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Interpenetrating polymer networks of polyurethane and epoxy

Y. C. CHERN, K. H. HSIEH
Chemical Engineering Department, National Taiwan University, Taipei, Taiwan 106
C. C. M. MA, Y. G. GONG
Chemical Engineering Department, National Tsing Hua University, Hsin-Chu, Taiwan 300

Interpenetrating polymer networks of polyurethane, based on poly(oxypropylene)triol grafted with polyacrylonitrile and epoxy, were prepared by a simultaneous polymerization technique. The mechanical properties and morphology of the networks were investigated. As the epoxy content increased, the tensile strength of the interpenetrating polymer networks or the graft networks (in which some grafting reaction has taken place between polyurethane and the pendant hydroxyl group of epoxy) decreased. The shifts of the loss modulus peaks of the interpenetrating polymer networks and the graft-IPNs were different and their tan δ peaks shifted to a high temperature as the epoxy content increased.

1. Introduction

Polyurethane has been widely applied to elastomer, foam, coating fibre, artificial leather and fibre treatment agents [1]. In order to improve the mechanical properties, thermal resistance and damping properties of polyurethane, several researchers have proposed to introduce epoxy to polyurethane systems to form epoxy/polyurethane interpenetrating polymer networks (IPN) structures [2–10]. A number of methods to broaden the damping peaks are adopted by using the structures of IPNs [11, 12]. This paper investigates the use of the IPN structure to achieve high damping properties over a selected temperature range. Different epoxy contents in IPNs and graft-IPNs were prepared. The effects of epoxy content on the tensile strength, loss moduli (E''), loss tangent ($\tan\delta$) and morphology of these IPNs and graft-IPNs were investigated.

2. Experimental procedure

2.1. Materials

The materials used in this study are summarized in Table I. The polyol and epoxy were degassed at 60 °C with magnetic stirring in the flask for 8 h and the MDI was melted at 65 °C before it was used. The TDMP used as a catalyst of epoxy was employed as-received.

2.2. Preparation of epoxy/polyurethane IPNs and graft-IPNs

The preparation of epoxy/polyurethane IPNs was carried out with the polyurethane synthesized via a one-shot method. The IPNs and graft-IPNs were synthesized by mixing two components; one component consisted of POPT, DBTD and DGEBA, the other one contained MDI and TDMP. For the graft-IPN system, one component consisted of POPT, DBTD, and TDMP. The other component contained the epoxy grafted by MDI with its secondary hydroxyl groups and suitable amounts of MDI. The mixture of IPNs or graft-IPNs was prepared by mixing the two components and then vigorously stirring for 60 s with a high-torque mechanical stirrer at room temperature. It was then poured into a hot mould (80 °C) and cured for 1 h at 80 °C in a hot press under a pressure of ~ 13.72 MPa. Finally, it was postcured at 110 °C for 2 h. After the samples were removed from the mould, they were conditioned in a desiccator at 50% relative humidity for at least 3 days before testing.

2.3. Testing method

The tensile strength and elongation were measured using a Tensilon (Mode: TCF-RC; Yashima Works Ltd, Japan), The test procedure was followed with the specifications of ASTM D412-Die C type with a cross-head speed of 200 mm min^{-1}. At least five specimens were taken for the test

Dynamic mechanical analysis (DMA) was carried out on a DuPont 983 DMA from − 100 to 150 °C with a heating rate of 5 °C min^{-1}. The measurement was performed at a fixed frequency (1 Hz) and a fixed amplitude of 0.3 mm. The dimensions of the specimens are approximately 20 × 2 × 7 mm. Morphological studies were performed by using scanning electron microscopy (SEM). Microphotographs were taken on the surface which was made by fracturing the specimen in liquid nitrogen and then coating it with gold powder.

