

Highly ductile glassy epoxy systems obtained by network topology modification using partially reacted substructures

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ABSTRACT

A strategy for toughening epoxy thermosets via topological rearrangement of cross-linked networks is presented. Amine-cured epoxy systems were modified by mixing partially reacted substructures (mPRS), which were synthesized by partially curing tetraglycidyl ether of diaminodiphenylmethane (TGDDM) and polyether monoamine (Jeffamine M1000) to provide free unbound surfaces that enhance protovoid formation during deformation. The influence of mPRS conversion and weight ratio on the properties of diglycidyl ether of bisphenol A (DGEBA) and TGDDM systems cured with Jeffamine D230 was investigated. Adding mPRS resulted in high T_g systems capable of exceptional strain at failure in tension: 43% for the DGEBA ($T_g = 75^\circ\text{C}$) and 20% for the TGDDM ($T_g = 135^\circ\text{C}$). The addition of mPRS, however, decreases T_g relative to unmodified systems. SEM and SAXS characterization provide evidence of protovoid (18–34 nm) formation. Quasi-static compressive tests conducted at testing temperatures selected to maintain a constant ($T_g - T_{\text{test}}$) reveal the protovoid opening mechanism plays a dominant role in enhanced ductility.

1. Introduction

Epoxy resins are an important class of thermoset polymers with wide industrial applications, including matrix materials for structural composites, protective coatings, and adhesives. Epoxy thermosets have excellent mechanical properties and good thermal and chemical stability due to their highly cross-linked networks; however, the cross-linked structure also makes epoxies intrinsically brittle. To counter this brittleness, the major toughening strategies have focused on incorporating secondary additives. The additives can be divided into two main categories: soft toughening particles [1–3] and rigid nanofillers [4–6].

Recently, a series of coarse-grained molecular simulations conducted by Mukherji et al. suggested that a void-growth mechanism in highly-crosslinked thermosets could be used to improve the ductility of polymer without sacrificing mechanical properties such as tensile strength and Young's modulus [7–9]. Based on these simulation results, an epoxy toughening method was proposed by Sharifi et al. wherein molecular surfaces were created within a highly-crosslinked epoxy system by curing the epoxy system in the presence of dichloromethane [10]. Upon thermally removing the solvent, surfaces previously in contact with the solvent form collapsed voids, termed protovoids. These modified systems exhibit significantly greater degrees of plastic deformation than

similar epoxies cured without solvent, but unlike other toughening methods, the properties of the material such as Young's modulus, tensile yield strength, and glass transition temperature were not affected. These studies revealed that the protovoid opening mechanism allowed the glassy material to dissipate more energy and deform more under loading; however, due to the presence of organic solvent during the curing process and an additional drying step, this method is not practically useful.

In order to circumvent processing challenges associated with the use of solvents, another processing method was developed by Sharifi et al., wherein partially reacted substructures (PRS) were incorporated into a reacting epoxy mixture, to create the protovoids without the use of solvent [11]. The PRS was synthesized by reacting standard epoxy monomers with long-chain diamine. The long-chain diamines were expected to reduce the crosslink density locally, thus mimicking collapsed voids. The results showed the PRS modification toughened the epoxy system but did not increase plasticity, as observed in the solvent-based systems. It was suggested that the long-chain diamines used in the PRS were connected covalently at both ends, reducing the ability of the system to generate free molecular surfaces upon loading. Based on this hypothesis, Sharifi et al. [12,13] proposed and tested a new partially reacted substructure for toughening that used long-chain monoamine

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molecules in the epoxy system instead.

The use of mPRS creates local concentrations of chain ends that are not covalently bound to the network. When deformed, these chain ends are expected to easily separate, effectively forming protovoids within the network that increase plasticity. Thus, assuming that unbound molecular surfaces are a key factor that affects the ductility of thermosets, then the size and the weight ratio of such molecular surfaces would be controlling factors influencing behavior. Fig. 1 shows schematically two cases that illustrate this point. If the soluble long-chain monoamine is directly added into the epoxy system, it will disperse and cure uniformly into the system, represented in Fig. 1a. However, if the monoamine and epoxy are first partially reacted to some degree of polymerization and this mPRS is added into the epoxy system, the long-chain monoamine

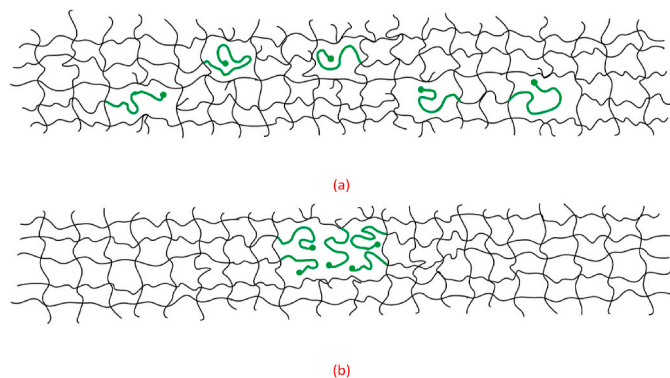


Fig. 1. Polymer network structures of (a) the 0% reacted mPRS system, and (b) the partially reacted mPRS modified system.

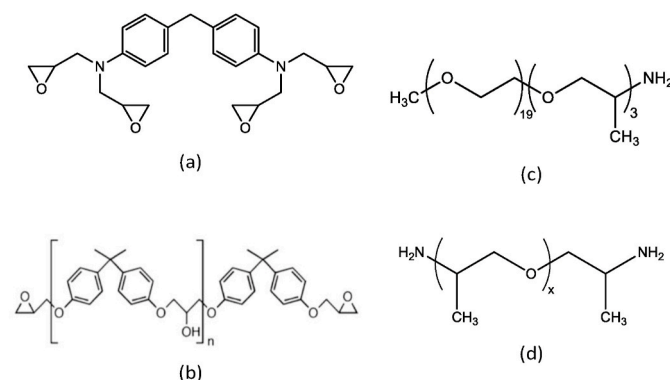


Fig. 2. Chemical structures of epoxy and amine used in this study. (a) tetraglycidyl ether of diaminodiphenylmethane (TGDDM), (b) Diglycidyl ether of bisphenol A (DGEBA EPON 828 $n \approx 0.1$), (c) Polyether monoamine (Jeffamine M1000, MW ≈ 1000 g/mol), (d) Poly(propylene oxide) diamine (Jeffamine D230, MW ≈ 230 g/mol, $x \approx 2.5$).

can be localized to form larger unbound molecular surfaces as shown in Fig. 1b. Note that in such systems, the overall chemical composition of the two systems is the same but the spatial distributions of the long-chain monoamine molecules differ greatly. Thus, using the same chemical composition, it is possible to create networks with different topologies, which we call network isomers.

