Mechanical and Thermal Properties of Novel Rubber-Toughened Epoxy Blend Prepared by In Situ Pre-crosslinking

Heng-Shi Zhou, Xiao-Xue Song, Shi-Ai Xu

Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
Correspondence to: S.-A. Xu (E-mail: saxu@ecust.edu.cn)

ABSTRACT: A novel method is used for preparing liquid rubber-toughened epoxy blend, in which an initiator was added to the liquid rubber–epoxy mixture to initiate crosslinking reaction of liquid rubber, and then curing agent was added to form the thermoset. Two epoxy blends with carboxyl-terminated butadiene-acrylonitrile copolymers were prepared using traditional and novel methods respectively. Results indicated that the novel rubber-toughened epoxy blend exhibited much better mechanical properties than its traditional counterpart. The morphologies of the blends were explored by transmission electron microscopy (TEM), it was revealed that the use of the novel method formed a local interpenetrating network structure in the blend, which substantially improved the interfacial adhesion. The impact fracture surfaces of the two blends were observed by scanning electron microscopy (SEM) to explore the toughening mechanism, it was found that crack pinning was the major toughening mechanism for the novel rubber-toughened epoxy blend. Dynamic mechanical analysis (DMA) was applied to determine the T_g values of the blends, which were found to be close. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41110.

INTRODUCTION

Epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, and electrical laminates because of their rigidity, high temperature resistance, chemical tolerance, and adhesive properties.[1,2] Cured epoxy resins are typical thermosetting polymers with highly crosslinked network structure. The materials have inherently low impact resistances that limit their potential uses in many fields. Thus, imparting good fracture toughness to epoxy resins is necessary to ensure the feasibility of materials for practical applications.[3] This procedure has been thoroughly investigated.[2]

Attempts to toughen epoxy resins were initiated by researchers from B. F. Goodrich Company and were first reported by McGarry.[4] In the original study, McGarry used a liquid carboxyl-terminated butadiene-acrylonitrile (CTBN) copolymer to modify the diglycidyl ether of bisphenol A (DGEBA) epoxy. Following the research, extensive analyses have been performed to explore the toughening mechanism of rubber-toughened epoxies.[5–13] Several reviews have likewise been published.[2,3,14,15]

The improvement in toughness inevitably coincides with a significant loss in elastic modulus and yield stress. Epoxy resins can be substantially toughened by the addition of liquid rubber. To maintain good stiffness, inorganic particles were used to toughen the materials. Glass beads or ceramic particles with diameters between 4 and 100 μm were typically used. The toughness of epoxy can be improved by the addition of inorganic particles without lowering the elastic modulus. However, the relatively large particles significantly increase the viscosity of the resin, thereby reducing the processability of the resulting composites.[16] In contrast to neat epoxy, the composites exhibit markedly lower yield stresses. Preparing nanocomposites with small rigid particles is a good way to toughen the epoxy, which increases the mechanical performance of such thermosetting polymers. Rigid nanoparticles increase the toughness of the epoxy polymer and improve the Young's modulus.[16–20] Although the nanocomposites of epoxy show good balance properties, the toughening effect of inorganic nanoparticles is less prominent compared with that of liquid rubber.

Thus, liquid rubber is a widely used toughener for epoxy at the expense of the modulus, whereas inorganic particles in micro- or nano-size can improve the toughness of epoxy without decreasing its stiffness. However, in most cases, the yield stresses of the composites decrease after the addition of either organic or inorganic particles.

Table I. Sample Identifications and Formulations of Traditional and Pre-crosslinked CTBN/epoxy Blends

Sample ID[a]	CTBN (phr)[b]	BPO (wt %)[c]	Piperidine (phr)[d]
Epoxy-P	0	0	5
Tra-C	5	0	5
Cro-C	5	1.0	5

[a] Epoxy-P, Tra-C and Cro-C represent pure epoxy, the traditional CTBN/epoxy blend, and the pre-crosslinked CTBN/epoxy blends, respectively, all of the samples were cured with piperidine.
[b] The rubber content for all blends is 5 phr (parts per hundred of E51 resin).
[c] The BPO content is relative to the rubber weight.
[d] The dosage of piperidine is 5 phr (relative to the weight of E51 resin).

Block copolymers may segregate into nanoscale micellar structures in an epoxy matrix at low loadings, which have minimal impact on the glass transition temperature and Young's modulus. Moreover, block copolymers may provide a dramatic increase in the fracture resistance.[21–25] However, synthesis of block copolymers is expensive, and controlling their micellar structures is difficult.