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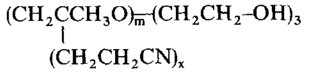
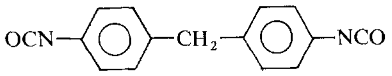
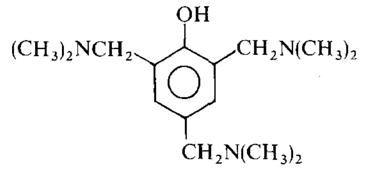
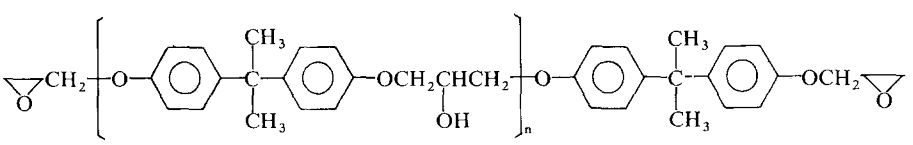
TABLE I Materials used in this study.

Designation	Description	Source
POPT	Poly(oxypropylene)triol, ethylene oxide capped and grafted with 21 wt % acrylonitrile. MW = 6000.  $(CH_2\underset{\substack{\vert \\ (CH_2CH_2CN)_x}}{C}CH_3O)_m(CH_2CH_2\text{-}OH)_3$	Chiung Long Co.,Taiwan
MDI	4,4′-diphenyl methane diisocyanate. Eq. wt = 125. 	BASF Wyandotte Co., Germany
TDMP	2,4,6, tri(dimethyl aminomethyl) phenol. 	Ciba-Geigy Co., Switzerland
DBTD	Dibutyltin dilaurate (catalyst Sn% = 18). $(C_4H_9)_2\,Sn\,(COC_{10}H_{20}CH_3)_2$	Merk Co., Germany
DGEBA	Diglycidyl ether of biphenol A EEW = 186, n = 0.11267. 	Dow-Chemical, USA

3. Results and discussion

3.1. Infrared spectrum

The epoxide group does not react with the isocyanate during the grafting reaction at 65 °C. Hence, the intensity of the i.r. absorption peak of the epoxide group at 915 cm^{-1} should not change during the grafting reaction. The intensity ratio of the isocyanate peak (2278 cm^{-1}) to the epoxide peak (915 cm^{-1}) was employed as an indication of the degree of grafting reaction between the isocyanate groups of MDI and pendant hydroxyl groups of the epoxy resin. As shown in Fig. 1, the intensity ratio was high at the beginning of the grafting reaction; as the reaction proceeded, it decreased and reached a constant value. This indicates that the pendant hydroxyl groups of the epoxy had been reacted completely and grafted with the isocyanate groups of the MDI. In this grafting reaction, the ratio of isocyanate groups of MDI to the hydroxyl groups of the epoxy was 2:1. The remaining isocyanate in the system was further polymerized simultaneously to form graft-IPNs by the addition of suitable amounts of polyol.

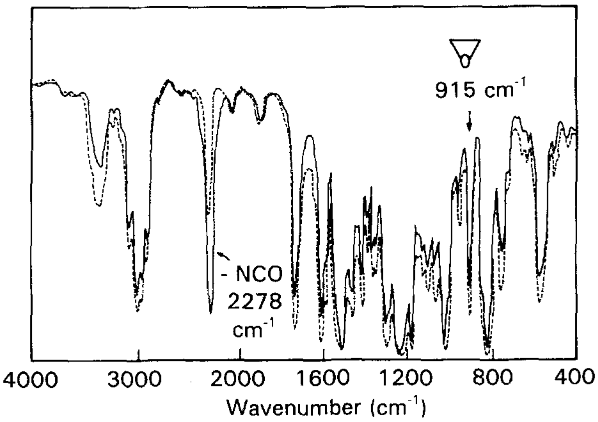


Figure 1 Infrared spectra during the reaction between isocyanate of MDI and pendant hydroxyl group of epoxy. (——) Beginning, (- - -) end of reaction.

