

Epoxy-Amine Networks with Varying Epoxy Polydispersity

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ABSTRACT: Solid, high molecular weight DGEBA-based epoxies were blended with high purity liquid DGEBA to create several resins with equivalent epoxy equivalent weights, but with polydispersity indices (PDIs) ranging from 3 to over 10. The resins were cured with a stoichiometric amount of polyetheramine and compared to a nonblended epoxy with PDI of 1.8. Modulus, glass transition temperatures, and molecular weight between cross-links were measured using dynamic mechanical analysis. Coefficients of thermal expansion (CTE) were measured and used to extend room temperature density measurements as a function of temperature. Fracture properties were also measured. Overall, the increased polydispersity has almost negligible effect, with the main difference occurring in the slope of the glassy CTE, with more polydisperse epoxies having a slower increase in CTE. In comparison to previous work where bimodal amines were blended with DGEBA, we conclude that epoxy resins are far more sensitive to distributions in the flexible portion, rather than the more rigid one. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41503.

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INTRODUCTION

Worldwide, approximately 75% of epoxy resins are derived from diglycidyl ether of bisphenol A (DGEBA) whose structure is shown in Figure 1(A). The value of n , the number of additional repeat units per molecule, can range from <0.1 for liquid epoxies to over 35 for Type 10 solid epoxy resins.¹ Epoxies can be characterized by the n value, but they are more often characterized by their epoxy equivalent weight (EEW) which is the molecular weight of the molecule normalized by the number of epoxy groups per molecule. While many epoxies are used in protective coating applications, highly cross-linked epoxies also find use in structural composites. Solid epoxies are widely used in coatings while the lower molecular weight liquid epoxies tend to be used where their low viscosity eases processing, such as flooring and composite applications. Solid epoxies have longer backbones giving more distance between cross-links, resulting in improved toughness.² The additional repeat units also incorporate additional hydroxyl functionality that can be reacted with isocyanates or other cross-linkers. High molecular weight epoxies are made by two processes: the taffy process and the fusion process. The taffy process is called such due to the taffy-like appearance of high molecular weight epoxy during the process. The process uses epichlorohydrin, bisphenol A, and a stoichiometric amount of sodium hydroxide; it generates an

epoxy distribution with both odd and even numbers of repeat units. The fusion process generates epoxy with mostly even numbers of repeat units by combining low molecular weight DGEBA with bisphenol A. The fusion process is more widely used in commercial manufacturing.¹

Attempts to achieve increased toughness through the incorporation of higher molecular weight epoxies into blends with lower molecular weight epoxies have resulted with mixed results. A bimodal blend of low and high molecular weight DGEBA-based vinyl esters resulted in increased the toughness compared to the toughness of a single molecular weight distribution.³ Bimodal blends of epoxies cured with a single amine led to increased toughness, but the different molecular weights resulted in phase separation.⁴ Mirsa et al.⁵ created a range of theoretical molecular weights between cross-links (M_c) values using Epon resins 825 (EEW = 176 g/mol), 828 (190 g/mol), 834 (296 g/mol) and 1001F (500 g/mol) along with blends of 825 and 1004F (998 g/mol). Three of these blends matched the EEWs of Epon 828, Epon 834, and Epon 1001F. All formulations were cured with MDA (4,4'-methylenedianiline). The bimodal blends matching Epon 828 and Epon 1001F had similar glass transition temperatures (T_g s) and rubbery moduli compared to the single molecular weight epoxy. The blend of 825 and 1004F matching 834 had a T_g 15°C lower but similar glassy and rubbery moduli.

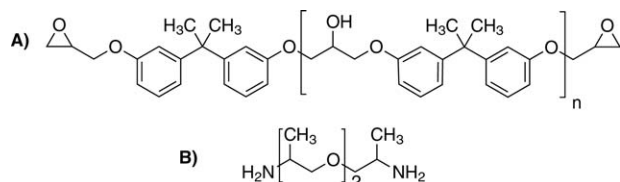


Figure 1. Structure of (A) DGEBA and (B) D230, $n \sim 2.5$.

The difference was suggested to be due to the longer chain epoxies reacting first, resulting in a microgel with the shorter epoxies reacting later forming an interpenetrating network. Room temperature tensile experiments also showed no dependence on the M_c or M_w distribution. This was attributed to restricted motion of the main chains at room temperature, which continued above T_g , as shown by creep experiments.

Vakil and Martin investigated yield and fracture behavior of various epoxies, including two bimodal blends, cured with *m*-phenylenediamine.⁶ Their blends were mixtures of Epon 825 (EEW = 175 g/mol) with Epon 1004F (833 g/mol) matching the EEW of 1001F (545 g/mol) and Epon 825 with Epon 1001F to match Epon 836 (EEW = 315 g/mol). They concluded that fracture properties are not sensitive to epoxy molecular weight distributions, although the two blends appear to be only briefly examined.

Haris et al. blended Epikote 828 (EEW = 190 g/mol) with Epikote 1001 (EEW = 475 g/mol) in various proportions from pure 828 to pure 1001.^{7,8} The blends were cured with an anhydride curing agent. The temperature of maximum $\tan \delta$ was decreased from either epoxy for all blends, while the fracture toughness steadily increased with increasing amount of 1001, the higher molecular weight epoxy.

Our previous work showed that distributions of polyetheramines reacted with high purity DGEBA can greatly increase the breadth of the glass transition.⁹ A distribution in the epoxy with a constant amine molecular weight could yield similar results. The previous studies with blends of various molecular weight epoxies only used aromatic or anhydride curing agents,^{5–8} so there was little flexibility in the resulting networks; any influence the epoxy distribution had could have easily been masked. In addition, few of the prior studies had a comparable single distribution epoxy for reference. In this work high purity DGEBA was blended, individually, with several higher molecular weight epoxies to match the EEW of a semi-solid DGEBA epoxy ($n \sim 0.5$) and any effects on thermal and mechanical properties were investigated.