In this work, we continue to investigate the toughening of epoxy via the rearrangement of network topology using the mPRS approach. In particular, the influence of mPRS conversion, mPRS weight ratio, and temperature on mechanical behavior will be evaluated and compared for two base epoxy systems, each with a different average cross-link density.

2. Experimental

Materials. The molecular structures of the materials used in this study are shown in Fig. 2. Two epoxy resins used were diglycidyl ether of bisphenol A (DGEBA EPON 828) obtained from Miller-Stephensen and tetraglycidyl diaminodiphenylmethane (TGDDM) obtained from Sigma-Aldrich. Poly(propylene oxide) diamine Jeffamine D230, with approximately 2.5 propylene oxide units along the backbone was provided by Huntsman Corporation and used as the primary curing agent. Polyether monoamine Jeffamine M1000 was also provided by Huntsman Corporation and used to prepare the mPRS. The ratio of propylene oxide to ethylene oxide in M1000 is about 3–19 (manufacturer).

Preparation and characterization of mPRS. The modifying agent mPRS was prepared by partially reacting a stoichiometric mixture of TGDDM and Jeffamine M1000 to a controlled degree of conversion. A stoichiometric mixture of TGDDM and Jeffamine M1000 was prepared. Jeffamine M1000 is solid at room temperature, so it was melted at 50 °C before being added to the TGDDM. The preheated Jeffamine M1000 and TGDDM were then mixed at 80 °C until a transparent mixture was obtained. Then, the mPRS mixture was further stirred and heated at 80 °C in an oil bath until the desired conversion of epoxy was achieved.

To monitor the degree of reaction of the mPRS, Fourier transform infrared spectroscopy (FTIR) was used in the near-IR region. Fig. 3 shows the FTIR spectra of the mPRS resins over a period of 2500 min. By quantifying the peak height at 4520 cm^{-1} that corresponds to the stretching and bending of the oxirane ring, a plot of fractional epoxy conversion as a function of time was constructed and is shown in Fig. 4. The molecular weight distribution of mPRS was evaluated using a Waters ACQUITY Gel Permeation Chromatograph (GPC) equipped with two sub-3- μm ethylene bridged hybrid (BEH) particle packed columns with 45 Å pore size in series. The column effluent was monitored using two detectors: A UV/Visible detector operating at 315 nm and a refractive index (RI) detector. DMF containing 10 mM LiBr was used as the mobile phase at a flow rate of 0.3 ml/min. Samples (1.5 mg) were dissolved in DMF (10 mM LiBr) solution (2 mL) and filtered before being injected into the column operating at 60 °C. The total running time for each sample was 20 min.

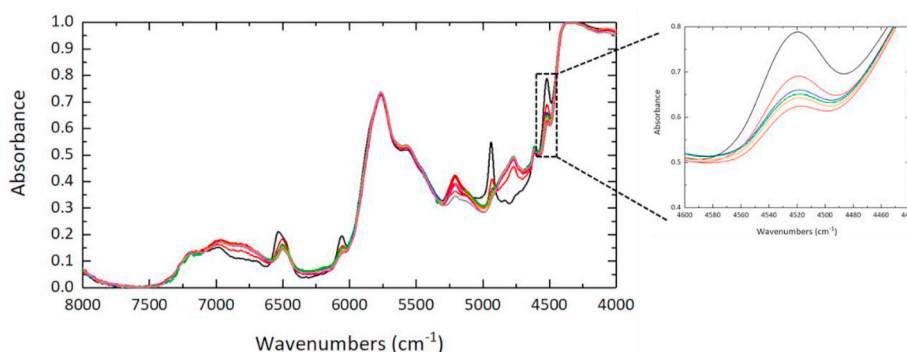


Fig. 3. FTIR spectra (near IR) of the mPRS resins at 80 °C over a period of 2500 min.

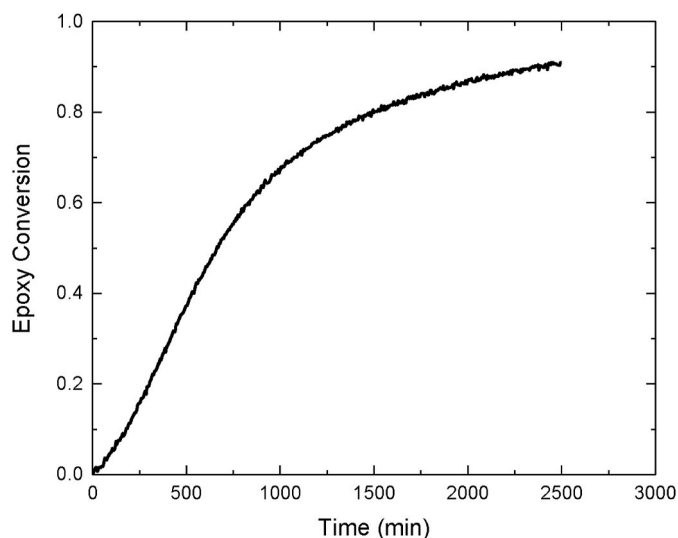


Fig. 4. The degree of polymerization of the mPRS resins. The reaction temperature was held at 80 °C.

mPRS synthesis at 75% conversion (mPRS-75) was used to investigate the influence of network topology on protovoids formation and the mechanical behavior of thermosets. At this conversion, the material still flows but should contain significant branching as well as unreacted sites for reaction into the network. For comparison, 0% conversion mPRS (mPRS-0), i.e., the unreacted stoichiometric mixture of TGDDM and M1000 was also evaluated.

Sample preparation and cure. The polymers were prepared by mixing stoichiometric blends, i.e., one epoxy per amine hydrogen, of TGDDM or DGEBA with Jeffamine D230 and mPRS at various weight ratios. To investigate the influence of mPRS structures on mechanical behavior, mPRS-0 and mPRS-75 were added to the epoxy systems. The resins were well mixed and degassed using a centrifugal mixer, cured at 80 °C for 24 h, and post-cured at 160 °C for 3 h. Adhering to the reaction temperature schedule is important since it has been reported that for epoxy-amine systems the relative rate of primary amine-epoxy and secondary amine-epoxy reactions depends on temperature [14]. This suggests that changing temperature could affect network topology and the interest herein is to evaluate the influence of mPRS on network topology and mechanical behavior. In addition to the samples cured with mPRS-0 (mPRS-control) and mPRS-75 (mPRS-modified), the unmodified systems (blank) were also prepared and tested.

