Polymer Vol. 37 No. 5, pp. 785–792, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

Interpenetrating polymer networks of poly(allyl diglycol carbonate) and polyurethane: effect of composition and crosslink density on morphology and mechanical properties

Susan Dadbin, R. P. Burford and R. P. Chaplin*
Department of Polymer Science, The University of New South Wales, Sydney 2052, Australia
(Received 11 May 1994; revised 9 August 1994)

Simultaneous interpenetrating polymer networks (SINs) of poly(allyl diglycol carbonate) (ADC) and a polyurethane (PU) were synthesized. The effects of the network composition and the crosslink density of the PU phase on the morphology, mechanical properties and thermal transition behaviour of the PU/ADC SIN were studied. At 10% composition, dynamic mechanical analysis revealed complete phase miscibility. As the PU content increased, although phase separation occurred, the samples retained their optical transparency. Modulus and tensile strength decreased, whilst elongation increased, as the PU content increased. At 30% PU content, transmission electron micrograph studies revealed a co-continuous phase morphology, and the domain sizes increased as the PU crosslink density increased. Modulus, tensile strength and fracture toughness also increased with increasing crosslink density.

(Keywords: simultaneous IPNs; crosslink density; mechanical properties)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymers in a network form, in which at least one of them is synthesized and/or crosslinked in the immediate presence of the other[1,2]. When both polymers are polymerized and crosslinked simultaneously with non-interfering modes, such as stepwise and chain polymerization, the IPN is known as a simultaneous interpenetrating network (SIN).

Most IPNs involve heterogeneous systems, with one phase elastomeric and the other phase glassy. This combination of elastomeric and glassy networks allows IPNs to range in properties from filler-reinforced elastomers to rubber-reinforced (high-impact) plastics, depending on which component becomes the continuous phase[3].

Meyer *et al.*[4–7] and Lipatov *et al.*[8,9] have studied the interconnection between properties and microphase separation in a number of IPN systems. They have shown that differing rates of polymerization of the networks that make up the IPN can produce materials with changing morphologies and mechanical properties.

The degree of intermixing of SINs is mainly affected by the compatibility of the components, the relative rate of network formation, the composition, the degree of crosslinking and the mobility of polymer chains at the time of phase separation[10]. However, complete compatibility is not essential to achieve complete phase mixing, since the permanent entanglements can effectively limit the extent of phase separation. It is believed that phase separation may be kinetically hindered by the simultaneous polymerization and gelation of two networks, i.e. the chain entanglements and crosslinking associated with simultaneous polymerization would be expected to restrict phase separation[11,12].

Maximum restriction of phase separation should result when the polymer begins to gel near or before phase separation of the two components. If phase separation precedes gelation, the domains will be relatively large and the crosslinking stabilizes the phase-separated morphology[12].

Alternatively, a greater degree of intermixing is achieved as the rates of network formation (gelation time) of the two constituent components approach equality[3,10,13]. Changing the crosslink density of one of the networks may also have a similar effect[14]. This also has been shown to result in an increase in mechanical properties, such as tensile strength and fracture toughness[15,16].

However, in simultaneous interpenetrating networks based on a polybutadiene-based polyurethane/poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate) it was found[15] that increasing the crosslink density of the first-formed network, the polyurethane phase, did not change the morphology of the SINs, and in all cases

---

* To whom correspondence should be addressed

domain sizes of about a few micrometres were observed. The stiffness and strength of the SINs increased with increasing crosslink density of the polyurethane phase until an optimum value was reached. These properties then decreased as the crosslink density increased further. In these IPNs the onset of polymerization of both networks was simultaneous.

Meyer *et al.* also reported an optimum level of crosslink density of the first-formed network to obtain higher stiffness and strength in the SINs of polyurethane/poly(methyl methacrylate)[17,18]. In this case the polyurethane was first gelled at room temperature, followed by polymerization of the methyl methacrylate. However, no details of the effect of the change in crosslink density on the morphology of the networks were presented.

Lee and Kim[14] also investigated the effect of crosslink density of the first-formed network in SINs based on polyurethane (PU) and polystyrene (PS). They found that increasing the PU crosslink density decreased the domain size from 5–10 to 3–5 nm in the IPN containing 50 wt% of the polyurethane.

These studies indicate that the effect of crosslink density in full SINs is different in each individual case and depends on the kinetics of network formation and phase separation.

Bulk polymerization of allyl diglycol carbonate (ADC) monomer gives a clear, colourless, abrasion-resistant polymer that offers advantages over glass and acrylic plastics for optical applications. ADC resins are highly crosslinked materials used primarily for optical applications, but possess a low fracture toughness. Some

Table 1 Materials used in the preparation of the IPNs

Material description	Source	Code
Isophorone diisocyanate	Aldrich	IPDI
1,4-Butanediol	Aldrich	BDO
Trimethylolpropane	Aldrich	TMP
Poly(caprolactone) diol *MW* 530	Aldrich	PCL
Allyl diglycol carbonate	SOLA Inc.	ADC
Benzoyl peroxide (ADC initiator)	Interox	BP
Dibutyltin dilaurate (PU catalyst)	Aldrich	T12