In the conventional process for rubber-modified epoxies, the liquid rubber is dissolved in the epoxy by mechanical mixing until a homogenous solution is formed. The reaction-induced phase separation occurs during the curing process of epoxy, and the rubber particles precipitate as a second phase. The principal liquid rubber used for toughening epoxies is CTBN copolymer. The chemical linkage between the CTBN and the matrix is expected to occur because the carboxyl groups in CTBN can react with the matrix; however, this chemical linkage is very weak.[17] Therefore, the interfacial interaction between the rubbery phase and the matrix is also weak, which causes low modulus and tensile strength of liquid rubber-modified epoxies.

Researchers initially attempted to toughen polystyrene by simple mechanical blending with rubber. However, the mixture as whole exhibited poor mechanical properties compared with the parent polystyrene because the two phases were only bonded together by weak van der Waals forces. The modulus and strength of the hybrid greatly decreased after addition of rubber. The problem was solved by graft polymerization technique, which resulted in better mixing and interfacial bonding than mechanical blending. The rubber-toughened polystyrene produced by graft polymerization is well known as high impact polystyrene (HIPS). Aside from a higher level of toughness, the blends produced by graft polymerization show a much higher yield stress than that of the simple blends produced by mechanical blending.[26]

Inspired by the preparation of HIPS, a novel method that involves a pre-crosslinking process was developed to improve the interfacial adhesion between the liquid rubber and the matrix.[27] A previous study revealed that the novel rubber-toughened epoxy blends showed much better mechanical properties compared with traditional rubber-toughened epoxies. Moreover, the novel method was proven to be universal. In this study, two epoxy blends with liquid rubber (CTBN copolymer)
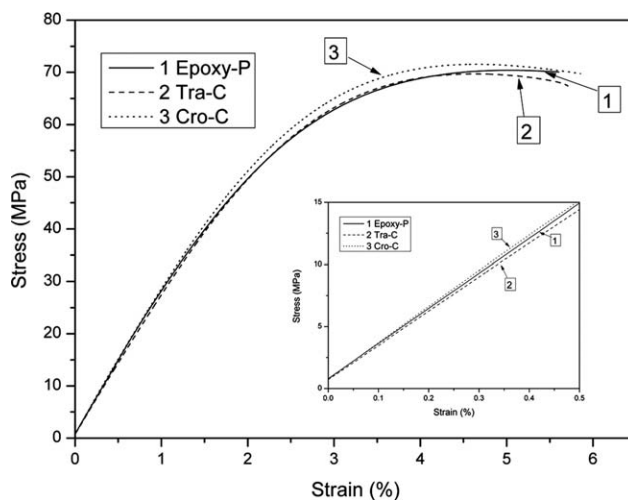
Figure 1. Stress-stain curves of pure epoxy, and its traditional and pre-crosslinked CTBN/epoxy blends.

were prepared using traditional and novel methods. The morphology, as well as mechanical and thermal properties, of the two blends were extensively studied and compared.

EXPERIMENTAL

Materials
Diglycidyl ether of bisphenol A, i.e., DGEBA (E51, epoxide equivalent weight of 185–210) was purchased from Shanghai Resin Co. Ltd. (Shanghai, China). The curing agent piperidine and the initiator benzoyl peroxide (BPO) were obtained from Shanghai Reagent Co. CTBN (molecular weight, 2000 g/mol to 3000 g/mol; acrylonitrile content, 25 wt %) copolymers were used as tougheners and were purchased from Zibo Qilong Chemical Industry Co. Ltd. (China).

