

# Dynamic Mechanical Properties of Castor Oil-Based Polyurethane/Epoxy Graft Interpenetrating Polymer Network Composites

Shoubing Chen,<sup>1,2</sup> Qihua Wang,<sup>1</sup> Xianqiang Pei,<sup>1</sup> Tingmei Wang<sup>1</sup>

<sup>1</sup>State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

<sup>2</sup>Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Received 11 July 2009; accepted 25 March 2010

DOI 10.1002/app.32518

Published online 28 May 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of graft interpenetrating polymer networks (IPNs) were prepared from epoxy (EP) and castor oil-based polyurethane (PU). The dynamic mechanical properties, as well as the tensile and impact strength, of the IPNs were studied systematically. Results revealed that PU/EP IPNs showed improved damping properties compared with that of EP matrix. In addition, the PU content and testing frequencies had much influence on the damping properties of the IPNs. The IPN composites showed better damping properties with higher PU content or under higher testing frequencies.

Mechanical analysis showed that the tensile strength of IPN composites was higher than that of pure EP. However, higher PU content (beyond 5 wt %) impaired the impact strength of the IPNs. It is expected that PU/EP IPNs may be potentially used as structural damping materials. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1144–1151, 2010

**Key words:** interpenetrating polymer networks; castor oil-based polyurethanes; dynamic mechanical properties; tensile strength; impact strength

## INTRODUCTION

With the development of modern industry, the damping of vibration has become a critical problem in the design of structural components. Excessive vibration can cause damage to either the surroundings or to the source. Application of polymer composites is a possible way to avoid these problems.<sup>1</sup> Epoxy (EP) resins based on diglycidyl ether of bisphenol-A, which are associated with high modulus and strength,<sup>2</sup> have been widely studied and used in many kinds of structural composites.<sup>3,4</sup> However, EP resins are generally brittle polymers, which restrict their application in damping materials. Polyurethane (PU), a flexible and elastic polymer, is one of the most versatile polymers, which is widely used in coatings, adhesives, thermoplastic elastomers, and composites. The application of PU in the structural

materials is limited because of its low-mechanical strength.

Interpenetrating polymer networks (IPNs) are polymer alloys consisting of two or more polymers in a network form, held together by permanent entanglements with only occasional covalent bonds between the chains of the two different types of polymers. One of these polymers is synthesized and/or crosslinked in the presence of the others. It is held together by permanent entanglement and shows excellent thermal stability and mechanical properties because of a synergistic effect induced by the forced compatibility of individual components. Dean et al.<sup>5</sup> studied IPNs which were prepared from a model vinyl ester resin and two EP resin systems, and the curing kinetics were monitored via NIR and rheometry at 70°C. Qin et al.<sup>6,7</sup> investigated damping properties and morphology of a series of PU/vinyl ester resin simultaneous and gradient IPNs and showed that the damping temperature range is broadened by controlling the techniques of gradient IPN and different microstructure of IPN determines their different damping properties. They also studied the vibration damping properties of gradient PU/VER (BMA) IPN as coatings, polysulfide rubber modified EP resin without fillers and with common inorganic fillers and whisker crystals as constrained layer.<sup>8</sup> Lee et al.<sup>9</sup> prepared IPN membranes of PU and poly(methyl methacrylate) crosslinked with

Correspondence to: T. Wang (wangtin3088@sina.com).

Contract grant sponsor: Knowledge Innovative Engineering of Chinese Academy of Sciences; contract grant number: KG CX3-SYW-205.

Contract grant sponsor: The Innovative Group Foundation from NSFC; contract grant number: 50721062.

Contract grant sponsor: The National 973 Project of China; contract grant number: 2007CB607606.

*Journal of Applied Polymer Science*, Vol. 118, 1144–1151 (2010)  
© 2010 Wiley Periodicals, Inc.