Tensile testing. To investigate the influence of mPRS on mechanical behavior, quasi-static tensile testing was performed on two different crosslink density epoxy systems: low crosslink density DGEBA 828 system and high crosslink density TGDDM system. Testing was conducted according to ASTM D638-14. For each system, six dog-bone shape specimens were prepared using silicone rubber molds and were well polished before testing. Each specimen had an average thickness of 1.7 mm, an average width of 3.8 mm, and a gauge length of 25 mm. The quasi-static tensile test was carried out using a servo-hydraulic INSTRON 8872 with a 1 kN load cell, at a crosshead speed of 1 mm/min. Two 2716-015 wedge action tensile grips with flat serrated faces were used to prevent specimen slippage. A dynamic extensometer with 12.5 mm gauge length was used to obtain tensile Young's modulus, the values were determined within the first 1% strain.

Compressive testing. In order to investigate the influence of mPRS and temperature on mechanical behavior, the quasi-static compressive testing was performed on the TGDDM system. Testing was conducted according to ASTM D695-15. For each system, resin plates were prepared using glass molds and six cylindrical specimens were obtained by core drilling the plates. Each specimen had an average thickness of 5 mm, an average diameter of 5 mm. Quasi-static compressive testing was

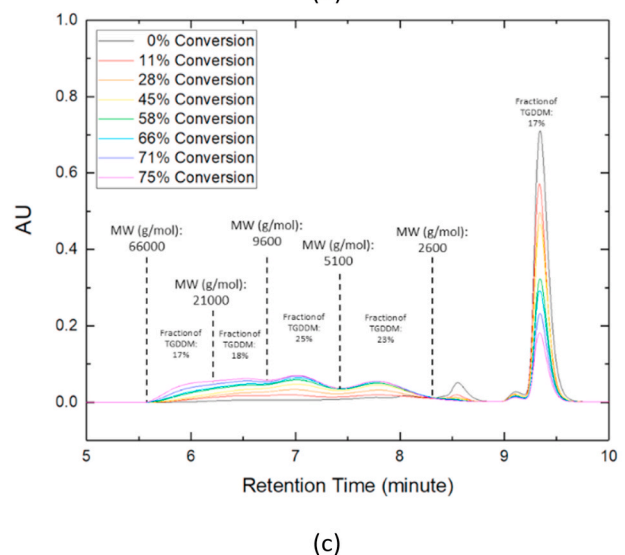
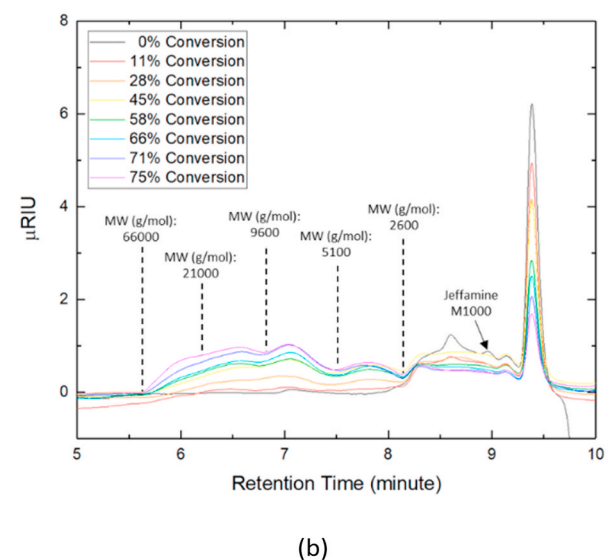
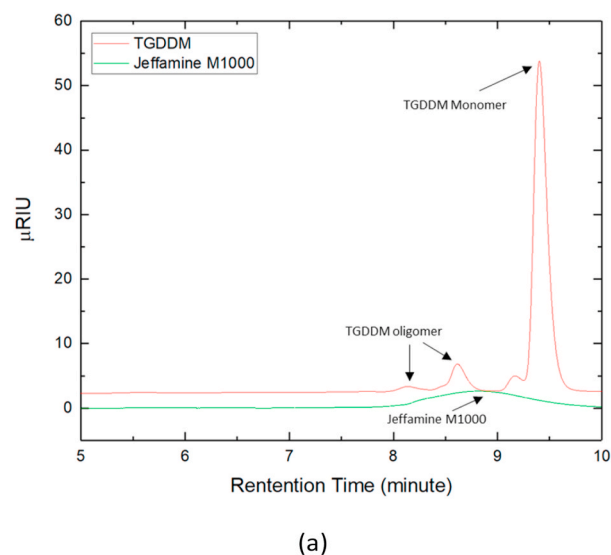


Fig. 5. (a) GPC RI traces of TGDDM and Jeffamine M1000, (b) GPC RI traces of the mPRS mixtures from 0 to 75% conversion, and (c) GPC UV traces of the mPRS mixtures from 0 to 75% conversion.

carried out using an INSTRON 5985 with a 250 KN load cell. An environmental chamber was used to control the testing temperature. All compressive tests were performed using 0.001/s strain rate.

Small angle X-ray scattering (SAXS). X-ray scattering measurements were performed using a Rigaku SMAX-3000 with a MicroMax-002 sealed tube x-ray source operated at 45 kV and 0.88 mA. Cu-K α radiation is generated with a wavelength of 0.154 nm. A gas filled proportional type detector collects scatter that is 200 mm in diameter with a 20- μ m resolution. The SMAX-3000 environment is 3 m long and is fully evacuated prior to sample exposure. The beam focal spot is 20 μ m $\times$ 20 μ m. Samples are placed in a holder mounted to a X-Y scanning motor, allowing for precise 2D sample mapping. The scattering vectors that can be collected range from 0.0067 to 0.16 $\text{\AA}^{-1}$. Silver behenate is used to calibrate for the small-angle measurements. The 2D WAXS patterns obtained were analyzed using the Datasqueeze software package.

Scanning electron microscopy (SEM). The high-resolution micrographs were taken with a Zeiss Supra 50VP equipped with an in-lens imaging detector. The fractured surface of the samples was platinum sputtered for 15 s prior to imaging.

Dynamic mechanical analysis (DMA). A TA instrument Q800 DMA apparatus was used to measure the viscoelastic properties and T_g of the cured systems. All specimens were tested at a constant frequency of 1 Hz. The oscillation amplitude was kept at 10 μ m in single-cantilever mode. All samples were cast in silicone rubber molds and then sanded into rectangular slab geometry (35–36 mm in length, 10–12 mm in width, and approximately 3 mm in thickness). The test was conducted with a scanning rate of 2 $^{\circ}\text{C}/\text{min}$ starting from -100°C to 200°C to obtain sufficient data below and above the glass transition temperature. The crosslink density, ν , was calculated using the following equation:

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

where E' is storage modulus at T_g (loss modulus) + 50 $^{\circ}\text{C}$, R is the gas constant and $T = T_g + 50$ is the absolute temperature.