3.2. Stress–strain properties

The tensile strength of the IPNs and graft-IPNs is shown in Fig. 2. The tensile strength value of the IPNs was much lower than that of epoxy (42 MPa) [6], due to the incompatibility of the epoxy and polyurethane in the IPN system. When the epoxy content increased, the tensile strength of the IPNs and graft-IPNs gradually decreased. As shown in the figure, the tensile strength of the IPNs was lower than that of the graft-IPNs. This effect was attributed to the lower interpenetration degree between the epoxy and polyurethane in the IPNs. In the graft-IPNs, some urethanes were grafted to the pendant secondary hydroxyl groups of the epoxy through the reaction with the isocyanate, and hence enhanced the intermolecular force as shown in Fig. 3. Therefore, it was found that the tensile strength of graft-IPNs is higher than that of the IPNs in Fig 2. Fig. 4 illustrates the elongation of IPNs and graft-IPNs. As the epoxy content increased, the elongation of the IPNs decreased. As the graft-IPNs possess chemical bonds between epoxy and polyurethane, the elongation of the graft-IPNs was lower than that of the IPNs.

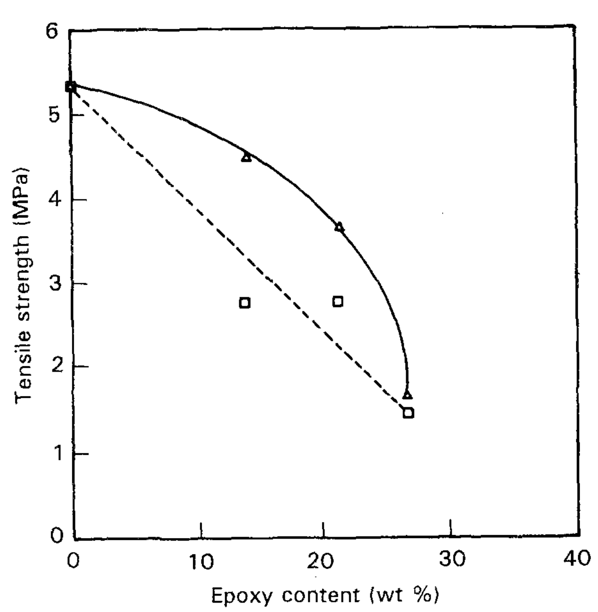


Figure 2 Tensile strength of epoxy/polyurethane IPNs at various epoxy contents. △ Graft-IPN; □ IPN.

