

Effect of Conversion on the Structure–Property Relationships of Amine-Cured Epoxy Thermosets

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ABSTRACT The effects of conversion beyond the gel point on the structure–property relationships of epoxy thermosets using formulations representative of the most commonly used epoxy resin and amine curing agents at balanced stoichiometry with an emphasis on the thermal, tensile, and fracture properties were studied. The range of T_g from just beyond the gel point to full conversion typically is >100 °C. Fracture toughness (as K_{Ic}) of the epoxy thermosets cured with relatively flexible amines such as ethylenediamine (EDA), diethylenetriamine (DETA), and *m*-xylylenediamine (MXDA) reaches near its full cure value at only ~ 65 – 70 % conversion. The maximum in K_{Ic} for these types of epoxy thermosets is at ~ 90 % conversion for EDA and DETA but just below its full cure for MXDA. Isophoronediamine represents a special case for fracture behavior because of its apparent substantial cyclization during cure. In the 4,4'-diaminodiphenylsulfone series, K_{Ic} generally increases with conversion as the concentrations of their strongly antiplasticizing soluble and pendant fractions decrease. A uniform trend of decreasing tensile modulus with increasing conversion was observed in each formulation and is consistent with the expected decrease in the cohesive energy density as monomer glass is transformed into polymer glass.

KEYWORDS: epoxy • thermoset • conversion • structure–property relationships

INTRODUCTION

Epoxy thermosets remain one of the most widely used high-performance polymeric materials because of their rich variety of compositions (epoxy resins and curing agents), cure processes, and resultant properties (1), and much is known about their chemistry, cure kinetics, and thermal and mechanical behavior (2). It is widely assumed that optimum properties of epoxy thermosets are achieved upon full cure, but in practice cure conditions are typically controlled to balance the final properties and processing time rather than to achieve complete functional group conversion. While the effects of conversion on the glass transition temperature (T_g) are well studied (3), its relationship to epoxy thermoset mechanical properties, particularly glassy modulus and fracture toughness, is much less understood.

Previous work on the structure–property relationships of epoxy thermosets as a function of conversion is somewhat inconsistent and limited in scope. A study on the fracture properties of epoxy thermosets made from a commercial grade (D.E.R. 332* epoxy resin) of bisphenol A diglycidyl ether (BADGE) and tetraethylenepentamine showed that the tensile modulus *decreases* whereas the fracture toughness, as measured by the modulus-dependent strain energy release rate (G_{Ic}), *increases* with increasing postcure temperature (4). It is apparent from those results that conversion increased with higher postcure temperatures, but the data

provided do not allow its estimation. Similarly, using a much more rigid curing agent, a study using another commercial grade of BADGE and 4,4'-diaminodiphenylsulfone (DDS) showed increasing T_g and decreasing glassy modulus with increasing cure temperature (5). These trends were also observed in a study on the physical aging of thermosets made from a BADGE resin and another specialty aromatic diamine (6).

Another report which evaluated a broader range of compositions showed that the maxima of the flexural or tensile modulus and Charpy impact resistance appeared well below full conversion and depended on the number-average functionality of the curing system (7). This wide-ranging study did, however, employ some relatively uncommon amine curing agents and did not achieve full cure of many of the compositions evaluated. A later detailed study on thermosets from D.E.R. 332 epoxy resin and 4,4'-diamino-3,3'-dimethyldicyclohexylmethane, a specialty cycloaliphatic diamine also used in the above work, showed the tensile modulus decreasing from ~ 75 – 90 % conversion and a minimum in the fracture toughness as measured by G_{Ic} or the critical stress intensity factor (K_{Ic}) at ~ 90 % conversion (8). However, a study on the fracture properties of a BADGE resin cured with diethanolamine, which cures largely by unselective epoxy–hydroxyl reactions, showed *increasing* K_{Ic} up to nearly full cure under the conditions used (9). Other more recent reports on the properties of epoxy thermosets as a function of conversion focus on properties other than ambient mechanical properties, such as viscoelastic (10), thermal (11), and dielectric (12).

