Interpenetrating polymer networks of poly(diethyleneglycol bis(allylcarbonate)) and poly(urethane acrylates)

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Simultaneous full interpenetrating polymer networks of poly(diethyleneglycol bis(allylcarbonate)) and poly(urethane acrylates) have been synthesized and characterized by the measurement of mechanical properties, fracture toughness parameters, and by dynamic mechanical analysis. No evidence of phase segregation was detected in the interpenetrating polymer networks. The networks exhibited a single glass transition temperature at all the compositions studied. Significant enhancement in mechanical properties and fracture toughness was observed in one of the interpenetrating polymer networks which was characterized by high chain intermixing. The high optical transparency of the base resin system was retained in all the interpenetrating polymer network systems studied.

(Keywords: interpenetrating polymer networks; fracture; mechanical properties)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are intimate mixtures of crosslinked polymers held together by permanent entanglements. IPNs can be prepared either by swelling a crosslinked polymer with monomer and a crosslinking agent followed by *in situ* curing of the swollen polymer (sequential technique) or by blending monomers or prepolymers together with the respective crosslinking agents and curing the component polymers simultaneously (SIN technique). Although IPNs have been the subject of extensive study[1], little work has been done to use this type of polymer material in toughened systems.

Poly(diethyleneglycol bis(allylcarbonate)), also known as poly(allyldiglycol carbonate) or ADC, is a highly successful commercial resin with superior optical transparency. Fracture behaviour of ADC has been studied by the authors[2], and it was shown that plastic deformation is similar to that of those thermoplastic polymers in which shear yielding is the major stress-relieving process. Thermoplastic polymers such as poly(methyl methacrylate), which deform predominantly via shear bands[3,4], require a smaller optimum size of reinforcing agents than either acrylonitrile-butadiene-styrene (ABS) or high impact polystyrene (HIPS)[5,6], in which the major mode of deformation occurs via crazes or by a mixed mode process. Therefore forming IPNs in which domain phase size may be very small due to molecular entanglements may be considered as a toughening method for ADC resin. Moreover, forming IPNs in which domains are about 10–50 nm in size allows the essential transparency of ADC to be retained.

This paper describes novel poly(allyldiglycol carbonate)/poly(urethane acrylate) (PUA) simultaneous interpenetrating polymer networks or ADC/PUA IPNs. The major aim of the project has been to modify the yielding behaviour of ADC by the incorporation of another glassy polymer network, giving tough resins with higher ductility without loss in modulus, yield strength and of course optical qualities. For this purpose acrylated urethane oligomers were chosen. These resins can be incorporated as oligomers which can be subsequently polymerized to produce a polyurethane network that has the potential to combine the high abrasion resistance and toughness of the polyurethane backbone[7].

EXPERIMENTAL

Materials

The urethane acrylate oligomers were provided as development products by Polycure Australia Ltd. The trifunctional urethane acrylate oligomer was prepared by reacting propoxylated trimethylol propane with an average molecular weight of 430 with fully hydrogenated methylene 4,4′-diphenylene diisocyanate ($H_{12}MDI$) in appropriate proportions to produce an OH-terminated polyurethane oligomer with an average molecular weight of about 2000. This was then reacted with acrylic acid in the usual manner to produce the urethane acrylate oligomer, to which was added propoxylated glycerol triacylate (Aldrich). The difunctional urethane acrylate oligomer was prepared in exactly the same manner except that polypropylene glycol with an average molecular weight of 750 was reacted with the $H_{12}MDI$. These details are summarized in *Table 1*. Irgacure 651 (dimethoxy-2-phenyl acetophenone) from Ciba-Geigy Australia Ltd was the photoinitiator. Diethyleneglycol bis(allylcarbonate) monomer provided by SOLA International Holdings Ltd was used as received.