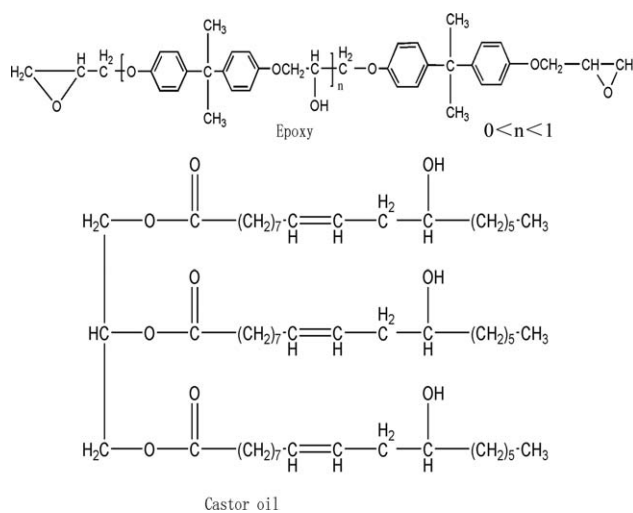
ethylene glycol dimethacrylate (EGDMA), and in the result of tensile test, the membrane crosslinked with 10 wt % EGDMA showed the maximum tensile strength. Trakulsujaritchook and Hourston<sup>10</sup> studied silicon-filled PU/poly(ethyl methacrylate) IPN at the 70PUR/30PEMA composition ratio. Results showed that the filler enhanced the damping ability of the IPN at certain temperature range and improved material strength. Li and Mao<sup>11</sup> studied an existing polyether PU product/EP semi-IPNs, and when formed the IPNs, damping properties and mechanical properties improved. Mahesh et al.<sup>12</sup> investigated IPNs of bismaleimide-modified PU-EP systems, proved that the incorporation of aromatic bismaleimide into the PU-modified EP system increased the glass transition temperature, thermal stability, and electrical properties. Liu and Bui<sup>13</sup> studied the castor oil-based PU and found that NCO/OH ratio had significant effects on their mechanical properties. On this basis, Raymond and Bui<sup>14</sup> studied the mechanical properties of EP and castor oil-based PU graft IPNs. The results showed that the tensile strength and thermal stability improved compared with those of the pure components; however, their impact energy obtained from instrumented impact testing did not show much enhancement except for a narrow PU composition gap between 25% and 30%. However, most of the studies focused on the mechanical properties of IPNs, the literatures on damping properties were few especially on the castor oil-based PU/EP IPNs.

In this study, isocyanate group terminated castor oil-based PU prepolymer was synthesized first. Then, a series of PU-modified EP graft IPN composites were prepared. Dynamic mechanical properties, tensile, and impact strength, and fracture surfaces of the composites were examined, and especially, we focused on the dynamic mechanical properties. The purpose of this research is to investigate the effects of the component ratios between castor oil-based PU and EP on the damping properties and mechanical properties of the composites, which is helpful in expanding the application scope of EP resins as structural damping materials. This work could also serve as the basis for further modification of the PU/EP graft IPN composites.

## EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol-A-based (DEGDA) EP resin WSR-618 (with an epoxide equivalent weight of 196 g/mol) was purchased from Wuxi Resin Factory of Bluestar New Chemical Materials (Jiangsu, China). 2,4-Toluene diisocyanate (TDI) was supplied by Shanghai Sanyou Chemical Reagent (Shanghai, China). Castor oil was obtained from Laiyang



**Scheme 1** The structural formulas of castor oil and epoxy.

Shuangshuang Chemical (Shandong, China). 2,4,6-Tris(dimethylaminomethyl)phenol (DMP-30, Jiangdu Dajiang Chemical Factory, Jiangsu, China) was used as a catalyst for the curing of EP. Castor oil and DGEBA were dried under a vacuum before use. The structural formulas of castor oil and EP are shown in Scheme 1. The equivalent weight per hydroxyl group of castor oil is 332.8 g and that of TDI per NCO group is 87.0 g. The two values were used to calculate the NCO/OH ratio for the synthesis of the PU phase.

