Polyurethane-modified polyester semi-interpenetrating networks

D. J. Hourston and Y. Zia
Department of Chemistry, University of Lancaster, Lancaster, LA1 4YA, UK
(Received 12 February 1979)

Four semi-interpenetrating polymer network materials based on a methyl acrylate modified crosslinked polyester and a polyurethane were synthesized and their dynamic mechanical and stress–strain properties were investigated. The tan δ-temperature dispersion of the semi-interpenetrating polymer network containing 70% polyurethane showed two maxima, while at 60% polyurethane a distinct shoulder is again to be seen at around the polyurethane glass transition temperature. At 30% and 50% by weight of polyurethane single, but rather broad, transitions occurred, despite the fact that at 30% and 60% polyurethane electron micrographs indicated a two-phase morphology. The stress at break was found to decrease approximately linearly with rubber content up to about 70% by weight.

INTRODUCTION

There are a variety of reasons why polymeric composites such as blends$^{1-6}$, grafts^{7,9}, and semi- and fully interpenetrating systems$^{10-16}$ are currently much studied. They include the desire to obtain better properties in the composite than are possessed by either of the constituents and the need to gain a better understanding of how phase separated polymeric materials behave mechanically. The latter objective is the one which is paramount in this case.

An interpenetrating polymer network is obtained when a second 3-D network is synthesized from a monomer which was dispersed in an already established network. There are a variety of methods of synthesis^{17}. For a semi-interpenetrating polymer network (semi-IPN) only one of the two constitutents is crosslinked. If the polymer synthesized first is crosslinked, the material is a semi-IPN of the first kind. A semi-IPN of the second kind (semi-2-IPN) is obtained when only the second polymer to be polymerized is crosslinked.

The materials in this study are believed to be best classified as semi-2-IPN's. They were prepared in a one shot, two stage process in which a diisocyanate prepolymer (Adiprene L-100) and butane-1,4-diol, the polyurethane precursors, were mixed with both an unsaturated polyester liquid resin (Crystic 191) and with methyl acrylate. The unsaturated polyester resin, which has a significant number of hydroxyl ends, contained 35% by weight of styrene as crosslinking agent. It is thought that the linear polyurethane which was formed at room temperature contains some polyester units and that the network component which is established at higher temperatures is a polyester crosslinked by both styrene and methyl acrylate. The latter serves to give a more flexible network.

EXPERIMENTAL

Materials

(i) Polyurethane. Adiprene L-100^{18}, kindly donated by Du Pont Ltd., an isocyanate-ended polyurethane precursor based on toluene diisocyanate, and butane-1,4-diol (BDH) Ltd.) were used in the polyurethane synthesis which was catalysed by di-n-butyl tin dilaurate (2% by weight of polyurethane). See *Table 1* for characterization data. 2,4-dihydroxybenzophenone at 1% by weight of polyurethane was added as a stabilizer.

Table 1 Characterization data

	Adiprene L-100	Crystic 191
$\bar{M}_n$^{a}	1990	650
$\bar{M}_w/\bar{M}_n$^{b}	2.0	1.46
Acid number (mg KOH/g)	–	31
Hydroxyl number (mg KOH/g)	–	165

[a] By vapour pressure osmometry
[b] By gel permeation chromatography

(ii) Polyester. A commercially available unsaturated polyester resin (Crystic 191) was kindly donated by the Scott Bader Company Ltd. This liquid resin, which is based on orthophthalic and maleic acids, contains 35% by weight of styrene as crosslinking agent. See *Table 1* for characterization data.

(iii) Methyl acrylate. Methyl acrylate (BDH Ltd.) was freed from inhibitor and distilled prior to use. In the preparation of the semi-IPN's the methyl acrylate to unsaturated polyester ratio was always 1 to 3 by weight. 2,2′-azobis-(2-methylpropionitrile), present at a level of 0.1% by weight of the methyl acrylate/unsaturated polyester resin component, was used as initiator.

All materials were carefully dried prior to use.

