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Structure−property relationships of controlled epoxy networks with quantified levels of excess epoxy etherification

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Abstract

Epoxy thermosets are commonly formulated with an excess of epoxy resin to ensure complete reaction of co-reactive hardeners and to optimize performance. However, the degree to which the reaction of the excess epoxy resin contributes to the thermal and mechanical properties of the thermoset is incompletely understood. In this report, the preparation of controlled epoxy thermosets containing varying amounts of excess epoxy resin having essentially complete excess epoxy conversion is described. The extent of conversion was determined using a solid-state ^{13}C NMR method with enhanced resolution due to solvent swelling of the thermosets. This etherification reaction increases the crosslink density of the epoxy thermosets but uniquely affects the thermal and mechanical properties of the materials. Significant property differences observed with respect to analogous thermosets made by varying crosslink density using different extender/hardener ratios are the sensitivity of T_g to the crosslink density and enhanced fracture toughness and tensile yielding with reduced bulk density.

Keywords: Epoxy; Thermoset; Etherification

1. Introduction

Many of the formulations used to prepare epoxy thermosets contain a stoichiometric excess of epoxy resin. To better understand the relationships between preparation conditions and material properties of epoxy thermosets, a wide range of topics related to their curing have been probed and several of these have employed excess epoxy resin [1]. The prior results are somewhat conflicting in regard to the fate of the excess epoxy functionality; in some cases the excess epoxy reacted while in other very similar formulations it did not. But there are no prior studies which have determined the effects of quantified degrees of various amounts of reacted excess epoxy resin on both the thermal and mechanical properties of epoxy thermosets.

Epoxy thermosets are generally prepared by the reaction of an epoxy resin with some type of co-reactive hardener like an amine or phenol that is incorporated stoichiometrically into the polymer network [2]. With co-reactive hardeners, the assumption is normally made that the epoxide groups react exclusively with the hardener. To a large extent, studies of relative reaction rates show this to be true [3], but in some formulations, particularly ones in which the epoxide is in stoichiometric excess, the etherification of the produced 2° hydroxyl groups by an epoxide can also proceed to some extent. Although efforts have been made to identify more selective hardeners and catalysts to minimize the extent of etherification [4−6], systematic evaluations of the thermal and mechanical structure−property relationships of thermosets cured through a combination of co-reaction with a hardener and etherification have not been reported. As a result, the potential advantages and disadvantages of these systems remain unclear. This report aims to resolve some of these questions.

The primary curing reaction between an epoxide and a hardener (R_2XH, where $X = -O-, -S-, -N-, -CO_2-$) results in an opening of the epoxide group to form a 2° hydroxyl group (Scheme 1). The formation of a uniform network with a hardener depends on significantly faster kinetics for the hardener reaction versus the etherification reaction and perfectly balanced

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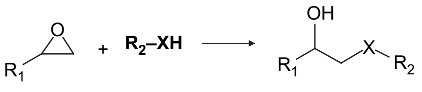
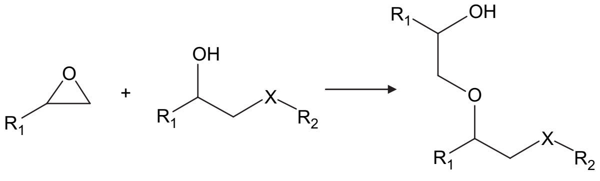


Scheme 1.



Scheme 2.

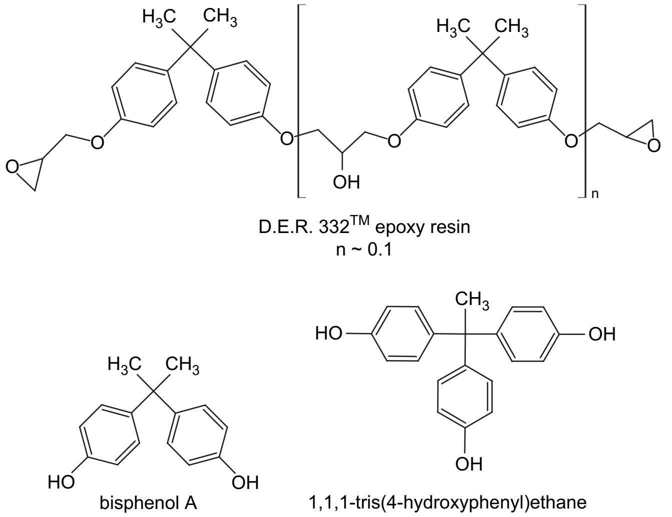
stoichiometry. In many systems, particularly those having a stoichiometric excess of epoxy resin, the 2° hydroxyl can then react with remaining epoxide groups via the etherification reaction [2,3,5,7–9]. This alkyl etherification reaction (Scheme 2) adds a branch point to the network for each additional epoxide reacted, causing a significant increase in the crosslink density of the cured material with the complete reaction of a diepoxide.

The effects of epoxy etherification on the thermal and mechanical properties of thermosets prepared with an excess of epoxy resin have not been fully determined. Since the etherification reaction is slow and typically does not proceed until the completion of the primary curing reaction, there is uncertainty as to the extent of completion of the etherification reaction. Measurements of parameters such as the glass transition temperature (T_g) indirectly indicate the effect of the added crosslinking due to the etherification reaction, but methods for directly measuring both the excess epoxy conversion and concomitant alkyl ether formation have not been available.

Most of the previous studies on epoxy thermosets with excess epoxy resin used amine curing agents and their results are somewhat contradictory. A series of epoxy thermosets using bisphenol A diglycidyl ether (BADGE) and poly(oxypropylene)diamine in various equivalent ratios showed increasing storage modulus (G') and T_g with increasing excess epoxy conversion as quantified by near-infrared spectroscopy [10]. Two studies on the reaction of BADGE with α,ω-diaminoalkanes also showed significant excess epoxy reaction, one by kinetic analysis [6] and the other by increases in T_g [11]. On the other hand, many more studies on very similar systems showed no evidence of the reaction of excess epoxy resin, such as BADGE and either 4,4′-diaminodiphenylmethane (DDM) or 1,6-diaminohexane [12], BADGE and isophoronediamine [13], or BADGE and 1,2-diaminoethane or DDM [14]. The inadvertent presence of catalysts for epoxy etherification may have complicated the former studies. The reaction of excess epoxy in a phenolic-type formulation was reported using BADGE and bisphenol A in the presence of an imidazole catalyst [15].

