JOURNAL OF MATERIALS SCIENCE **32** (1997) 3503–3509

Interpenetrating polymer networks of polyurethane cross-linked epoxy and polyurethanes

Y. C. CHERN, K. H. HSIEH*
Chemical Engineering Department, National Taiwan University, Taipei, 106 Taiwan
J. S. HSU
Chemistry Department, Chung-Shan Institute of Science Technology, Lung-Tan, Taiwan

Interpenetrating polymer networks (IPNs) were prepared from polyurethane (PU) cross-linked epoxy and polyurethanes based on the mixture of polydiol and polytriol by the one-shot method. The mechanical properties, dynamic mechanical properties, morphology and damping behaviour were investigated. The results show that the damping ability and mechanical strength are enhanced through the introduction of PU cross-linked epoxy into the PU matrix to form the IPN structure. As the epoxy content increases, the tensile strength of the two types of the IPNs decrease in low composition, then increase in high composition. The damping properties of the PU (polyether type) cross-linked epoxy/PU IPNs are much better than those of the PU (polyester type) cross-linked epoxy/PU IPNs, but the mechanical properties reveal an opposite tendency. The sample with 20 wt% epoxy content in the PU cross-linked epoxy/PU IPNs shows particle–matrix morphology and exhibits good damping properties.

1. Introduction

Viscoelastic polymeric materials are capable of attenuating the sound and damping the vibration. As the temperature or frequency varies, the loss modulus (E'') and loss tangent (tan δ) show a peak value, where damping reaches a maximum [1]. Therefore, the polymers are usually used as damping materials near their glass transition temperatures [2]. The ability for a polymer to dissipate sound and vibrational mechanical energy into heat depends on the intensity of loss modulus or tan δ value at the applying temperature. Generally, the damping peaks of homopolymers ranged only 20–30 °C, which is rather narrow for practical applications [3]. However, the temperature range for a good damping material is required to be at least 60–70 °C. In order to broaden the damping peaks and improve the damping behaviour, damping polymers of polyblends, copolymer, or interpenetrating polymer networks (IPNs) [4–10] were developed. In recent years, interpenetrating polymer networks have been widely applied as a damping material with satisfactory properties, for instant, poly(methyl methacrylate)/polyurethane (PU), and epoxy/PU IPN systems [11–19].

Two types of polyurethanes (polyether or polyester) cross-linked epoxy were introduced into polyurethane matrix to prepare the PU cross-linked epoxy/PU IPNs. In this paper, the LA (loss modulus area), TA (tan δ area) were measured to characterize damping property of the IPNs. The effect of the epoxy content in the IPNs and the type of PU cross-linked epoxy/PU IPNs on the damping behaviour, mechanical properties, dynamic mechanical properties, and morphology were investigated.

2. Experimental procedure

2.1. Materials

The materials used, and their designations, are listed in Table I. The polyol (PPG1000, PPG400, PBA1000, PPG3000 (polytriol) and epoxy (diglycidyl ether of bisphenol A) were degassed at 80 °C with magnetic stirring in the flask for at least 12 h and the 4,4′-diphenyl methane diisocyanate (MDI) was melted at 70 °C before they were used. The 2,4,6, tri(dimethyl aminomethyl) phenol (TDMP) used as a catalyst of epoxy was employed without further purification.

2.2. Preparation of polyurethane prepolymer

The polyurethane prepolymer were prepared by two equivalents of MDI and one equivalent of polyol (PPG1000 or PBA1000). The reaction of MDI and polyol was carried out at 70 °C under dry nitrogen.

---

* Author to whom correspondence should be addressed.

0022–2461 © *1997 Chapman & Hall*

TABLE I Materials used in this study

Designation	Description	Source
PPG400	Poly(oxypropylene)glycol MW = 400	ACRO Chem. Taiwan Co., Taiwan
PPG1000	Poly(oxypropylene)glycol MW = 1000	ACRO Chem. Taiwan Co., Taiwan
PBA1000	Poly(tetramethylene adipate)glycol MW = 1000	Tai Gin Co., Taiwan
PPG3000	Poly(oxypropylene)triol, ethylene oxide capped	ACRO Chem. Taiwan Co., Taiwan
MDI	4,4′-diphenyl methane diisocyanate. Eq. wt = 125	BASF Wyandotte Co., Switzerland
Epoxy	Diglycidyl ether of bisphenol A EEW = 186, $n = 0.11267$	Dow-Chemical Co., USA
TDMP	2,4,6, tri(dimethyl aminomethyl) phenol	Ciba-Geigy Co., Switzerland
DBTDL	Dibutyltin dilaurate (catalyst Sn% = 18)	Merck Co., Germany

The reaction was stopped, when the –NCO content, which was determined by the di-*n*-butylamine titration method [20], reached the theoretical value.