The degree of conversion of epoxy–amine thermosets can be controlled by curing below T_g of the fully cured

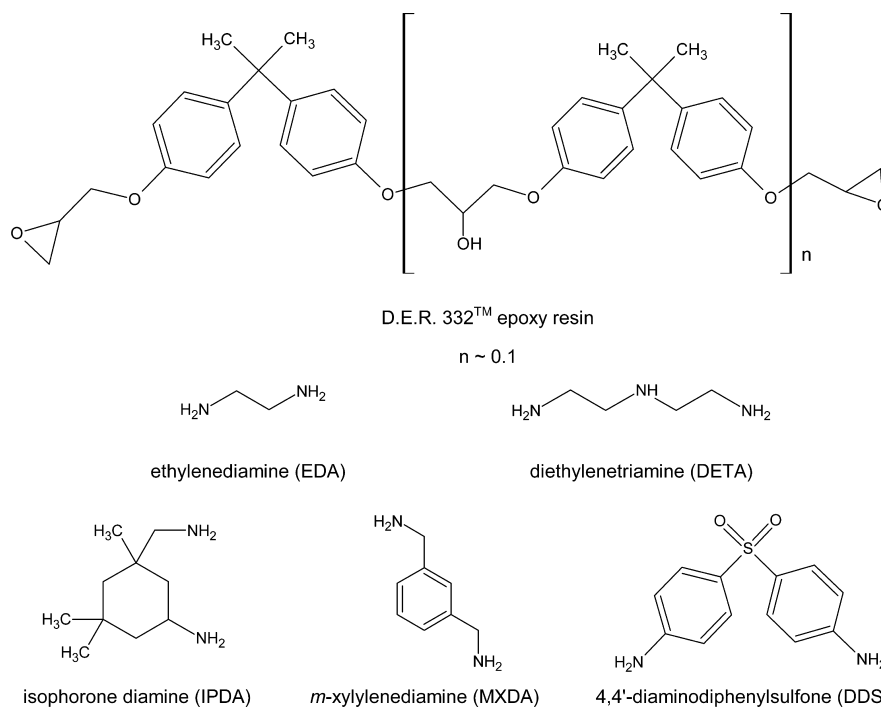
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Scheme 1. Epoxy and Diamine Monomers Used To Prepare DER 332–Amine Thermosets



polymer (5). However, quantifying the degree of conversion has proven more challenging. The disappearance of epoxide groups can be monitored by vibrational spectroscopy, such as IR, near-IR, and Raman spectroscopies, but these methods become less accurate as conversion increases and do not detect the formation of either products or a possible byproduct. A convenient calorimetric method, commonly known as the DiBenedetto approach (13, 14), relates changes in the thermoset heat capacity (ΔC_p) and T_g to conversion and has been shown to correlate well with the above spectroscopic methods up to just over 90% conversion (7).

The effect of conversion on the thermoset network structure is much more clearly defined (15). Polyfunctional epoxy resins and curing agents react to form fully soluble branched clusters up to the gel point, at which the weight-average molecular weight and viscosity approach infinity and the bulk material is no longer fully soluble. With increasing conversion beyond the gel point, the soluble fraction decreases, the pendant fraction, which is bound only at one terminus, first increases and then decreases, and the molecular weight between cross-links (M_c) decreases. Formulations having balanced stoichiometry have no soluble or pendant fraction at full conversion. How the counteracting influences of diminishing network defects and decreasing M_c coupled with formulation composition variations affect the mechanical properties of epoxy thermosets is difficult to anticipate. Indeed, the effects of these types of network defects in epoxy formulations having monofunctional components were recently shown to be very complex (16).

