Controlled Topology Toughening Epoxy via Incorporation of Partially Reacted Substructures

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ABSTRACT

This work investigates a new strategy to improve the toughness of epoxy resins by rearranging the topological structure of cross-linked networks. Amine-cured epoxy networks was modified with monoamine functionalized partially reacted substructures (mPRS), synthesized by partially curing tetraglycidyl ether of diaminodiphenylmethane (TGDDM) and a monoamine polyetheramine (Jeffamine M1000). mPRS resins with different degrees of polymerization were added to a mixture of Diglycidyl Ether of Bisphenol A (DGEBA) and cured with Jeffamine D230. The addition of mPRS increased failure strain and energy dissipation. The mechanical properties could be adjusted by controlling the conversion and concentration of mPRS, resulting in yield strength 39 to 59 MPa and failure strain 15% to 44%. The improved ductility was also observed from compression testing. The observed differences came from the conversion of mPRS, which locally influenced the epoxy network topology and further influenced the mechanical behavior of the epoxy systems.

1. INTRODUCTION

As one of the most important classes of thermoset polymers, epoxy resins are used across industries in matrix materials for composites and structural materials to protective coatings and adhesives. Their wide-spread use is due to their excellent thermal and chemical stability and good mechanical properties, which are caused by their highly cross-linked structure. Unfortunately, this highly cross-linked network also makes epoxies intrinsically brittle, so many techniques have been developed to reduce this brittleness and improve toughness. The major toughening strategies focus on incorporating secondary additives. The additives can be broken into two main categories: soft toughening particles[1-3] and rigid nanofillers.[4-6]

A recent series of coarse-grained molecular simulations were investigated by Mukherji et al. Their modeling results suggested that a void-opening mechanism in highly cross-linked thermosets could increase the ductility of thermoset materials without sacrificing important mechanical properties, like yield strength and Young's modulus.[7-9] Based this theory, Sharifi et al. proposed a novel epoxy toughening method that created molecular surfaces within a highly cross-linked epoxy-amine system. This was achieved by incorporating a partially reacted long-chain monoamine, called monoamine functionalized partially reacted substructures (mPRS), into the epoxy systems.[10] The inclusion of mPRS created a local concentration of long aliphatic chain ends that were not covalently connected to the network. As a result, when the modified material under tensile deformation, these unbound chain ends created microvoids within the polymer network, improving the ductility of the material. Assuming the unbound molecular surfaces directly influenced the polymer's ductility, then the size of these molecular surfaces should be a key factor affecting deformation behavior.

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For this work, we investigated the effectiveness of network topology rearrangement as a method for epoxy toughening to figure out how the conversion of mPRS affected the quasi-static tensile properties and the quasi-static compression properties of the epoxy systems.

2. EXPERIMENTATION

2.1 Materials

The molecular structures of the materials used in this study are shown in **Figure 1**. Two epoxy resins were used: Diglycidyl ether of bisphenol-A (DGEBA EPON 828) provided by Miller-Stephensen and tetraglycidyl diaminodiphenylmethane (TGDDM) provided by Sigma-Aldrich. Poly (propylene oxide) diamine Jeffamine D230, with approximately 2.5 propylene oxide units along the backbone, provided by Huntsman, was used as the primary curing agent. Jeffamine M-1000 polyether amine monoamine (PEA1000) with a ratio of propylene oxide to ethylene oxide of about 3 to 19, was used to prepare the mPRS.