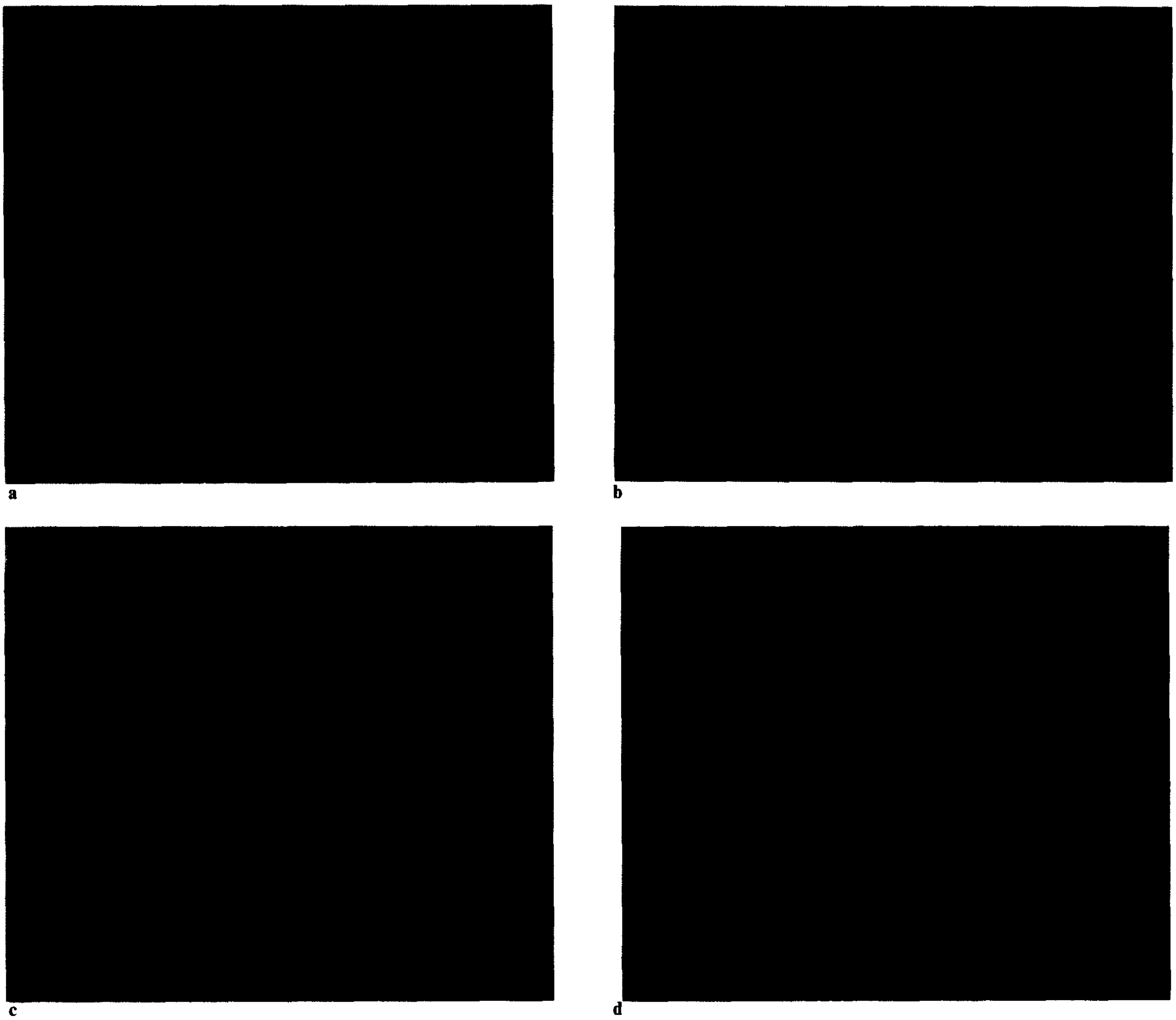
a
b
c
d

Figure 1 Transmission electron micrographs of polyurethane/allyl diglycol carbonate interpenetrating polymer network: (a) PU composition 10%, TMP = 0.8 equivalents, magnification 200000;(b) PU composition 20%. TMP = 0.8 equivalents, magnification 15000; (c) PU composition 30%, TMP = 0.8 equivalents, magnification 15000; (d) PU composition 30%, TMP = 0.8 equivalents, magnification 50000 attempts have been made to improve fracture toughness through the formation of a range of IPNs[16,19]. In the present work we introduce novel simultaneous interpenetrating networks based on poly(allyl diglycol carbonate) (ADC) and polyurethane (PU). The effects of SIN composition and crosslink density of network I (PU) on the morphology and mechanical properties of the SINs were investigated by transmission electron microscopy (TEM), dynamic mechanical analysis (d.m.a.), conventional tensile testing, and single-edge-notch tension fracture toughness methods. The effects of phase separation and rate of gelation on morphology and mechanical properties are discussed.

EXPERIMENTAL

Reagents

The raw materials used for this series of SINs and their description are listed in *Table 1*. They were used without further purification.