EXPERIMENTAL

Blend Formation

Seven Epon epoxies with molecular weights ranging from 352 g/mol to over 5000 g/mol were obtained from Momentive and their characteristics are listed in Table I. All of the 1000 series resins are solid at room temperature. Epon 825 is a liquid while 834 has a higher viscosity and is semi-solid. The epoxies' EEWs were taken from the manufacturer's certificates of analysis

Table I. Epoxy Equivalent Weights and Values of n

Resin	Epoxy equivalent weight (EEW) (g/mol)	Average n
Epon 825	176	0.04
Epon 834	246	0.54
Epon 1001F	528	2.52
Epon 1002F	663	3.47
Epon 1004F	853	4.81
Epon 1007F	1810	11.55
Epon 1009F	2774	18.34

and confirmed following ASTM D 1652-90 Test Method B.¹⁰ Epon 834 with an EEW of 246 g/mol was chosen as the basis of comparison. The blend ratios are given in Table II. To create the blends, appropriate amounts of 825 and a solid epoxy were heated in a glass jar and periodically stirred until the solid epoxy melted and a homogeneous mixture was obtained. Blends containing 1001F, 1002F, and 1004F were heated to 125°C while the blends containing 1007F and 1009F were heated to 150°C. The epoxy blends were degassed while warm to remove any volatiles or entrapped air. The resulting blends were clear, tacky semi-solids at room temperature. The EEWs of the blends were also tested and were confirmed to match the EEW (± 1) of Epon 834.

Polydispersity

Twice the EEW is equivalent to the number-average molecular weight assuming ideal structures; however it does not give any information on the weight-average molecular weight or polydispersity. Gel permeation chromatography (GPC) was performed to quantify the polydispersity of the as-received epoxies as well as the blends. A Waters 515 GPC was used with two 30 cm long, 7.5 mm diameter, 5 μ m styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45°C using tetrahydrofuran (THF, Sigma-Aldrich, 99.9%) as the elution solvent at a flow rate of 1 mL/min. The column effluent was monitored by two detectors operating at 25°C: a Waters 2410 refractive index (RI) detector and a Waters 2487 dual absorbance detector operating at 270 and 254 nm. Samples had concentrations of 1–2 mg epoxy per mL THF. Data from the RI detector was used for polydispersity analysis. The molecular weight calibration curve was based upon polystyrene standards for the higher molecular weights, and the discrete peaks for DGEBA with $n = 0, 1, \text{ and } 2$ for the low molecular weights.

Table II. Ratio of Components in Blends Matching 834's EEW

Resin	Weight % 825	Mol % 825
825-1001F	57.3	80.1
825-1002F	61.3	85.6
825-1004F	64.1	89.7
825-1007F	68.5	95.7
825-1009F	69.6	97.3

Resin Cure

The epoxy was heated to 80–85°C and a stoichiometric amount of Jeffamine D230 (Huntsman), a linear polyether diamine whose structure is shown in Figure 1(B), was added, with two epoxy groups per amine. The resin was thoroughly mixed by hand and then mixed and defoamed using an ARE-250 centrifugal mixer (Thinky Corp.) before being poured into silicone rubber molds (preheated to 80°C) and cured for 2 h at 80°C. The samples were removed from the mold and post cured for 2 h at 125°C. All cured samples were transparent indicating that macrophase separation did not occur.

Polymer Characterization

Near-infrared (NIR) spectroscopy was used to investigate the extent of cure. In the NIR region, epoxide groups show peaks at 4530 and 6060 cm^{-1} ; primary amines have a peak at 4925 cm^{-1} while a peak at 6534 cm^{-1} is caused by primary and secondary amines.¹¹ Spectra of the neat monomers and the cured samples were taken using a Nicolet Nexus 870 infrared spectrometer. The spectra of the cured samples were qualitatively examined for residual epoxy or amine functionality.

Samples with approximate dimensions of 35 × 12 × 3.25 mm were tested on a TA Instruments Q800 Dynamic Mechanical Analyzer using the single cantilever clamp, operating at 1 Hz with 7.5 μm displacement. Samples were allowed to equilibrate at 0°C for 10 min before increasing the temperature by 2°C/min to 200°C.

The temperature at which the peak in the loss modulus occurred was considered the T_g of the resin.¹² All samples had a definite point in the storage modulus where the rubbery modulus began to increase with increasing temperature; this point was used to calculate the molecular weight between cross-links, M_c . The theory of rubber elasticity was used to calculate the M_c , eq. (1), from dynamic mechanical analysis (DMA) data:

$$M_c = \frac{3RT\rho}{E'} \quad (1)$$

where R is the universal gas constant, T the absolute temperature, ρ the density, and E' the modulus of the rubbery plateau. Rubber elasticity applies to polymers with low cross-link densities and may not give completely accurate cross-link density measurements for highly cross-linked epoxies.¹³ Nonetheless, numerous researchers have used it as a measure of cross-link density, and it seems to show good trends for sample sets with similar chemistries.^{14,15}

The densities of all samples were measured using the water displacement method outlined in ASTM Standard D792–00.¹⁶ Density measurements were made using the broken pieces from the fracture tests, described in the following paragraph. The coefficients of thermal expansion, CTE or α , in both the rubbery and glassy regions were measured using a TA Instruments Q400 Thermomechanical analyzer. Samples for thermomechanical analysis (TMA) were made by cutting the fracture compliance samples into pieces approximately 5 × 5 × 12.7 mm. A constant force of 0.05 N was used for both the preload and the applied load. Samples were heated from room temperature to 125°C, cooled to –70°C, then heated to 150°C at 3°C/min. The