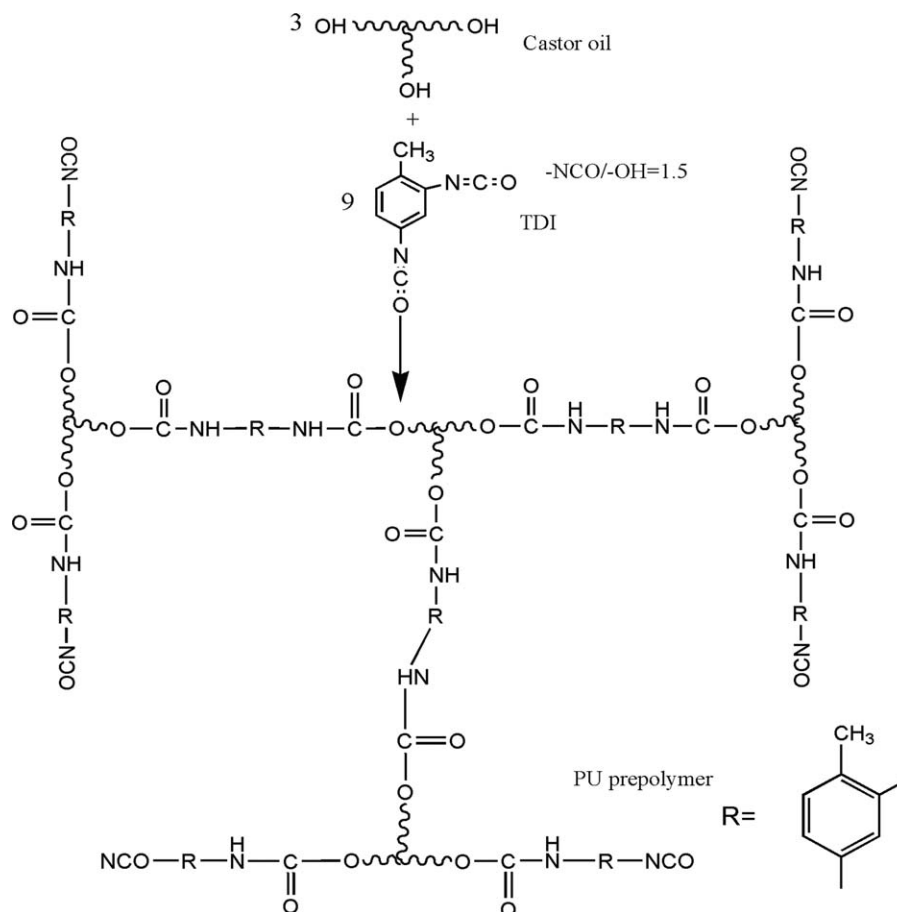
### Synthesis of EP/PU IPNs

A typical synthetic method was as follows: A weighed amount of castor oil was placed in a round-bottomed flask, heated until 60°C, and thoroughly mixed with a predetermined amount of TDI, which corresponds to a fixed NCO/OH ratio of 1.50.<sup>13</sup> The reaction system was stirred vigorously with mechanical stirring, under a dry nitrogen atmosphere, for about 45 min to form a urethane prepolymer. Then, a predetermined amount of DGEBA was added to the system which was stirred for a while before addition of 1.5 wt % of DMP-30 (based on the amount of DGEBA). The mixture was degassed under a vacuum for about 30 min (until bubbling ceased) and then poured into preheated molds made from Teflon. Finally, the samples were cured at 120°C for 6 h.<sup>14</sup> The preparing process of the PU/EP IPNs is shown in Schemes 2 and 3, during which the component ratios between castor oil-based PU (PU ratio from 5 to 30 wt %, and the alternation is 5 wt %) and EP were adjusted.

### Characterization and testing procedures

#### Structural analysis of the IPNs

The structure of the IPNs was analyzed using Fourier transform infrared (FTIR) spectra, which was



**Scheme 2** Formation of castor oil-based PU prepolymer.

recorded on an IFS 66v/s (Bruker, GER) infrared spectrophotometer.

#### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a DMA 242 C analyzer (NETZSCH Instruments, GER) with double-cantilever mode (3.2 cm × 1.0 cm) over a temperature range from  $-50^\circ\text{C}$  to  $150^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$  at 1 Hz, 10 Hz, 20 Hz, and 50 Hz. The samples were rectangular bars (6.0 cm × 1.0 cm × 0.4 cm). Five specimens were tested for each composition.

#### Tensile tests and impact tests

Tensile strength was carried out on an Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen Sans Testing Machine, China), according to GB/T1040.2-2006(ISO527-2:1993) using a standard sample size (ISO527-2/1BA). The Charpy impact strength of unnotched specimens (5.0 cm × 0.6 cm × 0.4 cm) was studied on a tester according to GB/T1043-93(ISO179-1982). Five specimens were tested for each sample.

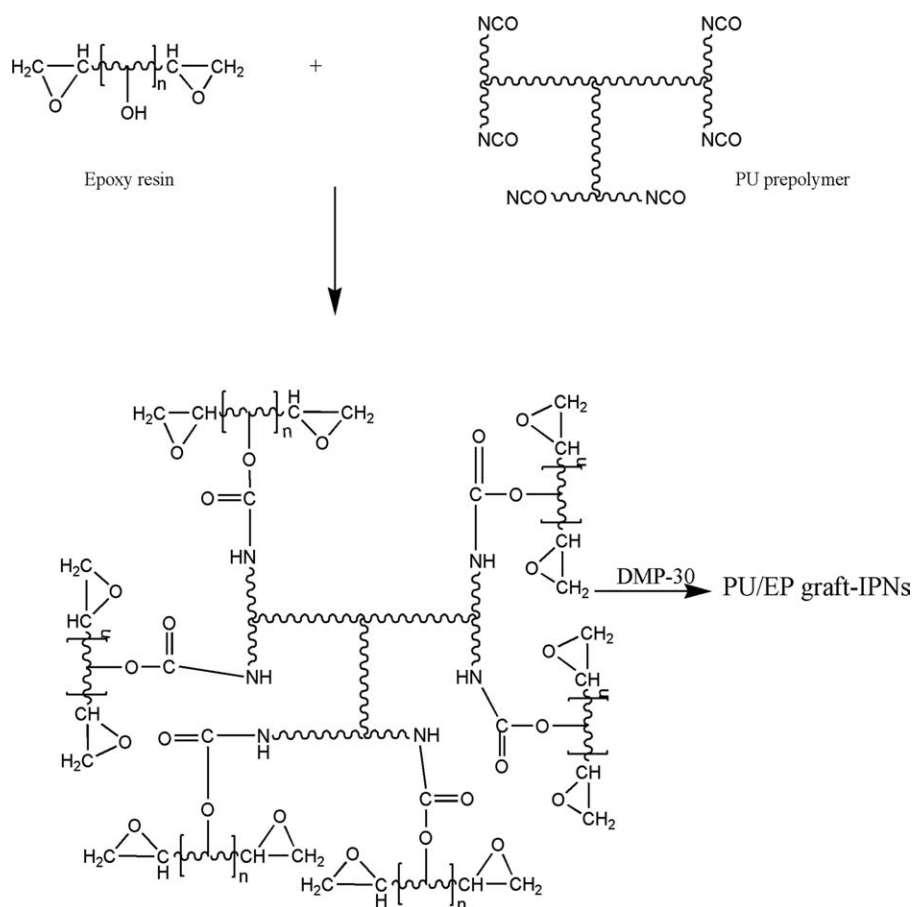
#### Surface morphologies of fractured surfaces