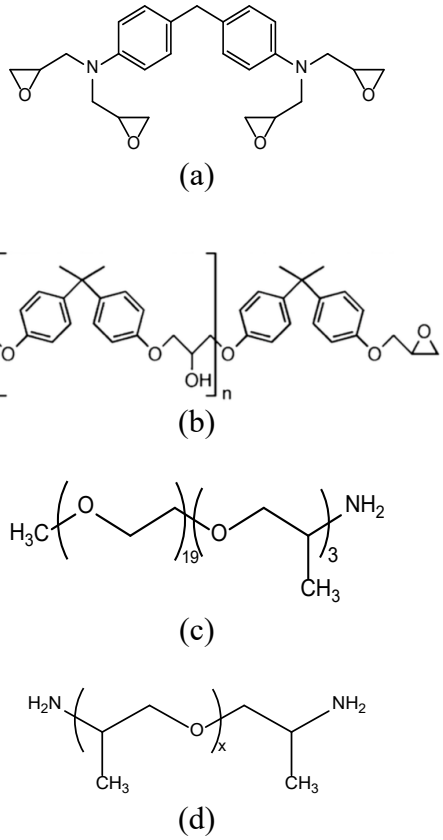

Figure 1. Chemical structures of the epoxy and amine were used in this study: (a) tetraglycidyl of diaminodiphenylmethane (TGDDM), (b) Diglycidyl ether of bisphenol-A (DGEBA EPON 828 n≈0.1), (c) Polyetheramines (Jeffamine M1000, MW≈1000 g/mol), (d) Poly (propylene oxide) diamine (Jeffamine D230, MW ≈ 230 g/mol, x≈2.5).

2.2 Preparation of mPRS resins.

The toughening agent mPRS was synthesized by partially reacting a stoichiometric mixture of TGDDM and Jeffamine M1000 to controlled degrees of polymerization. The preheated TGDDM and Jeffamine

M1000 were mixed at 80 °C until a transparent (no phase separation) mixture was obtained. Then, the mPRS mixture was further stirred and heated at 80°C in an oil bath until the desired epoxy and amine conversion was achieved. To monitor the degree of reaction, Fourier transform infrared spectroscopy (FTIR) was used in the near-IR region. The results of epoxy conversion versus time were obtained by quantifying the peak height at 4520 cm^{-1} that corresponded to the stretching and bending of the oxirane ring. To study the relationship between the size of the molecular surface and the mechanical behavior of thermosets, four different mPRS conversions were synthesized: 0%,70%,75% and 80%. The 75% conversion was chosen as the central conversion based on TGDDM structure, which has four epoxy functional groups. To synthesize the biggest substructures which have the functional groups left to connect to the network, it was best to react three of four epoxy groups. For comparison, 0%, 70% and 80% conversion mPRS were also synthesized.

2.3 Resin Preparation and Cure.

The polymers were prepared by mixing stoichiometric blends (i.e., one epoxy per amine hydrogen) of DGEBA with Jeffamine D230 and mPRS at different concentrations. To investigate how the size of free molecular surfaces (conversion of mPRS) impacted mechanical behavior, 0%, 70%, 75%, and 80% conversion mPRS were added to the epoxy system. 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. For epoxy-amine systems, the curing procedure is important because it has been reported that the relative rate of primary amine-epoxy and secondary amine-epoxy reactions depends on temperature.[11] This suggests that changing temperature could affect network topology, and the interest herein is to evaluate the influence of mPRS on topology and mechanical behavior. Accordingly, in this paper, cured samples with no mPRS resins are referred to as “blank,” samples with 0% conversion mPRS resins are “mPRS-control,” and samples with 70%, 75% and 80% conversion mPRS resins are “mPRS-modified.”

2.4 Tensile Testing.

To investigate the influence of mPRS on mechanical behavior, quasi-static tensile testing was performed on DGEBA system. Testing was conducted according to ASTM D638-14. For each system, six dog-bone shaped specimens were prepared. Each specimen had an average thickness of 1.7 mm, an average width of 3.8 mm, and a gauge length of 27 mm. The quasi-static tensile test was carried out using a servo-hydraulic INSTRON 8872 with a 1000 N load cell apparatus at a crosshead speed of 1 mm/min.

2.5 Compression Testing.

To investigate the influence of mPRS on mechanical behavior, quasi-static compression testing was performed on the DGEBA system. Testing was conducted according to ASTM D695-15. For each system, six cylindrical specimens were prepared. Each specimen had an average thickness and average diameter of 5 mm. The quasi-static compression test was carried out using an electric INSTRON 5985 with a 250 KN load cell. All compression tests were performed under 0.001/s strain rate.

2.6 Dynamic Mechanical Analysis (DMA).

A TA instrument Q800 DMA apparatus was utilized to measure the viscoelastic properties and Tg. All specimens were tested at a constant frequency of 1 Hz. The oscillation amplitude was kept at 15 μm in single-cantilever mode. All samples were sanded into rectangular slab geometry (35–36 mm in length, 12–13 mm in width, and approximately 3 mm in thickness). The test was conducted with a scanning rate of 2 °C /min starting from -100 °C to 200 °C to obtain sufficient data below and above the glass transition temperature. Due to the inclusion of the low Tg mPRS, the loss modulus curve always has a broad peak. For this reason, the Tg value in this study was chosen from the peak of tan delta curve.