2.3. Preparation of polyurethane cross-linked epoxy

PU (PPG1000 or PBA1000) prepolymer was put into a reaction kettle which was maintained at about 70 °C under dry nitrogen. A suitable amount of epoxy (the equivalent ratio of –NCO group of the PU prepolymer and hydroxyl group of the epoxy is 1.05) was then poured into the kettle under vigorously mixing. The cross-linking reaction occurred between the pendent hydroxyl groups of the epoxy resin and the isocyanate groups of polyurethane prepolymer. Several drops of dibutyltin dilaurate (DBTDL) were added and vigorously agitated with the mixture to accelerate the reaction for several hours. The intensity of the infrared spectrum absorption peak (2270 cm^{-1}) of the isocyanate was measured periodically to detect the degree of reaction. When the NCO– absorption peak at 2270 cm^{-1} disappears, it indicates that the pendent hydroxyl groups of epoxy completely react with the isocyanate groups of the polyurethane prepolymer.

To cure PU cross-linked epoxy by 3 phr (per hundred resin) of catalyst (TDMP) was added and followed by vigorously stirring with the PU cross-linked epoxy for 60 s with high torque mechanical stirrer at about 60 °C. It was then poured into a hot mould at 90 °C and cured in a hot press under pressure of 13.7 MPa for 2 h. The sample was then postcured at 110 °C for 24 h.

2.4. Preparation of PU cross-linked epoxy/PU IPNs

The preparation of PU cross-linked epoxy/PU IPNs was carried out with the polyurethane (PU) synthesized via a one-shot method. The IPNs were prepared by mixing two components together; one component consisted of PU (PPG1000 or PBA1000) cross-linked epoxy and MDI, the other one contained the mixture of the PPG400, PPG3000 and TDMP. The mixture was vigorously stirred for 60 s with high torque mechanical stirrer at about 60 °C. The curing steps of the IPNs are the same with the preparation of PU cross-linked epoxy, as described previously. Finally, the samples were removed from the mould and placed in a desiccator, where the relative humidity was maintained at 50%, for at least 3 days before they were tested.

2.5. Testing method

The tensile strength and modulus were measured by using a Tensilon (Mode: TCF-RC). The test procedure followed the specifications of ASTM D412-Die C type with strain rate of 100% min^{-1} and at least five specimens were taken for the test.

The dynamic mechanical analysis (DMA) was carried out on a Perkin-Elmer DMA-7 form -100 °C to 150 °C with a heating rate of 3 °C min^{-1}. The measurement was performed on the extension mode with fixed dynamic and static stress with force control. The frequency was set at 1 Hz. The dimensions of the specimens were approximately $5 \times 1.5 \times 1$ mm.

The loss modulus area (LA) under the curve of loss modulus versus temperature and the tan δ area (TA) under the curve of tan δ versus temperature are calculated by integrating from -70 to 60 °C.

Morphological studies were performed by using scanning electron microscopy (SEM). Microphotographs were taken on the surface which was made by breaking the specimen in liquid nitrogen and then coated with gold powder.

3. Results and discussion

3.1. Dynamic mechanical properties

Fig. 1 illustrates the loss moduli (E'') from dynamic mechanical analysis of the epoxy cross-linked with polyurethane (PU) based on polyether (PPG)- and polyester (PBA)-type polyols. Two distinct transition peaks of the neat epoxy are observed at -88 °C (T_{gl}) and 91 °C (T_{gh}). Both the T_{gh} and T_{gl} of the epoxy shift to higher temperatures when the epoxy is cross-linked with polyether-type PU. This behaviour indicates that both the soft and hard domains of the epoxy dissolves in the soft and hard segments of the PU respectively to form another hard-segment domain and soft segment domains containing both polymer components [21]. Another PU cross-linked epoxy based on polyester-type PU shows that the T_{gh} and T_{gl} move inward and the intensity of the high transition peak show much higher. It may show the more compatible nature of polyester-type PU with the hard and soft segments of epoxy results in shifting inward of the two transition peaks. In the other words, it indicates that the PU dissolves in hard and soft segment domains of

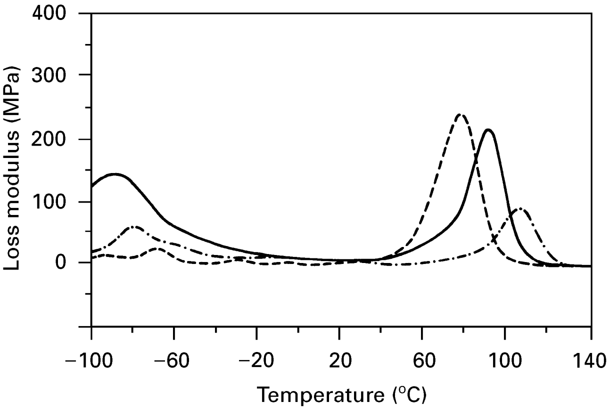

Figure 1 Loss modulus (E'') versus temperature of PU cross-linked epoxy (———) epoxy; (— · — · —) PU (PPG1000) cross-linked epoxy; (- - -) PU (PBA1000) cross-linked epoxy.

