

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. IV. Grafted Semi-1-Interpenetrating Polymer Networks

D. J. HOURSTON and Y. ZIA, *Department of Chemistry, University of Lancaster, Bailrigg, Lancaster, LA1 4YA, United Kingdom*

Synopsis

A series of semi-1-IPNs containing 40% polyurethane and 60% polymethyl acrylate was synthesized using Adiprene L-100, trimethylol propane, and polybutadiene diol. This diol was chosen to yield polyurethanes with a large number of potential graft sites for the methyl acrylate which was polymerized after the polyurethane network had been formed. A series of linear polyurethane–poly-methyl acrylate blends, covering a range of compositions, was also prepared. The polyurethane for these polyblends was synthesized from Adiprene L-100 and butane-1,4-diol. Both sets of materials were investigated by dynamic mechanical analysis. On the basis of a comparison of solubility parameters, the polyurethanes and polymethyl acrylate would be expected to be incompatible. In the dynamic loss modulus–temperature plots of the polyblends there was a significant shift of the polyurethane T_g to higher temperature, but the polymethyl acrylate transition did not shift. The polyurethane transitions of the semi-1-IPNs were also shifted, but considerably more than in the case of the polyblends. For both systems, it was postulated that grafting had occurred to a significant extent. With the semi-1-IPNs, it was found that as \bar{M}_c decreased the extent of grafting apparently increased. This was rationalized on the grounds that as the network chain lengths decrease, a higher proportion of the methyl acrylate monomer, prior to polymerization, was close to polyurethane segments and that this is a situation likely to lead to more grafting.

INTRODUCTION

An interpenetrating polymer network (IPN) is formed when a material, composed of two crosslinked components, is prepared in such a way that at least one of the networks is synthesized and/or crosslinked in the presence of the other. If only one of the components is crosslinked, the material is referred to as a semi-IPN. When only the first formed polymer is a network, a semi-1-IPN results. IPNs and semi-IPNs have been the subject of several recent reviews.^{1–4}

In earlier papers,^{5–7} the synthesis and properties of semi-1- and semi-2-IPNs based on polyurethanes and polymethyl acrylate have been reported. This paper reports the dynamic mechanical properties of polyurethane–poly(methyl acrylate) semi-1-IPNs in which the polyurethane has a substantial degree of unsaturation, allowing the monomer of the second formed polymer, methyl acrylate, sites for grafting. Such a material is known as a grafted semi-1-IPN.

Touhsaent et al.^{8,9} have reported studies of various epoxy–acrylic compositions. Later Scarito and Sperling¹⁰ repeated this work adding glycidyl methacrylate to the system. They reported that even 3% of glycidyl methacrylate, which was incorporated in both components during a simultaneous network formation, was enough to cause sufficient mixing to yield materials showing only one glass

transition temperature T_g . Beachall et al.¹¹ grafted vinyl monomers to preformed polyurethanes. The method used was a two-step one involving proton abstraction from the urethane nitrogen with sodium hydride followed by reaction with various halides such as bromoethyl acrylate, to yield a substituted polyurethane with pendant ethyl acrylate groups which can take part in the subsequent vinyl polymerisation. Solution properties of these grafted polyurethanes were studied.¹¹

The present grafted semi-1-IPNs were prepared by polymerizing methyl acrylate in the presence of a crosslinked polyurethane which contained a large number of double bonds. Also, a series of polyblend samples were prepared by polymerizing methyl acrylate in the presence of a linear polyurethane. Certain properties of the grafted semi-1-IPNs are contrasted with those of the polyblends.

EXPERIMENTAL

A supply of Adiprene L-100 was kindly donated by DuPont Ltd. (U.K.). This isocyanate-terminated commercial prepolymer¹² had a number average molecular weight of 1990 g/mol and a weight average molecular weight of 3980 g/mol. To form the polyurethane networks with the unsaturation, Adiprene L-100, trimethylol propane, and polybutadiene diol, which had a number average molecular weight of 2800 g/mol and which contained 60% *trans* 1,4-, 20% *cis* 1,4-, and 20% 1,2- groups, were used. Both the diol and the triol were supplied by Aldrich Chemicals. The linear polyurethane component of the polyblends was prepared from Adiprene L-100 and butane-1,4-diol. This diol and the methyl acrylate were supplied by B.D.H., Ltd. For both polyurethanes the isocyanate to hydroxyl ratio was 1.1.