The quantification of both the conversion of excess epoxy resin and the yield of the derived alkyl ether branched sites in epoxy thermosets has proven to be quite challenging. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been used to study epoxy thermosets, but the rigidity of the epoxy network has severely limited the resolution of ^{13}C spectra in these studies preventing the identification and quantitation of the chemically different reacted glycidyl groups in the network [16–19]. One reported method that was able to detect etherified epoxides did so for a network designed to be flexible, circumventing the rigidity normally typical in epoxy thermosets [7]. There have also been ^{1}H NMR methods presented that relate crosslink densities of epoxy thermosets with different relaxation times, but these techniques typically do not offer a straightforward method for quantitatively measuring crosslink densities, particularly for highly crosslinked samples [20,21]. To directly measure the epoxy conversion and the extent of branching due to the etherification reaction shown in Scheme 2, we have developed a method for collecting high resolution ^{13}C magic angle spinning (MAS) NMR spectra of solvent-swollen epoxy thermosets.

The term "controlled epoxy networks" (CENs) is used in our studies to mean epoxy network polymers synthesized and evaluated under well-controlled conditions. Key aspects of the CEN approach are the use of monomers having well defined structures, known stoichiometry, consistent reaction conditions, and known functional group conversions. This paper first presents the structure–property relationships of a series of CENs made from a commercial source of BADGE, bisphenol A (BA) as chain extender, and 1,1,1-tris-(4-hydroxyphenyl)ethane (THPE) as curing agent (Scheme 3). These CENs were prepared using a phosphonium salt catalyst which gives high selectivity to phenolic–epoxy coupling [22] and demonstrate the effects of crosslink density on the properties of this model system for phenolic-cured epoxy thermosets. Two other families of CENs were prepared with varying amounts of excess epoxy resin catalyzed using 1-benzyl-2-methylimidazole (1B2MZ) to obtain different levels of extra crosslinking due to epoxy etherification. The solid-state NMR method mentioned above was used to measure the alkyl ether branching in these CENs. The thermal and mechanical properties of the CENs were then evaluated to determine the structure–property



Scheme 3.

relationships for these materials with the goal of identifying the effect of excess epoxy etherification on the properties of these controlled networks.

2. Experimental

2.1. CEN preparation

D.E.R.™ 332 epoxy resin (equivalent weight[2] = 173 g/eq), PARABIS™ bisphenol A (99.9%), both from The Dow Chemical Co., and 1,1,1-tris-(4-hydroxyphenyl)ethane (THPE, 99%, Sigma–Aldrich), each used as received, were mixed by melting at 180 °C in a 1 L 3-necked round bottomed flask. The mixture was then cooled prior to catalyst addition: to 120 °C for the phenolic-only cured mixtures using A-1 catalyst (70% w/w ethyltriphenylphosphonium acetate–acetic acid complex in methanol, Morton Chemical, Garden Grove, CA) and to 80 °C for 1-benzyl-2-methylimidazole (Air Products and Chemicals, Curezol 1B2MZ). The mixture was degassed either by vacuum using A-1 (to remove methanol) or by centrifugation using 1B2MZ and a 1/8″-thick plaque was cast and cured at 200 °C for 2 h. Details of the CEN formulations are given in Table 1.

2.2. Solid-state MAS ^{13}C NMR characterization

The degree of epoxy etherification in the cured plaques was measured by single-pulse magic angle spinning (MAS) ^{13}C NMR. Experiments were performed on a Bruker Avance 400 spectrometer (Bruker BioSpin, Billerica, MA) operating at a resonance frequency of 100.56 MHz with a 7 mm MAS-II probe. Ground CEN samples for analysis were swollen in *N*,*N*-dimethylformamide (approximately 2:1 solvent/CEN by mass) to enhance resolution. NMR spectra were collected at an MAS speed of 4800 Hz, collecting 3000 scans with a time domain size of 3072, a sweep width of 30 030.03 Hz, a receiver gain of 1820, a dwell time of 33.3 μs, and a pre-scan delay of 6 μs. Acquisition time was 0.136 s. The appropriate recycle delay was determined by measuring the T1 relaxation times for both the oxirane carbon resonance at 50.6 ppm and resonances for the product of the oxirane ring-opening around 70 ppm. Based on a T1 of 4.5 s for the oxirane carbon and 0.6 s for 70 ppm resonances the recycle delay was set to 25 s to ensure that the quantitative results were not influenced by the long relaxation times.

Table 1
CEN formulations prepared

CEN	Amount of each component (g)			
	DER 332	BA	THPE	Catalyst (mL A-1)
Phenolic-only CENs BA/THPE (mol)				
0.63	289.0	70.0	100.3	0.1
1.75	289.2	116.0	59.1	0.1
4.00	288.9	146.0	32.3	0.1
8.60	289.7	163.3	16.9	0.1
%Equivalents excess epoxy, BA/THPE = 1.75				(g 1B2MZ)
5	250.5	100.0	51.0	5.0
10	254.4	96.5	49.4	5.2
20	262.6	91.2	46.6	5.4
40	276.2	82.2	42.0	5.6
62	289.7	74.8	38.2	4.7
104	310.5	63.4	32.4	6.2
%Equivalents excess epoxy, BA/THPE = 4.00				
5	249.1	124.0	27.8	5.2
11	254.3	120.4	27.0	5.0
20	261.0	113.9	25.5	5.4
41	276.1	102.7	23.0	5.7
60	286.1	93.6	21.0	5.8
100	303.8	79.4	17.8	6.1
Epoxy only	407.4	–	–	8.3

2.3. Thermal and mechanical characterization

Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments (New Castle, DE) Q-1000 Calorimeter. Two scans from an equilibrated temperature of 35 °C–275 °C at 10 °C/min under nitrogen with an interim cool-down at 10 °C/min were performed for each sample in an open aluminum pan. Reported T_g values were measured from the inflection point of the heat capacity curve on the second scan.