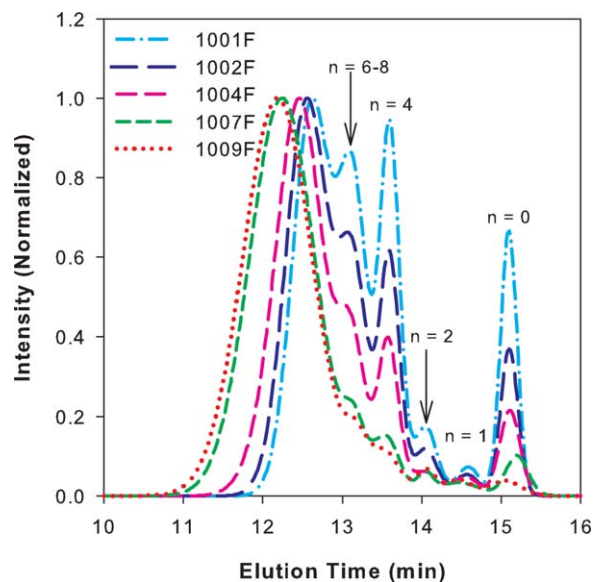


Figure 2. GPC spectra of epoxies, normalized to their most intense peak. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

initial heating cycle was to remove any residual stress. The CTE values from the final cycle, –70 to 150°C, were used to calculate the density as a function of temperature assuming isotropic behavior. Four samples per resin were tested for density measurements and two to three samples per resin for CTE measurements.

Fracture toughness, K_{Ic} , was measured using the compact tension geometry according to ASTM D5045.¹⁷ Samples were cured in silicone rubber molds with nominal dimensions of 30.5 × 32 × 12.7 mm. A 10 mm long notch was cut into each sample with a diamond saw. The samples and single edged razors were placed in a freezer overnight (approximately –20°C) to ensure all samples were well within their glassy region when starter cracks were made. Samples and razor blades were removed from the freezer; the razor was inserted into the notch and tapped with a hammer, until a crack propagated ~9 mm into the sample, leaving a ligament of ~13 mm for the crack to propagate through during testing. These cracks were of the “instantly propagated” type, shown by Ma et al. to give minimum K_{Ic} values.¹⁸ Seven samples per resin were tested at room temperature. After fracture, the unmodified fracture surfaces were imaged using an Olympus MX50 optical microscope.

RESULTS AND DISCUSSION

GPC Results

The Epon 1000 series of epoxies used in this work are reported to be fusion grade epoxies, meaning predominately even numbers of repeat units were expected. However, depending on the batch used, the molecular weight (MW) distribution of the epoxy can vary. Previous work showed that a batch of Epon 1004F manufactured prior to 2004 had components up to $n = 6–8$ and a PDI of 1.3.³ A more recent batch, manufactured in 2008 and used in this work, contained monomers with $n = 0$, small quantities of $n = 1$ and $n = 2$, then the maximum

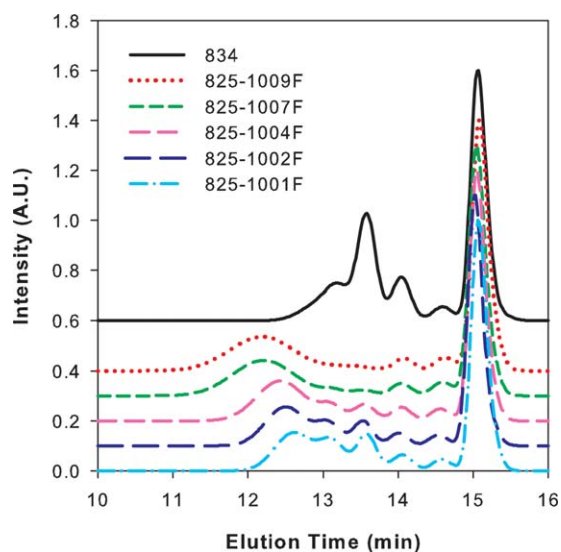


Figure 3. GPC spectra of blends and 834, normalized to their most intense peak ($n = 0$). All resins have equivalent EEWs and are shifted vertically for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matching $n = 14$, as shown in Figure 2, with a PDI of 2.82. Although the PDIs were very different for these batches, the EEWs were similar, 900 and 853, respectively. Misra et al. identified the components of their blends,⁵ which included Epon 1004F with a major component of $n = 12$, but did not quantify the PDI. Vakil and Martin did not consider molecular weight distributions of their epoxies.⁶

Figure 2 shows the processed GPC spectra of the higher molecular weight epoxies. In all cases, the most intense peak comes from high molecular weight epoxies ($n \geq 12$). Though in the 1001F, 1002F, and 1004F there are significant peaks representing DGEBA with $n = 0, 1$, or 2. Figure 3 shows the GPC spectra of the blends, along with that of 834. For all the blends, the peak

Table III. M_n from Epoxy Titrations and GPC Data Along with PDI of Epoxy Resins and Blends

Individual epoxies	M_n (g/mol) (2x EEW)	M_n (g/mol) (GPC)	PDI (GPC)
825	352	365	1.06
834	492	557	1.81
1001F	1056	1331	2.22
1002F	1326	1648	2.34
1004F	1706	2069	2.82
1007F	3620	3284	3.82
1009F	5548	4256	3.62
Blends			
825-1001F	493	546	2.98
825-1002F	490	566	3.68
825-1004F	492	550	4.83
825-1007F	493	542	9.50
825-1009F	490	522	10.71