Sample Preparation
The traditional CTBN/epoxy and the pre-crosslinked CTBN/Epoxy blends were prepared according to the procedures described in Refs. 17 and 27, respectively. Table I lists the identifications and formulations of all the samples.
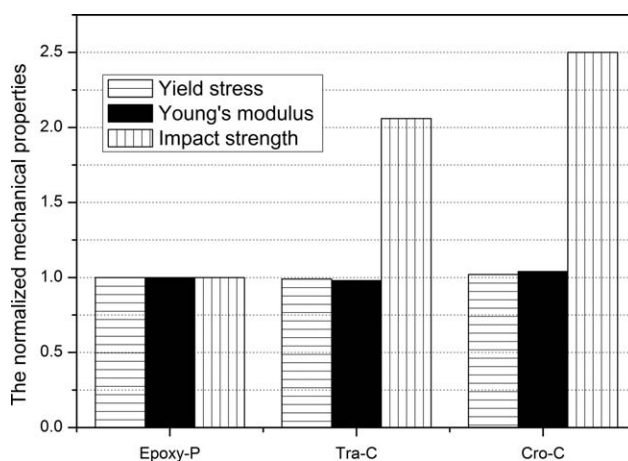
Figure 2. Normalized mechanical properties of pure epoxy, as well as traditional and pre-crosslinked CTBN/epoxy blends.
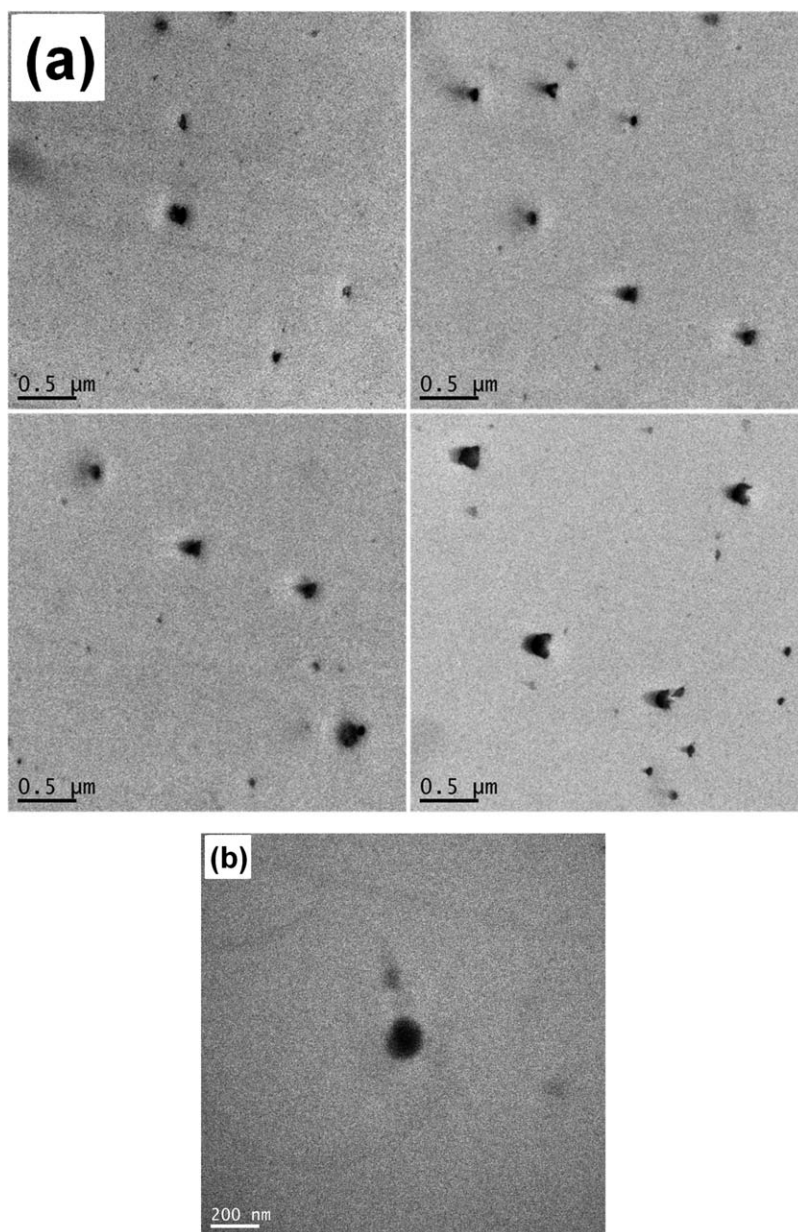
Figure 3. TEM micrographs of the traditional CTBN/epoxy blend (a) at low magnification; (b) at high magnification.

Characterization

The tensile strengths of the cured specimens were measured using an electric universal testing machine (SANS, China) at a cross-head speed of 2 mm/min based on ASTM D638-10. Izod impact test was conducted with a cantilever impact tester (SANS, China) at room temperature based on ASTM D256-10. The fracture surfaces of the specimens were observed by scanning electron microscopy (SEM) using a HITACHI S-4800 microscope (Hitachi Ltd., Japan). Prior to examination, the fracture surfaces were sprayed with a thin layer of evaporated gold to improve the conductivity of the blends. Transmission electron microscopy (TEM) was performed using a JEOL JEM-1400 electron microscope (Japan). The samples were trimmed using a microtome machine, and the section samples were stained with OsO_4 to enhance the contrast. The glass transition temperature T_g was determined by dynamic mechanical analysis (DMA) using a Q800 dynamic mechanical analyzer (TA Instruments, Inc., USA). Dynamic mechanical spectra were obtained at 1 Hz, and the rectangular specimen was tightened on the clamp at a torque of 20 Nm.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the stress-stain curves of pure epoxy and its traditional and pre-crosslinked CTBN/epoxy blends. It can be seen that the elongation at break for the three samples are very close, however, their Young's modulus and yield stress are different. The inset is enlarged view of the initial parts of the three curves.