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Synthesis of ADC/PUA simultaneous IPNs

ADC/PUA IPNs were polymerized as flat sheets 3.3 mm thick. The urethane acrylate oligomers containing 0.5% w/w Irgacure 651 were added to ADC monomer containing 3% w/w anhydrous benzoyl peroxide. Concentrations of 10, 20 and 30 wt% of the urethane acrylates were used. The reaction mixture was poured into glass plate moulds and irradiated by a Fusion Systems Ultraviolet Radiation source rated at 300 W in^{-1}. Conditions of operation of the UV system to obtain 100% conversion of the urethane acrylate moiety were determined in separate experiments. After polymerization of the urethane acrylate oligomer the ADC monomer was polymerized as detailed previously[2]. The IPN samples were then removed from the moulds and annealed at 110°C for 2 h. This procedure ensured that the ADC monomer was completely polymerized, as confirmed by infra-red spectroscopy.

Dynamic mechanical analysis

The glass transition temperature (T_g) for each sample was determined in a DuPont 983 dynamic mechanical analyser at a heating rate of 20°C min^{-1} in resonant mode over a temperature range from -100 to 200°C.

Transmission electron microscopy

A small sample of each IPN was stained overnight in 2% aqueous osmium tetroxide. The samples were then sectioned by using a Reichert-Jung Ultra Cut E ultramicrotome with a diamond knife. The electron micrographs were observed in a H-7000 Hitachi electron microscope operating at 100 kV.

Determination of mechanical and fracture properties

Tensile stress, strain, flexural modulus and fracture toughness were determined using an Instron Model 1122 universal testing machine at a crosshead travel speed of 1 mm min^{-1} at room temperature. Tensile stress and strain were determined on unnotched bars of dimensions 3.3 x 12 x 120 mm. The flexural modulus was measured on unnotched bars (3.3 x 14 x 80 mm) in three-point flexure mode with a distance of 60 mm between supports. The critical stress intensity factor K_c was obtained using single-edge notched bend (SENB) and single-edge notched tensile (SENT) test specimens. In all cases K_c was determined by the following general formula[8]:

$$K_c = \sigma_c Y a^{1/2}$$

with σ_c the critical stress for crack initiation, Y the shape factor, and a the notch length. The notches were produced with a sharp razor blade to produce a sharp notch whose radius was smaller than 10 μm. At least five test specimens were broken per sample. Testing was performed according to the methods described in ref. 9.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The T_g values recorded in *Table 2* were determined from the maximum in the tan δ *versus* temperature plots. The results in *Table 2* show that the ADC/PUA IPNs which used the L1 urethane acrylate oligomer are single-phase materials, which indicates complete segmental mixing of the two networks. *Figures 1* and *2* are plots of tan δ *versus* temperature for both L1 and L2 IPNs and show that the T_g values of both the L1 and L2 IPNs decreased with increasing concentration of the urethane acrylate. The heights of the tan δ curves also consistently increase with increase in urethane acrylate concentration. For all the compositions studied, one single T_g was observed, which also agrees with the transmission electron micrographs which show extremely small phase domains of either component. A typical electron micrograph of the L1 IPN (composition 75% ADC/25% PUA) is shown in *Figure 3*. The sizes of the domain phases are indeed on a molecular scale.

Frisch and co-workers[10] developed an equation to describe the relationship between glass transition temperature and degree of interpenetration in mutually compatible IPNs:

$$\frac{T_g - T_g(\text{av})}{T_g(\text{av})} = -\frac{\theta}{(1+\theta)}$$

Table 1 Chemical description of urethane acrylate oligomers

Urethane acrylate prepolymer	Designation code of IPN	Equivalent weight of UA	Functionality, F_n	Acrylic monomer, wt% in prepolymer
Aliphatic polyether	L1	430	3	PGTA[a], 20
Aliphatic polyether	L2	750	2	0

[a] Propoxylated glycerol triacrylate

Table 2 Glass transition temperatures of L1 IPNs

ADC/PUA IPN composition (wt%)	T_g (°C)			
	Experimental	Equation (1)	Equation (2)	θ
100 ADC	130.60			
90 ADC/10 PUA	120.57	123.7	123.7	0.026
80 ADC/20 PUA	99.76	117.1	117.1	0.174
100 PUA	71.05			