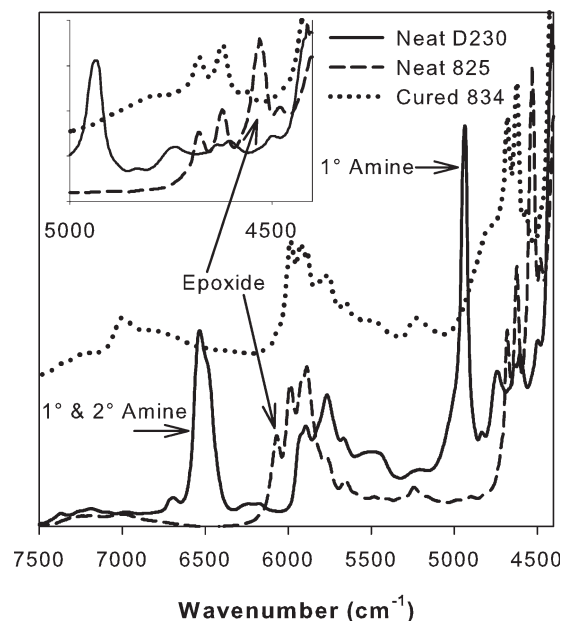


Figure 4. FTIR spectra of neat components and cured 834-D230. Inset shows the epoxide peak at 4530 cm^{-1} .

for pure DGEBA ($n = 0$) is the strongest, though in 834's case, the $n = 4$ peak is also very strong. With the shift of the other peaks to shorter elution times (higher molecular weights), the PDI of the blends increased. Even though the blends are only composed of two epoxies, the broad distributions disqualify them from being termed "bimodal" as Vakil did, while instead "polydisperse" better represents these epoxy blends.

Number and weight average molecular weights (M_n and M_w , respectively) were calculated from the GPC results. Igor Pro (WaveMetrics) was used to remove noise and flatten the baseline. The weight fraction eluted at time i , w_i , was calculated by

$$w_i = \frac{I_i}{\sum_i I_i} \quad (2)$$

where I_i is the intensity of the spectrum at time i . Using w_i , the number and weight average molecular weights were calculated according to eqs. (3) and (4), and the polydispersity index (PDI) by M_w/M_n .

$$M_n = \sum \frac{M_i}{w_i} \quad (3)$$

$$M_w = \sum w_i M_i \quad (4)$$

The molecular weight eluted at a given time (M_i) was determined from the calibration curve. Table III shows the calculated molecular weights of the individual epoxies and blends along with their PDIs.

The M_n calculated from the GPC results did not match the epoxy titration results for several reasons. The calibration curve was a best fit line between the elution times of known molecular weights, resulting in some mismatch. Also, the calculation of w_i assumes a continuous molecular weight distribution. Ideally the distribution should be discrete weights separated by

Table IV. Resin Properties

Resin	30°C storage modulus (MPa)	T_g (°C)	T_g breadth (°C)	Tan δ max (°C)	Minimum storage modulus (MPa)	Temperature at min. modulus (°C)	Density at 23°C (g/cm ³)
834	2310 ± 80	97.0 ± 1.7	10.8 ± 1.2	102.3 ± 1.1	15.7 ± 0.4	124.4 ± 2.3	1.1613 ± 0.0005
825-1001	2290 ± 90	97.5 ± 1.7	10.5 ± 0.7	102.8 ± 1.0	15.3 ± 0.8	125.1 ± 0.7	1.1603 ± 0.0002
825-1002	2300 ± 50	98.5 ± 0.9	10.1 ± 0.3	103.5 ± 0.6	16.5 ± 0.5	124.9 ± 2.8	1.1597 ± 0.0004
825-1004	2230 ± 10	98.5 ± 0.7	10.0 ± 0.4	103.5 ± 0.7	16.5 ± 0.2	124.6 ± 2.3	1.1597 ± 0.0005
825-1007	2340 ± 50	96.8 ± 2.3	10.5 ± 0.8	102.1 ± 2.1	15.1 ± 0.6	138.8 ± 5.1	1.1599 ± 0.0006
825-1009	2370 ± 40	97.6 ± 1.3	10.3 ± 0.7	102.8 ± 1.0	15.4 ± 0.5	136.8 ± 7.3	1.1604 ± 0.0005

multiples of 284 g/mol, the value of the repeat unit in Figure 1(A). While the ideal structure may be present for the lower molecular weight epoxies, the ideal di-functional form is not always present in higher molecular weights as shown by Julka et al. who tentatively identified nine types of nonideal species, with one to three epoxy groups in solid epoxies.¹⁹ These combine to result in the mismatch between the titration and GPC results. These results could indicate that Epon epoxies are not fully epoxidized; however, past results have confirmed agreement between epoxy titration and nuclear magnetic resonance spectroscopy with slight differences from the SEC results.³ These results showed that the epoxies contain a very high fraction of diepoxidized monomers and no significant fraction of mono-functional epoxies and nonepoxidized bisphenol A.³

Extent of Cure

After cure, no trace of the amine peaks at 4925 cm⁻¹ and 6534 cm⁻¹ was observed, as shown in Figure 4. The epoxide peak at 4530 cm⁻¹ had also completely vanished. It was less clear if there was a residual epoxide peak at 6066 cm⁻¹ because that peak overlaps with the aromatic peak at 5960 cm⁻¹ and must be deconvoluted for analysis.¹¹ The 4530 cm⁻¹ peak provides a direct means of monitoring epoxy concentration²⁰ and the absence of it and the amine peaks confirmed complete reaction.