3. Results and discussion

3.1. Molecular weight distribution of mPRS resins

Fig. 5a shows the GPC RI traces of TGDDM and Jeffamine M1000. Fig. 5b shows the GPC RI traces of mPRS mixtures corresponding to different stages of reaction identified by the epoxy conversion, ranging from 0% to 75% conversion. Fig. 5c contains the corresponding traces obtained using the UV detector. In the chromatogram shown in Fig. 5a, the main TGDDM monomer peak is found at 9.31 min, two smaller TGDDM oligomer peaks are also observed at 8.04 min and 8.53 min. The Jeffamine M1000 shows a broad peak at 8.78 min. Fig. 5b and c shows that the TGDDM peaks decreased with the epoxy conversion. In both RI and UV chromatographs, several broad peaks were identified at higher conversions. These peaks are delineated by local minima and were found in the following ranges: from 5.63 min to 6.18 min, from 6.18 min to 6.78 min, from 6.78 min to 7.47 min, and from 7.47 min to 8.36 min. These peaks develop and increase in intensity as conversion increases and represent the main products of mPRS at higher degrees of conversion. Based on polystyrene standard calibrations, the molecular weight (MW) ranges corresponding to these four main product peaks were 66,000–21,000 g/mol, 21,000–9600 g/mol, 9600–5100 g/mol, and 5100–2600 g/mol, which are shown in Fig. 5b and c. Integration of the UV chromatographs shows that at 75% conversion, the fractions of TGDDM associated with these peaks are 17%, 18%, 25%, 23%, respectively, with the remaining 17% attributed to completely unreacted TGDDM. Interestingly, the oligomeric TGDDM impurities are not present at this stage. Assuming an average repeat unit of mPRS consists of 1/2 TGDDM molecule and 1 Jeffamine M1000 molecule ($MW_{\text{repeat}} = 1211$ g/mol), then we would have roughly 23% mPRS with 2–4

Jeffamine M1000 chains, 25% mPRS with 4–8 chains, 18% mPRS with 8–17 chains, and 17% mPRS with 17–55 chains. Because of the tetra-functional nature of TGDDM, the mPRS molecules will be highly branched. In addition to differences in the chemical composition of mPRS relative to polystyrene, polymer architecture also needs to be taken into account when estimating MW. Overall, the polystyrene calibration most likely underpredicts the molecular weight of mPRS. Note that the radius of gyration of 66 k MW polystyrene in a good solvent like THF is 10.5 nm [15] and that DMF is a better solvent. Using the polystyrene MW analysis, the minimum size of mPRS in an un-swollen state ranges from 1 to 5 nm diameter (the density of mPRS was taken as 1100 kg/m^3). It is likely that when mPRS-75 is mixed with epoxy resin that substructures on the order of 10 nm with a significant size distribution will be incorporated.

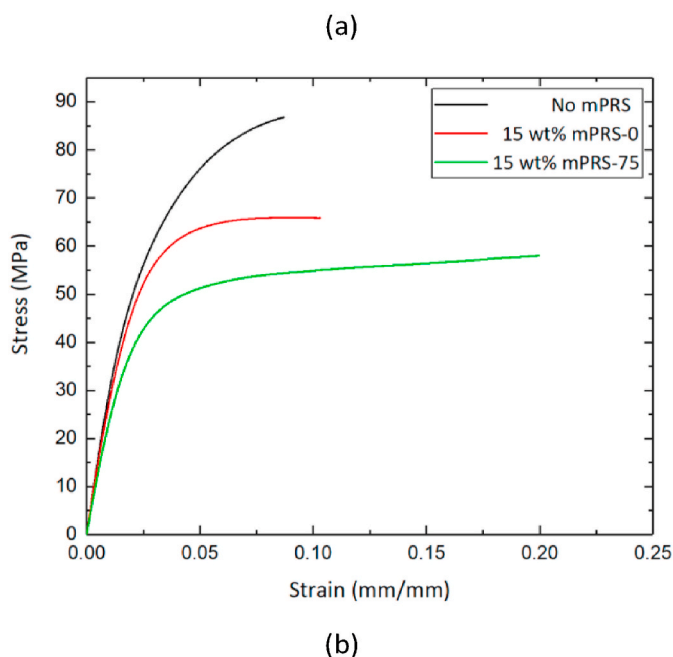
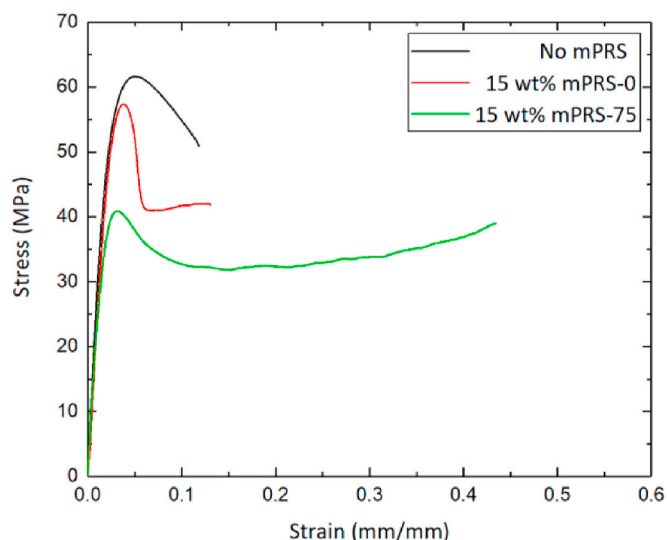
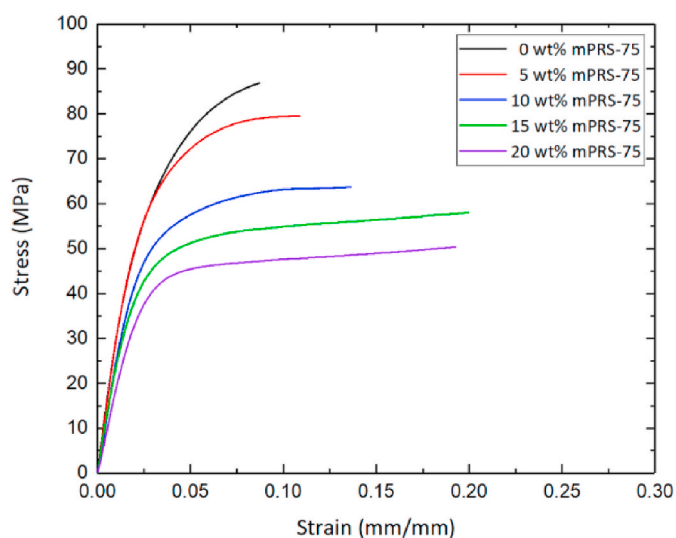


Fig. 6. Representative stress-strain curves of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) (a) DGEBA-D230 system and (b) TGDDM-D230 system.