Thermomechanical analysis (TMA) experiments used a TA Instruments Q-400 with a micro expansion probe. For samples dried in a dessicator overnight, the temperature was ramped twice to 275 °C at 10 °C/min. T_g and coefficients of thermal expansion (CTEs) were calculated from the second scan.

Dynamic mechanical thermal analysis (DMTA) was performed on an ARES LS rheometer (Rheometric Scientific, Piscataway, NJ) equipped with an environmental controlled oven chamber and rectangular plate fixtures. For 1.75″ × 0.5″ × 0.125″ samples, a 0.1% strain was applied at 1 Hz while ramping to 250 °C at 3 °C/min.

For thermogravimetric analyses (TGA) experiments on a TA Instruments Q-50, dry samples were analyzed by a ramp from room temperature to 600 °C at 10 °C/min under a nitrogen atmosphere. The degradation temperatures (T_d) were determined as the intersection of the tangents of the weight/temperature curve drawn prior to the degradation.

Fracture toughness was measured in accordance with ASTM D-5045 at room temperature. Samples from the cured materials were cut by the Hydrocut Company (Angleton, TX) using a water-jet cutter. A minimum of five analyses were performed and averaged. Tensile testing was performed at room temperature on selected samples according to ASTM D638 with the exception of sample size. For these tests, the nominally 1/8″-thick thermoset plaques were cut into 0.5″ × 2.75″ pieces with a 1/8″ gauge width. Bulk density was measured on plaque pieces using ASTM D792, method A.

3. Results and discussion

3.1. Kinetic study

To estimate whether the cure conditions used would be adequate for the desired complete conversion of the phenolic

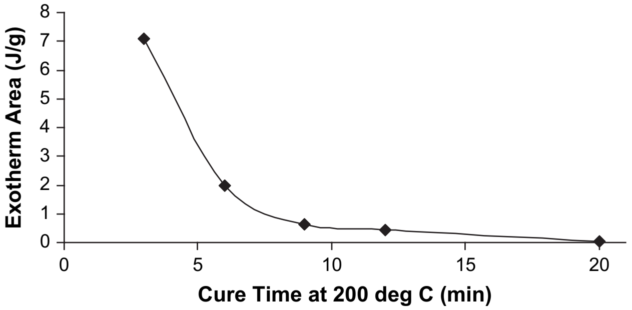


Fig. 1. Kinetics of CEN curing at 200 °C with 60% excess epoxide resin, BA/THPE = 1.75.

monomers and excess epoxy resin, the curing kinetics for an uncured mixture with a 60% excess of equivalents of epoxy resin and an extender/hardener ratio of 1.75 were studied by DSC. For these experiments, the sample was rapidly heated (at ~100 °C/min) to 200 °C and held there for the specified time followed by a rapid cool to room temperature (at ~60 °C/min). The area of the exotherm peak was then recorded on a scan at 10 °C/min to 275 °C. The results (Fig. 1) indicate that the reaction is essentially complete after ~20 min. and that curing for 2 h at 200 °C gives phenolic and epoxy functional groups conversion to their ultimate degrees.

3.2. Branching level

The degree of etherification in the CEN plaques prepared with excess epoxy was calculated from the NMR spectra (i.e. Fig. 2b) by taking the ratio of the amount of etherified glycidyl groups detected to the total amount of glycidyl groups detected. Defined in this way, the branching level is a measure of alkyl ether branching due only to the etherification reaction excluding chain extension/crosslinking by the aryl ethers formed from BA and THPE, respectively, and is a measure of the conversion of the excess epoxy in the formulation. Barring loop formation, each branch point adds another crosslink junction to the epoxy network.

The results of these calculations are shown in Fig. 3. At 100% conversion of the excess epoxy to alkyl ether groups, the % equivalents of excess epoxy should equal the %branching level. At low to moderate levels of excess epoxy, the observed %branching closely matches the % excess epoxy added. With greater amounts of excess epoxy resin, the measured branching level is lower than expected for complete epoxy conversion. Unfortunately, the resonance due to the methine carbon in the alkyl ether groups (B2 in Fig. 2) is small relative to the resonances of the carbons in the non-etherified groups and the methylene carbons in the alkyl ether groups centered around 70 ppm (A1, A2, and B1). Also, the broadening of the peaks at higher crosslink densities made accurate measurement of the B2 peak difficult, creating a source of uncertainty in the measurement.

We know of no other technique available to directly measure the degree of etherification to confirm the accuracy of the NMR branching level determination, but several other pieces of information help exclude some of the likely sources of error. Unreacted epoxy was not detected for any of the CENs indicating nearly complete epoxy conversion, but as described above the samples having higher levels of excess epoxy do not show correspondingly high degrees of branching. Rather, increasing line broadening with higher levels of excess reacted epoxy apparently results in poorer resolution of the alkyl ether resonance and thereby reduced integrated intensities.