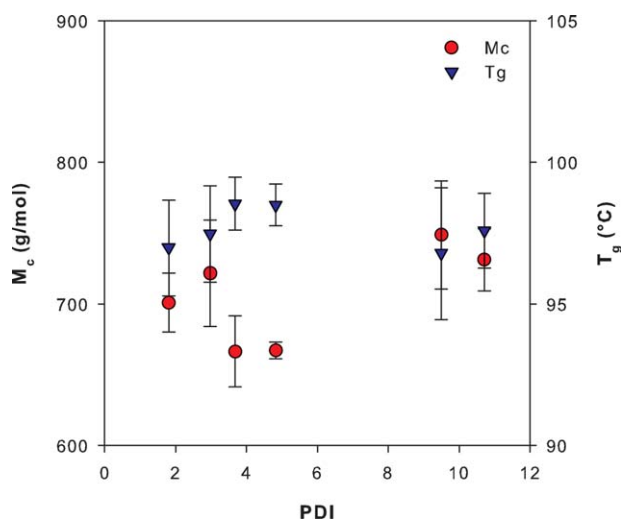


Figure 5. M_c and T_g versus epoxy polydispersity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMA Results

The DMA results showed very little difference among the blends (Table IV). The 30°C storage moduli were 2.2–2.3 GPa and the T_g s ranged from 97.0 to 98.5°C. Using the full width at half max (FWHM) of the tan δ curve as the breadth of the glass transition, there was still no change as the PDI of the epoxies increased. This is contrary to the behavior seen when the distribution of linear amines was increased; in those cases the breadth of transition greatly increased and the modulus at 30°C decreased.⁹ The temperature at which the minimum in the storage modulus occurred did increase for 825-1007F and 825-1009F but those samples also showed the greatest variation in those temperatures. The moduli values of those minima were similar to the other resins. Using those minimum rubbery modulus values and density at those temperatures (extrapolated from room temperature measurements using TMA data as discussed in the next section), M_c values for the resins were calculated. Figure 5 shows the M_c values and T_g s versus the PDI of

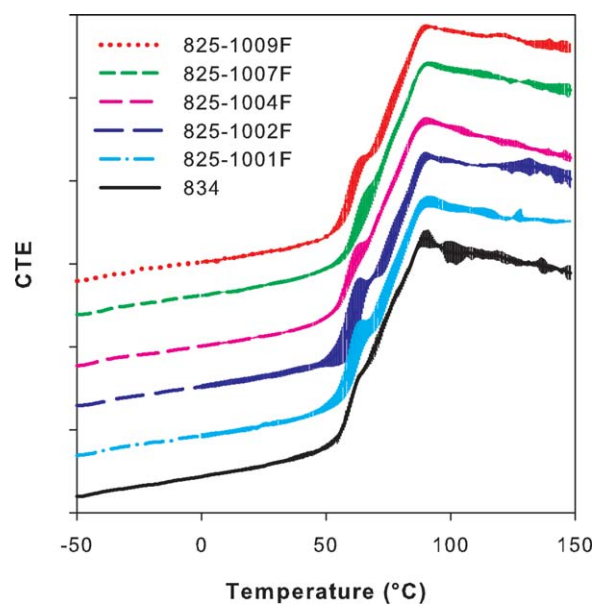


Figure 6. CTE curves, shifted vertically for clarity. Error bars are most noticeable in the transition region, but are present throughout, except below 0°C, where they were removed to enhance distinction between the curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

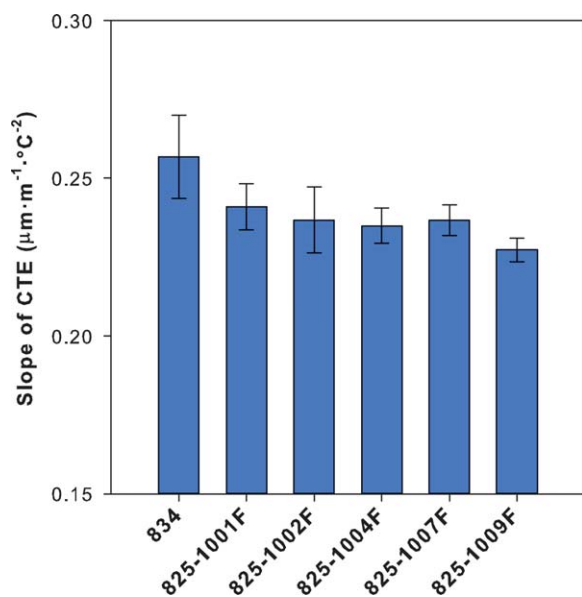


Figure 7. Slope of the glassy CTE (-50 – 40°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the epoxies. Within error, there is no trend between M_c or T_g with increasing polydispersity; however, M_c and T_g do show the typical inverse correlation.

Density and CTE

All samples had very similar room temperature densities, with the slight variations following no pattern. Also, all samples had similar CTE behavior, shown in Figure 6. While a constant or mean value for glassy CTE is often reported,^{21–24} CTEs for epoxies are temperature dependent.^{25,26} Here from -50°C to 40°C the CTEs changed from $\sim 60 \mu\text{m m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ to over $80 \mu\text{m m}^{-1} \text{ }^{\circ}\text{C}^{-1}$. For comparison over a similar temperature

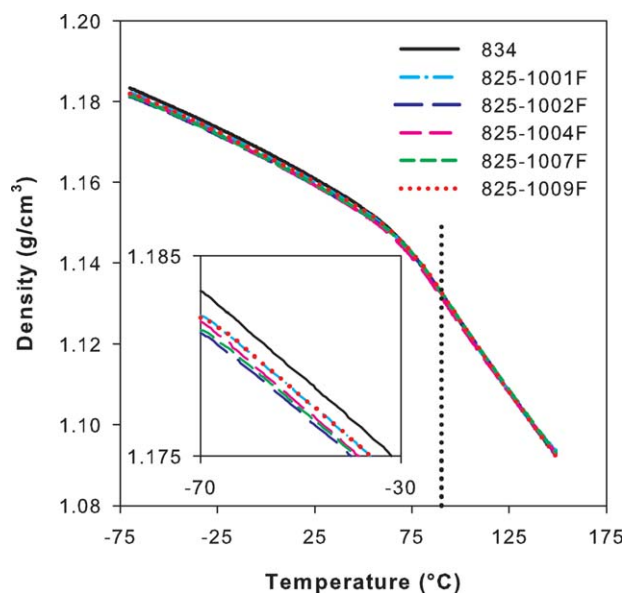


Figure 8. Density as a function of temperature; the dotted line indicates the maximum in CTE values. Inset shows that the room temperature differences extend through the glassy region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