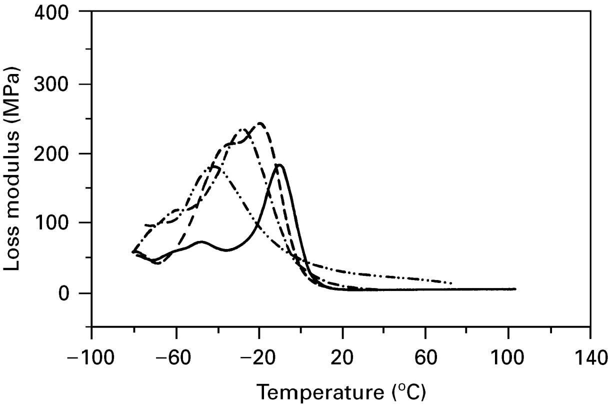

Figure 2 Loss modulus (E'') versus temperature of PU (PPG) cross-linked epoxy/PU IPNs at various epoxy contents. (———) 0 wt%; (- - -) 10 wt%; (— · — · —) 20 wt%; (– · · – · · –) 30 wt%.

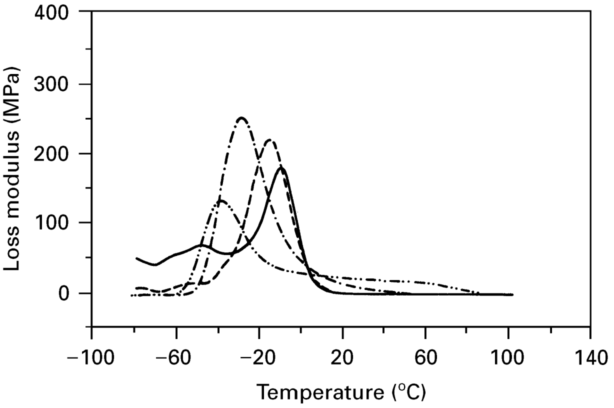

Figure 3 Loss modulus (E'') versus temperature of PU (PBA) cross-linked epoxy/PU IPNs at various epoxy contents. (———) 0 wt%; (- - -) 10 wt%; (— · — · —) 20 wt%; (– · · – · · –) 30 wt%.

epoxy. Thus, the mechanical properties of the PU (PBA) cross-linked epoxy are superior to those of the PU (PPG) cross-linked epoxy.

Figs 2 and 3 show the loss moduli of the PU (PPG) cross-linked epoxy/PU IPNs and the PU (PBA) cross-linked epoxy/PU IPNs, respectively. As can be seen from the width and intensity of the loss modulus peak of different types of the IPNs, the transition peaks are affected by the types of PU used. The peaks of the loss moduli become broader and their intensity increases as the epoxy content of the IPNs increases. This is due to the dissolution of PU chains of the PU cross-linked epoxy networks into the PU matrix phase and the epoxy formed a micro-heterogeneous domain dispersed in the PU matrix.

The PU (PPG) cross-linked epoxy reveals phase separation, as shown in Fig. 1 and Fig. 8b. Usually, the heterogeneous morphology causes a broader glass transition peak. Therefore, the breadth and the area under the loss modulus peak of the loss modulus curve (LA) of the PU (PPG) cross-linked epoxy/PU IPNs are larger than those of the PU (PBA) cross-linked epoxy/PU IPNs. Since the polyether-type PU segment is immiscible with epoxy of the PU (PPG) cross-linked epoxy/PU IPNs, the loss modulus curve appeared as a shoulder at the left-hand side of the peak. This shoulder is gradually separated from the main peak with the epoxy content increasing up to 30 wt%, as shown in Fig. 2. On the other hand, this behaviour does not appear in the PU (PBA) cross-linked epoxy/PU IPNs, as shown in Fig. 3. This is because the polyester-type PU is more compatible with epoxy than is the polyether-type PU. It results in less microphase separation for the PU (PBA) cross-linked epoxy/PU IPNs.

In the polyurethane-dominated matrix, incorporation of PU cross-linked epoxy in the matrix leads to shift of the loss transition temperature and broaden of the loss modulus peak. For the PU (PPG) cross-linked epoxy/PU IPNs with 30 wt% epoxy, another loss modulus peak appears at a higher temperature in addition to the main peak. This indicates that the epoxy gradually forms continuous phase and exhibits its intrinsic properties.