The carefully dried polyurethane precursors, including, as catalyst, di-*n*-butyl tin dilaurate (2% w/w of polyurethane) were dissolved in the appropriate amount of destabilized methyl acrylate. The solutions were degassed and poured into metal molds⁵ and maintained at 20°C for 24 h to allow the polyurethane formation to occur. The temperature was then taken to 60°C for 18 h, followed by a further 6 h at 90°C, to polymerize the methyl acrylate which was initiated with AIBN (0.2% w/w).

The linear polyurethane and the polyurethane homopolymer networks were prepared as in the first stage of the semi-1-IPN preparation, but in inhibited methyl acrylate, which was subsequently removed, slowly, under vacuum. The polymethyl acrylate homopolymer was also prepared in the same type of mold under the conditions detailed above. All the materials were stored under vacuum at 20°C for at least 10 days prior to testing.

The molecular weights between crosslinks, \overline{M}_c , were determined by swelling measurements.⁵

The dynamic mechanical data were obtained using a Rheovibron dynamic viscoelastometer (Model DDV-II-B) at a heating rate of approximately 1°C/min.

RESULTS AND DISCUSSION

The molecular weight between crosslinks of the polyurethane component of the grafted semi-1-IPNs was varied (10,600, 18,800, and 30,000 g/mol), but the

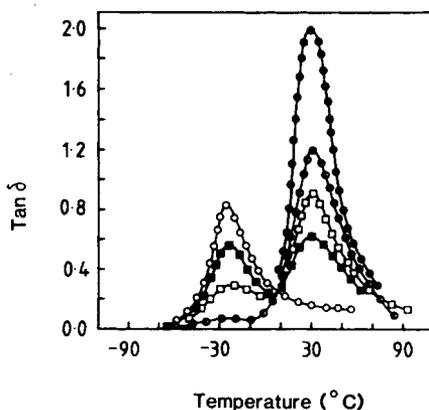


Fig. 1. $\tan \delta$ -temperature plots (11 Hz) of linear polyurethane (○), polymethyl acrylate (●), and of the polyurethane-polymethyl acrylate blends containing 20% (●), 40% (□), and 60% (■) by weight of polyurethane.

overall composition was kept constant (w/w) at 40% polyurethane-60% polymethyl acrylate. The solubility parameter⁵ was $19.2 \times 10^3 \text{ (J/m}^3\text{)}^{1/2}$ for all three polyurethane networks.

When blends of the linear polyurethane and polymethyl acrylate are prepared either by milling and hot pressing or by solvent casting, they show gross phase separation,¹³ which is visible to the naked eye. This is not surprising as the solubility parameter of polymethyl acrylate is $20.7 \times 10^3 \text{ (J/m}^3\text{)}^{1/2}$,¹³ which is $1.5 \times 10^3 \text{ (J/m}^3\text{)}^{1/2}$ greater than that of the polyurethane. However, if the blends are made by mixing all the reagents together and conducting both polymerizations in the molds already described,⁵ the materials are at least visually homogeneous. Three such blends containing 20%, 40%, and 60% by weight of polyurethane were prepared. The polyurethane in these blends is structurally different from the polyurethane component of the grafted semi-1-IPNs, but, as both polyurethanes have the same solubility parameter, their tendencies to mix with polymethyl acrylate should be similar.

