely to occur as the amount and degree of connectivity of the soft phase increases. Crack propagation will then occur through the pre-formed craze. In contrast, crack propagation will be enhanced for a material with a high degree of microgel formation. Because energy is consumed by the crazing process, the fracture toughness is likely to be higher for off-stoichiometry samples that contain a larger percentage of the low density phase.

CONCLUSIONS

The EPON 828-PACM 20 epoxy–amine system exhibits a two-phase structure consisting of a hard microgel phase and a dispersed phase of soft, unreacted and/or partially reacted material. This two-phase structure is inherently fractal, exhibiting a single glass transition temperature, T_g. For stoichiometric compositions cured for 2 h at 80°C, the microgel phase comprises a large percentage of the volume and the connectivity of the dispersed phase is extremely low. However, even a low percentage of the soft phase is apparently enough to suppress the T_g of the epoxy. After postcuring, the extent of reaction of the stoichiometric sample approaches 100% and the soft phase disappears, allowing the T_g to increase significantly. T_g and elevated-temperature properties reach maximum values for the stoichiometric composition, and thus are directly correlated with crosslink density and the percentage of microgel phase observed in microstructure studies. Postcuring is not expected to change the microstructure significantly and, thus, does not affect room-temperature properties such as modulus.

For epoxy-rich samples, the size of individual microgel regions is smaller on average than microgel sizes in stoichiometric samples. This decrease in microgel size might result in an increase in packing efficiency that could be partially re-sponsible for the observed increase in density. The amount and the connectivity of the softer phase also increases for increasingly epoxy-rich samples, causing a substantial decrease in T_g. This decrease in T_g, in turn, causes a decrease in room-temperature free volume that could also be related to the observed increase in density with decreasing amine content below the stoichiometric point. Postcuring epoxy-rich samples results in a small increase in T_g, most likely due to etherification reactions.

The size distribution of the microgel regions tends to increase with increasing amine content above 28 pph. Concurrently, the connectivity of the softer phase increases dramatically. These two effects result in a more open microgel structure, and thus a further decrease in density with increasing amine content. Also, the fracture toughness at room temperature increases with increasing amine content, most likely due to the increased presence of the soft phase, which absorbs more energy during crack growth. Postcuring amine-rich samples results in observable color changes caused by oxidation of unreacted amine. Very little change in T_g is observed after postcuring, because the extent of reaction of epoxy groups reaches 100% during the standard cure.

Changes in modulus values at 30°C with postcuring were not observed, and for a wide range of composition, these modulus values are similar. These results were explained by considering the variation of the effective aspect ratio of the microgel structures with stoichiometry. Off-stoichiometry samples tend to have microgels with less dense network structures, which corresponds to a higher aspect ratio. A higher aspect ratio corresponds to a higher load-bearing efficiency and, thus, to a higher values of modulus. At very high and very low amine contents, aspect ratio will begin to decrease with decreasing microgel volume fraction, causing the modulus of the epoxy to decrease.

Although the size of interphase regions in composite materials is predicted to be significantly smaller than the observed sizes of microgels, a significant percentage of the soft phase could form near the fiber surface due to preferential amine segregation, causing lower values of T_g and reducing elevated-temperature properties. This hypothesis could explain the large decreases of interfacial shear strength and intralaminar fracture toughness with temperature at temperatures much less than T_g, as reported elsewhere.[7–9,20] It is also consistent with the observations by Kardos[28] of a distinct change in microstructure of an epoxy system

within 100 nm of a glass fiber. Thus, the preferential adsorption of reacting species to solid surfaces appears to be a controlling mechanism of interphase formation, and the resulting interphase properties are a function of the resulting microstructure, which contains unreacted and/or partially reacted material.

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