The objective of this study is to determine the effects of conversion beyond the gel point on the structure–property relationships of epoxy thermosets using formulations representative of the most commonly used epoxy resin and amine curing agents at balanced stoichiometry with an

Table 1. Monomer Amounts for DER 332–Amine Thermosets

amount of DER 332 (g)	amine	
	type	amount (g)
400.00	EDA	34.74
325.00	DETA	39.45
350.00	IPDA	85.98
350.00	MXDA	68.79
300.00	DDS	107.51

emphasis on thermal, tensile, and fracture properties. D.E.R. 332 epoxy resin was chosen because it is the most pure of the commercially available sources of BADGE. Five amines were selected to represent the various classes of these curing agents: ethylenediamine (EDA) and diethylenetriamine (DETA) for the alkyleneamines, isophoronediamine (IPDA) for the cycloaliphatic amines, *m*-xylylenediamine (MXDA) for the aralkylamines, and DDS for the arylamines (Scheme 1). Conversion was determined using the DiBenedetto calorimetric method for each of these thermoset systems.

EXPERIMENTAL SECTION

Chemicals. D.E.R. 332 epoxy resin (“DER 332”) and DETA (D.E.H. 20* epoxy curing agent, $\geq 98.5\%$) were obtained from The Dow Chemical Co. IPDA (Vestamin IPD, $\geq 99.7\%$) was obtained from Evonik Ind. EDA ($> 99\%$), MXDA (99%), and DDS (97%) were obtained from Aldrich Chemical Co. Monomers were used as received.

Thermoset Preparation. Thermosets having balanced epoxide and amine equivalents were prepared using the general procedure and equipment as previously described (10). The epoxy resin was first thoroughly degassed under vacuum at 60 °C, and then the diamine was added over 5 min (Table 1). For the EDA thermosets, the amine was added to the resin at 55 °C. For the DETA, IPDA, and MXDA thermosets, the amine

Table 2. DSC Analysis of Uncured (0) and Fully Cured (∞) DER 332–Amine Thermosets

diamine	$T_g(0)$ (°C)	$\Delta C_p(0)$ (J/g · °C)	$T_g(\infty)$ (°C)	$\Delta C_p(\infty)$ (J/g · °C)	λ	$T_g(\infty)^{lit.}$ (°C)
EDA	−41	0.37	140	0.25	0.68	150 ^a (17)
DETA	−40	0.44	149	0.21	0.48	146(18)
IPDA	−37	0.64	171	0.25	0.39	169(19)
MXDA	−43	0.66	127	0.25	0.38	121 ^a (20)
DDS	0	0.60	225	0.13	0.22	215(21)

^a By DMA.

was added to the resin at 60 °C. The above monomer mixtures were degassed at the indicated temperature, poured into a preheated aluminum mold, and cured for 1 h at 60 °C and for another 1 h at the maximum cure temperature (Table S1 in the Supporting Information). Those samples having a maximum cure temperature of <60 °C were cured at the indicated temperature for 2 h. For the DDS thermosets, the diamine was dissolved into the resin at 130 °C, allowed to cool to 80 °C while degassing under vacuum, poured into a preheated aluminum mold, and cured for 2 h at the maximum cure temperature (Table S1 in the Supporting Information). About 5 g of each monomer mixture was quenched by pouring into an aluminum dish, sealing into a freezer bag, and cooling to −20 °C.