Synthesis

The materials were dissolved in the methyl acrylate and carefully degassed. The di-n-butyltin dilaurate was added just before degassing. The mixtures were then poured into a steel mould sealed with a teflon-coated rubber gasket. The lid of the mould was spring-loaded to compensate for con-

0032–3861/79/121497–04$02.00

Table 2 Composition of Semi-IPN's

Code	Polyurethane (wt %)	Methyl acrylate (wt %)	Polyester (wt %)
A[a]	100		
B	70	7.5	22.5
C	60	10	30
D	50	12.5	37.5
E	30	17.5	52.5
F[b]	0	25	75

[a] Synthesized (20°C; 24 h) from Adiprene L-100 and butane-1,4-diol in inhibited methyl acrylate

[b] Synthesized at 70°C for 4 h and then 100°C for another 4 h

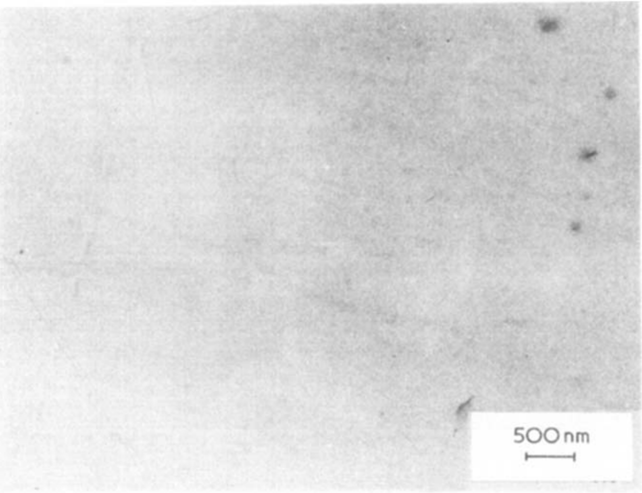

Figure 1 Electron micrograph of methyl acrylate modified crosslinked polyester resin

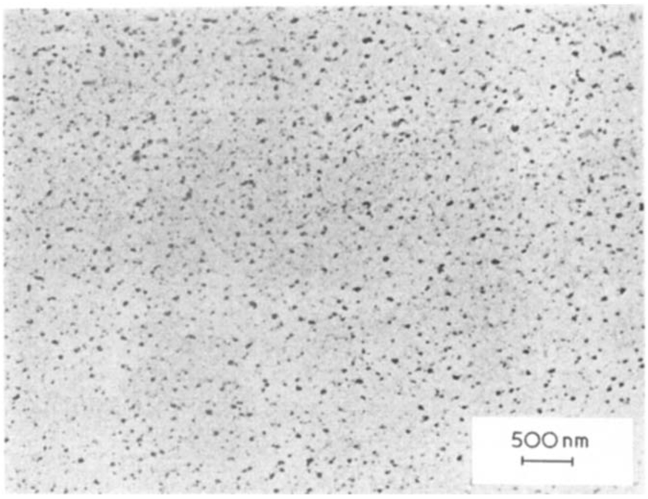

Figure 2 Electron micrograph of semi-IPN containing 30% by weight of polyurethane (sample E)

traction on polymerization. It was then left at 20°C for 24 h to allow the polyurethane to form. The methyl acrylate-modified crosslinked polyester component was formed by raising the temperature first to 70°C for 4 h and then to 100°C for a further 4 h.

All samples (see *Table 2* for details of composition) were placed in a vacuum oven at 20°C for at least 10 days prior to testing.

Techniques

(i) Electron microscopy. Transmission electron micrographs were obtained using a Hitachi electron microscope (model HU-11B). The samples were stained for several days in osmium tetroxide vapour.

(ii) Stress–strain measurements. The stress-strain characteristics of dumb-bell specimens of the materials were investigated at 20°C using a Howden tensometer. The initial gauge length was 2 cm and an extension rate of 2.5 cm/min was used.

(iii) Dynamic mechanical measurements. A Rheovibron dynamic viscoelastometer (model DDV-II) was used at a frequency of 11 Hz. The temperature ranges covered were scanned at a rate of 1–2°C/min.