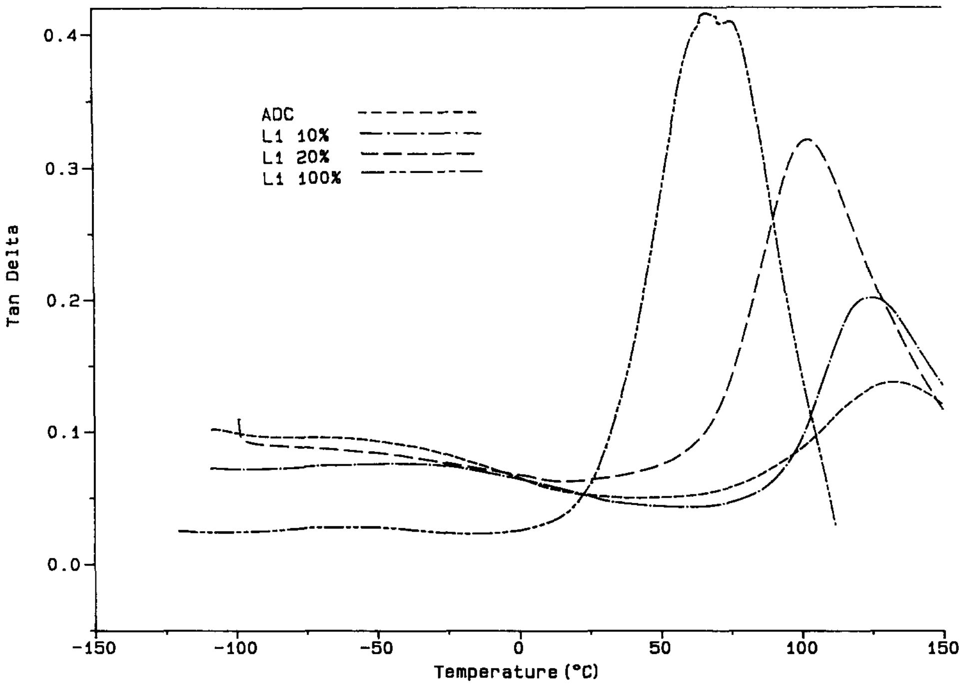

Figure 1 DMA tan δ of the L1 ADC/PUA IPN as a function of composition

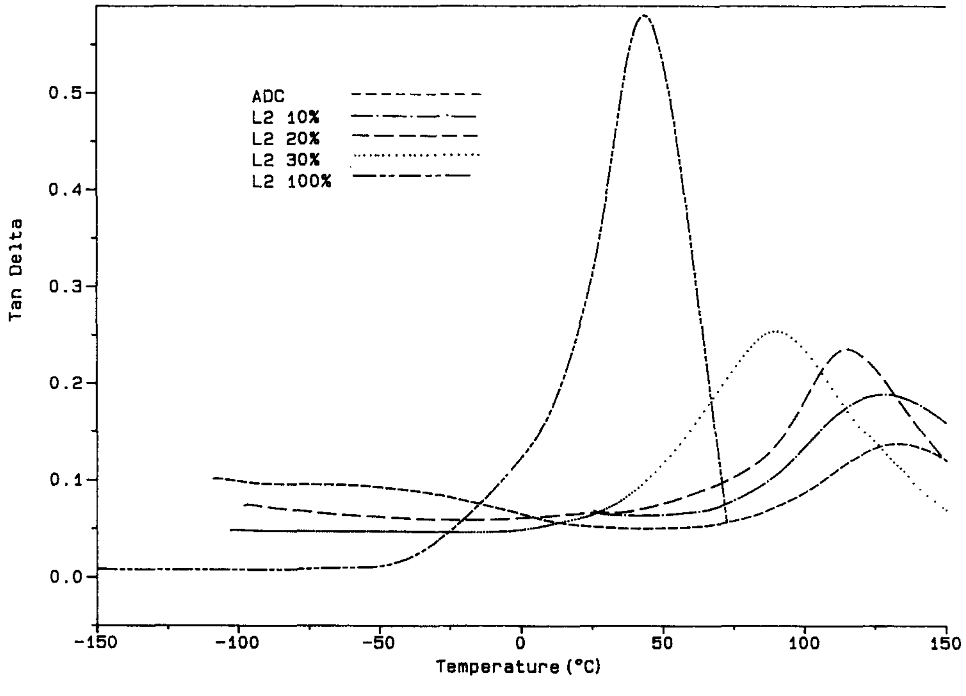

Figure 2 DMA tan δ of the L2 ADC/PUA IPN as a function of composition

where θ is a measure of interpenetration, T_g is the measured glass transition of IPN and $T_g(\mathrm{av})$ is the average T_g calculated from equations (2) or (3):

$$T_g = w_1 T_{g1} + w_2 T_{g2} \qquad (2)$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (3)$$

where T_{g1} and T_{g2} represent the glass transition temperatures of polymer 1 and polymer 2 and w_1 and w_2 are the weight fractions. Equation (1) predicts that the T_g of an IPN would be less than or equal to $T_g(\mathrm{av})$ for positive θ values. The higher value of θ indicates higher segmental mixing between the two networks.

Results of these calculations have been presented in *Tables 2* and *3* for L1 and L2 IPNs. As shown, the T_gs of the IPNs are lower than those of the average values calculated from equations (2) and (3). The θ value in L1 IPNs increases with urethane acrylate content, while in L2 IPNs, negative θ values were found at up to 20% urethane acrylate content. Only in the higher urethane acrylate content (30%) IPN was a positive θ value found. The calculated θ values suggest that the best segmental interpenetration in these series should appear in the L1 IPNs.