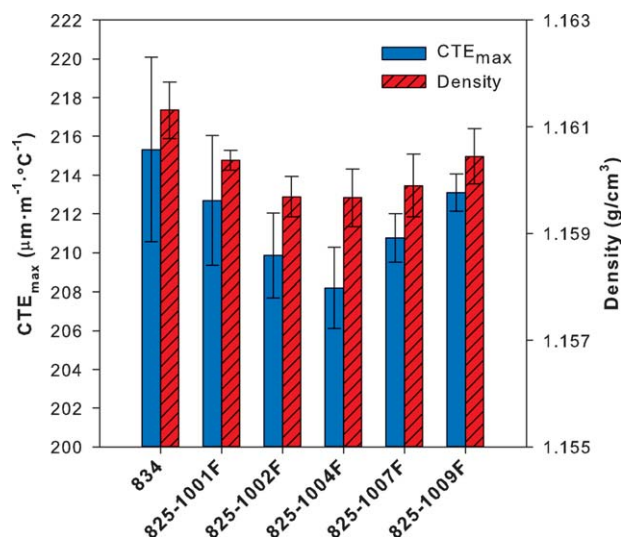


Figure 9. Maximum CTE and measured (at 23°C) densities of resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range, pure aluminum's CTE changes by only $1.6 \mu\text{m m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ (Ref. 27). The slopes of the CTEs in the glassy region were calculated by averaging the best-fit linear curves from -50°C to 40°C , with the results shown in Figure 7. All linear fits had R^2 values greater than 0.99 except for one sample of 825-1009F ($R^2 = 0.987$). A trend appears in these slopes, with the slope decreasing with increasing epoxy PDI. This declining rate of change in CTE could be a result of the increased softening point of the higher molecular weight epoxies. The increasing number of secondary hydroxyl groups with increasing molecular weight increase the softening points of the solid epoxies due to

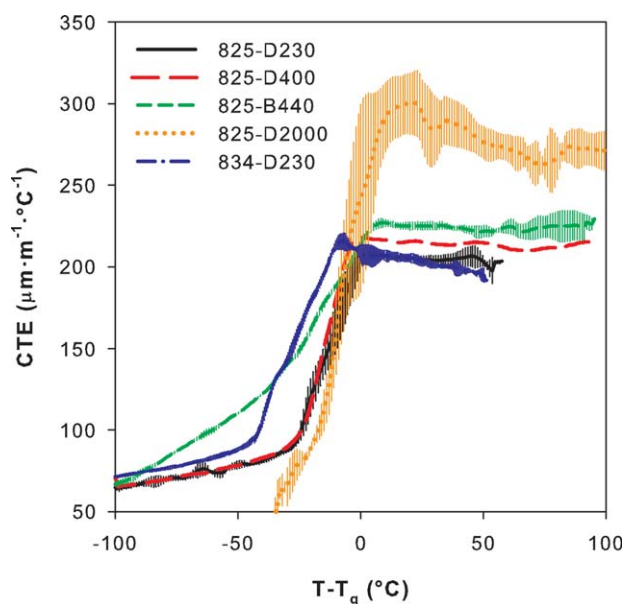


Figure 10. Averaged CTEs of 834 and related resins. Data are shifted to $T-T_g$ for ease of comparison. Error bars are the standard deviations from three runs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

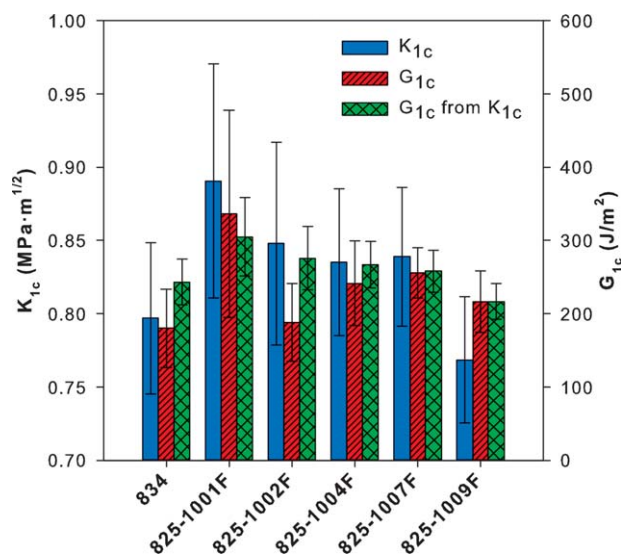


Figure 11. Fracture properties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen bonding; 1007 and 1009 have softening points of 125°C and 135°C, respectively.²⁸ While the blends should have similar amounts of hydroxyl groups and bonds, the distribution of hydroxyls was altered, possibly allowing for better hydrogen bond alignment, resulting in decreased rate of change in CTE.

Above the T_g , the CTEs drop slightly and could be indicative of rubber elasticity contraction of the samples¹³; however, this may be an artifact due to the compression of the then-rubbery samples. Elsewhere CTEs of epoxies above the T_g are shown to be slightly increasing when measured using a lower applied force.²⁹

By assuming isotropic expansion, the CTE measurements were used to transform the measured room temperature densities into a function of temperature. The resulting curves are shown in Figure 8. The glassy densities of the resins followed the same pattern as observed at room temperature while above the T_g s the densities collapse onto one curve.