RESULTS AND DISCUSSION

Morphology

Figures 1–3 show the electron micrographs of the modified polyester material and the semi-IPN's containing 30% and 60% polyurethane. In *Figure 1* it is clear that at this resolution the second component in these semi-2-IPN's appears quite homogeneous. This is taken as evidence, but not proof, that both the styrene and the methyl acrylate are involved in crosslinking the polyester resin and that relatively little linear polymethyl acrylate is present. This proposition is supported later by the stress-strain results.

In *Figures 2 and 3* the dark domains, in which at very much higher magnifications there is no evidence of substructure, are composed of the linear polyurethane which has some unsaturation as a result of the incorporation of hydroxyl-ended polyester molecules. It was shown by gel permeation chromatography that only a small quantity of the polyester resin is incorporated in the polyurethane. In other words, at least up to 60% by wt of polyurethane, these semi-2-IPN's may be viewed as rubber-modified glassy polymer systems.

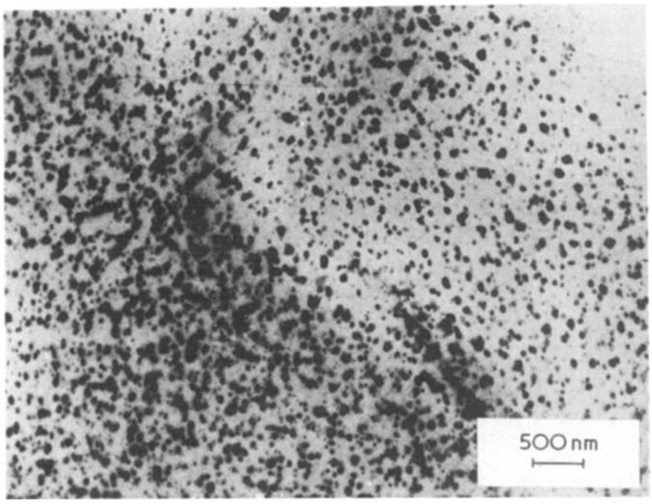

Figure 3 Electron micrograph of semi-IPN containing 60% by weight of polyurethane (sample C)

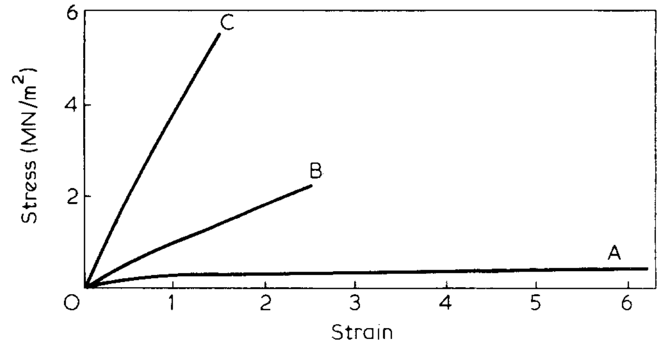

Figure 4 Stress–strain curves for linear polyurethane (A) and the semi-IPNs containing 70% (B) and 60% (C) by weight of polyurethane, respectively

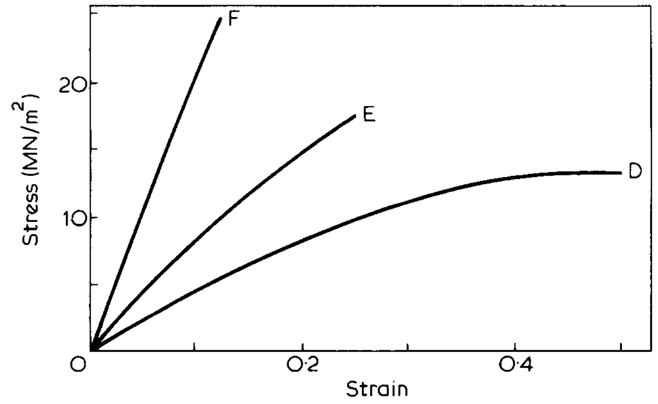

Figure 5 Stress–strain curves for the semi-IPN's containing 50% (D) and 30% (E) by weight of polyurethane and for the modified polyester resin (F)