Table 1Tensile properties and T_g of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) DGEBA-D230 system and TGDDM-D230 system.

mPRS Content	Young's Modulus E (GPa)	Yield Strength σ_Y (MPa)	Failure Strength σ_F (MPa)	Failure Strain ϵ_F (%)	T_g (Loss Modulus) ($^{\circ}$ C)	T_g (Tan Delta) ($^{\circ}$ C)	Crosslink Density (mol/m ³)
DGEBA-D230 System							
No mPRS	2.67 $\pm$ 0.02	60.9 $\pm$ 1.1	49.5 $\pm$ 1.1	11.5 $\pm$ 0.2	87	95	1400
15 wt% mPRS-0	2.54 $\pm$ 0.04	59.0 $\pm$ 1.5	42.9 $\pm$ 1.4	13.9 $\pm$ 4.7	61	73	1600
15 wt% mPRS-75	1.69 $\pm$ 0.11	38.9 $\pm$ 1.5	39.5 $\pm$ 1.2	42.8 $\pm$ 3.3	63	75	1400
TGDDM-D230 System							
No mPRS	2.94 $\pm$ 0.07	83.4 $\pm$ 1.0	86.3 $\pm$ 0.6	8.7 $\pm$ 0.8	142	155	5400
15 wt% mPRS-0	2.63 $\pm$ 0.02	65.2 $\pm$ 0.8	65.2 $\pm$ 0.5	10.3 $\pm$ 2.8	100	126	4400
15 wt% mPRS-75	2.25 $\pm$ 0.06	53.8 $\pm$ 0.6	57.6 $\pm$ 1.5	20.0 $\pm$ 1.6	105	135	4100

**Fig. 7.** Representative stress-strain curves of mPRS-75 (modified) at different weight ratios in the TGDDM-D230 System.

3.2. Quasi-static tensile properties

Influence of mPRS conversion at the same weight ratio. For the purpose of this discussion, the unmodified resin system is referred to as “blank”, the system modified with mPRS-0 is referred to as “mPRS-control,” and the system with mPRS-75 is referred to as “mPRS-modified”. Fig. 6 shows the representative quasi-static tensile stress-strain curves of blank, 15 wt% mPRS-control, and 15 wt% mPRS-modified (a) DGEBA 828-Jeffamine D230 systems and (b) TGDDM-Jeffamine D230 systems. These curves show clearly that mPRS conversion influences the ductile behavior of both systems. Higher conversion results in a more ductile system. These curves also show that adding mPRS

reduces yield strength significantly. Table 1 contains tensile Young's modulus, yield strength, failure strength, failure strain, T_g obtained by loss modulus and tan delta, and crosslink density for all these systems.

For both epoxy systems, the blank system possesses the highest yield strength, Young's modulus, failure stress, and T_g , but it also possesses the lowest failure strain. Adding the mPRS increases failure strain but reduces T_g and yield strength in both cases. It is interesting to note that the mPRS-control and the mPRS-modified systems have a similar T_g for the DGEBA-based system and that the mPRS-modified system has a slightly higher T_g for the TGDDM-based networks. The mPRS-control and mPRS-modified systems can be considered network isomers since their chemical compositions are identical but their network topology differ based on the sequence of reactions (see Fig. 1). Yet, there is a clear difference in the deformation behavior of these two mPRS systems. The mPRS-modified DGEBA system exhibits a 270% increase in failure strain as a result of necking. Necking was not observed for the TGDDM systems, nevertheless, failure strain was enhanced by roughly 130% for the mPRS-modified TGDDM system. The mPRS-modified systems reveal lower yield strength, Young's modulus, and failure stress. The results suggest that controlling the placement of long-chain monoamine within the network using partially reacted substructures results in materials with exceptional plasticity while preserving T_g . However, a concomitant decrease in yield strength and glassy modulus was observed.

Influence of mPRS weight ratio. Results of the previous section showed that the inclusion of mPRS-75 resulted in significant ductility enhancement. It was also clear that yield strength and T_g are reduced when the mPRS is added. Therefore, understanding the influence of mPRS weight ratio on performance is important to be able to balance performance characteristics like modulus, yield strength, and T_g against ductility and toughness. The influence of mPRS ratio was evaluated on the mPRS-75. Fig. 7 shows representative quasi-static tensile stress-strain curves of the mPRS-75 at 0%, 5%, 10%, 15%, and 20% weight ratios in the TGDDM system. Table 2 contains the tensile Young's modulus, yield strength, failure strength, failure strain, T_g obtained by loss modulus and tan delta, and crosslink density for all these mPRS-

Table 2Tensile properties and T_g of mPRS-75 at different weight ratios in the TGDDM-D230 System.

mPRS Weight Ratio	Young's Modulus E (GPa)	Yield Strength σ_Y (MPa)	Failure Strength σ_F (MPa)	Failure Strain ϵ_F (%)	T_g (Loss Modulus) ($^{\circ}$ C)	T_g (Tan Delta) ($^{\circ}$ C)	Crosslink Density (mol/m ³)
0 wt% mPRS-75	2.94 $\pm$ 0.07	83.4 $\pm$ 1.0	86.3 $\pm$ 0.6	8.7 $\pm$ 0.8	142	155	5400
5 wt% mPRS-75	2.89 $\pm$ 0.04	77.3 $\pm$ 1.7	79.5 $\pm$ 1.2	10.8 $\pm$ 0.5	134	142	5800
10 wt% mPRS-75	2.54 $\pm$ 0.05	64.2 $\pm$ 1.0	64.1 $\pm$ 1.7	13.6 $\pm$ 0.3	120	139	4800
15 wt% mPRS-75	2.25 $\pm$ 0.06	53.8 $\pm$ 0.6	57.6 $\pm$ 1.5	20.0 $\pm$ 1.6	105	135	4100
20 wt% mPRS-75	1.82 $\pm$ 0.08	45.4 $\pm$ 0.3	50.9 $\pm$ 2.0	19.2 $\pm$ 2.3	96	123	3400

modified systems.

As shown in Fig. 7 and Table 2, increasing mPRS weight ratio up to 15 wt% increases failure strain from 9% to 20%. However, decreases in Young's modulus, yield strength, failure strength, and T_g are also observed. It also appears that ductility gains diminish above 15 wt% as the 20 wt% mPRS-modified system shows similar elongation at break to the 15 wt% case. Thus, the addition of more mPRS into the epoxy system does not always result in improved performance. The 15 wt% mPRS-modified system shows the highest energy absorption, calculated as the area under the plastic deformation curves. It also has the highest energy absorption and a relatively high T_g .

3.3. Quasi-static compressive properties

Influence of mPRS conversion at the same weight ratio. Results of the previous sections showed the influence of mPRS on the quasi-static tensile properties, but studying the compressive behavior of these polymer systems can provide a better understanding of yielding behavior as it reduces the influence of specimen polishing and eliminates necking, making it easy to study true strain behavior. Therefore, quasi-static compressive tests were also performed on TGDDM-D230-mPRS systems. Fig. 8 shows the representative quasi-static true compressive stress-strain curves of blank, 15 wt% mPRS-control, and 15 wt% mPRS-modified TGDDM-Jeffamine D230 systems. The true stress and true strain were converted from engineering stress and engineering strain based on equations (1) and (2).