The measured densities and maximum CTE values follow the same trend, with 834 having the highest values, 825-1002F and 825-1004F having the lowest values, and the value increase again for 825-1007F and 825-1009F, as shown in Figure 9. In the rubbery regime, the densities converge to the same value. This is contrary to our previous work where the densities diverged in the rubbery regime.⁹ The diverging densities were seen in formulations with varying amine molecular weights and amounts, whereas the converging densities seen here had formulations with the same amount of a single molecular weight amine. These suggest that the amine controls the ultimate expansion as the polyether chains are more flexible than the aromatic epoxy. This density convergence begins before the questionable rubbery CTE region and therefore is not suspect. In the glassy regime, the differences in density may be due to packing differences caused by structural differences in the higher molecular weight epoxies. As mentioned above, nonideal structures can be found in solid epoxies, it is possible that more nonideal structures were present in the 1002 and 1004 resins than the others, leading to poorer packing and lower glassy densities.

As the CTEs and densities of the resins are, in general, similar, it is insightful to compare those properties to other related systems. Figure 10 shows the CTEs of 834-D230 along with 825 cured with D230 and two other molecular weights of the polyetheramine, D400 and D2000. In addition, 825 cured with a blend of D230 and D2000 with an average molecular weight equivalent to D400 (here termed B440) is also shown. The experimental details of these other resins are described elsewhere.⁹

Compared with the 825 resins, 834 and the more polydisperse epoxies have slightly higher glassy CTEs. Above T_g , the CTEs are similar to the 825-D230, but lower than 825-D400, 825-B440, and 825-D2000, again suggesting that the more flexible amine controls the high temperature expansion. For the transition region from glassy to rubbery, the 834 shows a broader transition, 34°C, than the 825 with single amines, 25, 19, and

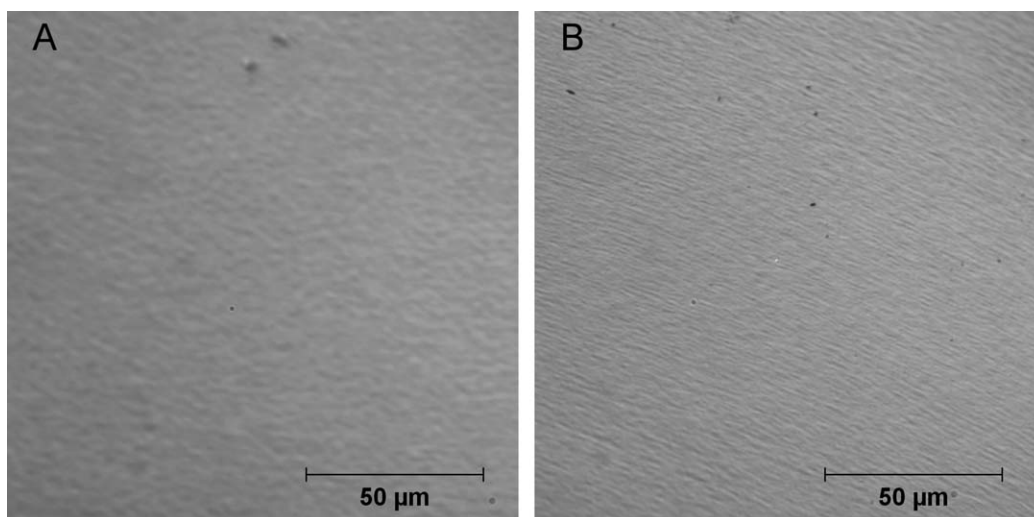


Figure 12. Fracture surface of (A) 834 and (B) 825-1009F. Crack propagation is right to left.

25°C for D230, D400, and D2000 respectively, but much less than the resin with blended amines, 825-B440, 43°C. Increasing the epoxy polydispersity from 1.81 to 10.71 does not change this transition region, whereas changing it from 1.06 to 1.81 and decreasing the EEW does (comparing Epon 825 to Epon 834). Despite this broader transition region as measured by TMA, the DMA breadth of T_g for the polydisperse epoxies are very similar compared with high purity DGEBA cured with D230.⁹

Fracture Toughness

As with the DMA results, the fracture toughness results also presented a null change, shown in Figure 11. Although 825-1001F, 825-1002F, 825-1004F, and 825-1007F appear to have slightly higher fracture properties than 834 and 825-1009F, the toughness values were similar within the error of the tests. G_{1c} was similar whether calculated from K_{1c} using the DMA modulus or from the area under the load displacement curve. Given these results, it is possible that resins with a high weight percentage of higher molecular weight component, as in the 825-1001F blend have high toughness and as the weight percent of higher molecular weight component decreased, the toughness decreased to a minimum of that of the 834 and the 825-1009F samples. However, given the error in the result, it is not possible to make this conclusion. Furthermore, in a similar experiment using bimodal amines, we measured significant increases in fracture toughness for blends relative to nonblended samples and changes in fracture behavior, showing that changing the amine polydispersity has a much more pronounced effect on fracture toughness than epoxy polydispersity. Here, all samples showed unstable stick-slip crack propagation, as has been seen elsewhere for unmodified epoxies.³⁰ In comparison, when the amine is blended, the fracture behavior changed compared to the single amine counterpart—from unstable for the single amine to slip-stick at room temperature and from brittle-stable to stable-unstable slip-stick at -20°C .⁹ The -20°C results may be more relevant when the amine is blended as -20°C is $\sim 75^\circ\text{C}$ below those resins' T_g , whereas room temperature is $\sim 75^\circ\text{C}$ below the polydisperse epoxies' T_g . It appears that changing the amine's dispersity slightly blunted the growing crack while changing the dispersity of the stiff epoxy has no effect on crack growth.