Table 3 Stress and elongation at break

Code	Stress at break (*MN/m*^{2})	Elongation at break (%)
A	0.4	620
B	2.4	250
C	5.5	150
D	12.9	50
E	17.8	25
F	25.0	12

Tensile behaviour

Figures 4 and *5* and *Table 3* show the tensile behaviour of the linear polyurethane, the four semi 2-IPN's and the modified polyester. The behaviour ranges from the rubbery characteristics of the linear polyurethane, which in this sample does not contain the low level of polyester residues found in the polyurethane component of the semi-IPN's, through to the rather stiff modified polyester. The fact that this latter material has an elongation at break of 12% is clear indication of the substantial involvement of the methyl acrylate in the crosslinking process. The elongation and stress at break expected for a pure crosslinked polyester of this type would be around 2% and 55 MN/m^2, respectively[19].

Figure 6 shows that the stress at break decreases approximately linearly with rubber content up to around 70%. Somewhat above this level, it is likely that the polyurethane becomes the continuous phase.

Dynamic mechanical behaviour

Figure 7 shows the tan δ-temperature curves for the six materials. All show a single major transition with the exception of sample B, which contains 70% by weight of polyurethane, where a second transition at around –20°C, ascribed to polyurethane, occurs. The fact that this transition is about 6°C above that of the pure polyurethane may result because sample A does not contain the low level of Crystic residues known to exist in the semi-IPN polyurethane component. Sample C, which contains 60% by weight of polyurethane, shows a low temperature shoulder indicating that the dynamic mechanical technique can distinguish a polyurethane phase.

The methyl acrylate modified polyester has only one glass transition at 118°C indicating that if any linear polymethyl acrylate is formed it is a very minor component.

The samples containing 70% and 60% by weight of polyurethane show very broad compound transitions. The width of the transitions at half peak height are 132°C and 101°C, respectively. At lower polyurethane contents the single tran-