Mechanical properties and fracture toughness parameters

Variation in tensile stress and strain. *Figures 4* and *5* give the variation in the tensile strength and elongation for the L1 and L2 ADC/PUA IPNs, respectively, as a function of composition. The results show that the tensile strength increased from 39 to 48 MPa for the L1 IPN whilst the elongation increased marginally from 7.5 to 8%. In contrast, the tensile strength of the L2 IPN decreased significantly as the UA content increased. Concomitant with this decrease in tensile strength, the elongation at break increased from 7 to 16.5%.

Variation in the Young's modulus. *Figures 6* and *7* give the variation in Young's flexural modulus with composition for the L1 and L2 ADC/PUA IPNs, respectively. Whilst the Young's modulus remained essentially constant for the L1 IPN, it decreased steadily from 2.2 to 0.9 GPa as the UA composition increased to 20% for the L2 IPNs. This higher modulus of the L1 IPNs, as compared with the L2 IPNs, is due to the higher functionality of the UA network, which limits its capacity for reptation.

Variation in the stress intensity factor K_c. *Figures 8* and *9* show the variation in the stress intensity factor K_c as a function of composition for the ADC/PUA IPNs. For the L1 series the fracture toughness increased steadily from 0.68 to 1.15 MPa m$^{1/2}$ at 20% UA composition, whereas the L2 IPNs exhibited a slight decrease in