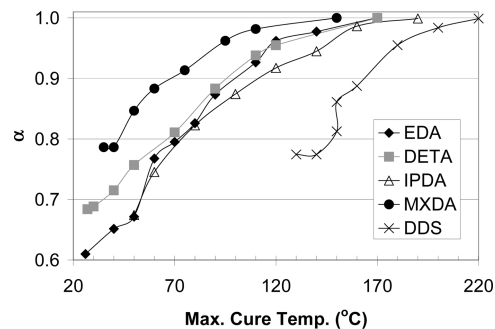
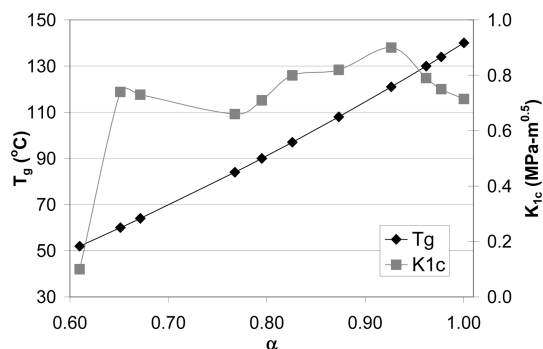
Analyses. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and fracture toughness using compact tension specimens were done as previously described (10). Tensile stress–strain testing was done in accordance with ASTM D638-03 using type I specimens and conditions on an Instron model 4505 test frame fitted with a 1000 lb. load cell and an Instron model 2630-115 extensometer. The fracture toughness and tensile data are reported as the average of five specimens (see Table S1 in the Supporting Information for the average error of each analysis).

RESULTS AND DISCUSSION

Conversion by DSC. The DiBenedetto calorimetric method relates T_g of the partially cured thermoset to conversion (α) using T_g of the unreacted monomer mixture [$T_g(0)$], T_g of the fully cured thermoset [$T_g(\infty)$], and the ratio (λ) of the ΔC_p values of the fully cured and unreacted materials (eq 1).

$$\frac{T_g - T_g(0)}{T_g(\infty) - T_g(0)} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha} \quad (1)$$

The $T_g(0)$ values for DER 332–amine monomer mixtures are each approximately −40 °C except for that of DDS (Table 2). On the other hand, the $\Delta C_p(0)$ values vary differently; the values for the straight-chain alkyleneamines are ~0.4, while those of the cyclic amines are ~0.6. It should be noted that the preparation of homogeneous, completely unreacted epoxy–amine monomer mixtures is practically impossible, and undoubtedly a small extent of the reaction occurred prior to quenching. This experimental challenge is the probable source of the most error in the determination of α by this method. The $T_g(\infty)$ values vary as expected with amine flexibility and functionality and are near to those previously reported ($T_g(\infty)^{lit.}$) mostly by DSC for these fully cured epoxy thermosets. The $\Delta C_p(\infty)$ values are approximately 0.25 for each thermoset except for the most rigid DDS material. These nonsystematic trends in ΔC_p values result in their ratio λ being unique for each composition. A

**FIGURE 1.** α vs maximum cure temperature for DER 332–amine thermosets.**FIGURE 2.** T_g and K_{1c} vs α for a DER 332–EDA thermoset.

trend of decreasing λ with increasing amine rigidity and functionality is apparent.

Reduction of the maximum cure temperature was generally effective in controlling α as determined here by DSC using a heating rate of 10 °C/min (Figure 1). The maximum cure temperature was well above $T_g(\infty)$ of each composition to ensure complete cure and ranged from 150 °C for MXDA to 220 °C for DDS (Table S1 in the Supporting Information). The reaction exotherm arising from epoxide ring opening often gave actual cure temperatures significantly greater than the oven temperature for short periods. For this reason, T_g can be greater than the maximum cure temperature. The use of cure temperatures lower than those indicated in Figure 1 for MXDA or DDS as a curing agent gave conversion below the gel point, so the lower range of α for those compositions were not be prepared.

DER 332–EDA Thermosets. These compositions were cured from 170 °C to room temperature to achieve a conversion α from 1.00 to 0.61. The resulting T_g values decreased from 140 to 52 °C (Figure 2). Note that in all cases α is calculated using a first-order relationship with T_g (eq 1), so T_g always varies uniformly in these plots. Remarkably, K_{1c} increases to essentially its ultimate value at conversion only slightly above the gel point. The theoretical gel point for this type of thermoset (epoxy functionality = 2; amine functionality = 4) is at $\alpha = 0.58$, and all of the prepared samples in this series swelled but did not fully dissolve in tetrahydrofuran (THF), thereby confirming their conversion to beyond the gel point. The maximum in K_{1c} is observed at $\alpha = 0.93$ and is ~20% higher than the value at complete cure. The tensile modulus (E) and percent strain at break (ϵ_b) versus α also show counterintuitive trends (Figure 3). The tensile modulus is at its maximum at the lowest conversion