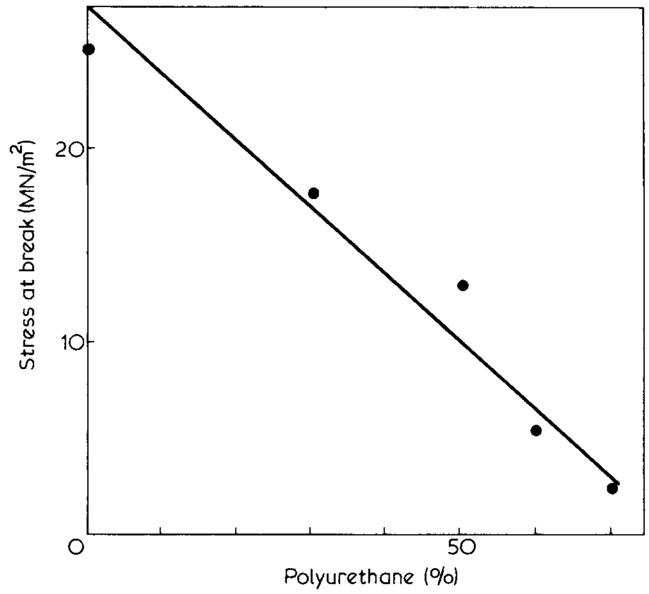

Figure 6 Curve showing stress at break *versus* weight % of polyurethane

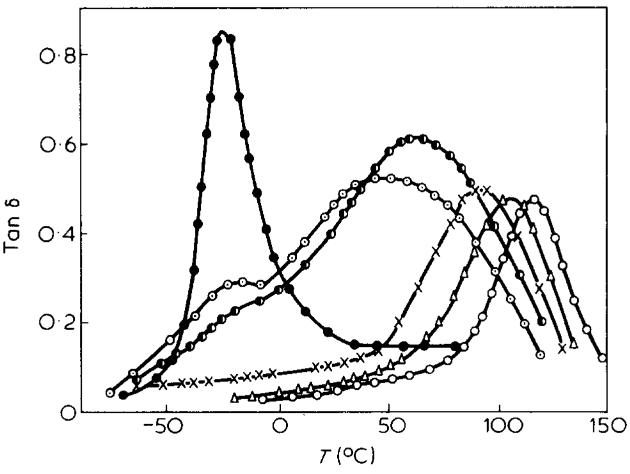

Figure 7 Tan δ *versus* temperature curves for polyurethane (●), modified polyester (○) and the semi-IPN's containing 70% (◎), 60% (◐), 50% (X) and 30% (△) polyurethane by weight

Table 4 Dynamic mechanical data

Code	Transition temperature (°C)	tan δ_{max}	Half peak width (°C)
A	−26	0.85	29
B	50 (−20)	0.52	132
C	63	0.61	101
D	93	0.50	60
E	106	0.48	50
F	118	0.47	39

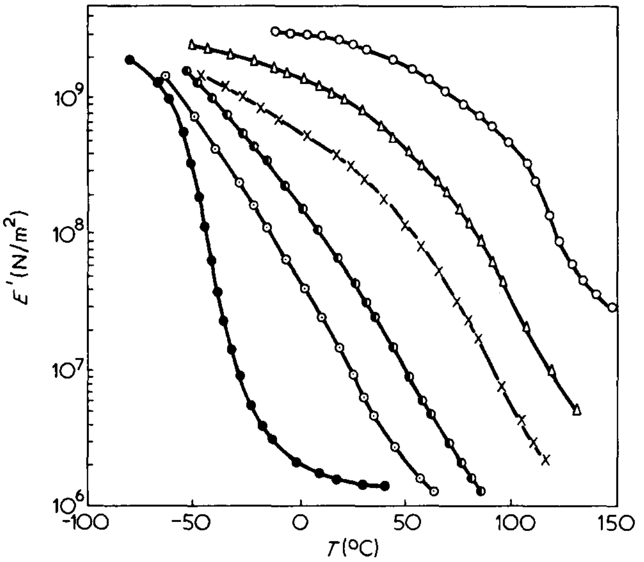

Figure 8 Dynamic storage modulus (E') *versus* temperature curves for polyurethane (●), modified polyester (○) and the semi-IPN's containing 70% (◎), 60% (◐), 50% (X) and 30% (△) polyurethane by weight

sitions are dramatically narrower. Meyer and Mehrenberger[20] have also reported a broad transition for a polyurethane–polyester IPN containing 7% by weight of polyurethane. The half peak widths, the maximum values of tan δ (tan δ_{max}) and the glass transition temperatures are given in *Table 4*.

Figures 8 and *9* show the dynamic storage modulus (E') and the dynamic loss modulus (E'') *versus* temperature curves, respectively, for all samples.

Kaplan[21] has made the suggestion that for phase-separated polymer systems there is a critical domain size of around 15 nm of the occluded phase which leads to a high and sustained level of damping between the glass transition temperatures of the two components themselves. From *Figure 3* it is clear in this case that the discrete phase is much coarser than 15 nm, but nonetheless a broad loss region (*Figure 7*) occurs. It is seen from *Table 4* that as the rubber content is increased the half peak width also increases. The existence of only a single relaxation process is, of course, conventionally taken as evidence of a certain degree of compatibility, but even at 30% by weight of polyurethane (*Figure 2*) the system is seen to be phase separated. Exactly how the loss transition broadens with increasing polyurethane content is not clear, but perhaps the mechanism proposed by Kaplan[21] offers at least a partial explanation. Alternatively, the broadening may be concerned with the nature and the extent of the interfaces between phases.