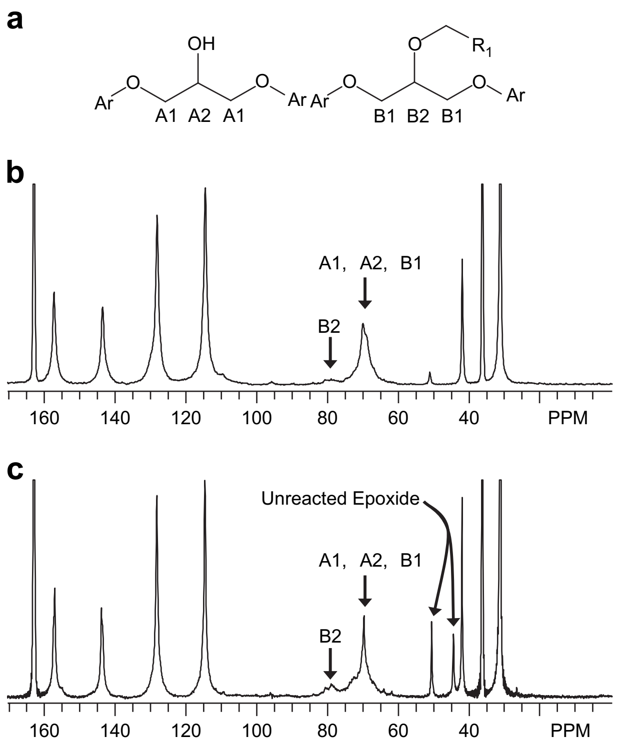


Fig. 2. Example NMR spectra of CENs: (a) key for NMR assignment of reacted glycidyl groups. Initial reaction of epoxide, left, and etherification, right; (b) NMR spectrum of CEN with 20% excess epoxy, BA/THPE = 1.75; (c) NMR spectrum of partially cured epoxy thermoset prepared with only epoxy resin and 1B2MZ catalyst.

To confirm that unreacted epoxides would be detected if present, a plaque containing only epoxy resin and 1B2MZ catalyst was prepared. Its incomplete cure was confirmed by the presence of a large exotherm peak in its initial DSC scan. The NMR spectra (Fig. 2c) contained the expected resonances at

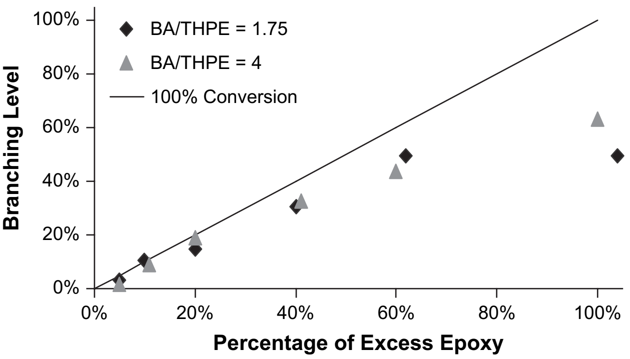


Fig. 3. Alkyl ether branching levels calculated from NMR spectra for plaques with excess epoxy.

44.4 and 50.6 ppm corresponding to the two epoxide-ring carbons, confirming both that the unreacted epoxide groups would be detected by the NMR method if present and that the swelling solvent does not interfere with the epoxide determination. Note that the weak resonance at 51.4 ppm is due to the methane carbon originating from THPE; this resonance appears as a shoulder on the nearby epoxide resonance (Fig. 2c) or alone at complete epoxy conversion (Fig. 2b).

It was also confirmed that the NMR sample preparation method did not fractionate the samples to remove unreacted epoxy components. With larger amounts of excess epoxy, a soluble fraction containing some of any unreacted epoxides may have been extracted by the swelling solvent and subsequently excluded from the NMR analysis. To test this possibility, solvent extracts in DMF of three samples, the two different CENs with 100% excess epoxy and the epoxy only thermoset, were analyzed by liquid chromatography to measure any soluble fraction in the CENs. No soluble fraction was detected for the two 100% excess epoxy CENs, and the epoxy only sample contained only ~1000 ppm of soluble material. These very low levels of soluble fraction indicate that essentially all of the starting materials were likely incorporated into the network.

The conclusion from these experiments is that conversion of the excess epoxy in these CENs approaches 100%. The lower values determined by the NMR branching level measurements are likely caused by increasing broadening of the alkyl ether resonance as M_c decreases which decreases the accuracy of the measurement of the B2 peak. Specifically, as M_c and the NMR resolution decrease, the peak corresponding to the B2 resonance and the peak corresponding to the resonances of A1, A2, and B1 begin to overlap. Since the determined branching level depends directly on the relative areas of these two peaks, the reduced accuracy of the areas resulting from the overlap impacts the sensitivity of the branching level determination. Because NMR analysis shows neither any remaining epoxide resonances at all crosslink densities nor the appearance of additional epoxide-derived resonances, the material properties of the CENs in this study are compared based on their M_c values assuming 100% conversion of the excess epoxy.

3.3. Calculation of average mass between crosslinks, M_c

Values for the crosslink densities of the networks with excess epoxy resin are calculated from the prepared stoichiometries for the phenolic-only CENs but ignoring the slight excess epoxy used to ensure complete phenolic conversion. For the CENs containing excess epoxy, the crosslink densities are calculated using 100% conversion of the excess epoxy. Complete conversion of the BA extender and THPE hardener is justified under these conditions considering the favorable kinetics of the epoxy–phenolic coupling reaction vs. epoxy–hydroxyl etherification [2] and by the high selectivity [21] of the phophonium salt catalyst. Thus, the crosslink density, X, is given by:

$$X = \frac{n_{\mathrm{THPE}} + n_{\mathrm{ExcessEpoxide}}\left(C_{\mathrm{ExcessEpoxide}}\right)}{m} \tag{1}$$

where n_{THPE} is the number of moles of THPE, $n_{\mathrm{ExcessEpoxide}}$ is the number of moles of excess epoxide groups (since each excess epoxide group can introduce a crosslink), $C_{\mathrm{ExcessEpoxide}}$ is the conversion of the excess epoxide (zero for the phenolic-only CENs or 100% for the CENs with excess epoxy), and m is the total mass of the network. The average molecular weight per crosslink, M_{pc}, is simply the inverse of the crosslink density:

$$M_{\mathrm{pc}} = \frac{1}{X} \tag{2}$$

Finally, the average molecular weight between crosslinks, M_c, is given by the relationship:

$$M_c = \left(\frac{2}{f_{\mathrm{avg}}}\right) M_{\mathrm{pc}} \tag{3}$$

where f_{avg} is the average functionality of the crosslinking groups [23]. Since each THPE hardener molecule and each reacted excess epoxide group introduce a single three-way branch point into the network, each has a functionality of three. As a result, $f_{\mathrm{avg}} = 3$. Calculated values of M_c for the CENs prepared are listed in Table 2.