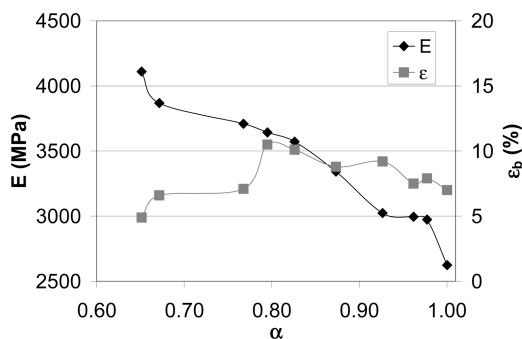


FIGURE 3. E and ϵ_b vs α for a DER 332-EDA thermoset.

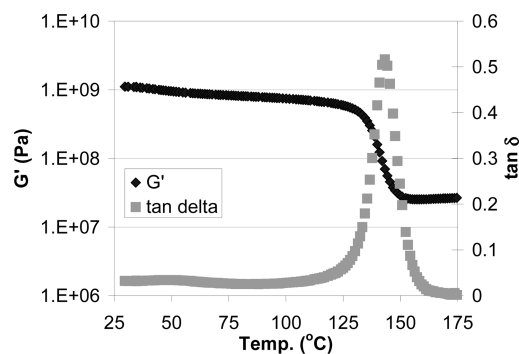


FIGURE 4. DMA of a DER 332-EDA thermoset; $\alpha = 1.00$.

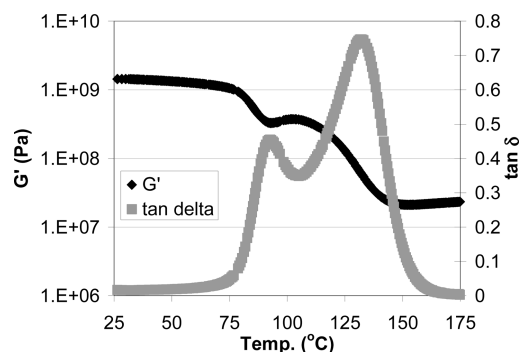


FIGURE 5. DMA of a DER 332-EDA thermoset; $\alpha = 0.79$.

and decreases by $\sim 35\%$ to its minimum value at complete conversion, while ϵ_b varies between ~ 5 and 10% with a maximum at $\alpha \sim 0.8$.

DMA of the fully cured DER 332-EDA thermoset shows typical behavior: the storage modulus (G') decreases modestly from room temperature until T_g and then decreases by greater than 1 decade through T_g , followed by a rubbery plateau; $\tan \delta$ changes slightly below T_g , increasing to a sharp peak at T_g and returning to near zero above T_g (Figure 4). However, DMA of samples having $\alpha < 1.00$ gave unmeaningful results because they further cured during the analysis, which employed a heating rate of $3\text{ }^\circ\text{C}/\text{min}$. This effect manifests in a partial increase in G' after T_g , a broadening and eventual splitting of peak $\tan \delta$, and an equivalence of rubbery G' values (Figure 5). The reaction kinetics of the incompletely cured thermosets based on the other alkylamines and MXDA are also too fast for DMA under these conditions. Similarly, the thermal decomposition temperature (T_d) by TGA is invariant with α for each series because of further curing during the analysis (Table S1 in the Supporting Information).