The tan δ curves of the PU (PPG) cross-linked epoxy/PU IPNs and PU (PBA) cross-linked epoxy/PU IPNs show the same tendency, as seen in Figs 4 and 5. The tan δ peak values of PU (PPG) cross-linked epoxy/PU IPNs are larger than those of PU (PBA) cross-linked epoxy/PU IPNs. The tan δ (E''/E') value, which indicating the damping ability of the material, is the ratio of mechanical dissipation energy

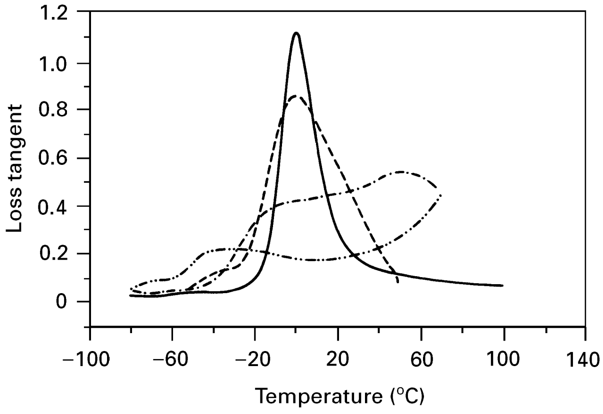

Figure 4 Loss tangent (tan δ) versus temperature of PU (PPG) cross-linked epoxy/PU IPNs at various epoxy contents. (———) 0 wt%; (- - -) 10 wt%; (— · — · —) 20 wt%; (– · · – · · –) 30 wt%.

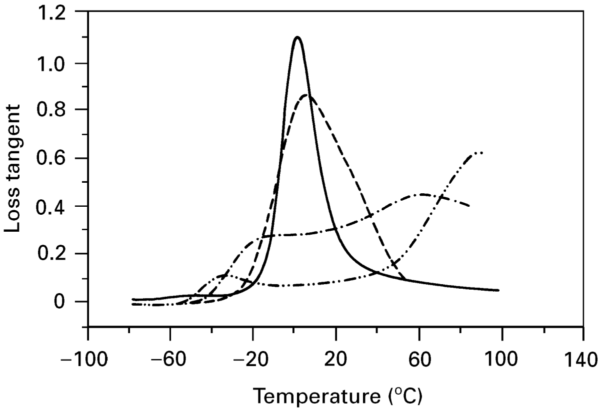

Figure 5 Loss tangent (tan δ) versus temperature of PU (PBA) cross-linked epoxy/PU IPNs at various epoxy contents. (———) 0 wt%; (- - -) 10 wt%; (—·—·—) 20 wt%; (–··–··–) 30 wt%.

to the storage energy. The tan δ peak is broadened and decreases in height as the epoxy content of these IPNs increases. At the composition of 20 wt% epoxy in both IPN systems, the tan δ curve exhibits a plateau of high tan δ value in the high temperature range. This material shows excellent damping property and has potential as a damping material. As the epoxy content in both IPNs is increased up to 30 wt%, the separation between two tan δ peaks becomes more pronounced, indicating a less degree of compatibility in the material. In other words, the reduction in height and separation of the two tan δs at high epoxy content indicate that the dual phase continuity is gradually formed.

3.2. Damping behaviour

The area under the loss tangent curve (TA) (integrated from −70 to 60 °C) and the temperature range of the tan δ value higher than 0.3 are listed in Tables II and III. It is found that the TA and the temperature range of the PU (PPG) cross-linked epoxy/PU IPNs are larger than those of the PU (PBA) cross-linked epoxy/PU IPNs. It indicates that the polyether-type PU cross-linked epoxy/PU IPNs have better damping properties than the polyester-type PU cross-linked epoxy/PU IPNs. The maximum tan δ value and the tan δ value at 20 °C decrease as the epoxy content increases in each IPN system.

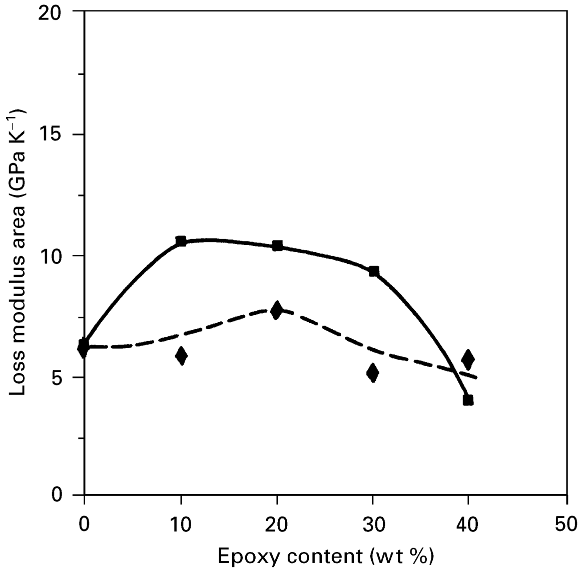

Figure 6 Loss area modulus (LA) of PU cross-linked epoxy/PU IPNs at various epoxy contents. (■) PU (PPG1000) cross-linked epoxy/PU IPNs; (◆) PU (PBA1000) cross-linked epoxy/PU IPNs.