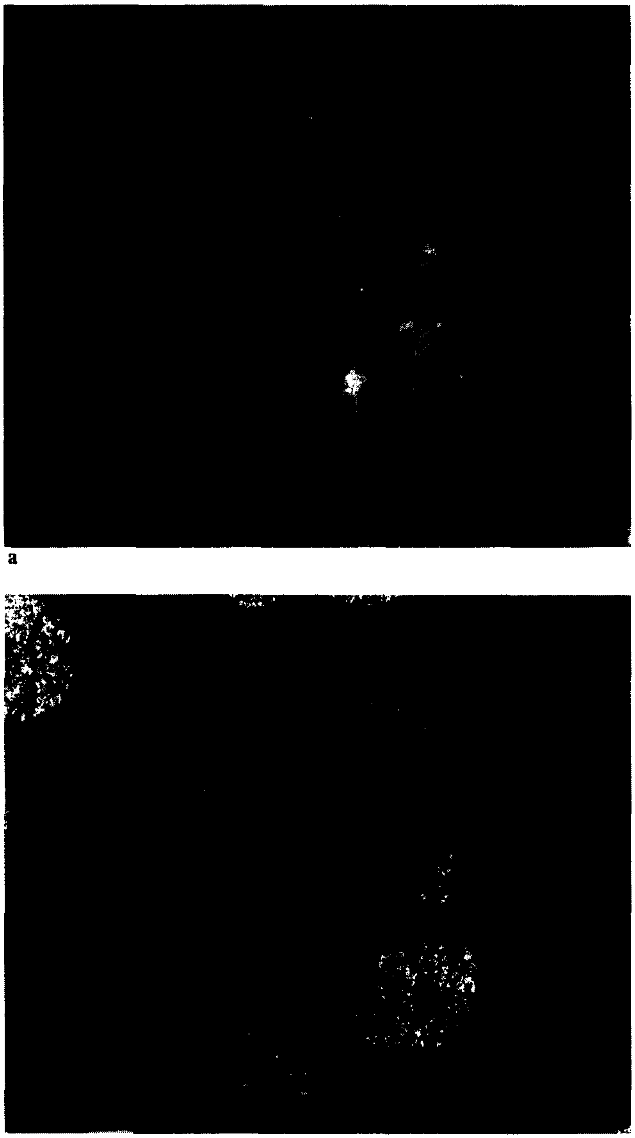

Figure 2 Transmission electron micrographs of polyurethane/allyl diglycol carbonate interpenetrating polymer network: PU content 10%, T12 content 0.5%, TMP = 0.8 equivalents; (a) magnification 15000, (b) magnification 2500

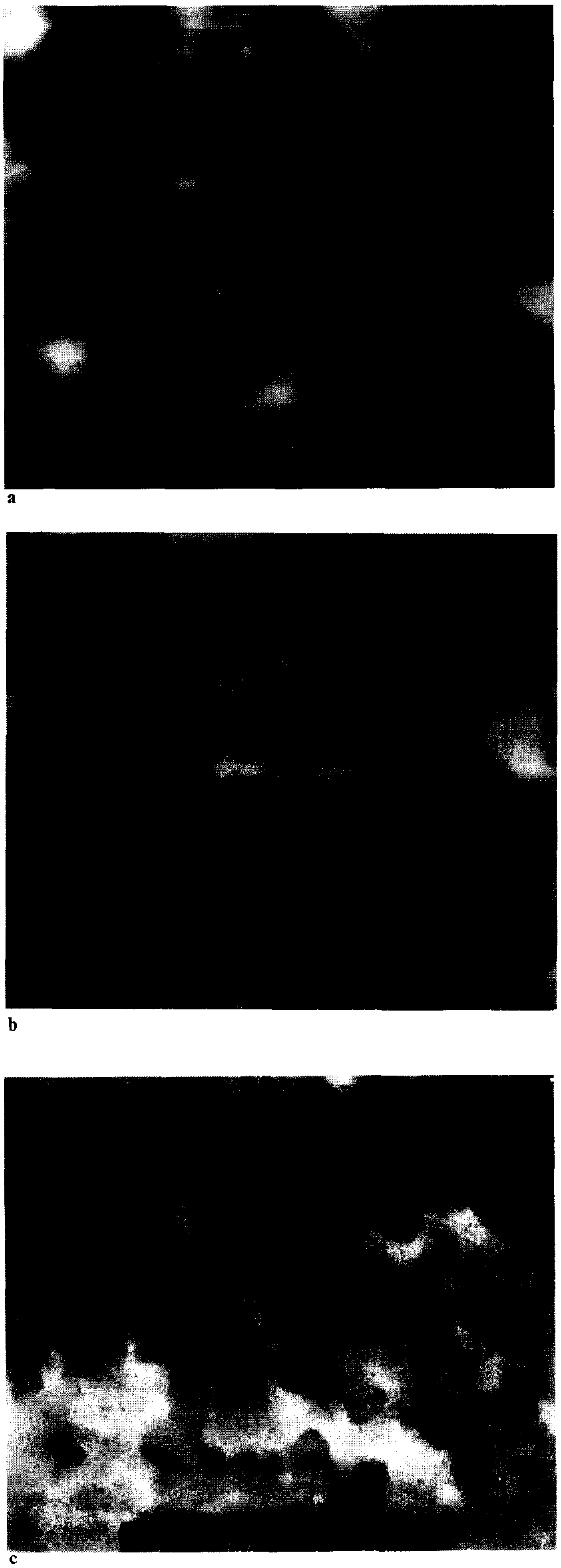

Figure 3 Transmission electron micrographs of polyurethane/allyl diglycol carbonate interpenetrating polymer network, PU content 30%: (a) TMP = 0.0 equivalents, magnification 50000; (b) TMP = 0.4 equivalents, magnification 50000; (c) TMP = 1.6 equivalents, magnification 30000

Synthesis

Casting of ADC homopolymer. Dried benzoyl peroxide powder as radical initiator was dissolved (3 wt%) in ADC monomer with vigorous stirring at 50°C. The solution was degassed and then poured into a glass mould and polymerized as flat sheets 3 mm thick, in a temperature-programmed oven. The temperature was slowly increased from 50°C to 85°C over a period of 22 h. The ADC samples were then removed from the mould and annealed at 105°C for 2 h.