The fracture surface morphologies of the composites were observed and analyzed by JSM-5600 scanning electronic microscope (JEOL, Japan) operated at 20 kV. The samples were coated with gold before observation.

## RESULTS AND DISCUSSION

#### Structural analysis of the IPNs

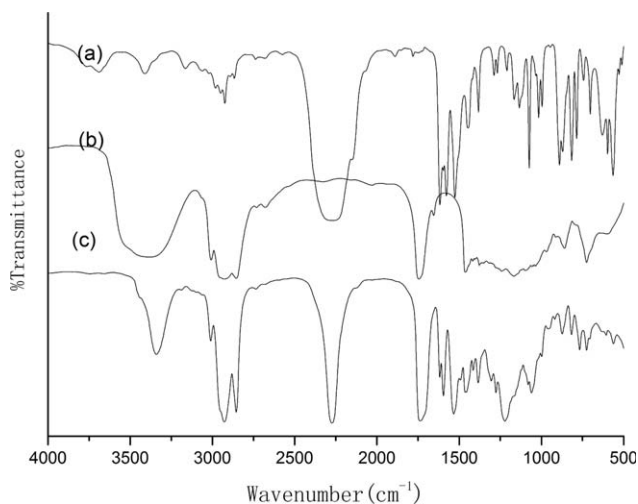
To confirm the formation of PU prepolymer and inter crosslinked network of PU and EP, the FTIR spectra of both the raw materials and products is shown in Figures 1 and 2, respectively. As can be seen from Figure 1, the characteristic bands of isocyanate group at  $2273 \text{ cm}^{-1}$  and  $-\text{NH}$  of secondary amide group at  $3338 \text{ cm}^{-1}$  indicated the formation of PU prepolymer. Because neither diisocyanate nor castor oil has the secondary amide group, it only appears in the PU prepolymer (Scheme 2). In addition, the formation of inter crosslinked network of PU and EP can be validated by the disappearance of isocyanate absorbing bands. With the reaction going



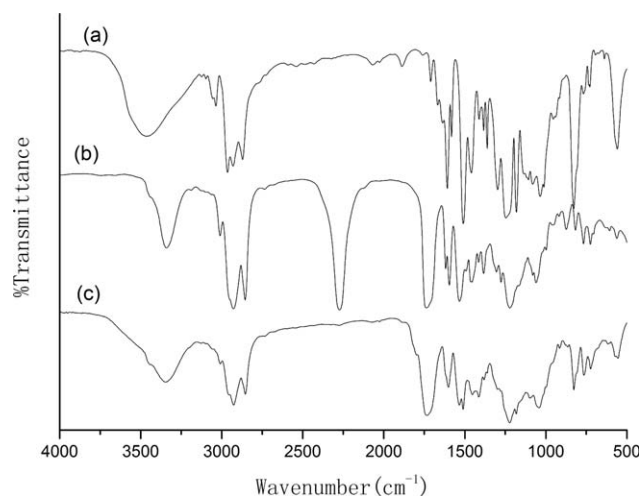
**Scheme 3** Formation of PU/EP graft interpenetrating polymer networks.

on, the intensity of the isocyanate group peak decreased and then disappeared when the reaction completed. In Figure 2, the characteristic groups of EP are aromatic rings ( $1500\text{--}1600\text{ cm}^{-1}$ ), EP and oxirane rings ( $\sim 1250\text{ cm}^{-1}$ ,  $800\text{--}890\text{ cm}^{-1}$ ), and