The values of area under loss modulus curve (LA) with the increase of epoxy content are shown in Fig. 6. As the epoxy content in these IPNs increases, the LA increases initially and then decreases. The LA value of the PU (PPG) cross-linked epoxy/PU IPNs with 10 ~ 30 wt% epoxy content are larger than that of the neat PU based on the same PU composition of the

TABLE II Tan δ and TA of the PU (PPG) cross-linked epoxy/PU IPNs

Epoxy (wt%)	PU in epoxy networks (wt%)	Tan δ maximum	Tan δ > 0.3 temperature range (°C)	Tan δ at 20 °C	Area of tan δ height (K)
0	0	1.11	− 11 ~ 20	0.29	31.6
10	2.3	0.85	− 19 ~ 35	0.58	41.1
20	4.5	0.53	− 22 ~ > 69	0.44	41.3
30	6.8	–[a]	56 ~ > 72	0.17	24.4

[a] Appears as two separated peaks.

TABLE III Tan δ and TA of the PU (PBA) cross-linked epoxy/PU IPNs

Epoxy (wt%)	PU in epoxy networks (wt%)	Tan δ maximum	Tan δ > 0.3 temperature range (°C)	Tan δ at 20 °C	Area of tan δ height (K)
0	0	1.11	− 11 ~ 20	0.29	31.6
10	2.3	0.87	− 15 ~ 40	0.66	39.5
20	4.5	0.45	− 8 ~ > 86	0.32	30.6
30	6.8	–[a]	60 ~ > 93	0.10	12.5

[a] Appears as two separated peaks.

IPNs. For the IPNs of PU (PBA) cross-linked epoxy/PU, the LA value has no significant change compared to that of the neat PU, except the appearance of a maximum value at 20% epoxy content. The LA value of the PU (PPG) cross-linked epoxy/PU IPNs is larger than that of the PU (PBA) cross-linked epoxy/PU IPNs. This effect is attributed to the formation of more micro-domains by PU (PPG) cross-linked epoxy in the matrix which contains much more ether groups (–O–) in the PU cross-linked epoxy networks [22]. The LA value indicates the ability of converting mechanical energy into heat through molecular motion. Therefore, the materials of higher LA value have good damping properties in selected temperature or frequency ranges.

3.3. Mechanical properties

The tensile strength of the PU (PPG) cross-linked epoxy/PU and PU (PBA) cross-linked epoxy/PU IPNs is shown in Fig. 7. As the epoxy content increases, the tensile strength of these two IPN systems decreases in the beginning and then increases. Since the tensile strength of the PU (PBA) cross-linked epoxy (75.9 MPa) is higher than that of PU (PPG) cross-linked epoxy (54.5 MPa), it may result from higher tensile strength in the corresponding IPN structure in addition to the better compatibility between PU (PBA) cross-linked epoxy and PU. Hence, the increase of tensile strength is more significant in the PU (PBA) cross-linked epoxy/PU IPNs than that in the PU (PPG) cross-linked epoxy/PU IPNs as the epoxy content increases in the IPNs. The tensile strength of the IPNs has no significant increase for the IPNs at 10 wt% epoxy content, as shown in Fig. 7, indicating that a lower degree of interpenetrating is obtained because of the low content of the PU cross-linked epoxy. When the epoxy content of the IPNs increases up to 30 wt%, the tensile strength increases rapidly. It demonstrates that the degree of interpenetrating between the PU cross-linked epoxy and the PU matrix increases. Hence, the intermolecular force and the reinforced rigid property through the epoxy in the IPNs are enhanced.

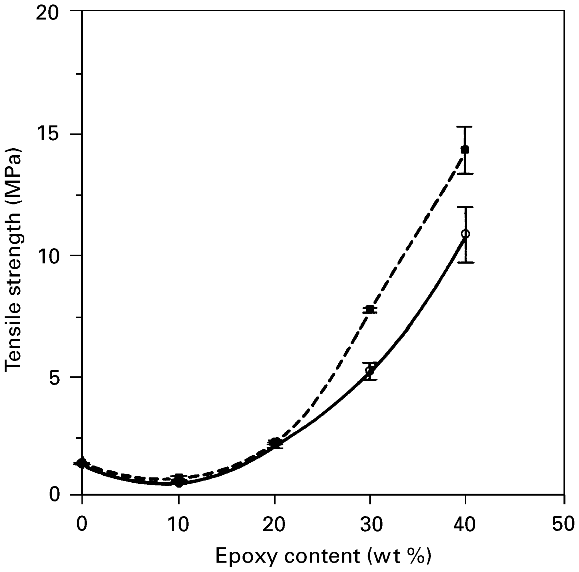

Figure 7 Tensile strength of PU cross-linked epoxy/PU IPNs at various epoxy contents. (○) PU (PPG1000) cross-linked epoxy/PU IPNs; (■) PU (PBA1000) cross-linked epoxy/PU IPNs.