Figure 1 shows the $\tan \delta$ -temperature dispersions for the linear polyurethane and polymethyl acrylate components as well as for the three blends. The glass transition temperatures are shown in Table I. For ease of reference, the lower transition for both the polyblends and for the grafted semi-1-IPN systems will be referred to as the polyurethane transition and the higher temperature tran-

TABLE I
Glass Transition Temperatures from the $\tan \delta$ -Temperature Curves of the Constituent Polymers and the Polyblends

Sample	Polyurethane T_g (°C)	Shift in polyurethane T_g (°C)	Polymethyl acrylate T_g (°C)
Polyurethane	-26		
60% Polyurethane	-25	1	30
40% Polyurethane	-22	4	31
20% Polyurethane	-24	2	30
Polymethyl acrylate			30

TABLE II
Glass Transition Temperatures from the E'' -Temperature Curves of the Constituent Polymers and the Polyblends

Sample	Polyurethane T_g ($^{\circ}\text{C}$)	Shift in Polyurethane T_g ($^{\circ}\text{C}$)	Polymethyl acrylate T_g ($^{\circ}\text{C}$)
Polyurethane	-67		
60% Polyurethane	-58	9	22
40% Polyurethane	-57	10	20
20% Polyurethane	-59	8	20
Polymethyl acrylate			20

sition as the polymethyl acrylate transition, even when there is some movement of the peaks indicating that their origin is probably in a mixed phase, rather than a pure one. There is no significant shift in the poly(methyl acrylate) transition, indicating that this component is present as a pure phase. The polyurethane transition is also apparently unmoved as the error in measuring T_g is about $\pm 1.5^{\circ}\text{C}$. Table II shows the same quantities as Table I, but based on dynamic loss modulus E'' transitions rather than on the $\tan \delta$ curves. From Table II, it is clear that there are significant shifts to higher temperatures of the polyurethane transition. These will be discussed later. There is no significant movement of the polymethyl acrylate transition. Figure 2 shows the full E'' -temperature data which has been briefly summarized in Table II.

Figure 3 shows $\tan \delta$ -temperature plots for the three grafted semi-1-IPNs, the polymethyl acrylate homopolymer and the crosslinked polyurethane with \bar{M}_c equal to 18,800 g/mol. As the T_g values of the three polyurethane networks were very similar, this one was chosen as being representative. No shift was observed in the polymethyl acrylate transition, but the polyurethane transitions are shifted, as shown in Table III, to much higher temperatures compared with the polyurethane network. These shifts are very much greater than those shown (Table II) by the 40% polyurethane-60% polymethyl acrylate polyblend. Figure 4 and Table IV show the same quantities, but based on E'' -temperature data. Clearly, these shifts are even more pronounced than those based on the $\tan \delta$ -temperature dispersions. The dynamic storage modulus E' -temperature plots also show (Fig. 5) this shift very clearly. Also from Figure 5, it is clear that the storage modulus of the grafted semi-1-IPN with the lowest \bar{M}_c is highest, at all temperatures.

TABLE III
Glass Transition Temperatures from $\tan \delta$ -Temperature Curves of the Constituent Polymers and the Grafted Semi-1-IPNs

Sample	Polyurethane T_g ($^{\circ}\text{C}$)	Shift in Polyurethane T_g ($^{\circ}\text{C}$)	Polymethyl acrylate T_g ($^{\circ}\text{C}$)
Polyurethane	-36		
Semi-IPN (10,600 g/mol)	-11	25	29
Semi-IPN (18,800 g/mol)	-14	22	31
Semi-IPN (30,000 g/mol)	-16	20	32
Polymethyl acrylate			30

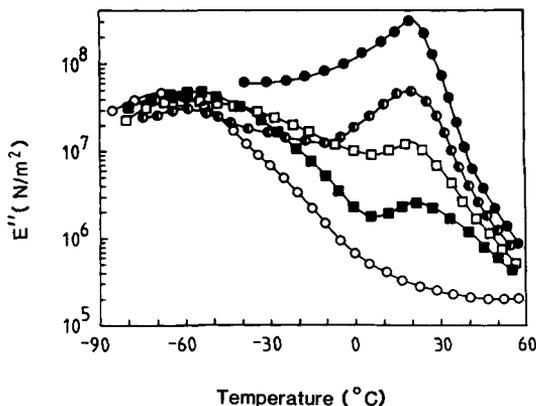


Fig. 2. E'' -temperature plots (11 Hz) of linear polyurethane (O), polymethyl acrylate (●), and of the polyurethane-polymethyl acrylate blends containing 20% (◐), 40% (◑), and 60% (■) by weight of polyurethane.