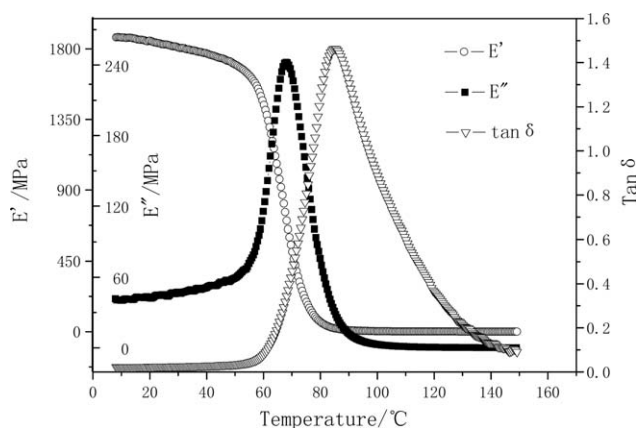
ether groups ( $1150\text{--}1050\text{ cm}^{-1}$ ). When the final polymer formed, aromatic rings ( $1500\text{--}1600\text{ cm}^{-1}$ ) and ether groups ( $1150\text{--}1050\text{ cm}^{-1}$ ) were not changed. The EP and oxirane rings ( $\sim 1250\text{ cm}^{-1}$ ,  $800\text{--}890\text{ cm}^{-1}$ ) opened when the EP cured, but it cannot be



**Figure 1** FTIR spectra of (a) TDI, (b) castor oil, and (c) polyurethane prepolymer.



**Figure 2** FTIR spectra of (a) unmodified epoxy, (b) polyurethane prepolymer, and (c) polyurethane-modified epoxy (PU20%).

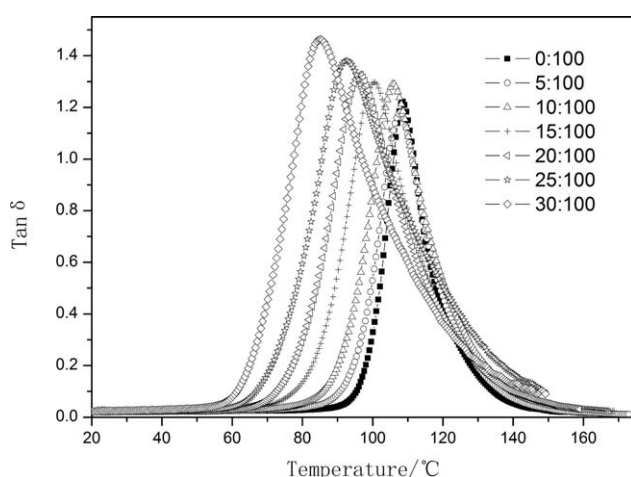


**Figure 3** Temperature dependence of  $E''$ ,  $E'$ , and  $\tan \delta$  for the composite with 30 wt % PU at 10 Hz.

opened completely. The variation of isocyanate band at  $2273 \text{ cm}^{-1}$  justified the formation of PU/EP IPN composites.

### Dynamic mechanical analysis

Figure 3 shows the temperature dependence of  $E''$ ,  $E'$ , and  $\tan \delta$  for the composite with 30 wt % PU at 10 Hz. It was clear that in the temperature range from  $50^\circ\text{C}$  to  $70^\circ\text{C}$ ,  $E'$  decreased sharply, whereas  $E''$  increased abruptly. At  $85.1^\circ\text{C}$ ,  $\tan \delta$  showed obvious peak, which corresponded to the glass transition temperature ( $T_g$ ). In this study,  $E''$  and  $\tan \delta$  both showed single peak, which indicated the polymer two-phase separation did not occur.<sup>15</sup> There are two points. At low temperature, the movement of chain segment of polymers is "frozen," when the force applies on the material,  $E'$  is high and the elastic deformation is small, the polymer material is in the



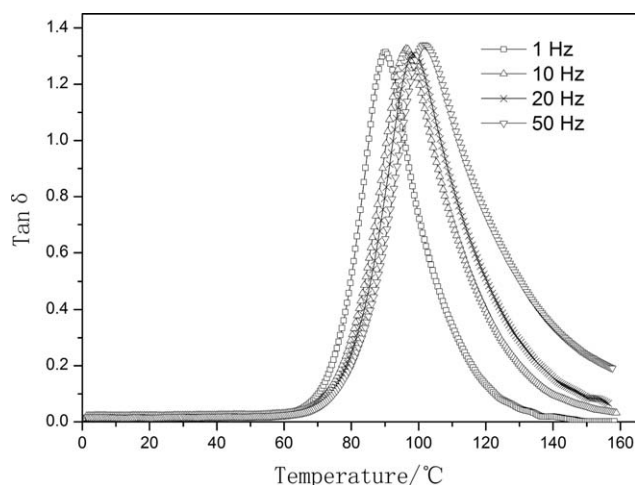
**Figure 4** DMA curves of PU/EP IPNs with component ratios from 0 : 100 to 30 : 70 at 10 Hz.