Table 2
Physical and mechanical properties of the CENs

CEN	Calc. M_c (g/mol)	Density (g/mL)	Fracture toughness K_{Ic} (MPa m$^{1/2}$)	Tensile properties	
				Tensile modulus (MPa)	Yield strength (MPa)
Phenolic-only CENs BA/THPE (mol)					
0.63	934	1.190	0.57	2336	75.4
1.75	1603	1.187	0.96	2452	70.4
4.00	2951	1.180	1.04	2449	69.9
8.60	5672	1.178	1.17	2729	71.1
%Equivalents excess epoxy, BA/THPE = 1.75					
5	1168	1.153	1.35	–	–
10	912	1.164	1.16	–	–
20	782	1.178	1.13	–	–
40	451	1.177	1.28	–	–
62	354	1.176	1.20	–	–
104	266	1.181	1.17	–	–
%Equivalents excess epoxy, BA/THPE = 4.00					
5	1648	1.124	1.70	3378	72.4
11	1170	1.137	1.38	–	–
20	799	1.160	1.19	–	–
41	500	1.179	1.17	–	–
60	389	1.177	1.46	3261	77.9
100	286	1.172	1.03	–	–

3.4. Thermal/mechanical characterization

Results of the thermal and thermomechanical analyses are listed in Table 3. The T_gs for these materials were measured

Table 3
Thermal and thermomechanical properties of the CENs

CEN	DSC	TMA			DMTA		TGA	
	T_g (°C)	T_g (°C)	CTE_g (ppm/°C)	CTE_r (ppm/°C)	T_g (°C)	G'_r (MPa), at $T_g + 40$ °C	T_d (°C)	Residue (%)
Phenolic-only CENs BA/THPE (mol)								
0.63	129	119	73	226	131	5.40	416	10.3
1.75	113	114	72	243	114	2.75	415	7.9
4.00	104	102	69	228	106	1.34	412	7.7
8.60	100	94	53	392	94	0.12	412	7.5
%Equivalents excess epoxy, BA/THPE = 1.75								
5	120	117	73	223	124	5.76	416	8.2
10	122	115	77	212	121	4.85	420	7.8
20	124	123	70	206	125	6.89	420	8.5
40	128	125	73	202	131	10.70	420	8.1
62	138	129	74	198	140	15.10	422	8.2
104	133	127	84	212	137	12.80	422	7.7
%Equivalents excess epoxy, BA/THPE = 4.00								
5	110	106	75	235	116	3.78	427	6.5
11	113	105	75	232	116	4.27	426	6.6
20	118	108	72	219	117	5.00	419	6.1
41	121	111	77	221	124	8.11	419	7.4
60	129	118	78	219	130	11.10	419	6.5
100	138	131	84	213	141	16.10	422	8.0

using three different techniques: DSC, TMA, and DMTA. Since the results are very consistent (Fig. 4) only the DSC results will be discussed in detail. First of all, no exotherms were observed in any of the DSC scans, indicating complete cure consistent with the absence of unreacted epoxides in the NMR spectra. The T_g values obtained from the second DSC scan are plotted against $1/M_c$ in Fig. 4a.

For the CENs from the phenolic-only series, T_g increases linearly with increasing crosslink density (increasing $1/M_c$). While the CENs containing excess epoxy exhibit the same general behavior, the slopes of the lines in Fig. 4 for the two series with varying amounts of excess epoxy (5.4 and 9.2 kg °C/mol for the series with varying amounts of excess epoxy with extender/hardener ratios of 1.75 and 4, respectively, based on the DSC measurements) are both significantly lower than the slope of the series with varying extender/hardener ratios (33.0 kg °C/mol). This difference is expected considering the greater rigidity of the THPE-derived crosslink junction compared to that formed by epoxy etherification and is consistent with results on stoichiometric epoxy thermosets having similar crosslink density but differing curing agent flexibility [24].

When plotted against $1/M_c$, G' in the rubbery region (G'_r) measured by DMTA falls on the same line for nearly every material evaluated, with the modulus increasing steadily with $1/M_c$ (Fig. 5). This behavior is consistent with an increase in material stiffness above T_g as the crosslink density increases. The only exception in this trend is for the excess epoxy sample having the lowest M_c. Note that this sample also has a slightly lower T_g compared to the previous sample in this series. These data can also be attributed to the greater flexibility of the excess epoxy network junctions, which in this sample have their greatest concentration relative to those from THPE.

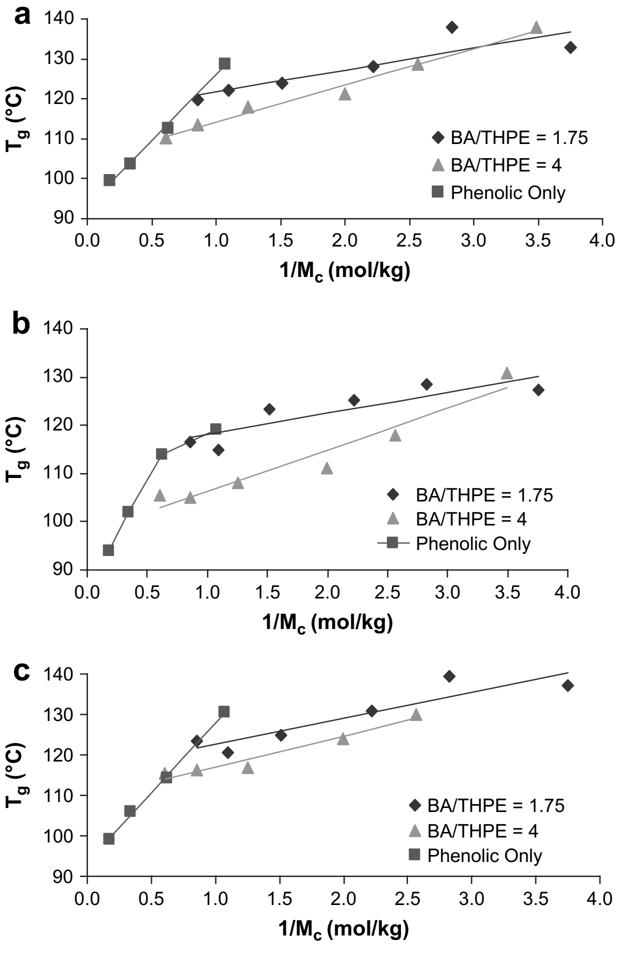


Fig. 4. Plots of T_g versus $1/M_c$ for data collected by (a) DSC, (b) TMA, and (c) DMTA.