The shift to higher temperatures of the polyurethane T_g 's of the grafted semi-1-IPNs may be caused by one or more of the following mechanisms. Grafting onto the polyurethane networks will cause some restriction of segmental motion. Turley,¹⁴ in studies of the effect of grafting in rubber modified polystyrenes, found that the T_g 's of the grafted rubbers were around 9°C higher than those of the corresponding ungrafted materials.

There are also possible mechanisms associated with mixing.

(a) Spontaneous mixing of the components.

(b) Grafting will cause some enforced mixing of polyurethane segments and polymethyl acrylate segments adjacent to graft points.

(c) It is known^{7,15,16} for IPNs and semi-IPNs that, as \bar{M}_c decreases, more mixing results.

Even with the polyblends discussed earlier, the shifts observed in the polyurethane T_g 's may also have more than one origin. Grafting as well as some spontaneous mixing may be occurring. At this point, it is not possible to be categorical in the assignment of mechanisms, but it seems likely that grafting is playing some part. The fact that the polymethyl acrylate transition does not move could support this contention, in that it may be only the polymethyl acrylate segments close to graft sites which mix with polyurethane segments. The remaining polymethyl acrylate segments constitute a pure phase.

TABLE IV

Glass Transition Temperatures from E'' -Temperature Curves of the Constituent Polymers and the Grafted Semi-1-IPNs

Sample	Polyurethane T_g (°C)	Shift in polyurethane T_g (°C)	Polymethyl acrylate T_g (°C)
Polyurethane	-77		
Semi-IPN (10,600 g/mol)	-42	35	20
Semi-IPN (18,800 g/mol)	-50	27	20
Semi-IPN (30,000 g/mol)	-54	23	23
Polymethyl acrylate			20

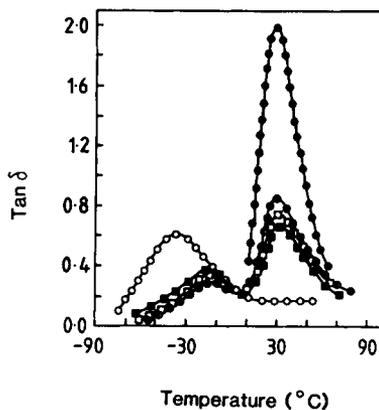


Fig. 3. $\tan \delta$ -temperature plots (11 Hz) of polyurethane network with \bar{M}_c of 18,800 g/mol (O), polymethyl acrylate (●), and of the 40% polyurethane-60% polymethyl acrylate grafted semi-1-IPNs with \bar{M}_c values of 10,600 g/mol (○), 18,800 g/mol (□), and 30,000 g/mol (■).

For the grafted semi-1-IPN with \bar{M}_c of 30,000 g/mol, there is a shift of the polyurethane transition of 20°C in the $\tan \delta$ data and a shift of 23°C in the E'' data. At such a high value of \bar{M}_c , the contribution to the shift from the cross-linking process^{7,15,16} will be small. Thus, the bulk of the shift may be attributed to the effects of grafting. As the \bar{M}_c value decreases, the shifts of the polyurethane transition measured by $\tan \delta$ data, and, particularly, by E'' data increase significantly. However, the transitions of the pure polyurethane networks, as they change from 30,000 g/mol to a value of 10,600 g/mol, show a shift of only a few degrees. Furthermore, the higher the \bar{M}_c value the greater will be the number of polybutadiene diol residues per network chain. It can be estimated, assuming an ideal network, that there are, on average, approximately two such residues per network chain for the material with \bar{M}_c equal to 10,600 g/mol. The corresponding numbers for the 18,800 g/mol and 30,000 g/mol materials are three

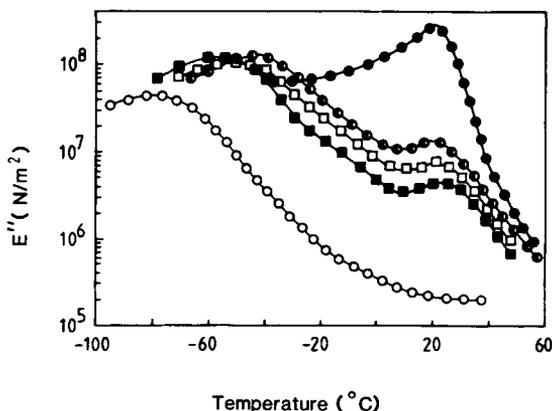


Fig. 4. E'' -temperature plots (11 Hz) of polyurethane network with \bar{M}_c of 18,800 g/mol (O), polymethyl acrylate (●), and of the 40% polyurethane-60% polymethyl acrylate grafted semi-1-IPNs with \bar{M}_c values of 10,600 g/mol (○), 18,800 g/mol (□), and 30,000 g/mol (■).