The absolute values of the mechanical properties have been previously provided.[27] For comparison, the values of the
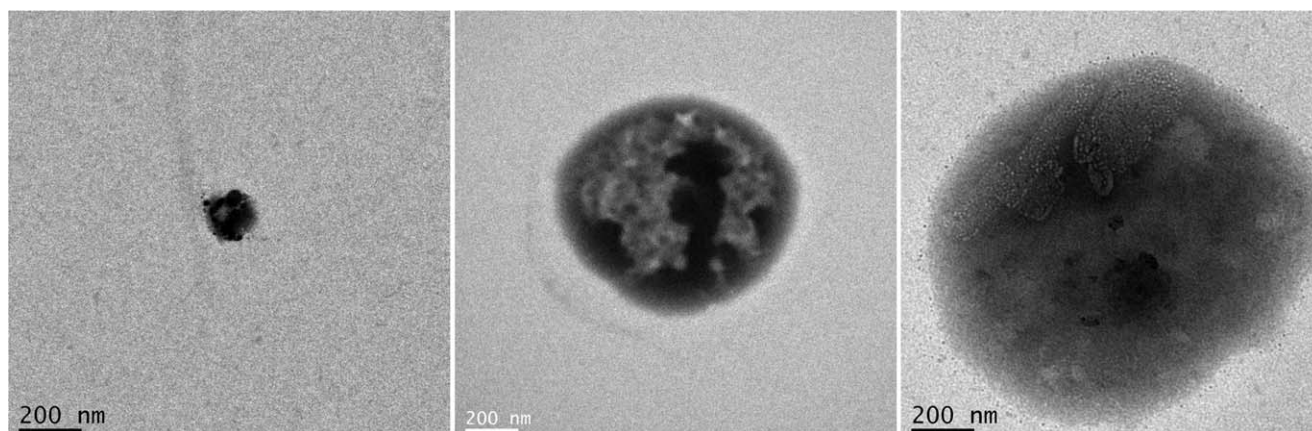
Figure 4. TEM micrographs showing the internal structure of rubber particles in the pre-crosslinked CTBN/epoxy blend at high magnification.

mechanical properties for Epoxy-P are normalized to 1 (Figure 2). The impact strength of the traditional blend substantially increases by more than 100% after addition of 5 phr (parts per hundred) CTBN, which is similar to the previous reports.[7,14,17] However, the yield strength and Young's modulus of the traditional blend slightly decrease. By contrast, the pre-crosslinked blend prepared by the novel method exhibits improved performance; the yield strength, Young's modulus and impact strength of the blend respectively increase by 2.7%, 5.5%, and 20.9% compared with the traditional blend. In particular, the yield strength and Young's modulus of the pre-crosslinked CTBN/epoxy blend are slightly higher than those of pure epoxy.

Morphology

The traditional method has been used for liquid CTBN-modified epoxies since 1970.[4] Theoretically, the carboxyl groups in CTBN can react with the epoxide groups of epoxy and amine groups of piperidine, resulting in a chemical linkage formed between CTBN and the matrix. However, only a small portion of CTBN molecules reacts with the matrix in traditional CTBN/epoxy blends because the reaction speed of the carboxyl group with the epoxide group is slow during curing; the reduction in

reaction speed is attributed to the competing reaction between epoxides and amine groups.[17] The weak chemical linkage between the rubbery phase and the matrix cannot guarantee the effective transfer of stress in the presence of an external force, which decreases the yield strength and Young's modulus following the addition of CTBN. During pre-crosslinking, the mixture
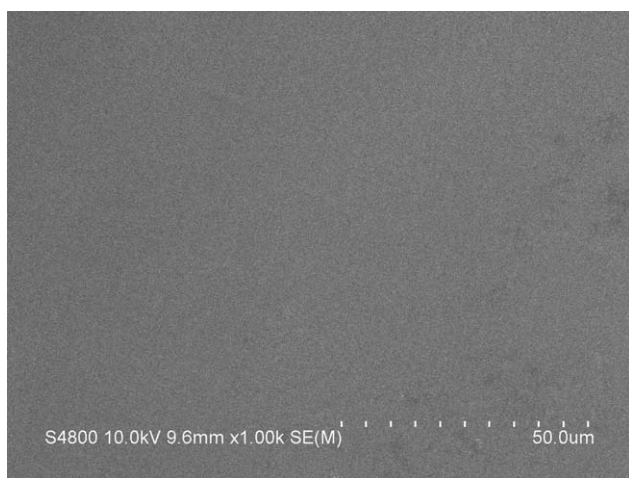