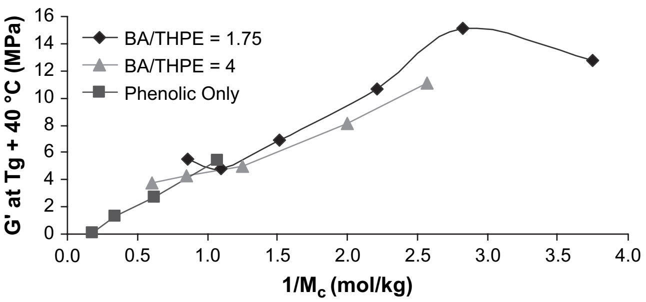


Fig. 5. G' of the CENs measured at $T_g + 40$ °C.

The phenolic-cured formulations also exhibit damping above T_g which increases in magnitude with increasing M_c, possibly due to network defects (pendant and sol fractions) arising from the small amounts of excess epoxy in these samples. The imidazole cured CENs prepared with excess epoxy show no damping in this region, an additional indicator of the high conversion of the excess epoxy present.

Examination of the tan δ curves from the DMTA experiments reveals one final point of interest concerning the T_gs of these materials. For the phenolic-only CENs, the breadth of the tan δ curves remains relatively constant across the range of M_cs evaluated (Fig. 6a). With the excess epoxy CENs, however, as the amount of excess epoxy in the formulation increases, the breadth of the T_g transition increases as well, although the area under the tan δ curves remains constant. An example of this is shown in Fig. 6b for one series. This behavior is not seen when M_c is varied by altering the extender/hardener ratio because of post-T_g damping as M_c decreases. The orderly increase in the width of tan δ in the imidazole catalyzed CENs likely indicates a broadening of the spatial distribution of crosslink density [23,25].

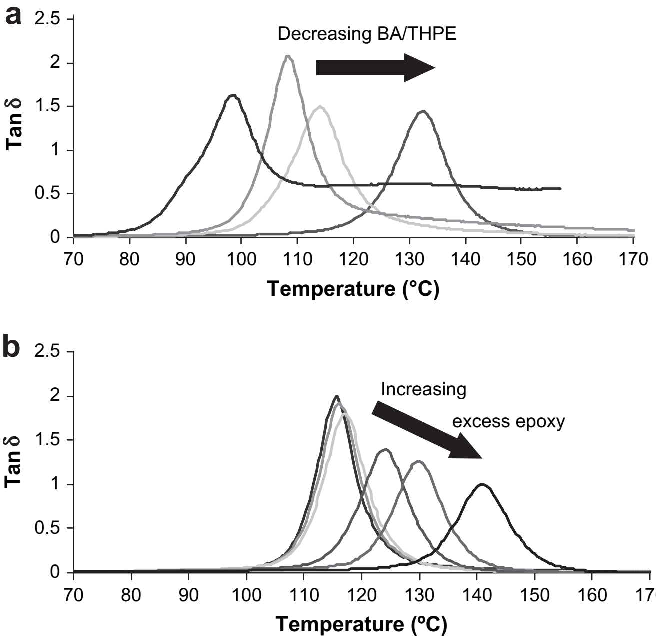


Fig. 6. The tan δ curves from DMTA for (a) the phenolic-only CENs and (b) the series of CENs with a bisphenol A/THPE ratio of 4. From left to right, the curves are for formulations containing (a) BA/THPE = 0.63, 1.75, 4.00, and 8.60, and (b) 5%, 11%, 20%, 41%, and 100% excess epoxy.

The T_d values for the CENs are consistently well above 400 °C (Fig. 7). Among the materials with higher M_c values, some small differences in T_d are observed between the CENs made with and without excess epoxy crosslinking, but the variations are very small with a maximum difference of less than 4%.

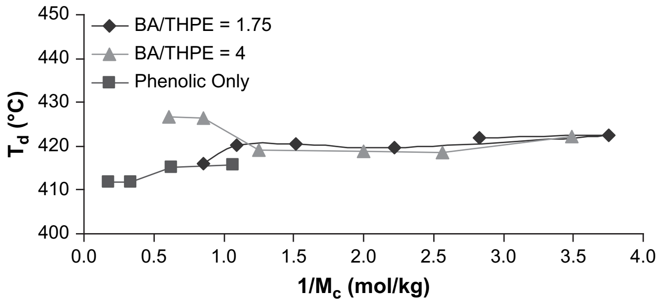


Fig. 7. Degradation temperature for the CENs tested by TMA.

With only one exception, for all of the networks tested the CTE for the materials in the glassy region ($T < T_g$, CTE$_g$) as measured by TMA demonstrate a very slight decrease with increasing M_c, ranging from 69 to 78 ppm/°C with no apparent trends (Fig. 8). The exception lay in the highest M_c sample from the phenolic-only series. This sample has a M_c significantly higher than any other in this study and exhibits a large drop in its CTE$_g$. In the rubbery region ($T > T_g$, CTE$_r$), aside from the same excepted network, the CTE$_r$ values tend to increase slightly with increasing M_c, ranging from 198 to 243 ppm/°C. In this series, though, the high M_c network has a much higher CTE$_r$ than the other thermosets.