**TABLE I**  
DMA Data of PU/EP IPNs with Different Component Ratios at 10 Hz

PU/EP (wt %)	Temperature range ( $^\circ\text{C}$ ) Tan $\delta > 0.3$	Tan $\delta$ (max.)	$T_g$ ( $^\circ\text{C}$ )
0 : 100	99.7–123.8	1.222	108.5
5 : 95	96.7–125.2	1.081	107.9
10 : 90	92.6–127.2	1.291	105.8
15 : 85	85.6–124.2	1.298	100.6
20 : 80	80.1–124.2	1.326	96.5
25 : 75	74.2–129.9	1.381	92.6
30 : 70	67.3–123.8	1.462	85.1

glass state, under which condition the  $\tan \delta$  ( $\tan \delta = E''/E'$ ) is low. When at high temperature (the polymers at the high elastic state), the chain segment will move freely, the deformation of material is large. However, the deformation can recover rapidly when the stress is revoked. So both the  $E'$  and  $\tan \delta$  are low in the high-elastic state. Only in the glass transition state,  $E'$  reduces and  $\tan \delta$  attains a peak value. So the glass transition temperature region is an important factor evaluating the dynamic mechanical properties in current work.<sup>15</sup> It is customary to take the temperature range ( $\tan \delta > 0.3$ )<sup>16</sup> as a standard to evaluate the dynamic mechanical properties of damping materials.

Figure 4 and Table I show DMA curves and data of PU/EP IPNs with different component ratios at 10 Hz. It can be seen that there was only one  $T_g$  peak for all the IPNs and that the component ratio exerted much influence on the damping properties. In addition, the damping temperature range became wider and the temperature for peak  $\tan \delta$  became lower with the increasing of PU content in the composites. This indicated that PU component



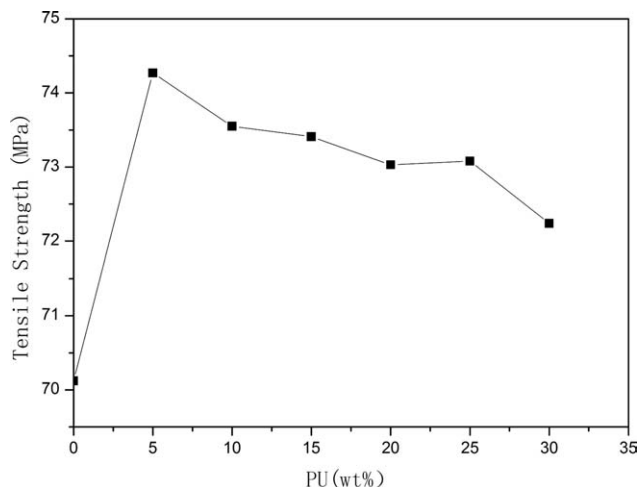
**Figure 5** DMA curves of PU/EP IPNs with component ratio 80 : 20 at different frequencies.

**TABLE II**  
DMA Data of PU/EP IPNs with Component Ratio 80 : 20 at Different Frequencies

Frequency (Hz)	Temperature range (°C) Tan $\delta > 0.3$	Tan $\delta$ (max.)	$T_g$ (°C)
1 Hz	76.6–111.5	1.315	90.1
10 Hz	80.1–124.2	1.326	96.5
20 Hz	81.6–129.3	1.306	98.4
50 Hz	83.2–143.4	1.340	101.6

improved the damping properties of the composites by forming IPN networks. The results showed that PU and EP were well compatible in the IPN networks. The two possible reasons are as follows: on the one hand, there are interpenetration and entanglement between PU and EP in the IPNs; on the other hand, there is higher degree of hydrogen bonding and crosslinking in the IPN system, which could also improve the compatibility of the two phases.

In addition to the component ratios, testing frequencies also had influence on the dynamic mechanical properties of the PU/EP IPNs. Figure 5 and Table II show the DMA curves and data of PU/EP IPNs with component ratio 80 : 20 at different frequencies, respectively. It can be seen that the  $T_g$  temperature of the IPNs became higher and the  $T_g$  region (tan  $\delta > 0.3$ ) became wider with increasing frequencies. The reason for the  $T_g$  shift was that at a fixed temperature, when the frequency was low enough and  $1/\omega \gg \tau$  (chain segment; the relaxing speed of chain segment from one equilibrium position to another was expressed with  $\tau$ ), the polymer showed high-elastic state. When the frequency was high enough and  $1/\omega \ll \tau$  (chain segment), the polymer showed glassy state.