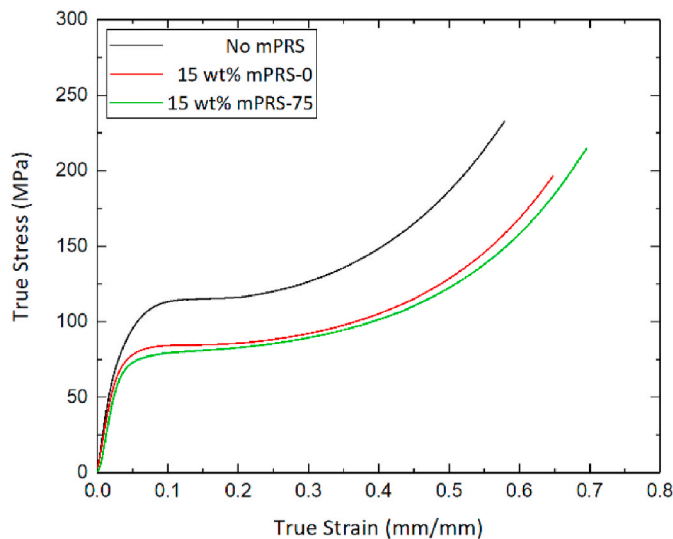
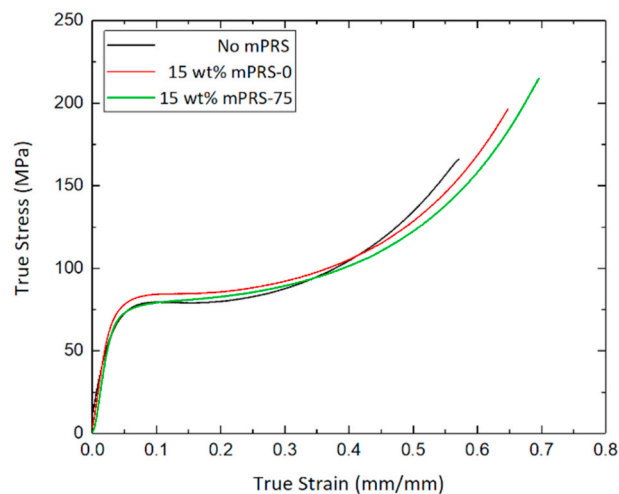


Fig. 8. Representative true compressive stress-strain curves of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) TGDDM-D230 system.

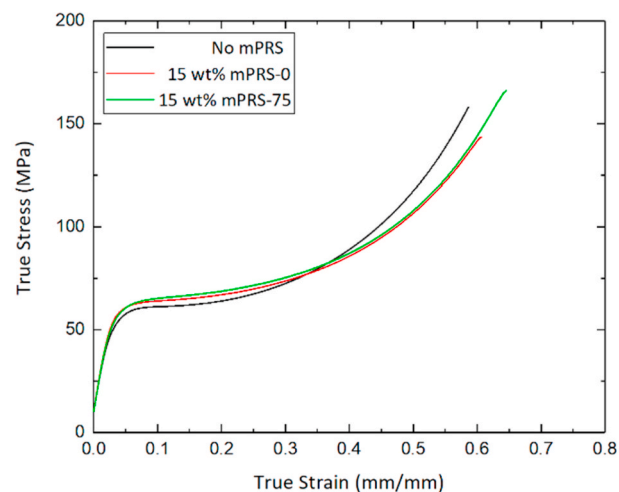
Table 3

True compressive properties of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) TGDDM-D230 system.

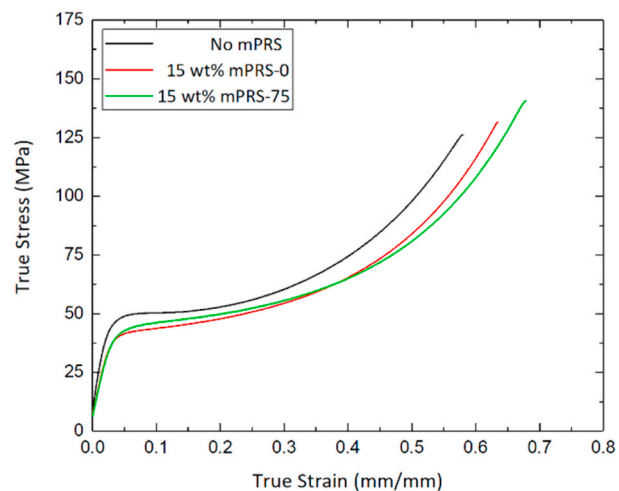
mPRS Content	Young's Modulus E (GPa)	Yield Strength σ_Y (MPa)	Failure Strength σ_F (MPa)	Failure Strain ϵ_F (%)
No mPRS	3.01 ± 0.02	113.5 ± 0.6	232.5 ± 4.1	57.9 ± 1.2
15 wt% mPRS-0	2.47 ± 0.03	85.3 ± 0.5	192.8 ± 3.1	64.2 ± 1.7
15 wt% mPRS-75	2.29 ± 0.08	77.9 ± 1.5	207.8 ± 6.8	69.6 ± 2.3



(a)



(b)



(c)

Fig. 9. Representative true compressive stress-strain curves of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) TGDDM-Jeffamine D230 systems at (a) T_g - 85 °C, (b) T_g - 65 °C, and (c) T_g - 45 °C.

$$\sigma_{\text{true}} = \sigma_{\text{engineering}} * (1 - \epsilon_{\text{engineering}}) \quad (2)$$

$$\epsilon_{\text{true}} = -\ln(1 - \epsilon_{\text{engineering}}) \quad (3)$$

Table 3 contains true compressive Young's modulus, yield strength, failure strength and failure strain for all systems.

Similar to the quasi-static tensile test results, the blank system possesses the highest yield strength, Young's modulus, and failure stress, but the lowest failure strain. Incorporating the mPRS gives the system a higher failure strain but a reduced Young's modulus and yield strength in both cases. Yet there is not a big difference in the Young's modulus and yield strength between the mPRS-control and the mPRS-modified systems, which differs significantly from tensile testing observations (see Fig. 6). More specifically, the difference in yield strength is significantly lower when measured in compression than in tension. The mPRS-control and the mPRS-modified systems have the same overall chemical composition. Also, these two systems have similar crosslink density based on the analysis of the rubbery region of the DMA results which suggests that yield strength of the two systems should be similar. The apparent difference in tensile and compressive yield strength behavior as a function of mPRS conversion could be attributed to topology differences. The protovoid structures (unbound molecular surfaces induced by mPRS) are more likely to be separated in tension than compression resulting in a greater reduction of yield strength. Nevertheless, as was observed in tension, the higher conversion mPRS-modified systems possess higher ductility as measured by the higher failure strain and failure stress.