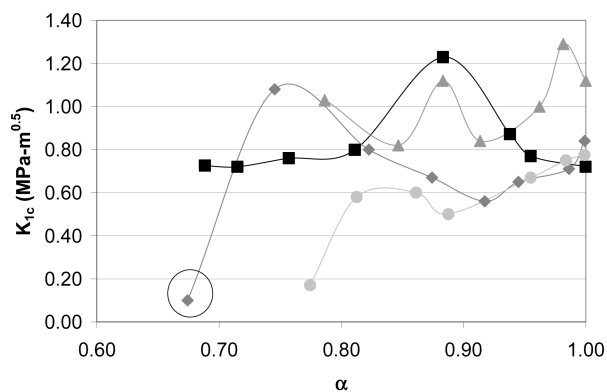


FIGURE 6. K_{1c} vs α for DER 332-DETA, -IPDA, -MXDA, and -DDS thermosets.

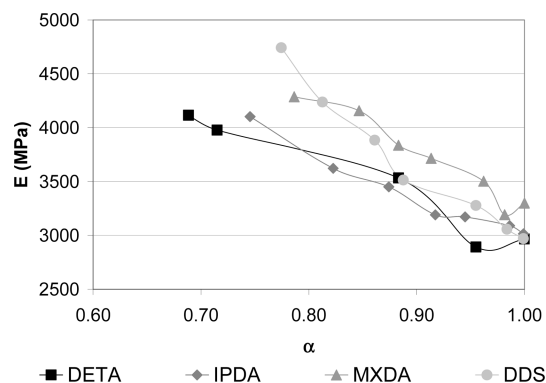


FIGURE 7. E vs α for DER 332-DETA, -IPDA, -MXDA, and -DDS thermosets.

DER 332-DETA Thermosets. The results of the DER 332-EDA thermosets were so striking that the study was repeated using DETA, a related but much more technologically important curing agent. This formulation was also cured from $170\text{ }^\circ\text{C}$ to room temperature and gave α from 1.00 to 0.68. The resulting T_g values decreased from 149 to $57\text{ }^\circ\text{C}$ (Table S1 in the Supporting Information). In this formulation, the reaction exotherm proved high enough to provide a room temperature cure to even further beyond the gel point compared to EDA. Here again K_{1c} at the lowest α values is equivalent to that at full conversion (Figures 6 and S1 in the Supporting Information). In this series, the variation in K_{1c} vs α is lower than that in the EDA series and the maximum value is again observed at $\alpha \sim 0.9$. The tensile modulus decreases and the percent strain at break varies only slightly with increasing α , as seen in the EDA series (Figures 7 and S2 in the Supporting Information).

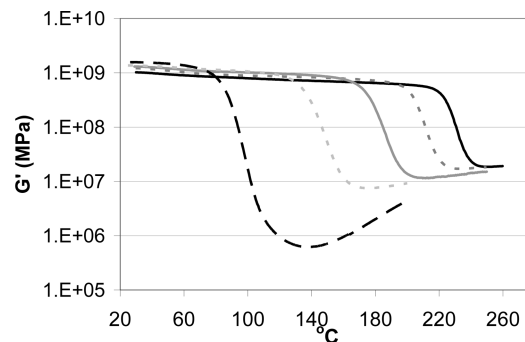
DER 332-IPDA Thermosets. IPDA was chosen to represent the cycloaliphatic amine curing agent family, and its cure behavior significantly differs from that of the ethyleneamines discussed above. This formulation was cured from 190 to $50\text{ }^\circ\text{C}$ to give $\alpha = 1.00-0.67$. Over this range of α , T_g decreases from $171\text{ }^\circ\text{C}$ at full cure to $56\text{ }^\circ\text{C}$ at the lowest degree of cure (Table S1 in the Supporting Information). However, the sample having the lowest degree of cure, which theoretically should be well above the gel point, actually was completely soluble in THF and is therefore uncross-linked (circled point, Figures 6 and S3 in the Supporting