Casting of SINs. All the hydroxyl components were first vacuum dried. Then the reagents including isophorone diisocyanate, poly(caprolactone) diol, trimethylolpropane (TMP), butanediol (BDO) and the ADC monomer containing the initiator were thoroughly mixed together at 50°C for about 30 min. A clear solution was obtained. In samples in which the polyurethane formation was promoted by catalyst, dibutyltin dilaurate (T12) was added last, as its catalytic action begins immediately upon contact with the polyurethane precursors. The mixture was then degassed for about 30 min at room temperature, after which it was introduced into the glass mould and polymerized using the same method as for the ADC homopolymer. The SINs were annealed at 105°C for 2 h. The completion of each component reaction was verified by the disappearance of the absorbance of the NCO peak at 2270 cm^{-1} and the allyl peak at 3092 cm^{-1} using *FT*i.r. spectroscopy. The NCO/OH ratio was kept constant at a level of 1.03 for all SIN samples. To investigate the effect of composition, three samples containing 10–30% PU were made at a TMP/BDO ratio of 2/3, which corresponds to 0.8 equivalents of TMP. In addition to these samples, other SINs containing 30% PU were prepared in which the TMP/BDO ratio was varied in order to study the effect of different PU crosslink densities on morphology and mechanical properties.

Mechanical properties

The stress–strain properties were determined on an Instron model 1115 universal testing machine. The specimens had dimensions of $120 \times 12 \times 3\,\mathrm{mm}^3$. The test procedure was carried out at a crosshead speed of 1 mm min^{-1} at 22°C using flat-faced grips at an inter-grip distance of 60 mm.

Fracture toughness was determined by the single-edge-notch tension method. Moulded sheets were cut into specimens, having dimensions of $120 \times 15 \times 3.4\,\mathrm{mm}^3$. The fracture toughness, or stress intensity at the onset of crack propagation, K_c, was measured at a crosshead speed of 1 mm min^{-1} at 22°C[20].

Thermal behaviour

The thermal transition behaviour was determined using a DuPont Dynamic Mechanical Analyser model 983 in resonance mode. The tan δ maximum was taken as the glass transition temperature.

Transmission electron microscopy

A small piece of each SIN sample was stained in 2% aqueous osmium tetroxide vapour for one week. The samples were trimmed and then thin-sectioned (80 nm) using a Reichert-Jung UltraCut E ultramicrotome. The electron micrographs were observed in a H-7000 Hitachi electron microscope. The polyurethane phase is stained with the osmium tetroxide and appears as the darker area in the TEM micrographs.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the transmission electron micrographs (TEM) of the full simultaneous interpenetrating networks (SINs) as the PU content varied from 10 to 30%. The TMP concentration has been kept constant at 0.8 equivalents. *Figure 1a* clearly shows a single-phase morphology for the PU10/ADC90 SIN. As the PU content is raised to 20% (*Figure 1b*), two-phase morphology with very fine structure was observed, indicating microphase separation. The domains are not well defined, probably indicating dual phase continuity.