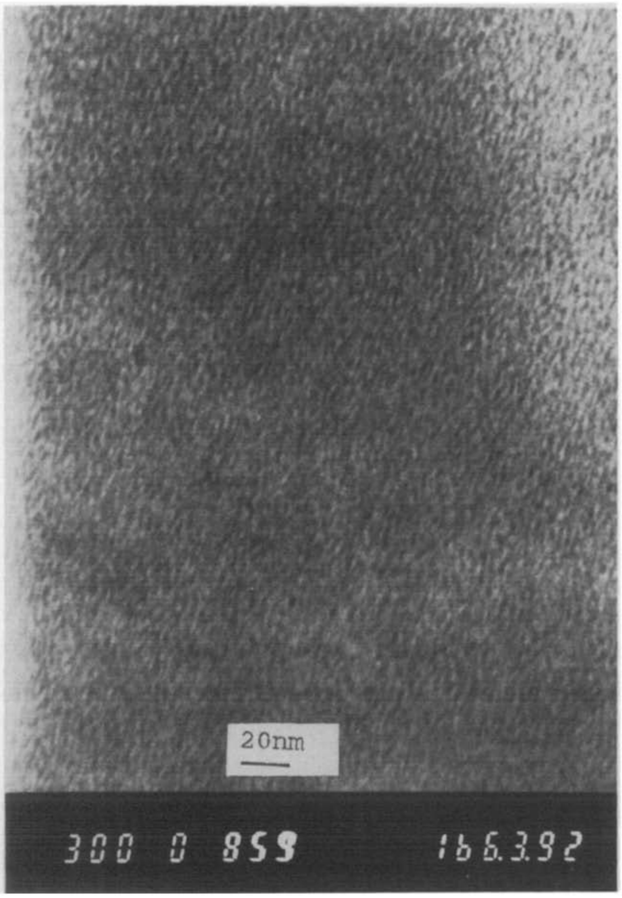

Figure 3 Transmission electron micrograph of the L1 IPN with composition 25% UA/75% ADC at a magnification of ×300000

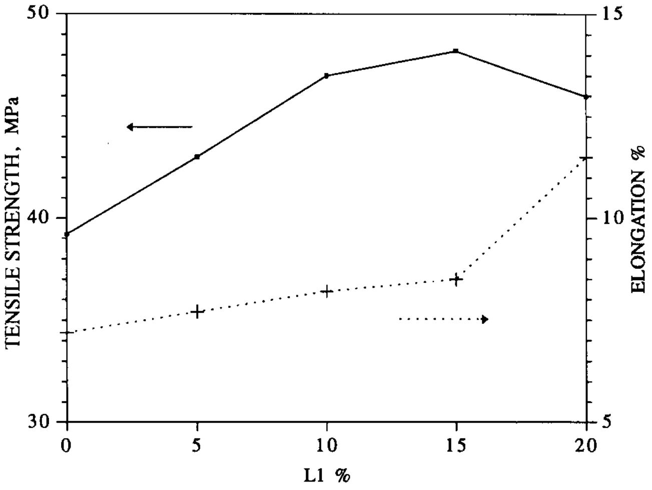

Figure 4 Variation of the tensile stress and elongation as a function of IPN composition for L1 IPN

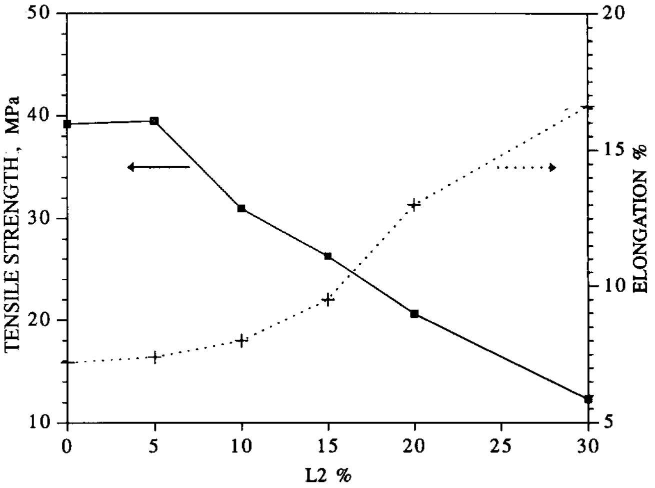

Figure 5 Variation of the tensile stress and elongation as a function of IPN composition for L2 IPN

Table 3 Glass transition temperatures of L2 IPNs

ADC/PUA IPN composition (wt%)	T_g (°C)			θ
	Experimental	Equation (1)	Equation (2)	
100 ADC	130.60			
90 ADC/10 PUA	126.32	119.8	119.8	−0.051
80 ADC/20 PUA	113.40	109.6	109.6	−0.033
70 ADC/30 PUA	89.71	99.9	99.9	0.114
100 PUA	43.78			