Information). A plausible explanation for the much higher than expected gel point in this formulation is a greater degree of cyclization of BADGE–IPDA oligomers compared to those derived from the ethyleneamines. In fact, a substantial degree of cyclization was observed in the polymerization of BADGE and cyclohexylamine (22). The variation of fracture properties with α of this formulation is also unique: the maximum in K_{1c} is observed for the sample just beyond the gel point ($\alpha = 0.75$), and K_{1c} at $\alpha \sim 0.9$ is the minimum value observed. The tensile modulus decreases $\sim 25\%$ from its maximum at lowest conversion while the percent strain at break generally increases from ~ 2 to 8% (Figures 7 and S4 in the Supporting Information). The fact that K_{1c} and ϵ_b show opposite trends with conversion is explicable considering the far different stress states and strain rates of the two tests (0.5 vs 5.1 mm/min, respectively) and the well-known dependency of epoxy thermoset fracture properties on the strain rate (23).

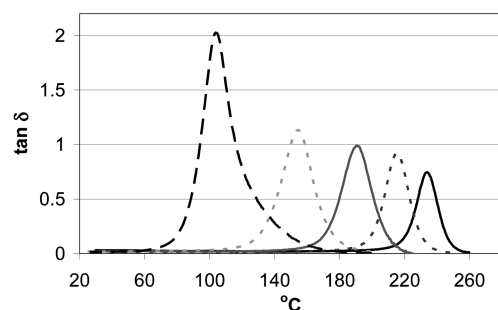
DER 332–MXDA Thermosets. The MXDA samples were cured at temperatures from 150 to 35 °C to result in a range of α from 1.00 to 0.79 . The exotherm in this formulation also cured the samples to T_g values well above their cure temperatures, so samples having conversion closer to the gel point were not obtained. T_g decreased from 127 °C at full cure to 56 °C at the lowest conversion (Table S1 in the Supporting Information). The fracture toughness oscillates with increasing α over a range of ~ 0.8 – 1.3 MPa \cdot m $^{0.5}$ (Figures 6 and S5 in the Supporting Information). K_{1c} for this series is only slightly lower at the minimum α compared to that at full cure and has a maximum value at just under full cure. This series also shows the tensile modulus decreasing and the ultimate elongation decreasing with increasing conversion (Figures 7 and S6 in the Supporting Information).

DER 332–DDS Thermosets. DDS is a much more rigid curing agent than the others studied here, and its thermosets show somewhat more intuitive structure–property relationships. These high-temperature thermosets were cured from 220 to 130 °C to give a minimum $\alpha = 0.77$ and a range of T_g values from 224 °C at full cure to 96 °C at the minimum conversion (Table S1 in the Supporting Information). Curing at 140 and 130 °C gave the same degree of cure, so samples having lower values of conversion were not obtained. The fracture toughness generally increases with increasing α , but there appears a broad discontinuity in this trend from $\alpha = 0.81$ to 0.86 (Figures 6 and S7 in the Supporting Information). The tensile modulus decreases markedly with increasing α , and the percent strain at break tends to increase uniformly from near zero to $\sim 10\%$ (Figures 7 and S8 in the Supporting Information).

The reaction kinetics of DER 332–DDS is slow enough to obtain more meaningful DMA results. The temperature sweeps of G' show changes typical for glassy to rubbery transitions (Figure 8). Glassy G' increases with decreasing α , consistent with the tensile modulus results. Samples having less than full cure show a minimum in their rubbery G' values, which reflects their increase in M_c with decreasing conversion. However, because these samples cure at sig-



MCT = — 220 °C - - - 200 °C — 180 °C ··· 150 °C - - - 140 °C
 FIGURE 8. G' by DMA for DER 332–DDS thermosets.



MCT = — 220 °C - - - 200 °C — 180 °C ··· 150 °C - - - 140 °C
 FIGURE 9. Peak $\tan \delta$ by DMA for DER 332–DDS thermosets.

nificant rates at ≥ 140 °C, the results for all but the sample at lowest α are not considered representative of their initial state of cure. This inconsistency is further observed in the trend of peak $\tan \delta$ with α (Figure 9).