Figure 5. SEM images of the fractured surface of the pure epoxy after impact test.
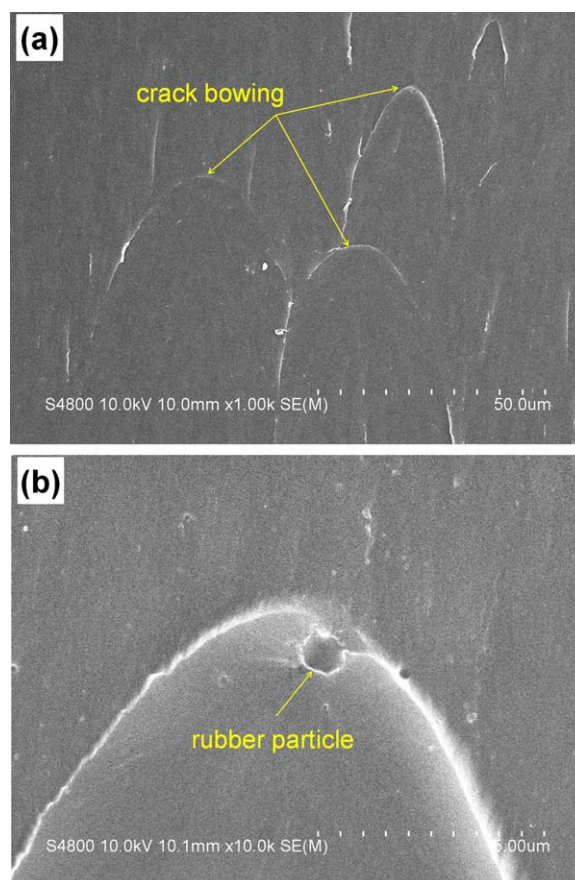
Figure 6. SEM images of the fractured surface of the traditional blend after impact test (a) at low magnification; (b) at high magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. SEM images of the fractured surface of the pre-crosslinked blend after impact test (a) at low magnification; (b) at high magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
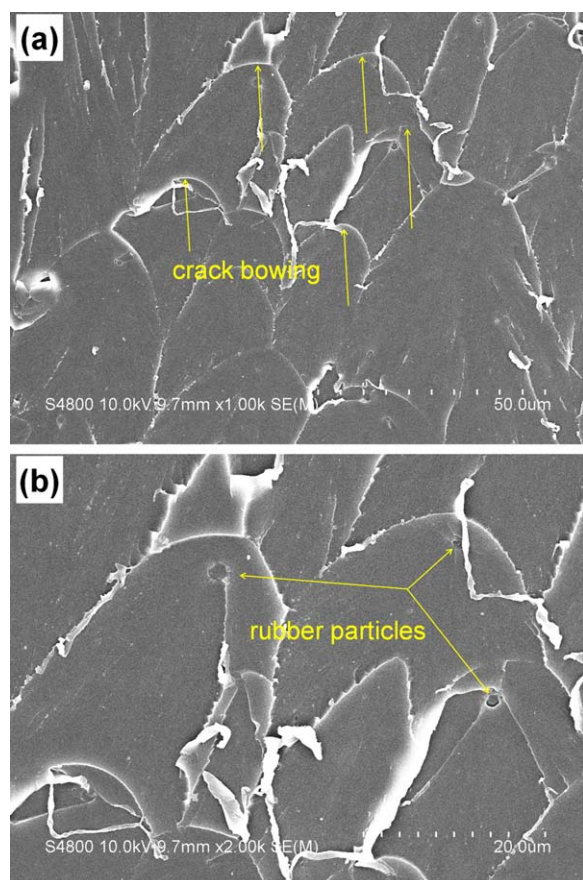
of CTBN with epoxy is heated before adding piperidine. The carboxyl groups in CTBN react with epoxy in the absence of amine groups of the curing agent. Therefore, increased chemical linkages are formed between CTBN and the matrix during curing.

In the traditional process, CTBN is first dissolved in epoxy, after adding the curing agent, the rubbery phase begins to precipitate to form a second phase as the epoxy resin begins to cure and the molecular weight begins to increase. The volume fraction and size of the rubbery domains are influenced by the degree of compatibility of the two phases and the kinetics of gelation.[28] CTBN molecules easily migrate during phase separation and agglomerate into large particles because of the low molecular weight of CTBN. By contrast, the homogenous mixture of epoxy resin with CTBN is kept heated in the presence of an initiator before adding the curing agent during pre-crosslinking. The initiator opens the double bond of C=C in liquid rubber, which initiates the crosslinking of CTBN molecules with each other.[29] Because CTBN molecules disperse homogenously in the epoxy resin, and additionally, the crosslinking reaction is conducted on stirring, CTBN cannot form a continuous phase.