3. RESULTS

3.1 Quasi-Static Tensile Properties

As discussed in the introduction section, mPRS resins can provide the molecular surface to improve the ductility of the highly cross-linked epoxy thermosets in the glassy state. The degree of ductility is related to the size of the molecular surface, which can be controlled by the conversion of mPRS. To study the relationship between the substructure size and ductility, quasi-static tensile testing was performed. **Figure 2** shows the representative quasi-static tensile stress-strain curves of blank system, and 15% weight ratio of four different conversions of stoichiometric mPRS: 0%, 70%,75% and 80% in the DGEBA 828–Jeffamine D230 system. **Table 1** contains Young's modulus, yield strength, failure strength, failure strain and Tg by tan delta of blank system and these different mPRS-modified systems. As shown in **Figure 2**, the blank system has the highest yield strength, Young's modulus, and failure strength, but it also has the lowest failure strain. If compare the mechanical behavior among the system modified with mPRS resins, the mPRS-control system shows the highest yield strength, Young's modulus, but the lowest failure strain. The 75% conversion mPRS-modified system has the highest failure strain and the largest area below the plastic deformation portion of the stress-strain curves. This means it could absorb the highest energy during the tensile testing. The 70% conversion mPRS-modified system shows the second highest energy absorption and slightly lower yield strength and failure strain than that of the 75% mPRS system. As previously mentioned, the key factor that can affect the ductility of the material is the size of the molecular surface. The 75% conversion of mPRS had on average three of the total four epoxy groups reacted with the monofunctional amine, which means, theoretically, it has the biggest substructures. By comparing the results of 70%, 75% and 80% mPRS-modified systems, the higher conversion of mPRS does not always lead to better mechanical properties.

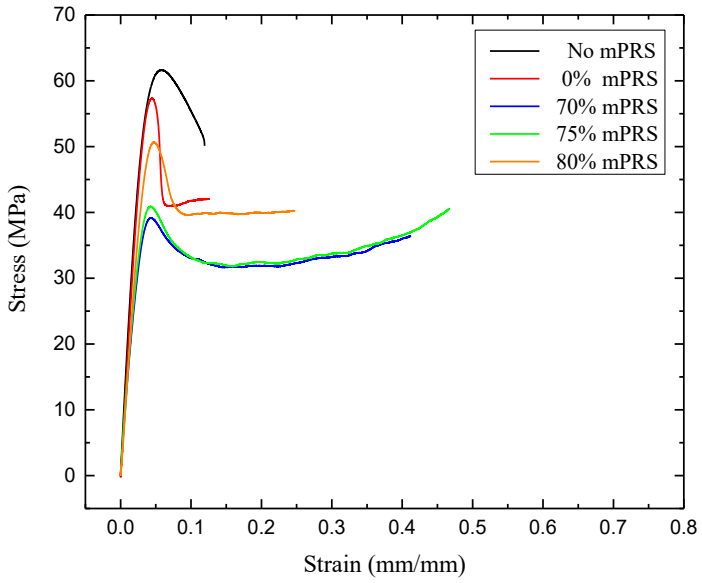

Figure 2. Stress-strain curves of blank system and 15% weight ratio of different mPRS in DGEBA-D230 System

Table 1. Mechanical properties and Tg of blank system 15% weight ratio of different mPRS in DGEBA-D230 System

mPRS Content	Young's Modulus E (GPa)	Yield Strength σ_y (MPa)	Failure Strength σ_f (MPa)	Failure Strain ε_r (%)	Tg (°C)	Crosslink Density (mol/m3)
No mPRS	2.67 ± 0.02	60.9 ± 1.09	49.5 ± 1.1	12.1 ±0.2	95	1400
0% 15%	2.54 ± 0.04	59.0 ± 1.5	42.9 ± 1.4	15.2 ± 4.7	73	1600
70% 15%	1.94 ± 0.02	39.5 ± 0.6	35.6 ± 0.7	39.1 ± 3.6	73	1400
75% 15%	1.69 ± 0.11	38.9 ± 1.5	39.5 ± 1.2	44.1 ± 3.3	75	1400
80% 15%	2.14 ± 0.07	51.1 ± 0.8	39.7 ± 0.8	23. 5 ± 2.7	71	1500