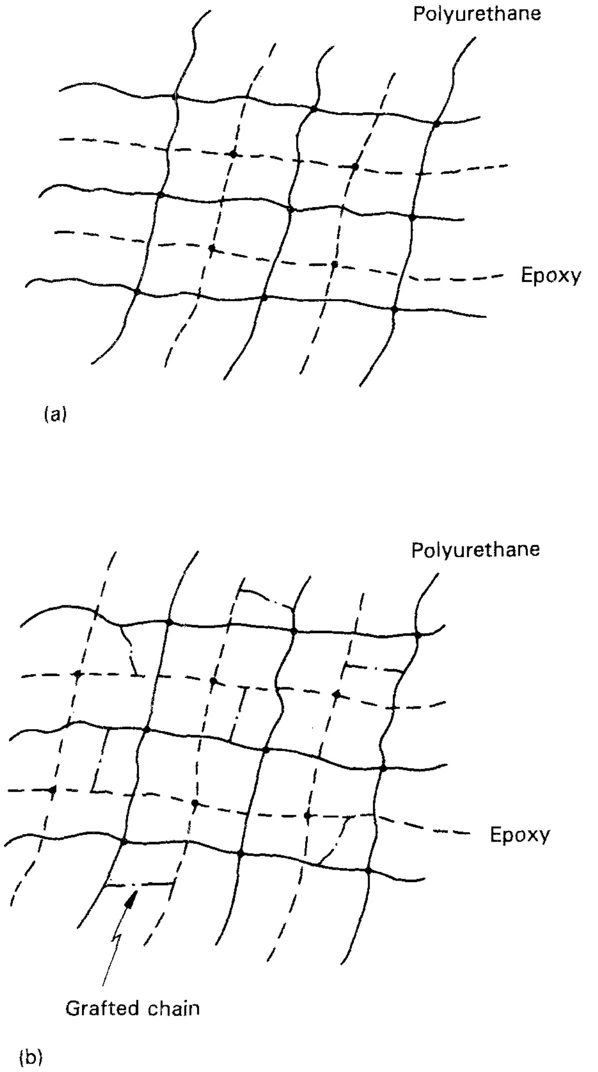


Figure 3 Structure of IPNs of polyurethane (——) and epoxy (- - -): (a) IPNs; (b) graft-IPNs.

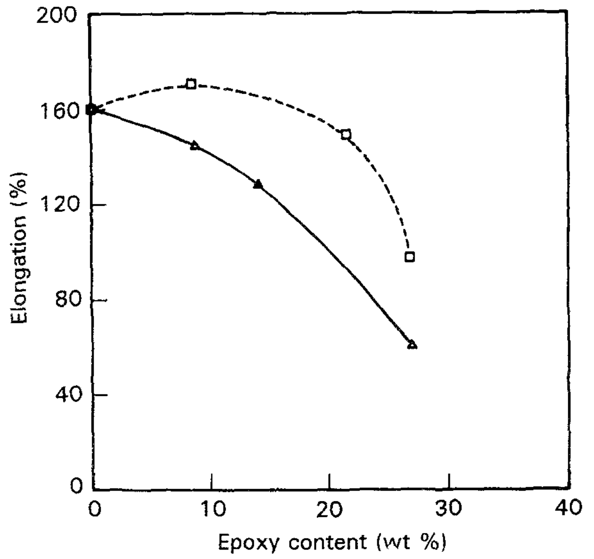


Figure 4 Elongation of epoxy/polyurethane IPNs at various epoxy contents. △ Graft-IPN; □ IPN.

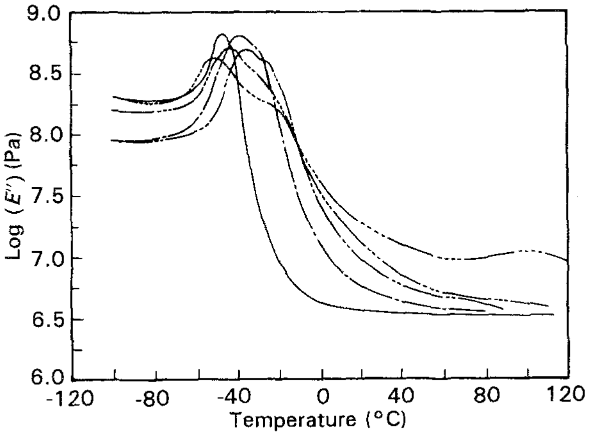


Figure 5 Loss modulus (E'') against temperature of epoxy/polyurethane IPNs at various epoxy contents. (———) 0; (- - - -) 14.0; (— - —) 21.6; (— - - - —) 26.8; (— - - - - —) 31.6 wt %.

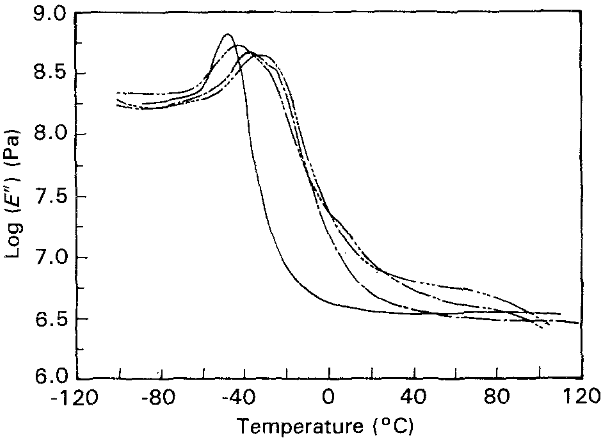


Figure 6 Loss modulus (E'') against temperature of epoxy/polyurethane graft-IPNs at various epoxy contents. (———) 0; (— - - - - —) 14.0; (— - - - —) 21.6; (— - - - —) 26.8 wt %.