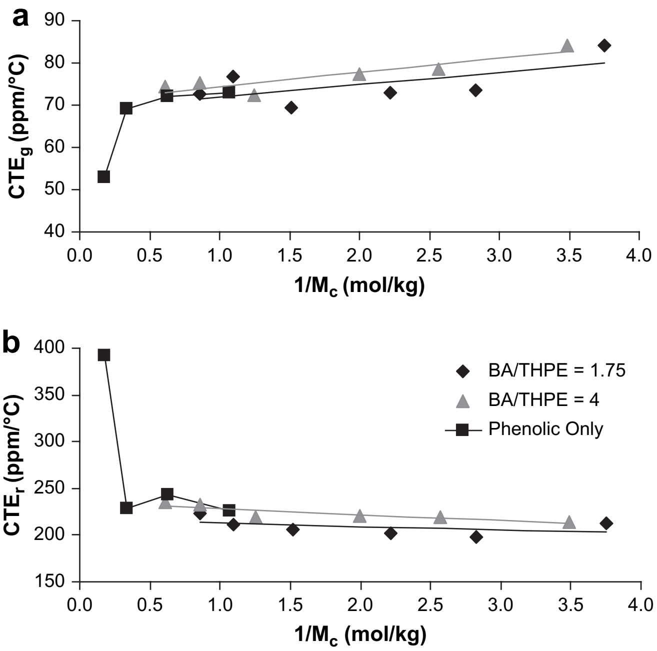


Fig. 8. CTE in the (a) glassy region and (b) rubbery region.

Fracture toughness testing of the CENs reveals one of the more interesting properties of the materials with epoxy etherification (Fig. 9). For the samples with M_c greater than ~1000 mol/g, the same trend is observed both with and without etherification: as the crosslink density increases, K_{Ic} decreases due to the increasing rigidity of the network [23]. The CENs with excess epoxy, though, have significantly greater fracture toughness than the CENs without etherification. We speculate that this could be a result of the increased free volume in these materials allowing more space for chain motions to accommodate the applied load.

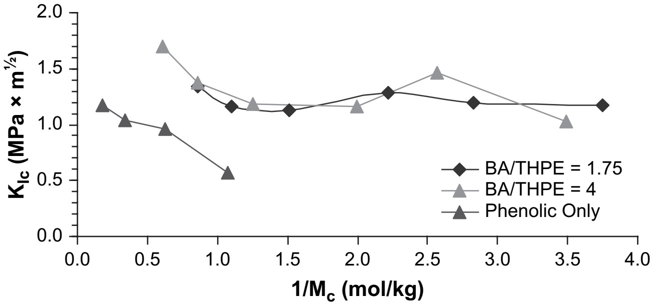


Fig. 9. Results of room temperature fracture toughness testing for CENs.

Density measurements of the networks listed in Table 2 further support this conclusion. Within each series, density increases with increasing crosslink density as might be expected with packing efficiency improving as the linear chain segments of the networks shorten (Fig. 10). In the networks with significant degrees of epoxy etherification, however, the ultimate density reached for the lowest M_c materials is slightly lower than that for the networks where the extender/hardener ratio is used to vary the crosslink density, and for a given M_c, there can be substantial differences in density, especially when M_c is high. These results offer further support that curing with a combination of phenolic hardeners and etherification creates a network with more free volume than when the resin is cured with phenolics alone. Furthermore, an experiment with one of the less dense CENs (BA/THPE = 4, 5% excess epoxy) yielded preliminary evidence that these materials can be densified under pressure at temperatures near T_g. In this sample, a pressure of 80 psi was applied to the 1/8″ plaque at 120 °C for 1 h which resulted in a material with a density nearer to that of the phenolic-only CENs, 1.190 g/mL. An identical experiment on a more dense CEN in this series (BA/THPE = 4, 60% excess epoxy) resulted in only a very small increase in density, from 1.177 to 1.185 g/mL.

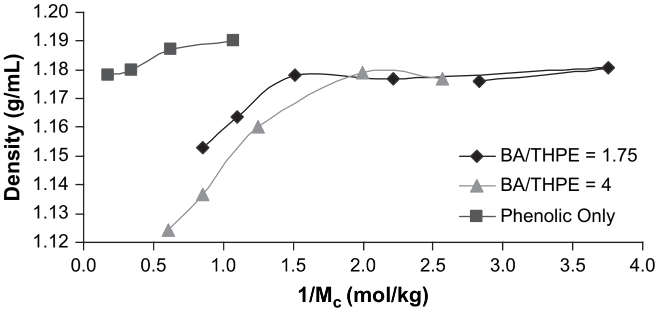


Fig. 10. Densities of the epoxy networks.

For the lower M_c networks, the K_{Ic} values level at a relatively high value near 1.0 MPa $m^{1/2}$. Closer inspection of both the fracture data and the broken pieces themselves revealed evidence for some degree of ductile yielding prior to fracture. Typically, materials with high crosslink densities such as these are extremely brittle, having low values of K_{Ic}. With these materials, this embrittlement is not observed. To further probe the apparent improved ductility of these epoxy thermosets, tensile testing was performed on selected samples – the phenolic-only CENs and the CENs at either extreme of the M_c range for the series with an extender/hardener ratio of 4. For the phenolic-only samples, the tensile modulus demonstrate an unexpected slight increase with increasing M_c, the opposite of the trend typically observed for glassy thermosets [23]. The stress–strain curves for these CENs are shown in Fig. 11. One likely explanation is that as M_c increases in these materials, secondary interactions such as inter-chain hydrogen bonding, dipolar interactions, and entanglement of the thermoset backbone become stronger.

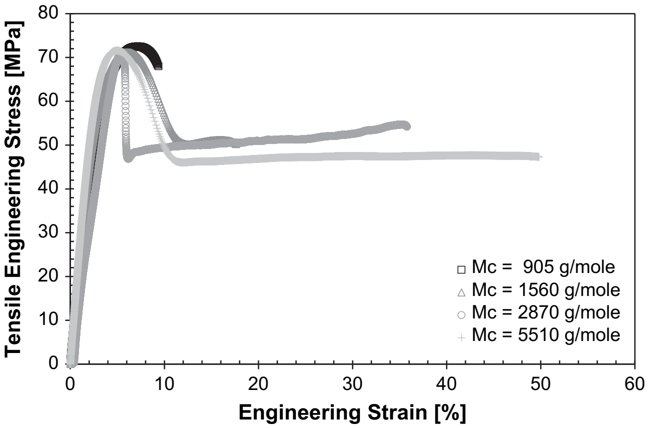


Fig. 11. Tensile behavior of the phenolic-only CENs at room temperature.