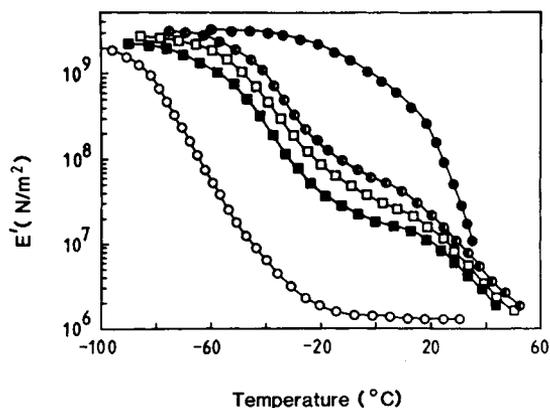


Fig. 5. E' -temperature plots (11 Hz) of polyurethane network with \bar{M}_c of 18,800 g/mol (O), polymethyl acrylate (●), and of the 40% polyurethane-60% polymethyl acrylate grafted semi-1-IPNs with \bar{M}_c values of 10,600 g/mol (○), 18,800 g/mol (□), and 30,000 g/mol (■).

and six, respectively. Therefore, despite the increase in the number of double bonds as \bar{M}_c increases, the shifts of the polyurethane glass transition increase as the network is made tighter. It is concluded, therefore, that the level of grafting increases as \bar{M}_c decreases. This may be rationalized by recognizing that the methyl acrylate initially exists as a swelling agent for the already established polyurethane network. As that network becomes more crosslinked, more of the methyl acrylate monomer will exist close to polyurethane segments, and, hence, have a greater opportunity to form grafts.

References

1. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
2. D. A. Thomas and L. H. Sperling, *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 2.
3. L. H. Sperling, *Polymer Alloys*, Plenum, New York, 1977.
4. H. L. Frisch, K. C. Frisch, and D. Klempner, *Pure Appl. Chem.*, **53**, 1557 (1981).
5. D. J. Hourston and Y. Zia, *J. Appl. Polym. Sci.*, **28**, 2139 (1983).
6. D. J. Hourston and Y. Zia, *J. Appl. Polym. Sci.*, **28**, 3745 (1983).
7. D. J. Hourston and Y. Zia, *J. Appl. Polym. Sci.*, **28**, 3849 (1983).
8. R. E. Touhsaent, D. A. Thomas, and L. H. Sperling, *Toughness and Brittleness of Plastics*, R. B. Deanin and A. M. Crugnola, Eds., Advances in Chemistry Series No. 154, American Chemical Society, Washington, D.C., 1976.
9. R. E. Touhsaent, D. A. Thomas, and L. H. Sperling, *J. Polym. Sci.*, **46C**, 175 (1974).
10. P. R. Scarito and L. H. Sperling, *Polym. Eng. Sci.*, **19**, 297 (1979).
11. H. C. Beachell, R. Blumstein, and J. C. Peterson, *J. Polym. Sci.*, **22C**, 569 (1969).
12. D. J. Hourston and Y. Zia, *Polymer*, **20**, 1497 (1979).
13. Y. Zia, Ph.D. thesis, University of Lancaster, 1979.
14. S. G. Turley, *J. Polym. Sci.*, **1C**, 101 (1963).
15. L. H. Sperling, *Recent Advances in Polymer Blends, Grafts and Blocks*, Plenum, New York, 1974.
16. G. Allen, M. J. Bowden, D. J. Blundell, F. G. Hutchinson, G. M. Jeffs, and J. Vyvoda, *Polymer*, **14**, 597 (1973).

Received May 13, 1983

Accepted August 3, 1983