3.3. Dynamic mechanical properties

The loss moduli (E'') of the epoxy/polyurethane IPNs and graft-IPNs are shown in Figs 5 and 6. As the length of the polyol chain is much longer than that of the epoxy chain, and the epoxy content is small compared with the polyurethane content, the peak of the hard segment of IPNs is not seen in these two figures. From Fig. 5, the peak of loss moduli (E'') of pure polyurethane (POPT) is very sharp at − 50 °C. When the epoxy content is increased, the peak of loss moduli (E'') shifted to a higher temperature and became broader and the intensity of the peak of the loss moduli (E'') decreased. The peak (transition temperature) of the loss moduli (E'') shifted to a higher temperature of 35 °C as the epoxy content increased up to 21.6 wt %. At the same time, as the epoxy content increased continuously beyond 21.6 wt %, a shoulder on the peak of the loss moduli (E'') appeared at the right hand side of the peak. This is due to the epoxy being incompatible with the soft segment of polyurethane – the epoxy was distributed heterogeneously in the polyurethane matrix and incorporated in the hard segment of polyurethane. This causes the soft segment domain of the polyurethane to form a 'purer', soft-segment domain in the matrix [14] and results in the main peak shifting back to a lower temperature and leaving the shoulder of the peak. This may imply that the shoulder on the loss moduli (E'') peak may be a mixture of the soft domain of epoxy and some hard segment of the polyurethane. However, there were more pure soft segments of polyurethane aggregating in the matrix, therefore the chain of the soft-segment domain moved more easily. This caused the transition temperature of the IPN to shift to a lower one than that of neat polyurethane. This behaviour indicated that the IPNs of epoxy/polyurethane were partially miscible and resulted in a heterogeneous matrix.

On the other hand, for the epoxy/polyurethane graft-IPNs as shown in Fig. 6, when the epoxy content falls below 21.6 wt %, the peak (transition temperature) of loss moduli (E'') of graft-IPNs is still the same as those of the IPNs shifting to a higher temperature. However, there is no shoulder on the peak of the loss moduli (E'') of graft-IPNs, as there is chemical grafting on both the polyurethane and epoxy through urethane chain. Thus it is difficult to separate completely the epoxy from the mixed hard/soft segment domains of the graft-IPNs. This indicates that the graft-IPN systems are more compatible than the IPN systems and result in less phase separation of the matrix.

The loss tangents (tan δ) of the IPNs and graft-IPNs are illustrated in Figs 7 and 8. As the storage moduli (E'') of these IPNs drops rapidly at the high-temperature region, even though there is little change in loss moduli, variations in the loss tangent ($\tan\delta = E''/E'$) at this region are apparently observed. Two peaks for the pure polyurethane from the polyol(POPT) were observed because the POPT had grafted with acrylonitrile. The low temperature peak is the transition of the soft segment of polyurethane, the second is the high transition temperature of the grafted polyacrylonitrile. As the epoxy content increased, the loss tangent (tan δ) of the IPNs and graft-IPNs shifted slightly to a higher temperature. The transition peak of the loss tangent (tan δ) was broadened and its intensity was reduced. Meanwhile a new obvious tan δ peak appeared at high temperature. This loss tangent (tan δ) first increased, then inversely decreased to a low value as the epoxy content beyond 21.6 wt %. Fig. 7 can be compared with Fig. 8: the intensity of the loss tangent (tan δ) peak of IPNs is higher than for graft-IPNs, as the motion of chains in the graft-IPNs is restricted by the partial chemical bonding structures between polyurethane and epoxy, as shown in Fig. 2b.