3.4. Morphology

As shown in Fig. 8, the fracture surface of the polyether- and polyester-type PU cross-linked epoxy show two distinctive types of morphology. The fracture surface of the PU (PBA) cross-linked epoxy shows a more homogeneous microstructure (Fig. 8a). On the contrary, the fracture surface of the PU (PPG) cross-linked epoxy has a phase-separated microstructure, as shown in Fig. 8b. The PU (PPG) rubber particles precipitate out from the epoxy matrix, resulting from the low compatibility between the two PU and epoxy components.

The micro photographs of fracture surface of the PU (PPG) cross-linked epoxy/PU IPNs with various epoxy content are shown in Fig. 9. When the epoxy content of the PU (PPG) cross-linked epoxy/PU IPNs increases, the small particles precipitate out from the matrix of these IPNs. It reveals the heterogeneous microstructures are formed below 20 wt% epoxy in the IPNs. For 20 wt% epoxy in the PU (PPG) cross-linked epoxy/PU IPN, the small particles dispersed on the matrix are observed, as shown

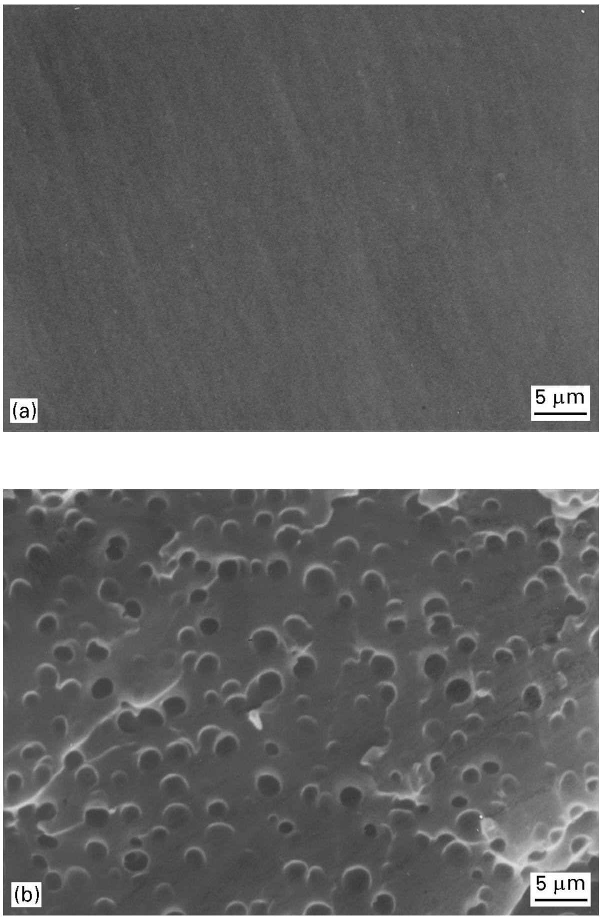

Figure 8 Microphotographs of PU cross-linked epoxy: (a) PU (PBA1000) cross-linked epoxy; (b) PU (PPG1000) cross-linked epoxy.