It is interesting that both the mPRS-control and mPRS-modified systems have the same Tg. These four systems can be considered as network isomers because the chemical composition of the four systems is identical but the network topology of the four systems differ. The difference is apparent in the deformation behavior of the four mPRS systems. In particular, the necking behavior of each system is different. The mPRS-modified systems show a broader necking region than the mPRS-control system in the stress-strain curves. The necking part would quickly spread to the whole testing specimen, unlike the mPRS-control system, which has demonstrated a large drop in stress after the yielding point. Comparing the necking region of the stress-strain curves revealed important relationships; the broader the necking region, the lower the yield strength and Young's modulus. Yet, the mPRS-modified materials can achieve higher failure strain and larger energy absorption. The study on the influence of the conversion of mPRS revealed that the mechanical properties can be adjusted (Yield strength from 59.02 MPa to 38.93 MPa, Young's modulus from 2.54 GPa to 1.69 GPa, failure strength from 42.89 MPa to 35.58 MPa, failure strain from 44.10% to 15.23%) without affecting the Tg by controlling the conversion of mPRS.

3.2 Quasi-Static Compression Properties

Results of the 3.1.1 section showed the influence of the conversion of mPRS on the quasi-static tensile properties. Next, we conducted compression testing for three reasons: (1) it is necessary for some applications, such as fiber composites; (2) compared to tensile testing, compression testing can make it easier to see true deformation instead of engineering deformation; and (3) it can reduce the influence of the specimen polishing. The quasi-static compression test was performed on DGEBA-D230-mPRS systems. **Figure 3** shows the representative quasi-static compression true stress-strain curves of the blank, the 15wt% mPRS-control, and the 15wt% mPRS-modified TGDDM- Jeffamine D230 systems. The true stress and true strain were converted from engineering stress and engineering strain, using equations (1) and (2).

$$\sigma_{ture} = \sigma_{engineering} * (1 - \varepsilon_{engineering}) \quad (1)$$

$$\varepsilon_{ture} = -\mathrm{Ln}(1 - \varepsilon_{engineering}) \quad (2)$$

Table 2 contains true Young's modulus, true yield strength, true failure strength, and true failure strain for all systems.

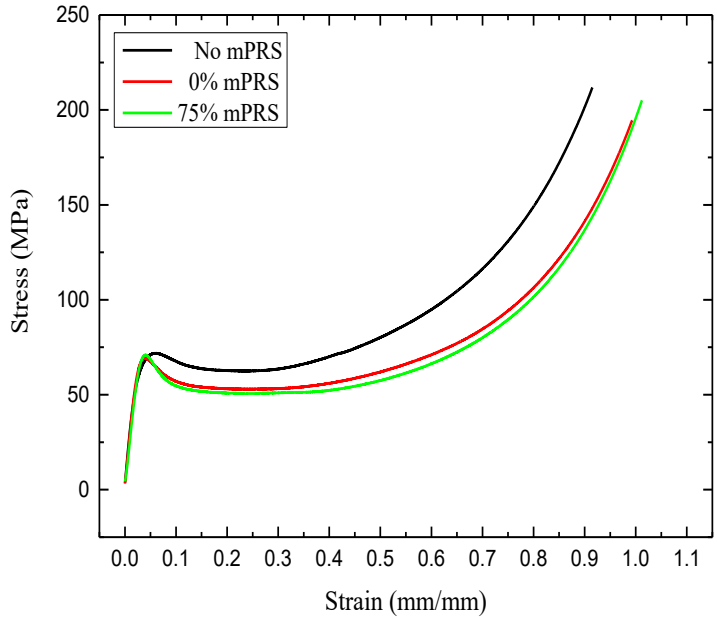

Figure 3. True stress-strain curves of blank, 15% weight ratio of 0% and 75% conversion mPRS in the DGEBA-D230 system.