Correlation of the conversion-dependent mechanical properties of these epoxy thermosets with the structures of the curing agents is a significant challenge. The fracture toughness of epoxy thermosets cured with relatively flexible amines such as ethyleneamines (EDA and DETA) and aralkylamines (MXDA) reaches near its full cure value at only ~ 65 – 70% conversion. The maximum in K_{1c} for these types of epoxy thermosets is at $\sim 90\%$ conversion for the former but just below full cure for the latter. For these systems, as conversion increases, there appears to be a general balance between decreasing M_c , which decreases the toughness, and decreasing concentrations of soluble and pendant network fractions, which increases the toughness (10). Cycloaliphatic amines like IPDA represent special cases for fracture behavior because of their apparent substantial cyclization during cure. Aromatic diamines (i.e., DDS) impart much greater chain rigidity as the thermoset network builds. The fracture toughness in these thermosets generally increases with conversion as the concentration of their strongly antiplasticizing soluble fraction decreases.

The uniform trend of decreasing tensile modulus with increasing conversion can be understood in terms of the changes in the network cohesive energy density as the curing material transforms from monomer glass into polymer glass (24). As the monomers cure, their nonbonded interactions decrease as their intermolecular distances increase because of the constraints of covalent bond formation. The resulting decrease in the cohesive energy density,

which is directly proportional to the bulk modulus, continues as the monomers and oligomers react to full conversion.

The implications of these results are important in virtually all epoxy thermoset applications. With all but the most rigid cross-linking agents, achieving full cure is not required to obtain good fracture toughness. This behavior explains why it is not necessary to achieve complete functional group conversion in most epoxy formulations to achieve targeted mechanical properties. These results also explain some apparent anomalous behavior, such as the effects of the coating thickness on their mechanical properties (25) and complications in the high-temperature testing of undercured epoxy electronics formulations (26).

CONCLUSIONS

The effect of conversion on the structure–property relationships of these amine-cured epoxy thermosets shows consistent trends with the amine structure for all of the properties evaluated except for the fracture toughness. The range of T_g from just beyond the gel point to full conversion typically is >100 °C. Some of the temperature-dependent behavior (TGA and DMA) were complicated by increasing cure during the analyses. With increasing conversion, the tensile modulus decreases ~ 25 – 30% from near the gel point to full conversion regardless of the amine curing agent. However, the trend of the tensile strain at break with increasing conversion depends on the class of the amine curing agent: ϵ_b changes irregularly within ~ 4 – 10% for the aliphatic (EDA, DETA, and IPDA) and aralkylamine (MXDA) thermosets but more uniformly from ~ 4 to 8% for the arylamine (DDS) materials.

The trends for the fracture toughness with increasing conversion are the most surprising and depend strongly on the structure of the curing agent. K_{Ic} for the EDA and DETA thermosets at just above the gel point are as high as that at full conversion, and the maximum value is at $\sim 90\%$ conversion. The result using MXDA is similar except that the maximum in K_{Ic} is closer to 95% conversion. The fracture toughness for IPDA thermosets is at its maximum just above the gel point, which is increased significantly above its theoretical value apparently because of cyclization. Only the most rigid epoxy thermoset (DDS) shows K_{Ic} generally improving with increasing conversion, behavior heretofore considered typical for thermosets in general.

The observed trend of decreasing tensile modulus with increasing cure can be explained by the decrease in the cohesive energy density as monomer glass transforms to polymer glass. However, the trends for the fracture tough-

ness appear to depend on the complex interactions of decreasing M_c , decreasing amounts of soluble and pendant fractions, and the plasticizing versus antiplasticizing nature of the soluble fraction.

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Supporting Information Available: Table S1 and Figures S1–S8 giving a detailed listing of the cure temperatures and properties versus conversion of the samples and plots of properties versus conversion for each of the materials not shown above. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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