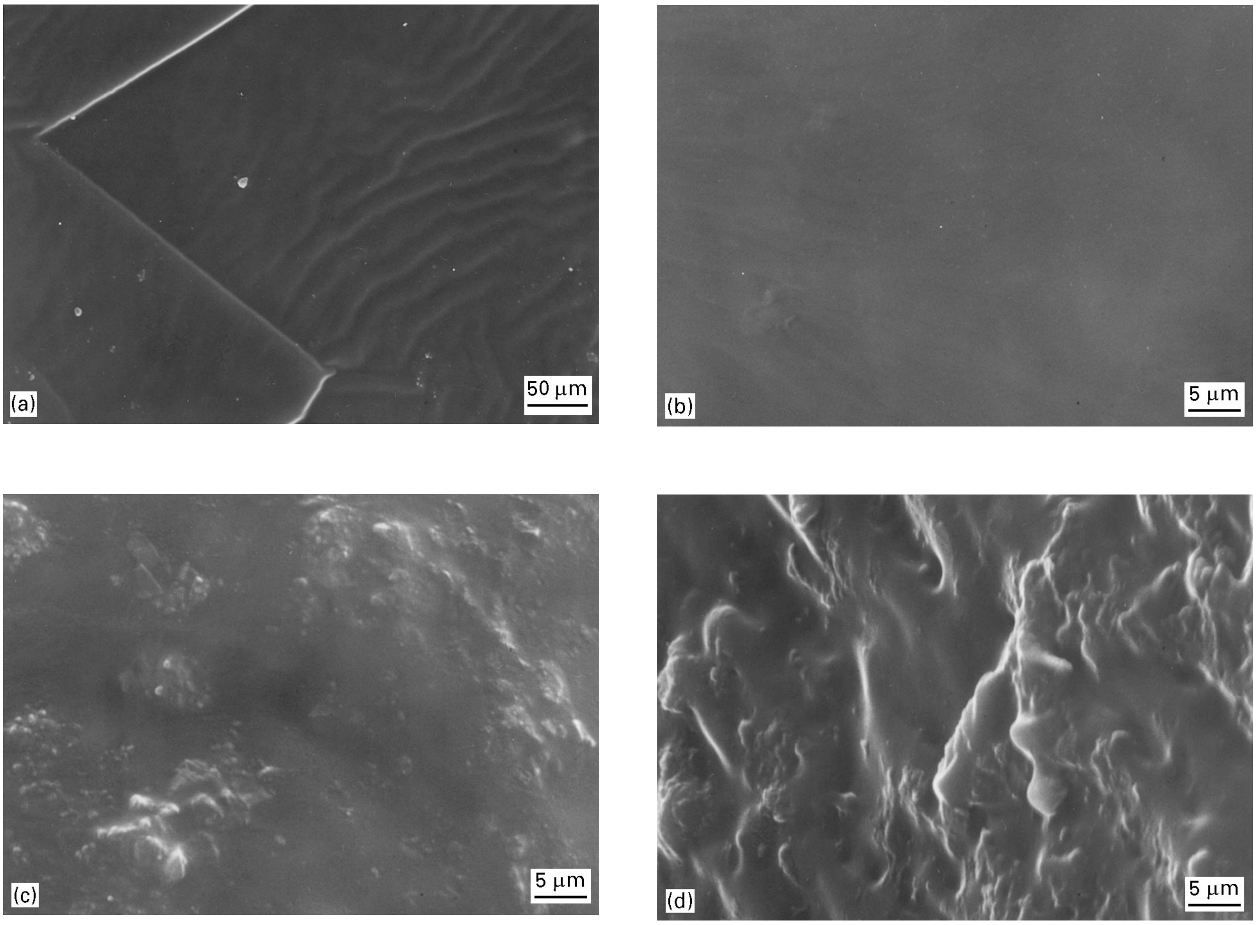

Figure 9 Microphotographs of PU (PPG) cross-linked epoxy/PU IPNs at various epoxy contents. (a) 0 wt %; (b) 10 wt %; (c) 20 wt %; (d) 30 wt %.

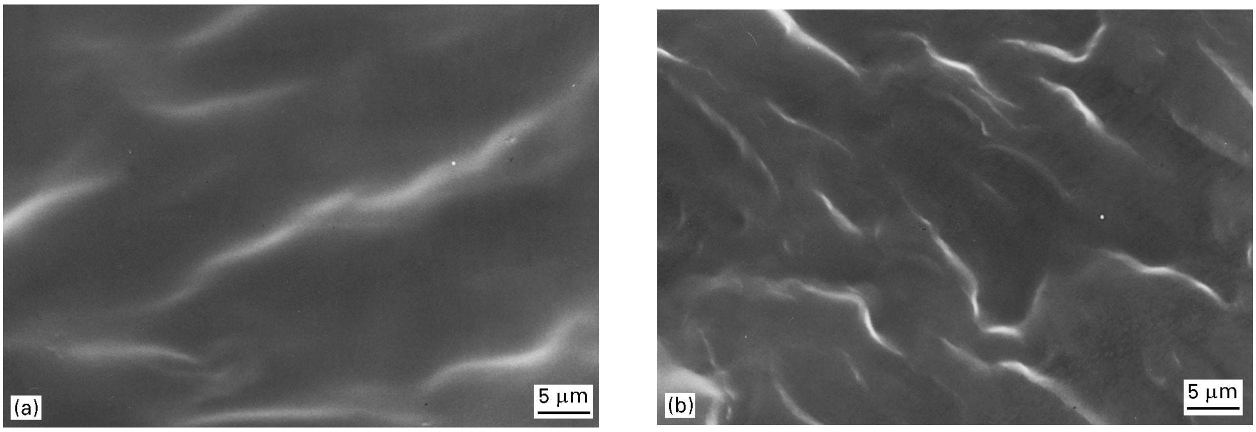

Figure 10 Microphotographs of PU (PBA) cross-linked epoxy/PU IPNs at various epoxy contents. (a) 20 wt %; (b) 30 wt %.

in Fig. 9c. This particle–matrix morphology corresponding to high values of LA and TA, as mentioned above, shows the excellent damping property of material. As the epoxy content of the PU (PPG) cross-linked epoxy/PU IPNs increases above 30 wt %, the fracture surface is rough because of the PU cross-linked epoxy turning into a continuous phase in the matrix. In the PU (PBA) cross-linked epoxy/PU IPN system, their fracture surfaces show few particles existed and are more homogeneous, as shown in Fig. 10. On the other hand, this morphology implies the damping properties of the PU (PBA) cross-linked epoxy/PU IPNs should be lower than those of the PU (PPG) cross-linked epoxy/PU IPNs. The result is consistent with that described previously.