The SIN with 30% PU (*Figure 1c*) shows how the

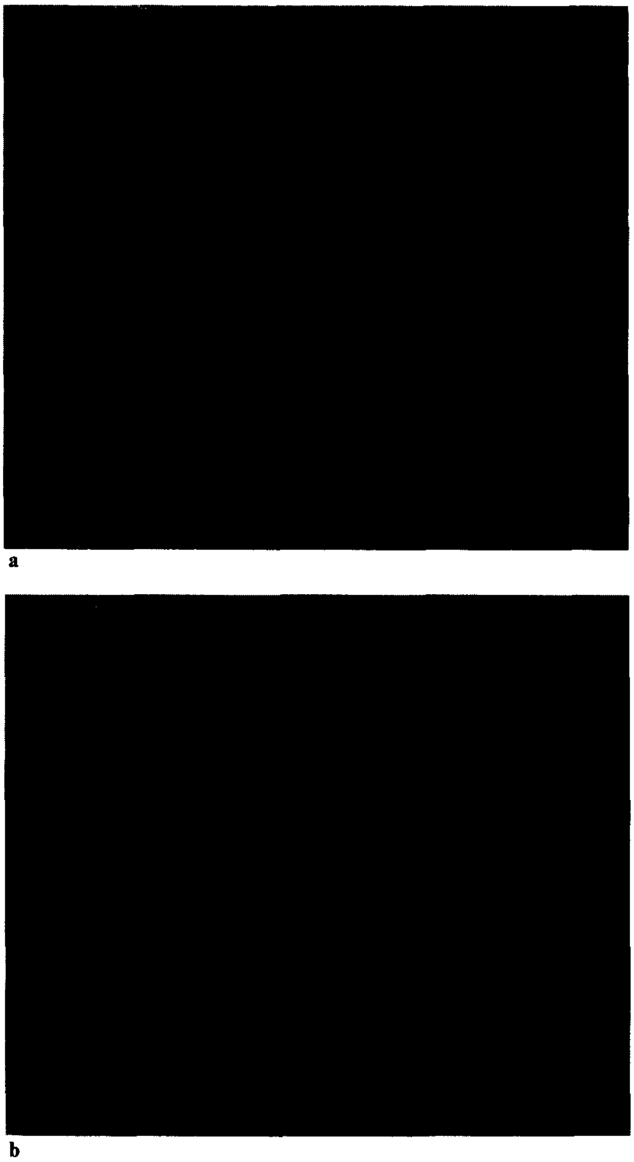

Figure 4 Transmission electron micrographs of polyurethane/allyl diglycol carbonate interpenetrating polymer network: PU content 30%, TMP = 2.0 equivalents; (a) magnification = 2500, (b) magnification = 15000

domain size has increased, indicating a higher degree of phase separation. As the TEM magnification was increased to 50 000 (*Figure 1d*), the dual phase continuity becomes apparent. This is most probably due to the fact that, as the PU concentration increases, the rate of PU network formation increases, which causes a reduction in gel time. Therefore, the interval time between PU gelation and that of ADC network formation also increases, which gives more time for the ADC monomer to phase separate and hence form larger domains.

When dibutyltin dilaurate was added, the PU network formed very rapidly. This had an even greater effect on the morphology as seen in *Figure 2*. The sample clearly possesses a dual phase morphology in which domains comprising both PU and ADC resin are distributed within the continuous ADC matrix. This rapid formation of the PU gel phase at the low concentration of 10% forms a microgel phase distributed within the ADC monomer. The PU microgel phase is swollen with the ADC monomer, which will form a separate phase due to the thermodynamic incompatibility of the two components.

As the crosslink density of the PU network is increased, the ADC domains increase in size as seen in *Figures 3* and *4*. This is a consistent response since, as the rate of the PU gel formation increases, it produces a greater phase separation. It is of interest to note that even these samples remain optically transparent, which, given the domain size of the ADC network, is an indication of a very close refractive index match between the two constituents.

Dynamic mechanical analysis

Figure 5 shows the d.m.a. thermogram of PU/ADC SINs containing 0, 10, 20 and 30% PU. With 10% PU the SIN has a single glass transition around 115°C, indicating single-phase morphology and complete miscibility. This is consistent with the TEM micrograph in *Figure 1a*.

As the PU content is increased to 30%, the d.m.a. thermogram shows two broad peaks with maxima at ~116°C and ~70°C, indicative of a two-phase structure and consistent with the TEM micrographs in *Figures 1b* and *1c*.

As the PU crosslink density is increased, the twin maxima in the tan δ thermogram gradually merge to produce a single maximum (*Figure 6*). Since the TEM micrographs indicate that the structures retain their two-phase morphology as the crosslink density of the PU network is increased, the formation of the single maximum is an indication of an increase in the T_g of the PU network with increase in crosslink density.

Mechanical properties

As the PU composition of the SINs was increased from 0 to 30%, the fracture toughness K_c increased from 0.6 to 1.2 MPa $m^{1/2}$ (*Figure 7*). However, this increase in fracture toughness was accompanied by a decrease in the modulus and a large increase in the elongation at break ϵ_b, as seen in *Figures 8* and *9*. The elongation at break increased from 6 to 23.5% whilst the modulus decreased from 1020 to 580 MPa. However, for the PU30/ADC70 IPN, as the PU network crosslink density increased