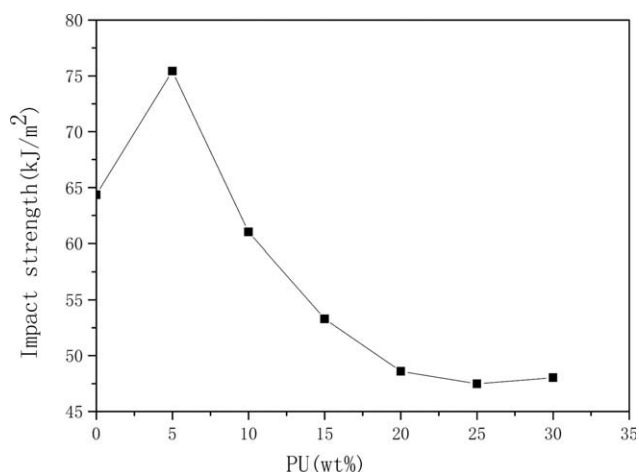
**Figure 6** Tensile strength of PU/EP IPNs as a function of PU composition.

However, when  $1/\omega \approx \tau$  (chain segment), polymers were at the glass transition state, and this state had good damping property. Thus, higher the frequency applied, higher temperature was required to achieve glass transition for the same kind of polymer. That was to say  $T_g$  temperature of the polymer became higher with increasing frequencies.<sup>15</sup> The results correspond to an Arrhenius dependence of  $\omega = \omega_0 \exp(\Delta H/RT)$ , where  $R$  is the universal gas constant,  $\Delta H$  is activation energy of the polymer chain segment, and  $\omega_0$  is a constant of the system.<sup>15,17</sup>

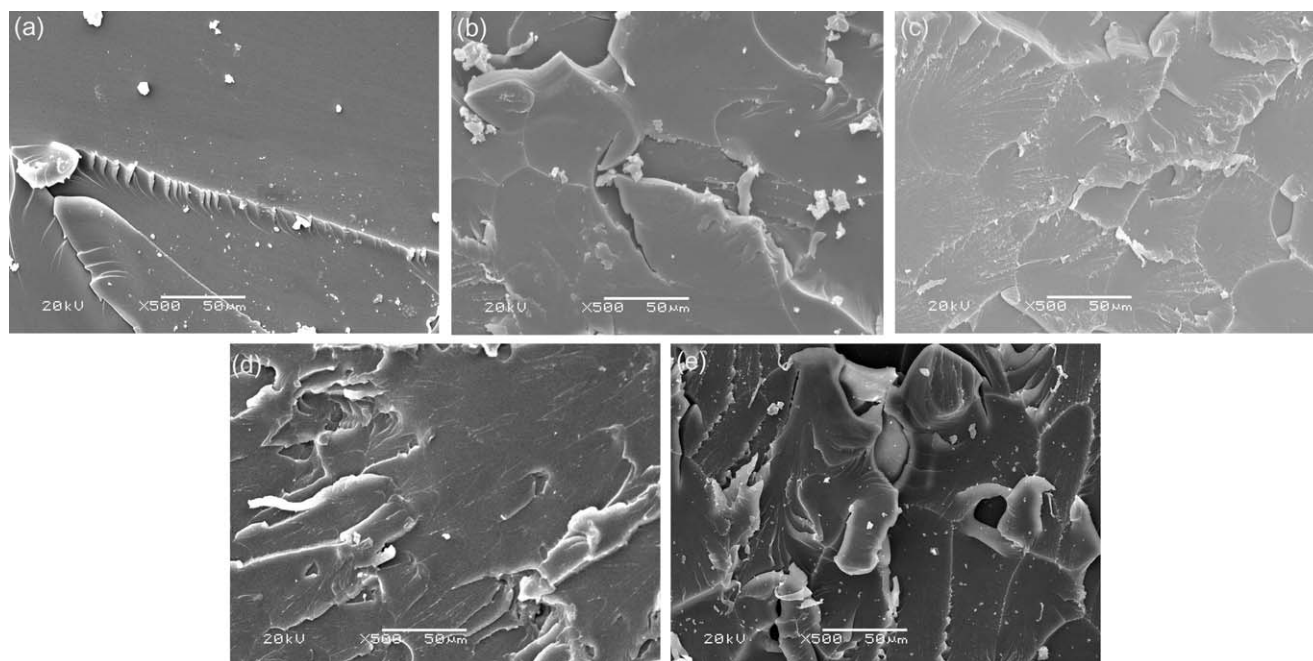
### Tensile strength and impact strength measurements

The tensile strength of the PU/EP IPNs is shown in Figure 6. It can be seen that the incorporation of PU into the EP system enhanced the tensile strength of the EP matrix. The result may be attributed to the increased degree of interpenetration in the graft IPNs.<sup>18</sup> The PU prepolymer first grafted onto EP precursor and then the EP precursor crosslinked at the existence of curing agent. As a result, the interpenetration and entanglement between PU and EP improved the tensile strength of EP matrix.