Influence of temperature on compressive behavior. Adding mPRS decreases the T_g of the systems so it is important to decouple the influence of T_g on mechanical behavior from the influence of network topology and composition. Generally, lower T_g systems exhibit higher ductility if tested at a temperature close to T_g . Therefore, to answer the question of whether the enhanced ductility observed by the inclusion of mPRS is a result of the variation of testing temperature relative to T_g or a result of differences in network structure, the quasi-static compressive testing was performed keeping the difference between T_g and testing temperature (T_{test}) constant at three conditions $T_g - T_{\text{test}} = 85^\circ\text{C}$, 65°C , and 45°C . Fig. 9 shows representative quasi-static true compressive stress-strain curves of blank, 15 wt% mPRS-control, and 15 wt% mPRS-modified TGDDM-Jeffamine D230 systems tested at (a) $T_g - 85^\circ\text{C}$, (b) $T_g - 65^\circ\text{C}$, and (c) $T_g - 45^\circ\text{C}$. The T_g used for selecting testing temperatures was based on the E'' peak. Table 4 contains true compressive Young's modulus, yield strength, failure strength, and failure strain data obtained for all testing conditions.

Table 4

True compressive properties of no mPRS (blank), 15 wt% mPRS-0 (control), and 15 wt% mPRS-75 (modified) TGDDM-D230 system at $T_g - 85^\circ\text{C}$, $T_g - 65^\circ\text{C}$, and $T_g - 45^\circ\text{C}$.

mPRS Content	Young's Modulus E (GPa)	Yield Strength σ_y (MPa)	Failure Strength σ_F (MPa)	Failure Strain ϵ_F (%)
Testing at $T_g - 85^\circ\text{C}$				
No mPRS	1.98 ± 0.07	78.9 ± 0.3	173.4 ± 7.2	58.1 ± 1.1
15 wt% mPRS-0	2.47 ± 0.03	85.3 ± 0.5	192.8 ± 3.1	64.2 ± 1.7
15 wt% mPRS-75	2.29 ± 0.08	77.9 ± 1.5	207.8 ± 6.8	69.6 ± 2.3
Testing at $T_g - 65^\circ\text{C}$				
No mPRS	1.82 ± 0.03	59.7 ± 0.7	152.4 ± 8.1	58.2 ± 0.8
15 wt% mPRS-0	1.92 ± 0.08	63.2 ± 0.5	145.1 ± 2.9	61.3 ± 1.6
15 wt% mPRS-75	1.86 ± 0.06	65.6 ± 0.9	155.5 ± 9.8	64.3 ± 1.2
Testing at $T_g - 45^\circ\text{C}$				
No mPRS	1.70 ± 0.03	50.2 ± 0.3	125.4 ± 1.1	58.6 ± 1.3
15 wt% mPRS-0	1.43 ± 0.06	44.3 ± 1.5	129.6 ± 2.6	63.3 ± 1.4
15 wt% mPRS-75	1.45 ± 0.03	45.8 ± 0.5	135.1 ± 7.8	67.8 ± 1.6

Note: The 15 wt% mPRS-0 (control) system was performed at $T_g - 80^\circ\text{C}$ instead of $T_g - 85^\circ\text{C}$ due to the temperature stability of the oven when operating at 5°C higher than room temperature.

As expected, Young's modulus and yield strength are inversely related to testing temperature for all systems. For a given testing temperature below T_g , the yield strength for the blank, the mPRS-control, and the mPRS-modified systems does not vary significantly. This is particularly evident for the $T_g - 65^\circ\text{C}$ and $T_g - 85^\circ\text{C}$ sets of experiments, which are well removed from T_g in the glassy state. For a given temperature below T_g , the blank, the 15 wt% mPRS-control, and the 15 wt% mPRS-modified systems show a similar Young's modulus and yield strength. An interesting observation is that the failure strain for each system does not vary significantly with testing temperature below T_g , while the failure strength decreases with increasing temperature. The most important observation obtained from the data in Table 4 is that for all three T_g normalized testing temperatures, the blank system shows the lowest failure strain, the mPRS-control system shows a slightly higher failure strain, and the mPRS-modified system shows the highest failure strain. This is also apparent when comparing the representative stress-strain curves in Fig. 9. Therefore, the results of these experiments successfully decouple the influences of T_g and network topology on ductility, and it is concluded that enhanced ductility of the mPRS modified systems is directly attributable to alterations made to network topology.

3.4. Protovoids and ductility

The significant improvement of failure strain and energy dissipation of the mPRS-modified system is thought to be related to a protovoid growth energy absorbing mechanism. This mechanism is enhanced by the presence of mPRS that provides topological domains on the order of 10 nm. The contribution of the protovoid growth in the mPRS-modified system is much greater than the mPRS-control system. This is related to the size of the molecular surfaces (conversion of mPRS) that are not covalently bonded and become protovoids. Evidence of protovoid growth was captured by SEM micrographs of fractured surfaces, and small angle X-ray scattering (SAXS) establishes the presence of the mPRS domains in cured systems. SEM images of the fracture surfaces of the blank sample, the 15 wt% mPRS-control sample and the 15 wt% mPRS-modified sample are depicted in Fig. 10. The SEM images clearly show the differences in the fracture surface of each sample: the blank sample has a very smooth surface, the mPRS-control sample has increased roughness, and the mPRS-modified sample system has many voids. Small angle X-ray scattering measurements were also performed on the blank, the 15 wt% mPRS-control, and the 15 wt% mPRS-modified samples, and the results are shown in Fig. 11. The SAXS results suggest there are 18–34 nm nanostructures on the fracture surface of the

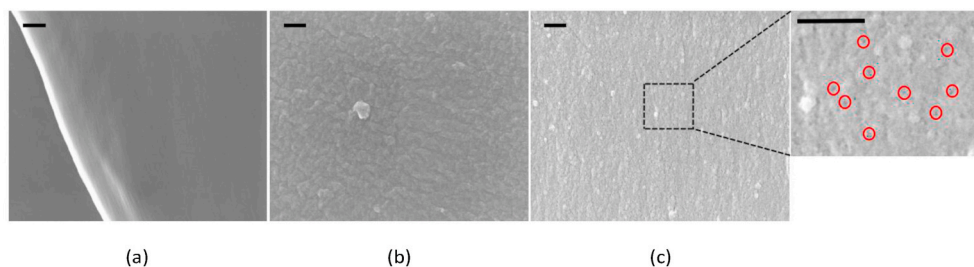


Fig. 10. SEM images of the fracture surfaces of (a) no mPRS (blank) sample, (b) 15 wt% mPRS-0 (control) sample, and (c) 15 wt% mPRS-75 (modified) sample. The scale bar is 200 nm.