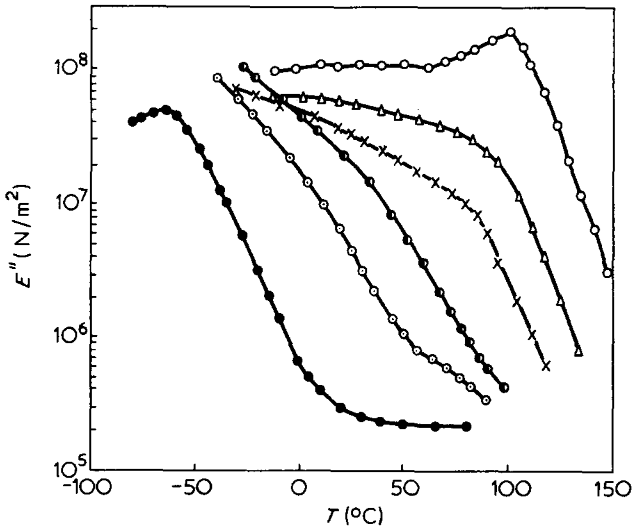

Figure 9 Dynamic loss modulus (E'') versus temperature curves for polyurethane (●), modified polyester (○) and the semi-IPN's containing 70% (◎), 60% (◐), 50% (X) and 30% (△) polyurethane by weight

REFERENCES

1 Boonstra, B. B. 'Polyblends and Composites' (Ed. P. F. Briens) Interscience, New York, 1970
2 Callan, J. E., Hess, W. M. and Scott, C. E. *Rubber Chem. Technol.* 1971, **44**, 814
3 MacKnight, W. J., Stoeltin, G. J. and Karasz, F. E. 'Multicomponent Polymer Systems' (Adv. Chem. Series No. 99), (Ed. N. A. J. Platzer) 1971, Ch. 3
4 Noland, J. S., Hsu, N. N. -C., Saxon, R. and Schmitt, J. M. 'Multicomponent Polymer Systems' (Adv. Chem. Series No. 99), (Ed. N. A. J. Platzer) 1971, Ch. 2
5 Hourston, D. J. and Hughes, I. D. *J. Appl. Polym. Sci.* 1977, **21**, 3099
6 Hourston, D. J. and Hughes, I. D. *Polymer* 1977, **18**, 1175
7 Turbak, A. F. 'Membranes from Cellulose and Cellulose Derivatives' (Appl. Polym. Symp. 13), Interscience
8 Matzner, M., Schober, D. L. and McGrath, J. E. *Eur. Polym. J.* 1973, **9**, 469
9 Szymczak, T. J. and Manson, J. A. *Mod. Plast.* 1974, **51**, 66
10 Donatelli, A. A., Thomas, D. A. and Sperling, L. H. 'Recent Advances in Polymer Blends, Grafts and Blocks' (Ed. L. H. Sperling), Plenum, New York, 1974
11 Sperling, L. H. and Sarge, H. D. *J. Appl. Polym. Sci.* 1972, **16**, 3041
12 Sperling, L. H. and Mihalakis, E. N. *J. Appl. Polym. Sci.* 1973, **17**, 3811
13 Allen, G., Bowden, M. J., Lewis, G., Blundell, D. J. and Jeffs, G. M. *Polymer* 1974, **15**, 13
14 Allen, G., Bowden, M. J., Lewis, G., Blundell, D. J., Jeffs, G. M. and Vyvoda, J. *Polymer* 1974, **15**, 19
15 Dickie, R. A. and Cheung, M. -F. *J. Appl. Polym. Sci.* 1973, **17**, 79
16 Dickie, R. A., Cheung, M. -F. and Newman, S. *J. Appl. Polym. Sci.* 1973, **17**, 65
17 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites' Plenum, New York, 1976
18 Ferguson, J., Hourston, D. J., Meredith, R. and Patsavoudis, D. *Eur. Polym. J.* 1972, **8**, 369
19 'Crystic Monograph No. 1' Scott Bader Co. Ltd. 1971
20 Meyer, G. C. and Mehrenberger, P. Y. *Eur. Polym. J.* 1977, **13**, 383
21 Kaplan, D. S. *J. Appl. Polym. Sci.* 1976, **20**, 2615