The stress–strain curves for the excess epoxy samples are shown in Fig. 12. For the high M_c network (with 5% excess epoxy in the formulation) the material exhibits typical yielding behavior under tension and a tensile modulus greater than any of the phenolic-only materials. For the network with a M_c of 389 (60% excess epoxy), the expected behavior would be for the material to fracture well prior to the yield point. A yield point is observed, however, with a slight necking just prior to fracture. This material also has a modulus greater than the phenolic-only CENs as well as higher yield strength. This behavior, unexpected in a network so tightly crosslinked and contrary to the yielding behavior of typical epoxy thermosets [23], confirms the ductility observed in the fracture toughness analyses. With crosslinks due to a combination of hardener and etherified resin, the toughness of the materials is significantly higher than materials with only phenolic curing and there is a degree of ductility at low M_c completely absent in the phenolic-cured networks.

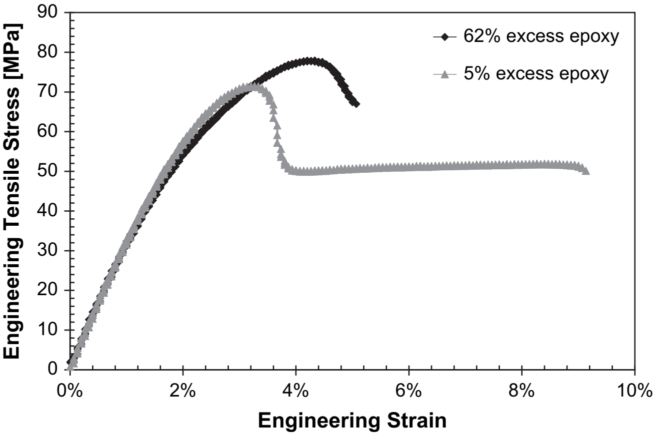


Fig. 12. Tensile behavior of selected samples with a BA/THPE ratio of 4 at room temperature.

4. Conclusions

The structure–property relationships of a series of new epoxy thermosets prepared from a combination of phenolic extender and hardener and a stoichiometric excess of fully reacted epoxy resin show unexpected trends in their thermal and mechanical properties compared to analogous thermosets prepared from the phenolic extender and hardener alone. Complete conversion of the excess epoxy resin was achieved using an imidazole catalyst and was quantified by a novel solvent-swollen NMR method. Reaction of the excess epoxy resin increases the crosslink density of the thermosets in proportion to the amount used (5–100 equivalent%). T_g generally increases with increasing crosslink density but to a maximum level dictated by the relative flexibility of the excess epoxy crosslink junction. This leveling behavior in thermal properties is also evidenced by DMTA. Glassy properties are markedly affected by excess epoxy etherification. Fracture toughness and tensile yielding are significantly improved compared to the phenolic-only analogs at the same crosslink density. This remarkable result is attributed to increased free volume introduced by virtue of the etherification reaction as evidenced by their lower bulk density.

Increasing crosslink density by excess epoxy etherification is surprisingly shown to improve both the heat resistance and fracture toughness of phenolic-cured epoxy thermosets. With these new structure–property relationships new epoxy thermoset formulations may be developed having significantly improved performance. Further studies on the structure–property relationships of related and other non-idealized types of epoxy thermosets are in progress.

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References

[1] Ellis B, editor. Chemistry and technology of epoxy resins. London: Blackie Academic and Professional; 1993.
[2] Pham HQ, Marks MJ. Epoxy resins, encyclopedia of polymer science and technology. New York: John Wiley and Sons, Inc.; 2004.
[3] Hale A, Macosko CW, Bair HE. J Appl Polym Sci 1989;38:1253.
[4] Gagnebien D, Madec PJ, Maréchal E. Eur Polym J 1985;21:273.
[5] Son PN, Weber CD. J Appl Polym Sci 1973;17:2415.
[6] Alvey FB. J Appl Polym Sci 1969;13:1473.
[7] Dušek K, Bleha M. J Polym Sci Polym Chem Ed 1977;15:2393.
[8] Wolff D, Schlothauer K, Tänzer W, Fedke M, Spèvácek J. Polymer 1991;32:1957.
[9] de Bakker CJ, St. John NA, George GA. Polymer 1993;34:716.
[10] Vazquez A, Ilavsky M, Dusek K. J Appl Polym Sci 1999;74:2877.
[11] Williams JG, Delatycki O. J Polym Sci Part A-2 1972;19:1297.
[12] Halary JL. High Perform Polym 2000;12:141.
[13] Won Y, Galy J, Gerard J-F, Pascault J-P, Bellenger V, Verdu J. Polymer 1990;31:1787.
[14] Charlesworth JM. Polym Eng Sci 1988;28:230.
[15] Heise MS, Martin GC, Gotro JT. J Appl Polym Sci 1991;42:1557.
[16] Chen W-Y, Wang Y-Z, Chang F-C. J Appl Polym Sci 2004;92:892.
[17] Ngono-Ravache Y, Foray M-F, Bardet M. Polym Adv Technol 2001;12:515.
[18] Tavares MIB, D'Almeida JRM, Monteiro SN. J Appl Polym Sci 2000;78:2358.
[19] Fischer A, Schlothauer K, Pfitzmann A, Spèvácek J. Polymer 1992; 33:1370.
[20] Schadt RJ, VanderHart DL. Macromolecules 1995;28:3416.
[21] Fry CG, Lind AC. Macromolecules 1988;21:1292.
[22] Shih W-C, Ma CM. J Appl Polym Sci 1999;73:2369.
[23] Lesser AJ, Crawford E. J Appl Polym Sci 1997;66:387.
[24] Pascault J-P, Sautereau H, Verdu J, Williams RJJ. Thermosetting polymers. New York: Marcel Dekker, Inc; 2002 [chapters 10–12].
[25] Nielsen LE. Mechanical properties of polymers and composites, vol. 1. New York: Marcel Dekker, Inc; 1974.