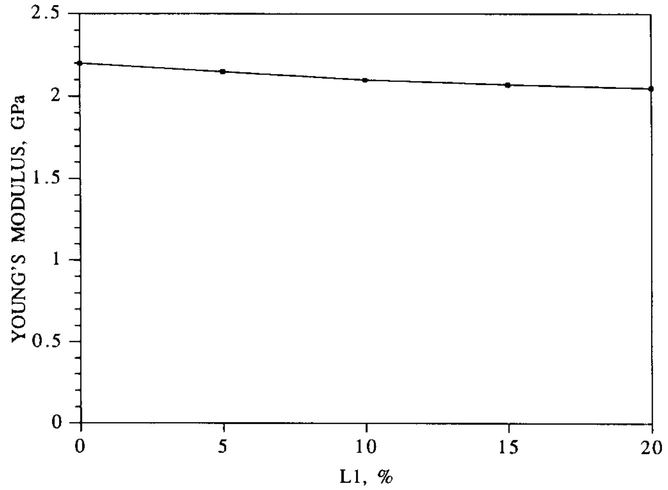

Figure 6 Variation of Young's modulus with IPN composition for L1 IPN

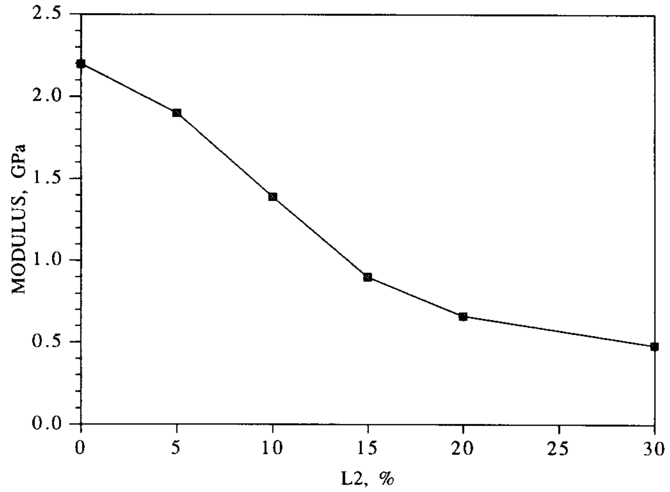

Figure 7 Variation of Young's modulus with IPN composition for L2 IPN

the fracture toughness as the UA content increased. This difference in properties relates to the molecular structure of these two IPNs. L1 urethane acrylate has a functionality of 3 and relatively low equivalent molecular weight (430), which leads to a tightly crosslinked rigid network. The increase in elongation at break and particularly the increase in toughness of the 80 ADC/20 PUA L1 IPN over the neat ADC resin verify that the increased entanglement between the ADC resin and L1 urethane acrylate have improved the ability of the highly crosslinked structure of the ADC resin to react in a more ductile fashion whilst retaining the desirable high stiffness (modulus) of ADC resin. Furthermore, in the absence of the phase-separated morphology usually seen in rubber-toughened thermosets, which have different toughening mechanisms, the only toughening mechanism should arise from shear yielding. Thus, the tight structure of the L1 urethane acrylate imparts ductility due to the inherent flexibility of the polyurethane backbone chain and at the same time imparts very high strength due to the highly crosslinked network structure. This results in significant increase in toughness of the ADC resin.

However, L2 IPNs have a urethane acrylate with a functionality of two and relativey high equivalent molecular weight (750) giving a looser network than L1. Although the L2 urethane acrylate has a more elastomeric structure than the L1 urethane acrylate, the elongation at break of L1 IPNs are very similar to L2 IPNs whilst the tensile strength and modulus of L2 IPNs are much lower than the L1 IPNs. Thus, the loose urethane network structure of the L2 IPNs, whilst it contributes ductility to the overall network, nevertheless causes significant deterioration in the overall strength and stiffness of the IPNs. This is almost certainly due to the fact that the L2 IPNs deform more easily by reptation.