3.4. Morphology

Fig. 9a illustrates the polyol of polyurethane grafted with polyacrylonitrile and the small particles of polyacrylonitrile distributed in the polyurethane matrix. When the epoxy content increased in the polyurethane matrix, the additional particles formed in these IPNs may be attributed to the cross-linked epoxy in the polyurethane matrix. The fracture surface of IPNs and graft-IPNs became rough gradually, as shown in Figs 9 and 10. Moreover, the fracture surfaces of the graft-IPNs were more rigid than those of the IPNs. The graft-IPNs exhibited more rigid properties, as the interpenetrating effect was more significant in graft-IPNs. As the epoxy content increased up to 31.6 wt %, the epoxy phase turned to form a continuous phase within the IPNs. At this composition, no large particles were separated out from the fracture surface, and the fracture surface was very rough, as shown in Fig. 9d. However, many small particles of the grafted polyacrylonitrile remained distributed in both the epoxy and polyurethane domains, implying that interpenetration existed in these IPNs.

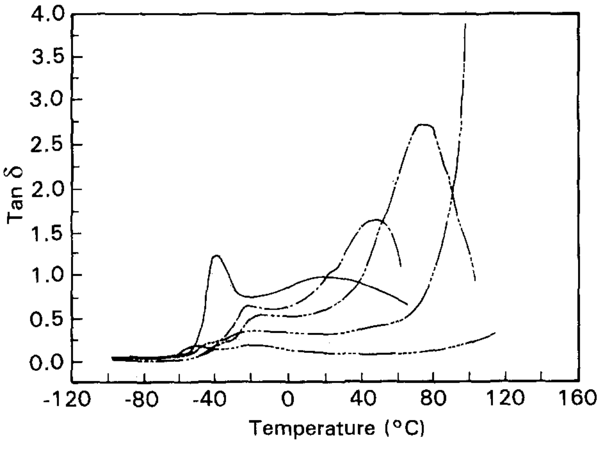


Figure 7 Loss tangent(tan δ) against temperature of epoxy/polyurethane IPNs at various epoxy contents. (———) 0, (—·—·—) 14.0; (— — —) 21.6; (—---—) 26.8; (------) 31.6 wt %.

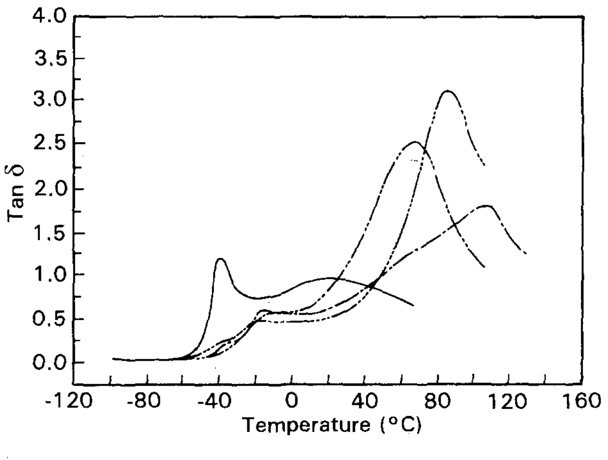


Figure 8 Loss tangent(tan δ) against temperature of epoxy/polyurethane graft-IPNs at various epoxy contents (———) 0; (—·—·—) 14.0; (— — —) 21.6; (—---—) 26.8 wt %.