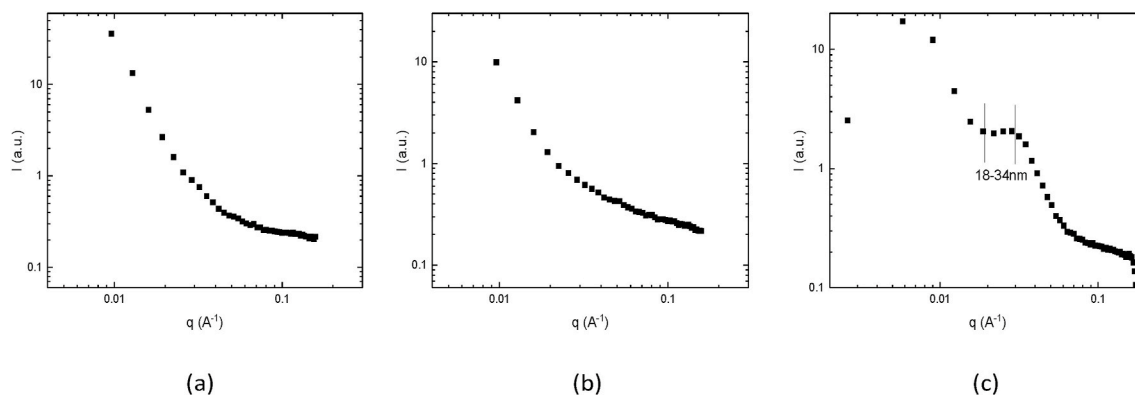


Fig. 11. SAXS plot of the fracture surfaces of (a) no mPRS (blank) sample, (b) 15 wt% mPRS-0 (control) sample, and (c) 15 wt% mPRS-75 (modified) sample.

mPRS-modified system; however, similar nanostructures were not detected on the fracture surface of the blank and the mPRS-control system.

4. Conclusions

A nano-scale epoxy toughening method was developed, and the resulting epoxy systems were characterized. According to the method, monoamine-functionalized partially reacted substructures (mPRS) were synthesized by partially curing a mixture of TGDDM and long-chain polyether monoamine (Jeffamine M1000). The influences of the degree of polymerization of mPRS (0% and 75%) and the weight fraction of mPRS (0 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%) in epoxy were studied by performing quasi-static tensile and compressive tests. Results reveal that in addition to maintaining high T_g , the systems prepared with higher conversion (larger size) mPRS modifier showed a significantly greater capacity to deform. Thus, providing evidence that the creation of protovoids within a network enhances ductility. For example, TGDDM tensile failure strain was improved from 9% to 20% by simply changing the degree of mPRS conversion from 0% to 75%, which also resulted in a slight T_g increase from 126 °C to 135 °C. Note that the overall chemical composition of these two systems was the same and that their network structures differed only in spatial arrangement of monomers within the network.

Adding mPRS at any conversion to the epoxy systems was found to increase ductility but also decrease T_g and mechanical characteristics including yield strength and modulus. Therefore, it was important to decouple the influences of T_g , network topology, and composition on mechanical behavior by performing mechanical characterization while keeping $T_g - T_{test}$ constant. Results of quasi-static compressive experiments conducted in this way were used to conclude that the enhanced ductility of the mPRS modified systems is directly attributable to the alterations made to network topology. Further evidence of protovoid and void formation was obtained by SEM and SAXS.

From a practical application standpoint, it was found that TGDDM

modified with 15 wt% mPRS-75 provides a good balance of properties (T_g , strength, and toughness). In addition to exceptional ductility, the mPRS-modified systems possess workable viscosity (0.9 Pa*s at RT) and may prove useful in coatings, adhesives, and composites applications. Furthermore, this toughening strategy should be applicable to other network forming systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2020.123260>.

References

- [1] F. Meng, S. Zheng, W. Zhang, H. Li, Q. Liang, *Macromolecules* 39 (2) (2006) 711–719, <https://doi.org/10.1021/ma0518499>.
- [2] R.A. Pearson, A.F. Yee, *J. Mater. Sci.* 26 (14) (1991) 3828–3844, <https://doi.org/10.1007/BF01184979>.
- [3] A. Kinloch, M. Yuen, S. Jenkins, *J. Mater. Sci.* 29 (14) (1994) 3781–3790, <https://doi.org/10.1007/BF00357349>.
- [4] J. Gao, J. Li, S. Zhao, B.C. Benicewicz, H. Hillborg, L.S. Schadler, *Polymer* 54 (2013) 3961–3973, <https://doi.org/10.1016/j.polymer.2013.05.033>.
- [5] B. Boesl, B.V. Sankar, W.G. Sawyer, *Proc. Am. Soc. Compos., Tech. Conf.* 21st (2006), 145/141–145/147.
- [6] Y.T. Park, Y. Qian, C. Chan, T. Suh, M.G. Nejjhad, C.W. Macosko, A. Stein, *Adv. Funct. Mater.* (2014), <https://doi.org/10.1002/adfm.201402553>.
- [7] Mukherji, C.F. Abrams, *Phys. Rev.* 78 (2008), 050801, <https://doi.org/10.1103/PhysRevE.78.050801>.
- [8] D. Mukherji, C.F. Abrams, *Phys. Rev.* 79 (2009), 061802, <https://doi.org/10.1103/PhysRevE.79.061802>.
- [9] C. Jang, M. Sharifi, G.R. Palmese, C.F. Abrams, *Polymer* 55 (2014) 3859–3868, <https://doi.org/10.1016/j.polymer.2014.06.022>.
- [10] M. Sharifi, C.W. Jang, C.F. Abrams, G.R. Palmese, *J. Mater. Chem.* 2 (2014) 16071–16082, <https://doi.org/10.1039/C4TA03051F>.
- [11] Majid Sharifi, Changwoon Jang, Cameron F. Abrams, Giuseppe R. Palmese, *Macromolecules* 48 (2015) 7495–7502, <https://doi.org/10.1021/acs.macromol.5b00677>.
- [12] M. Sharifi, and G. R. Palmese, Ph.D. Dissertation, May 2015.
- [13] M. Sharifi, G.R. Palmese, *J. Mater. Chem. A* (2020), <https://doi.org/10.1039/D0TA08158B>.
- [14] Leon Shechter, John Wynstra, and Raymond P. Kurkijy, *Ind. Eng. Chem. Vol.48*, No.1 DOI: 10.1021/ie50553a029.
- [15] L.J. Fetters, N. Hadjichristidis, J.S. Linder, J.W. Mays, *J. Phys. Chem. Ref. Data* 23 (1994) 619, <https://doi.org/10.1063/1.555949>.