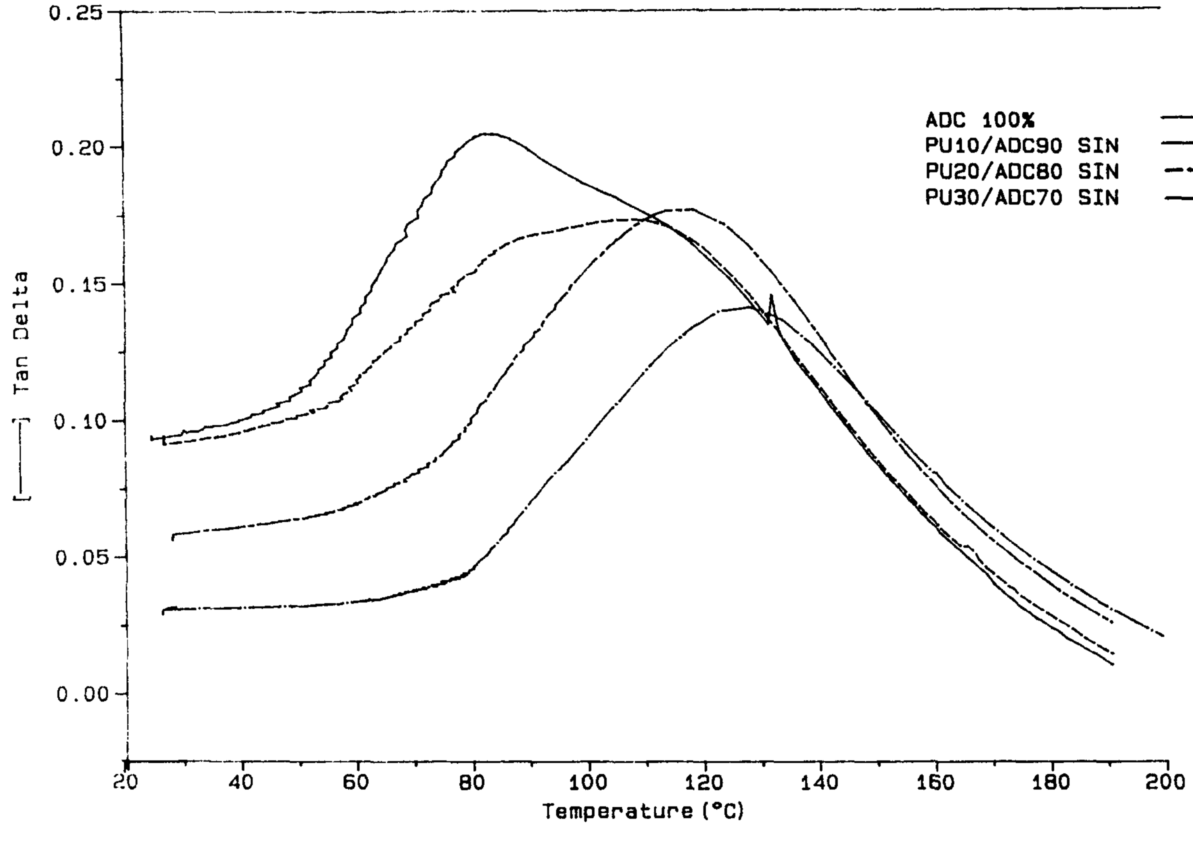

Figure 5 Dynamic mechanical analysis thermograms of polyurethane/allyl diglycol carbonate interpenetrating polymer network as a function of PU composition: 0% (–·–·–); 10% (– – –); 20% (- - - - -); 30% (——)

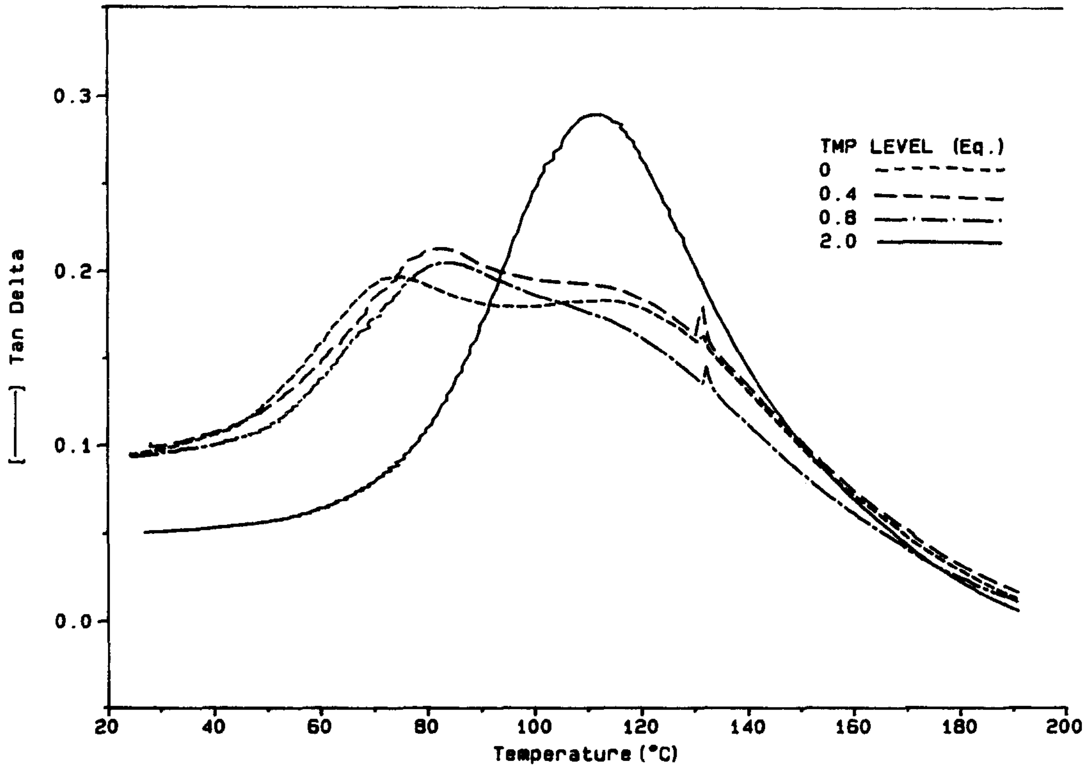

Figure 6 Dynamic mechanical analysis thermograms of polyurethane/allyl diglycol carbonate interpenetrating polymer network as a function of TMP content: 0.0 equivalents (- - - - -); 0.4 equivalents (– – –); 0.8 equivalents (—·—); 2.0 equivalents (——)

the modulus increased to 950 MPa, marginally less then the ADC resin itself, and the tensile strength increased to 35 MPa. This is shown in *Figures 10* and *11*. Concomitant with this increase in modulus, the stress intensity factor K_c also increased (*Figure 12*) to a maximum value of 1.4 MPa $m^{1/2}$, decreasing slightly as the crosslink density further increased.