In addition, the concentration of CTBN is very low compared with that of epoxy resin, CTBN molecules are far from each other, so the crosslinking degree is not high and the mixture remains macroscopically homogenous before curing. The carboxyl groups in CTBN react with epoxy to generate copolymers. During curing process, phase separation occurs as the molecular weight of epoxy increases. However, the molecular weight of CTBN is very high after pre-crosslinking, which is different from the traditional CTBN/epoxy system. Furthermore, the produced copolymers assembled on the interface between the two phases. These factors increase difficulty in the migration of CTBN and epoxy resin between the two phases during the phase separation process. Thus, a portion of epoxy is wrapped in the dispersed lightly crosslinked rubbery phase. As the curing proceeds, a localized interpenetrating polymer network is formed in the dispersed rubbery phase.[27]

The fine structures of CTBN/epoxy blends prepared using the two methods were explored by TEM to verify the toughening mechanisms. The samples were stained with OsO_4, in which the dark areas represent the rubber phase. Figure 3 shows the TEM micrographs of CTBN/epoxy blends prepared using the traditional process. The micrographs taken from four different areas are merged [Figure 3(a)]. CTBN rubber disperses in the matrix as particles, the shapes of the particles are irregular, and their size range between 100 and 200 nm. Figure 3(b) shows the TEM image of rubber particles at high magnification. The rubber phase is completely dark, implying that the dispersed phase comprises of pure rubber and no matrix component is included in the rubber phase. The morphology of the pre-crosslinked blend at low magnification is similar to that of the traditional blend, but the average size of the rubber particles in the pre-crosslinking blend is large. At high magnification, the rubber domains exhibit a totally different internal structure. Figure 4 shows the fine structures of the rubber particles with various sizes. The particles are white and dark instead of purely dark, which indicates that the interpenetrating network is formed in the rubber phase.[27] The internal structures in different rubber particles are dissimilar, although the interpenetrating network structure is clearly revealed.

Toughening Mechanisms

The impact behavior of the cured epoxies and the toughening mechanism are examined in terms of the morphology observed by SEM. The smooth and glassy surface (Figure 5) is a substantial evidence of the brittleness of the pure epoxy resin. The fracture surface of the CTBN-modified epoxy is much rougher than that of neat epoxy. Several stress whitening zones are observed. Figures 6 and 7 demonstrate the bowing of the crack front caused by the crack propagating through a particle-filled matrix, and the crack encounters the particles as obstacles and may be eventually pinned. The rubber particles cannot be identified on the fractured surfaces at low magnification due to their small size; however, it can be seen that the crack bowing is related to the rubber particles at high magnification [Figures 6(b) and 7(b)]. The crack length increases as the crack front extends by bowing, leading to a high line energy and enhancement of crack resistance.[30] Energy is absorbed when a material is subjected to an external force[31–33]; hence, crack pinning is a key toughening mechanism for CTBN-modified epoxies.
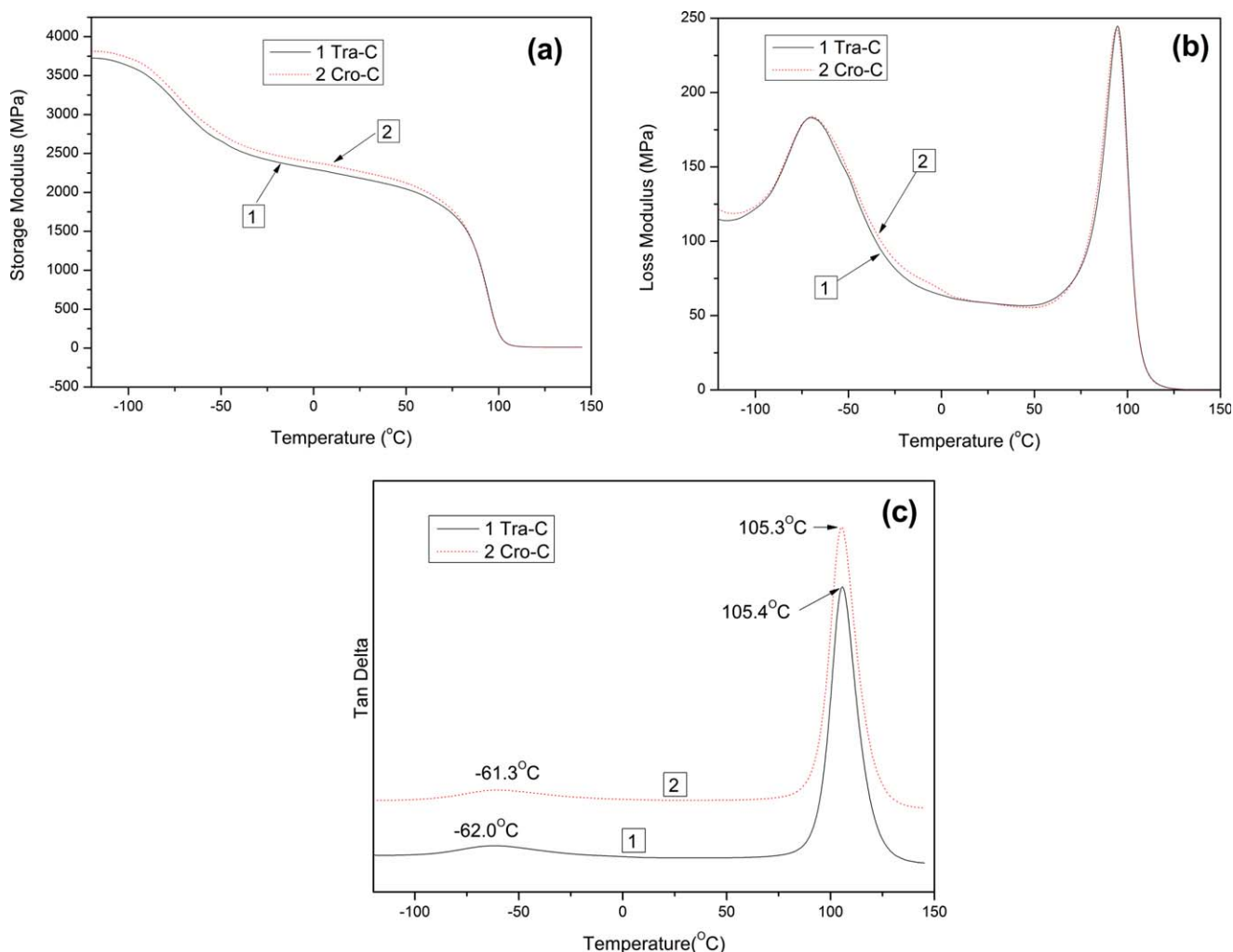
Figure 8. DMA curves of the two epoxy blends toughened with liquid rubber. 1, The traditional blend; 2, the pre-crosslinked blend. (a) Storage modulus; (b) loss modulus; (c) tan δ. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, the effectiveness of pinning is reduced by the breakdown of the particle/matrix interface. Coupling agents have been employed to enhance the strength of bonding between the particles and the matrix.[34] More crack front bowing is observed in Figure 7 compared with that in Figure 6, which is attributed to the formation of a localized interpenetrating polymer network in the dispersed rubbery phase in the pre-crosslinked blend. The special interpenetrating structure enhances the interfacial strength, and pulling out the particles becomes difficult during impact testing, which leads to much higher impact strength of the pre-crosslinked blend.