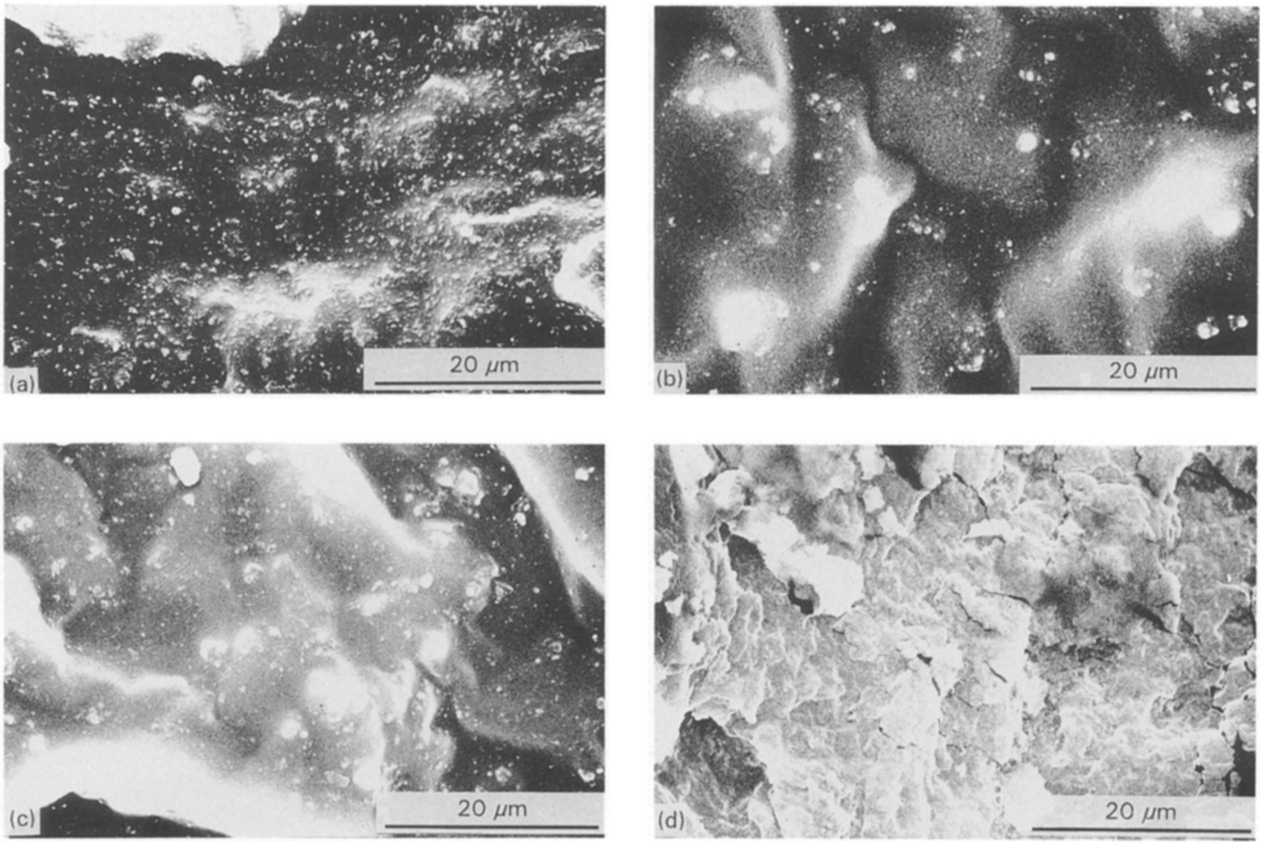


Figure 9 SEM micrographs of fracture surfaces from liquid nitrogen tests on IPNs at various epoxy contents: (a) 0; (b) 14; (c) 21.6; (d) 31.6 wt %.