As the level of TMP is increased, the phase regions of each network grow in size while the morphology remains co-continuous. The high fracture resistance of these IPNs indicates strong interfacial bonding of the two networks at all TMP levels. It may thus be inferred that each component contributes to the total toughness of the IPN system. This is consistent with the enhancement of fracture toughness of the SINs with the increase in strength of the PU phase as the TMP content and hence the crosslink density increases.

At very high PU crosslink densities, the fracture toughness slightly decreases, possibly due to a decrease in the toughness of the PU phase. Alternatively it may be attributed to the very large size of the domains, which have a relatively small interfacial area and so less interlocking between the two phases.

CONCLUSIONS

Optically clear simultaneous interpenetrating polymer networks based on poly(allyl diglycol carbonate) and a polyether polyurethane have been synthesized. As the

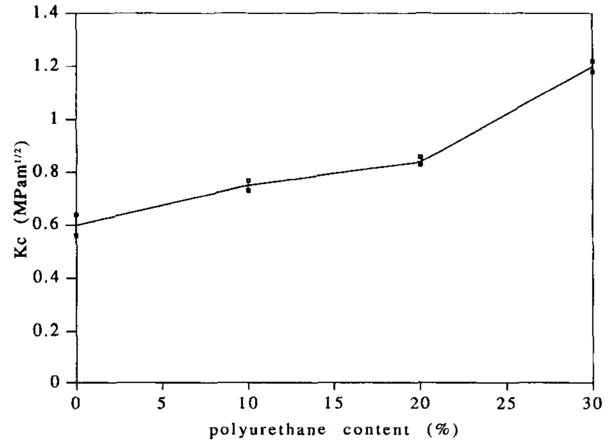

Figure 7 Variation of stress intensity factor K_c of PU/ADC IPNs as a function of PU content

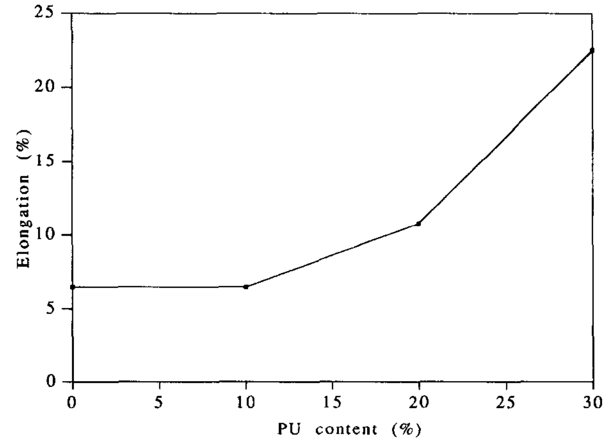

Figure 8 Variation of elongation at break of PU/ADC IPNS as a function of PU content

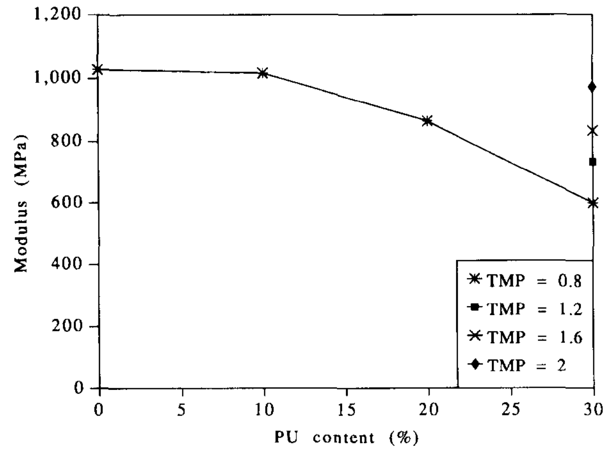

Figure 9 Variation of modulus of PU/ADC IPNs as a function of PU content

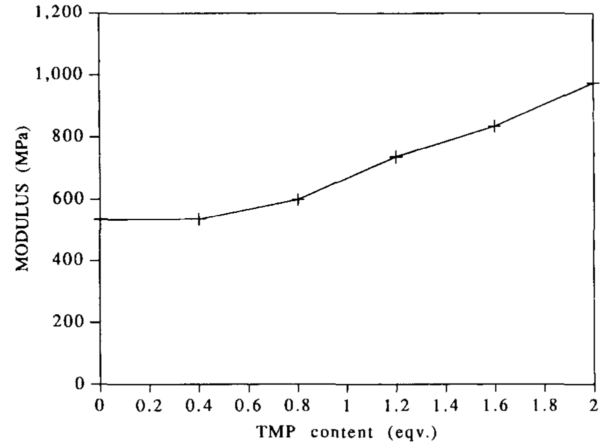

Figure 10 Variation of modulus of PU/ADC IPNs as a function of TMP content

polyurethane content is increased from 10% to 30%, the morphology changed from complete miscibility, through a phase-separated structure, to a structure that exhibited a co-continuous phase morphology. At 30% PU content, the domain sizes increased as the PU crosslink density increased. In addition the modulus and fracture toughness of this sample increased. Thus the modulus increased from 550 to 950 MPa, only slightly less than for ADC resin itself, whilst the stress intensity factor increased to a maximum value of 1.4 MPa $m^{1/2}$, a 105% increase over ADC resin.

ACKNOWLEDGMENTS

The authors would like to thank SOLA International Holdings for the provision of raw materials. One of us, SD, would like to thank the Australian Government for provision of an Overseas Postgraduate Research Scholarship. This research was supported by a grant from the Australian Research Council.