Dynamic Mechanical Properties

Figure 8 illustrates the DMA curves of epoxy resins modified with CTBN by the two processes. The storage modulus of the pre-crosslinked blend is slightly higher than that of the traditional blend below the glass transition temperature [Figure 8(a)], proving the strong interface adhesive strength in the pre-crosslinked blend from morphology observations. The storage moduli sharply decrease for both blends near the glass transition of the epoxy network and remain constant thereafter in the rubbery plateau region, which is typical for crosslinked polymers. Two relaxation peaks are observed in the plot of loss modulus versus temperature for the two blends [Figure 8(b)]. The α relaxation peak at high temperature corresponds to the T_g of the epoxy matrix, whereas the β relaxation peak at low temperature is attributed to the motions of glycidyl units in the network. T_g of the rubbery phase markedly overlaps with the β relaxation peak.[35,36] Similar results are observed in tan δ curves [Figure 8(c)], in which the glass transition temperatures of the two blends are determined. The temperatures are close to each other, implying that the preparation processes hardly affect the thermal properties of the blends.

CONCLUSIONS

The impact strength of CTBN/epoxy blends can be greatly improved without affecting the modulus by the pre-crosslinking process developed in this study. For blends with similar compositions, the yield strength, Young's modulus, and impact strength of the pre-crosslinked CTBN/epoxy blend respectively increase by 2.7%, 5.5%, and 20.9% compared with the corresponding traditional blend. The yield strength and Young's

modulus of the pre-crosslinked blend are even higher than those of pure epoxy.

The dispersed particles are pure rubber phases in traditional CTBN/epoxy blend, whereas the rubber phase and the matrix form a local interpenetrating network in the pre-crosslinked CTBN/epoxy blend. The local interpenetrating structure greatly improves the interfacial adhesion between the two phases, which improves the mechanical properties of the CTBN/epoxy blend prepared using pre-crosslinking process.

The effects of crack pinning in pre-crosslinking process are more prominent compared with those of the traditional blend because of the strong interface adhesion strength.

The glass transition temperatures of the blends prepared using traditional and pre-crosslinking processes are very close to each other.