CONCLUSIONS

Novel IPNs were prepared from ADC and urethane acrylate oligomers. All of the IPNs exhibited excellent optical transparency and a single glass transition. By appropriate selection of the urethane acrylate it is possible to modify yielding behaviour so that higher toughness is achieved without loss of other desirable properties. The mechanical and fracture properties of highly crosslinked IPNs were superior to those with a lower crosslink

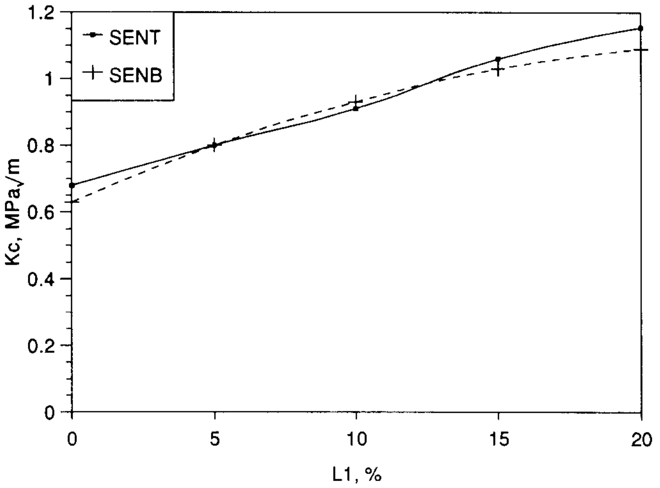

Figure 8 Variation of the critical stress intensity factor K_c as a function of the IPN composition for L1 IPN

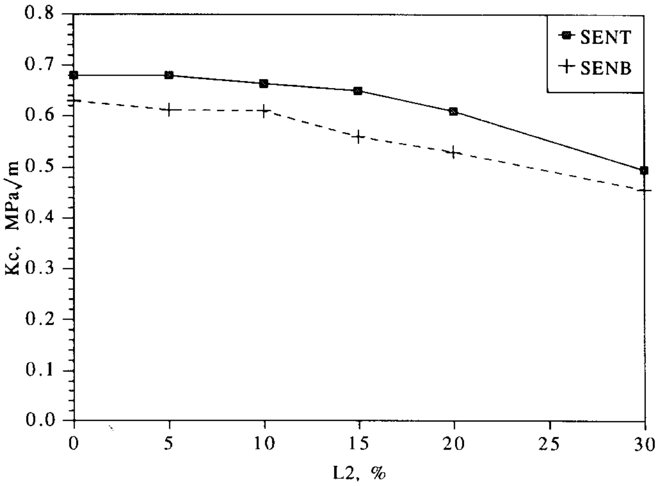

Figure 9 Variation of the critical stress intensity factor K_c as a function of the IPN composition for L2 IPN

density. This is due to a shift in glass transition temperature of the IPNs and can be correlated with their interpenetrating molecular structure.

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REFERENCES

1 Sperling, L. H. 'Multicomponent Polymer Materials' (Eds D. R. Paul and L. H. Sperling), Adv. Chem. Ser. no. 211, American Chemical Society, Washington DC, 1985, p. 21
2 Frounchi, M., Chaplin, R. P. and Burford, R. P. *Polymer* 1994, **35**, 752
3 Bucknall, C. B., Partridge, I. K. and Ward, M. V. *J. Mater. Sci.* 1984, **19**, 2064
4 Bucknall, C. B. and Marchettia, X. *J. Appl. Polym. Sci.* 1983, **28**, 2689
5 Donald, A. M. and Kramer, E. J. *J. Mater. Sci.* 1982, **17**, 1765
6 Donald, A. M. and Kramer, E. J. *J. Mater. Sci.* 1982, **17**, 2351
7 Frisch, K. C. and Reegen, S. L. 'Advances in Urethane Science and Technology', Vol. 7, Technomic, Westport, CT, 1979, p. 163
8 Williams, J. G. 'Fracture Mechanics of Polymers', Ellis Horwood, Chichester, 1984, pp. 63–70
9 Williams, J. G. and Cawood, M. J. *Polym. Testing* 1990, **9**, 15
10 Frisch, H. L., Frisch, K. C. and Klempner, D. *Polym. Eng. Sci.* 1974, **14**, 648