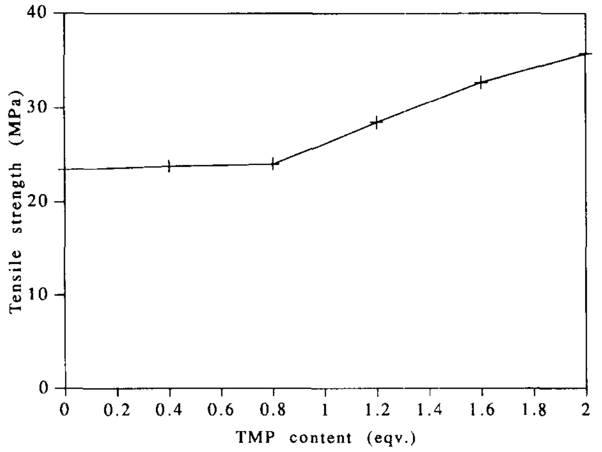

Figure 11 Variation of tensile strength of PU/ADC IPNs as a function of TMP content

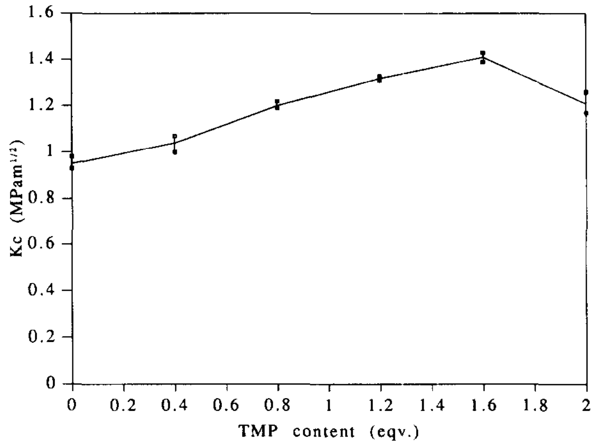

Figure 12 Variation of stress intensity factor K_c of PU/ADC IPNs as a function of TMP content

REFERENCES

1 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981

2 Sperling. L. H. 'Multicomponent Polymer Materials', (Eds. D. R. Paul and L. H. Sperling), Adv. Chem. Ser. 211, American Chemical Society, Washington, DC, 1986

3 Frisch, H. L. and Klempner, D. *Pure Appl. Chem.* 1981, **53**, 1557

4 Widmaier, J. M. and Meyer, G. C. 'Advances in Interpenetrating Polymer Networks' (Eds. D. Klempner and K. C. Frisch), Vol. 1, Technomic, Lancaster, PA, 1989, pp. 155–183

5 Jin, S. R. and Meyer, G. C. *Polymer* 1986, **27**, 592

6 Jin, S. R., Widmaier, J. M. and Meyer, G. C. *Polymer* 1988, **29**, 346

7 Tabka, M. T., Widmaier, J. M. and Meyer, G. C. in 'Sound and Vibration Damping with Polymers' (Eds. R. D. Corsaro and L. H. Sperling), American Chemical Society, Washington, DC, 1990, pp. 445–456

8 Lipatov, Y. S., Rosovizky, V. F., Datsko, P. V. and Maslak, Y. V. *J. Appl. Polym. Sci.* 1988, **36**, 1143

9 Lipatov, Y. S. *Macromol. Chem. Phys. (C)* 1990, **30**(2), 209

10 Park, I. H., Lee, J. H. and Kim, S. C. *Polym. Bull.* 1983, **10**, 126

11 Fox, R. B., Fay, J. J., Sorathia, U. and Sperling, L. H. in 'Sound and Vibration Damping with Polymers' (Eds. R. D. Corsaro and L. H. Sperling), Americal Chemical Society, Washington, DC, 1990, pp. 359–365

12 Touhsaent, R. E., Thomas, D. A. and Sperling, L. H. in 'Toughness and Brittleness of Plastics' (Eds. R. D. Deanin and A. M. Crugnola), Adv. Chem. Ser. 154, American Chemical Society, Washington, DC, 1976, pp. 206–223

13 Jia, D., Chen, L., Wu, B. and Wang, M. in 'Advances in Interpenetrating Polymer Networks' (Eds. D. Klempner and K. C. Frisch), Vol. 1, Technomic, Lancaster, PA, 1989, pp. 303–327

14 Lee, D. S. and Kim, S. C. *Macromolecules* 1984, **17**, 2193

15 Demin, J., Chen, L., Wu, B. and Wang, M. in 'Advances in Interpenetrating Polymer Networks' (Eds. D. Klempner and K. G. Frisch), Vol. 1, Technomic, Lancaster, PA, 1989, pp. 303–327

16 Frounchi, M., Burford, R. P. and Chaplin, R. P. *Polymer* 1994, **35**, 5073

17 Morin, A., Djomo, H. and Meyer, G. C. *Polym. Eng. Sci.* 1983, **23**, 394

18 Hermant, U., Damyanidu, M. and Meyer, G. C. *Polymer* 1983, **24**, 1419

19 Frounchi, M., Westgate, T. A., Chaplin, R. P. and Burford, R. P. *Polymer* 1994, **35**, 5041

20 Brown, W. F. Jr and Strawley, J. E. ASTM Special Technical Publication No. 410, 1986