REFERENCES

1. Lee, H. N. K. EPST, 1st ed., The Epoxylite Corporation, **1967**; Vol. *6*, pp 209–271.

2. Ratna, D.; Banthia, A. K. *Macromol. Res.* **2004**, *12*, 11.

3. Bagheri, R.; Marouf, B. T.; Pearson, R. A. *J. Macromol. Sci. C* **2009**, *49*, 201.

4. McGarry, F. J.; P. *Roy. Soc. A* **1970**, *319*, 59.

5. Bucknall, C. B.; Partridge, I. K. *Polymer* **1983**, *24*, 639.

6. Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. *Polymer* **1983**, *24*, 1341.

7. Yee, A. F.; Pearson, R. A. *J. Mater. Sci.* **1986**, *21*, 2462.

8. Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, *30*, 213.

9. Gilbert, A. H.; Bucknall, C. B. *Makromol. Chem. Macromol. Symp.* **1991**, *45*, 289.

10. Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. *Polymer* **1991**, *32*, 2020.

11. Kemp, T. J.; Wilford, A.; Howarth, O. W.; Lee, T. C. P. *Polymer* **1992**, *33*, 1860.

12. Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. *Polymer* **1993**, *34*, 4832.

13. Meijerink, J. I.; Eguchi, S.; Ogata, M.; Ishii, T.; Amagi, S.; Numata, S.; Sashima, H. *Polymer* **1994**, *35*, 179.

14. Unnikrishnan, K. P.; Thachil, E. T. *Des. Monomers. Polym.* **2006**, *9*, 129.

15. Garg, A. C.; Mai, Y. W. *Compos. Sci. Technol.* **1988**, *31*, 179.

16. Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D.; Taylor, A. C.; Sprenger, S. *Polymer* **2007**, *48*, 530.

17. Xu, S. A.; Wang, G. T.; Mai, Y. W. *J. Mater. Sci.* **2013**, *48*, 3546.

18. Chen, C. G.; Justice, R. S.; Schaefer, D. W.; Baur, J. W. *Polymer* **2008**, *49*, 3805.

19. Liang, Y. L.; Pearson, R. A. *Polymer,* **2009**, *50*, 4895.

20. Sprenger, S. *J. Appl. Polym. Sci.* **2013**, *130*, 1421.

21. Thompson, Z. J.; Hillmyer, M. A.; Liu, J.; Sue, H. J.; Dettloff, M.; Bates, F. S. *Macromolecules* **2009**, *42*, 2333.

22. Liu, J.; Sue, H. J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Phamc, H. *Acta. Mater.* **2009**, *57*, 2691.

23. Perez, C. D.; Redline, E. M.; Francis, L. F.; Bates, F. S. *ACS Macro. Lett.* **2012**, *1*, 338.

24. Redline, E. M.; Francis, L. F.; Bates, F. S. *J. Polym. Sci. Pol. Phys.* **2011**, *49*, 540.

25. Liu, J.; Thompson, Z. J.; Sue, H. J.; Bates, F. S.; Hillmyer, M. A.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H. *Macromolecules 43*, 2010, 7238.

26. Yee, A. F.; Du, J.; Thouless, M. D. Performance, Paul, D. R., Bucknall, C. B., Eds.; John Wiley & Sons: New York, **2000**; Vol. 2, Chapter 26.

27. Zhou, H. S.; Xu, S. A. *Mater. Lett.* **2014**, *121*, 238.

28. Manzione, L. T.; Gillham, J. K.; McPherson, C. A. *J. Appl. Polym. Sci.* **1981**, *26*, 889.

29. Hsu, Y. G.; Liang, C. W. *J. Appl. Polym. Sci.* **2007**, *106*, 1576.

30. Kinloch, A. J.; Maxwell, D.; Young, R. J. *J. Mater. Sci. Lett.* **1985**, *4*, 1276.

31. Wetzel, B.; Rosso, P.; Haupert, F.; Friedrich, K. *Eng. Fract. Mech.* **2006**, *73*, 2375.

32. Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D.; Taylor, A. C.; Sprenger, S. *Polymer* **2007**, *48*, 530.

33. Yang, J. P.; Feng, Q. P.; Chen, Z. K.; Fu, S. Y. *J. Appl. Polym. Sci.* **2011**, *119*, 863.

34. Spanoudakis, J.; Young, R. J. *J. Mater. Sci.* **1984**, *19*, 473.

35. Jyotishkumar, P.; Koetz, J.; Tiersch, B.; Strehmel, V.; Ozdilek, C.; Moklenaers, P.; Hassler, R.; Thomas, S. *J. Phys. Chem. B,* **2009**, *113*, 5418.

36. Mathew, V. S.; Jyotishkumar, P.; George, S. C.; Gopalakrishnan, P.; Delbreilh, L.; Saiter, J. M.; Saikia, P. J.; Thomas, S. *J. Appl. Polym. Sci.* **2012**, *125*, 804.