Figure 7 shows the impact strength of the PU/EP IPNs. It is clearly seen that the impact strength of EP matrix can be improved when the PU content is 5%. When the PU content beyond 5%, the impact strength of the IPNs decreased sharply and lower than pure EP. As is known, the state of the molecular chains of PU and EP exert much influence on the impact behavior of the IPNs. When the PU content was relatively lower (5%), this toughening effect was probably due to dissolution of the PU into the EP network. In this case, it was probably incorporating



**Figure 7** Impact strength of PU/EP IPNs as a function of PU composition.



**Figure 8** SEM micrographs of PU/EP IPN composites with various PU contents: (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 20 wt %, and (e) 30 wt %.

dispersed rubber particles into the continuous EP resin phase and the degree of grafting was low. The flexible and elastic nature of PU chain governed the impact behavior, which improved their impact strength. When the PU content increased further, the degree of grafting and the interpenetrating between PU and EP increased which restricted the mobility of the molecular chains. As a result, the IPN materials became brittle and the impact strength of the IPNs decreased sharply.

#### Morphologies of IPN fracture surfaces

Figure 8 shows the morphologies of the IPNs fracture surfaces with different content of PU. For pure EP, the fractured surface was very smooth, in which glassy homogeneous microstructures can be seen. However, heterogeneous morphologies dominated the fractured surfaces of the PU/EP IPNs. In addition, the microstructures of the IPNs became more and more heterogeneous with the increasing content of PU. The vibrations could be attributed to the increased grafting and interpenetrating between PU and EP.

#### CONCLUSIONS

1. The damping properties of EP matrix can be improved by forming graft IPNs with PU. With the increasing of the PU content, the

damping properties of the IPNs increased, whereas the glass transition temperature decreased. In addition, the PU/EP IPN composites showed better damping properties under higher frequencies.

2. By forming interpenetrating network with PU, the tensile strength of EP matrix was improved, whereas the formation of IPNs impaired the impact strength of EP matrix when the content of PU beyond 5 wt %.
3. Analysis of the fractured surfaces revealed that the homogeneous microstructures of EP matrix changed to heterogeneous morphologies after the formation of PU/EP IPNs.

The authors thank Xin Shao of Liaocheng University for the DMA analysis support.

#### References

1. Kang, S.; Hong, S. I.; Choe, C. R.; Park, M.; Rim, S.; Kim, J. *Polymer* 2001, 42, 879.
2. Petri, E. M. *Epoxy Adhesive Formulations*; McGraw-Hill: New York, 2005.
3. Krishnan, S.; Mohan, P. S. *J Coat Technol Res* 2007, 4, 89.
4. Gu, J.; Wu, G. H.; Zhao, X. *J Univ Sci Technol Beijing* 2008, 15, 509.
5. Dean, K.; Cook, W. D.; Rey, L.; Galy, J.; Sautereau, H. *Macromolecules* 2001, 34, 6623.
6. Qin, C. L.; Cai, W. M.; Cai, J.; Tang, D. Y.; Zhang, J. S.; Qin, M. *Mater Chem Phys* 2004, 85, 402.
7. Qin, C. L.; Tang, D. Y.; Cai, J.; Zhang, J. S.; Cai, W. M.; Sun, X. D. *J Mater Sci Technol* 2003, 19, 56.

8. Qin, C. L.; Zhao, D. Y.; Bai, X. D.; Zhang, X. G.; Zhang, B.; Jin, Z.; Niu, H. J. *Mater Chem Phys* 2006, 97, 517.
9. Lee, M. J.; Kim, H. S.; Kim, W. Y. *Polymer (Korea)* 1998, 22, 926.
10. Trakulsujarithchok, T.; Hourston, D. J. *Eur Polym J* 2006, 42, 2968.
11. Li, Y.; Mao, S. F. *J Appl Polym Sci* 1996, 61, 2059.
12. Mahesh, K. P. O.; Alagar, M.; Jothibas, S. *J Appl Polym Sci* 2006, 99, 3592.
13. Liu, T. M.; Bui, V. T. *J Appl Polym Sci* 1995, 56, 345.
14. Raymond, M. P.; Bui, V. T. *J Appl Polym Sci* 1998, 70, 1649.
15. Guo, M. *Dynamic Mechanical Thermal Analysis of Polymer Composites*; Chemical Industry Press: Beijing, 2002; Chapter 2.
16. Hu, R.; Dimonie, V. L.; El-Aasser, M. S.; Pearson, R. A.; Hiltner, A.; Mylonakis, S. G.; Sperling, L. H. *J Polym Sci Part B: Polym Phys* 1997, 35, 1501.
17. Compan, V.; DiazCalleja, R.; Ribes, A.; Andrio, A.; Lopez, M. L.; Riande, E. *J Appl Polym Sci* 1996, 60, 767.
18. Hsieh, K. H.; Han, J. L. *J Polym Sci Part B: Polym Phys* 1990, 28, 623.