The fracture surfaces of all samples were very smooth. Figure 12 is an optical microscopy image of the bulk surface. The surfaces had no visible differences between the low PDI and high PDI samples. Crack propagation is right-to-left in all images. The lack of degassing did result in some entrapped air in the samples that were visible during microscopy analysis; however they were few (0–2 per samples) and unlikely to affect the toughness. Air bubbles were not observed in the smaller DMA samples.

CONCLUSIONS

Epoxy blends were formulated that had large DGEBA molecular weight distributions, with PDIs ranging from 3 to over 10 while maintaining equivalent EEWs. When cured with a polyetherdiamine, the resins had similar T_g s, moduli, M_c values, densities, and fracture properties. Slight differences were seen in the slope

of the glassy CTE with the slope decreasing with increasing epoxy polydispersity. Despite these differences, the rubbery densities collapsed onto a single curve. The polydisperse epoxies did show broadening in the CTE transition region although narrower relative to bimodal amine blends; however, any epoxy polydispersity caused this broadening to appear. All resins exhibited the same slip-stick fracture behavior. These results corroborate the molecular weight distribution independence concluded from previous work with polydisperse epoxies cured with aromatic amines. This is in contrast to the distribution dependency seen for polydisperse linear amines cured with a single molecular weight epoxy, where T_g , breadth of T_g , and fracture toughness increased as a result of blending. Thus, we conclude that epoxy resins are far more sensitive to distributions in the flexible portion, rather than the more rigid one. In future work, we hope to show that flexible epoxies based on polyethylene glycol allow for more significant differences in T_g /breadth and fracture toughness to definitively prove this theory that the flexible component of the epoxy-amine network governs fracture properties.

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REFERENCES

1. Pham, H. Q.; Marks, M. J. In *Encyclopedia of Polymer Science and Technology*; Kroschwitz, J. I., Ed.; Wiley: Hoboken, NJ, 2004.
2. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1989**, *24*, 2571.
3. La Scala, J. J.; Orlicki, J. A.; Winston, C.; Robinette, E. J.; Sands, J. M.; Palmese, G. R. *Polymer* **2005**, *46*, 2908.
4. Zubeldia, A.; Larranaga, M.; Remiro, P.; Mondragon, I. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3920.
5. Misra, S. C.; Manson, J. A.; Sperling, L. H. In *Epoxy Resin Chemistry*; Bauer, R. S., Ed.; American Chemical Society: Washington, D.C., 1979; p 137.
6. Vakil, U. M.; Martin, G. C. *J. Mater. Sci.* **1993**, *28*, 4442.
7. Haris, A.; Adachi, T.; Hayashi, Y.; Araki, W. *J. Mater. Sci.* **2007**, *42*, 9859.
8. Haris, A.; Adachi, T.; Araki, W. *J. Mater. Sci.* **2008**, *43*, 3289.
9. McAninch, I. M.; Palmese, G. R.; Lenhart, J. L.; La Scala, J. *J. Appl. Polym. Sci.* **2013**, *130*, 1621.
10. D1652-11: Standard Test Method for Epoxy Content of Epoxy Resins; ASTM International, West Conshohocken, PA, 2011.
11. St. John, N. A.; George, G. A. *Polymer* **1992**, *33*, 2679.
12. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, NY, 1994.

13. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, **1953**.
14. Crawford, E.; Lesser, A. J. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *26*, 1371.
15. Nakka, J. S.; Jansen, K. M. B.; Ernst, L. J.; Jager, W. F. *J. Appl. Polym. Sci.* **2008**, *108*, 1414.
16. D792-00: Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement; ASTM International, West Conshohocken, PA, **2000**.
17. D5045-99 (Reapproved 2007): Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials; ASTM, West Conshohocken, PA, **1999**.
18. Ma, J.; Qi, Q.; Bayley, J.; Du, X.-S.; Mo, M.-S.; Zhang, L.-Q. *Polym. Test.* **2007**, *26*, 445.
19. Julka, S.; Cortes, H.; Harfmann, R.; Bell, B.; Schweizer-Theobaldt, A.; Pursch, M.; Mondello, L.; Maynard, S.; West, D. *Anal. Chem.* **2009**, *81*, 4271.
20. Raman, V. I.; Palmese, G. R. *Macromolecules* **2005**, *38*, 6923.
21. Jin, F.-L.; Han, M.; Park, S.-J. *Polym. Int.* **2006**, *55*, 1289.
22. Wong, C. P.; Bollampally, R. S. *J. Appl. Polym. Sci.* **1999**, *74*, 3396.
23. Ogata, M.; Kinjo, N.; Kawata, T. *J. Appl. Polym. Sci.* **1993**, *48*, 583.
24. Suzuki, T.; Oki, Y.; Numajiri, M.; Miura, T.; Kondo, K.; Shiomi, Y.; Ito, Y. *J. Appl. Polym. Sci.* **1993**, *49*, 1921.
25. He, Y.; Moreira, B. E.; Overson, A.; Nakamura, S. H.; Bider, C.; Briscoe, J. F. *Thermochim. Acta* **2000**, *357*, 1.
26. Tcharkhtchi, A.; Gouin, E.; Verdu, J. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 537.
27. E831-93: Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis; ASTM International, West Conshohocken, PA, **1993**.
28. Epon and Epi-Rez Epoxy Resins: Product Overview; Hexion Specialty Chemicals, Columbus, Ohio, **2009**.
29. Riesen, R. *Collected Applications Thermal Analysis: Thermosets*, Mettler Toledo: Switzerland, **2006**.
30. Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. *Polymer* **1983**, *24*, 1341.