Table 2. Mechanical properties and Tg of blank, 15% weight ratio of 0% and 75% conversion mPRS in the DGEBA-D230 system.

mPRS Content	Young's Modulus E (GPa)	Yield Strength σ_y (MPa)	Failure Strength σ_u (MPa)	Failure Strain ε_r (%)
No mPRS	3.03 ±0.02	72.1 ±0.6	212.2 ±4.7	91.5 ± 2.1
0% 15%	2.85 ± 0.05	69.4 ±0.5	199.8 ± 5.1	99.3 ± 1.4
75% 15%	2.64 ± 0.03	70.2 ±1.5	205.8 ± 3.7	101.2 ± 1.2

Like the quasi-static tensile test results, the blank system had the highest yield strength, Young's modulus, and failure stress but the lowest failure strain. In both cases, the inclusion of the mPRS caused the materials to have a higher failure strain but reduced the Young's modulus and yield strength. Compared to tensile test results, the compression test results show similar stress-strain curves for both the mPRS-control and mPRS-modified systems; in addition, the Young's modulus is similar and yield strength is almost the same. As previously explained, the mPRS-control and mPRS-modified systems can be considered network isomers. The DMA results also reveal the two systems have similar average crosslink density. As with tensile results the compression studies show that the inclusion of mPRS results in networks possessing higher ductility. Thus, the mPRS-modified system to have the higher failure strain and failure strength.

4. CONCLUSIONS

A nano-scale epoxy toughening method was developed, and the resulting epoxy systems were characterized. According to the method, a monoamine-functionalized partially reacted substructures resin (mPRS) was synthesized by partially curing a mixture of TGDDM and long-chain Jeffamine M1000 monoamine. The influence of the degree of polymerization of mPRS (0% 70%, 75%, and 80) were studied by performing the quasi-static tensile test and quasi-static compression test. Results of the quasi-

static tensile testing on the cured samples revealed that despite having the same Tg, the system prepared with the larger mPRS modifier showed a much greater capacity to deform, thus providing evidence that the creation of free surfaces (not bonded) within a network will enhance ductility. For example, tension failure strain could be improved from 15% to 44%, and the compression failure strain could be improved from 99% to 101%. By calculating the area below the plastic deformation portion of the stress-strain curves, the 75% conversion mPRS-modified system showed the highest capacity for energy absorption. Due to the low viscosity of the mPRS resins as well as good transparency of the cured mPRS-modified material, these systems may prove useful in coatings, adhesives, and composites applications.

5. ACKNOWLEDGMENT

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6. REFERENCES

1. Meng, F.; Zheng, S.; Zhang, W.; Li, H.; Liang, Q. Macromolecules, 2006, 39 (2), 711−719. DOI: 10.1021/ma0518499
2. Pearson, R. A.; Yee, A. F. J. Mater. Sci. 1991, 26 (14), 3828−3844. https://doi.org/10.1007/BF01184979
3. Kinloch, A.; Yuen, M.; Jenkins, S. J. Mater. Sci. 1994, 29 (14), 3781−3790. https://doi.org/10.1007/BF00357349
4. J. Gao, J. Li, S. Zhao, B. C. Benicewicz, H. Hillborg and L. S.Schadler, Polymer, 2013, 54, 3961-3973. https://doi.org/10.1016/j.polymer.2013.05.033
5. B. Boesl, B. V. Sankar and W. G. Sawyer, Proc. Am. Soc.Compos., Tech. Conf., 2006, 21st, 145/141-145/147 .
6. Y. T. Park, Y. Qian, C. Chan, T. Suh, M. G. Nejhad, C. W.Macosko and A. Stein, Advanced Functional Materials,2014. https://doi.org/10.1002/adfm.201402553
7. 2006, 39 (2), 711−719.D. Mukherji and C. F. Abrams, Physical Review E, 2008, 78, 050801. https://doi.org/10.1103/PhysRevE.78.050801
8. D. Mukherji and C. F. Abrams, Physical Review E, 2009, 79, 061802. https://doi.org/10.1103/PhysRevE.79.061802
9. C. Jang, M. Sharifi, G. R. Palmese and C. F. Abrams, Polymer, 2014, 55, 3859-3868. https://doi.org/10.1016/j.polymer.2014.06.022
10. M. Sharifi, and G. R. Palmese, Ph.D. Dissertation, May 2015
11. Leon Shechter, John Wynstra, and Raymond P. Kurkjy, Industrial and Engineering Chemistry Vol.48, No.1. DOI: 10.1021/ie50553a029