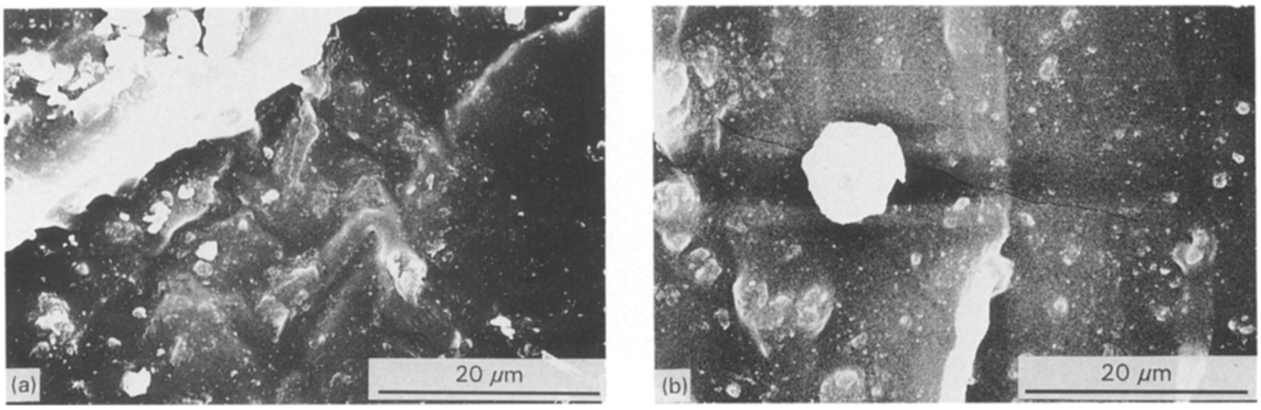


Figure 10 SEM micrographs of fracture surfaces from liquid nitrogen tests of IPNs at various epoxy contents: (a) 14.0; (b) 21.6 wt %.

4. Conclusions

When the epoxy content of the epoxy/polyurethane IPNs and graft-IPNs is increased, the mechanical properties of these IPNs are not improved by the one-shot technique. However, the mechanical properties of the graft-IPNs are better than those of the IPNs. There is a chemical bond between polyurethane and epoxy in the graft-IPNs which provides better compatibility and therefore better mechanical properties. It was also found in this study that the loss tangent (tan δ) was increased and the temperature range of the loss tangent (tan δ) was broadened for the epoxy/polyurethane IPNs and graft-IPNs. Good damping properties of the epoxy/polyurethane IPNs and graft-IPNs can be expected, and these materials may be utilized for vibration or energy absorption.

Acknowledgements

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References

1. G. OERTEL, "Polyurethane Handbook" (Hanser, New York, 1985) p. 15.
2. L. H. SPERLING, *Polym. Eng. Sci.* 25 (1985) 517.
3. K. C. FRISCH, D. KLEMPNER and S. K. MUKHERJEE, *J. Appl. Polym. Sci.* **18** (1974) 689.

4. E. F. CASSIDY, H. X. XIAO, K. C. FRISCH and H. L. FRISCH, *J. Polym. Sci. Polym. Chem. Ed.* **22** (1984) 2667.
5. *Idem, ibid.* **22** (1984) 1839.
6. K. H. HSIEH and J. L. HAN, *J. Polym. Sci. B.* **28** (1990) 623.
7. *Idem, ibid.* **28** (1990) 783.
8. R. PERNICE, K. C. FRISCH and R. NAVARE, *J. Cell. Plast.* **18** (1982) 121.
9. D. KLEMPNER, L. BERKOWSKI, K. C. FRISCH, K. H. HSIEH and R. TING, *Rubber World* **192** (1985) 16.
10. D. KLEMPNER, B. MUNI, M. OKOROAFOR and K. C. FRISCH, "Advances in Interpenetrating Polymer Networks" **II** (Technomic Publishing, 1990) p. 1.
11. L. H. SPERLING, "Interpenetrating Polymer Networks and Related Materials" (Plenum Press, New York, 1981) p. 224.
12. J. N. FOSTER and L. H. SPERLING, *J. Appl. Polym. Sci.* **33** (1987) 2637.
13. K. H. HSIEH, Y. C. CHIANG, Y. C. CHERN, W. Y. CHIU and C. C. M. MA, *Angew. Makromol. Chem.* **194** (1992) 15.

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