4. Conclusions

The damping and mechanical properties are significantly improved by introducing PU (PPG) cross-linked epoxy into the PU matrix to form IPNs. The loss modulus peaks of the PU (PPG) cross-linked epoxy/PU IPNs are very broad with a shoulder and the morphology shows a micro-heterogeneous structure. The PU (PBA) cross-linked epoxy is more compatible with the PU matrix than the PU (PPG) cross-linked epoxy through the dynamic mechanical analysis. However, the PU (PPG) cross-linked epoxy/PU IPN system with high loss modulus area, tan δ area, and broadened loss peak shows better damping ability and the PU (PBA) cross-linked epoxy/PU IPNs show higher tensile strength.

Acknowledgement

The authors acknowledge with gratitude the financial support from the Chung-Shan Institute of Science Technology (CSIST), Taiwan.

References

1. L. E. NILESLEN, "Mechanical properties of polymers and composites" Vol. 1 (Marcel Dekker, New York, 1974) p. 12.
2. J. A. GRATES, D. A. THOMAS, E. C. HICKEY and L. H. SPERLING, *J. Appl. Polym. Sci.* **19** (1975) 1731.
3. J. H. AKLONIS, W. J. MACKNIGHT and M. SHEN, "Introduction to polymer viscoelasticity" (Wiley-Interscience, New York, 1972) p. 38.
4. D. J. HOURSTON and I. D. AUGUHES, *J. Appl. Polym. Sci.* **21** (1977) 3487.
5. *Idem., ibid.* **26** (1981) 3093.
6. A. C. F. CHEN and H. L. WILLIANS, *ibid.* **20** (1976) 3403.
7. B. HARTMANN and G. F. LEE, *ibid.* **21** (1977) 1341.
8. J. N. FOSTER and L. H. SPERLING, *ibid.* **33** (1987) 2637.
9. D. J. HOURSTON and J. A. McCLUSKEY, *Polymer* **12** (1979) 1573.
10. D. SOPHIEA, D. KLEMPNER, V. SENDIJAREVIC, B. SUTHAR and K. C. FRISCH, in Advances in Chemistry Series No. 239, "Interpenetrating polymer networks" (American Chemical Society, Washington, DC, 1994) p. 39.
11. S. USMAN, Y. WILLIAM, A. QUEEN and D. TIMOTHY, US patent 5225498 (1991).
12. J. N. FOSTER and L. H. SPERLING, *J. Appl. Polym. Sci.* **34** (1987) 409.
13. Q. CHEN, H. GE, D. CHEN, X. HE and X. YU, *ibid.* **54** (1994) 1191.
14. A. TAKEMURA and H. MIZUMACHI, " Advances in interpenetrating polymer networks" III (Technomic Publishing, Pennsylvania 1991) p. 25.
15. S. USMAN, Y. WILLIAM and D. TIMOTHY, in ACS Symposium Series No. 424, "Sound and vibration damping with polymer" (American Chemical Society, Washington, DC, 1990) p. 382.
16. R. Y. TING, R. N. CAPPS and D. KLEMPNER, in ACS Symposium Series No. 424, "Sound and vibration damping with polymer" (American Chemical Society, Washington, DC, 1990) p. 367.
17. C. S. COUGHLIN, M. Q. SAMUELS and R. N. CAPPS, *Polym. Prep.* **34** (1993) 475.
18. Y. C. CHERN, K. H. HSIEH, C. C. M. MA and Y. G. GONG, *J. Mater. Sci.* **29** (1994) 5435.
19. D. KLEMPNER, L. BERKOWSKI, K. C. FRISCH, K. H. HSIEH and R. TING, *Rubber World* **192** (1985) 16.
20. C. HEPBURN, "Polyurethane elastomers" (Applied Science, New York, 1982) p. 280.
21. K. H. HSIEH, Y. C. CHANG, Y. C. CHERN, W. Y. CHIU and C. C. M. MA, *Angew, Makromol, Chem.* **194** (1992) 15.
22. T. HUR, J. A. MANSON and L. H. SPERLING, *J. Polym. Sci. Part B* **27** (1989) 2251.

Received 20 November 1995
and accepted 17 September 1996