Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. III. Polyurethane–Poly(methyl Acrylate) Semi-2-Interpenetrating Polymer Networks

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Synopsis

Two series of semi-2-IPNs based on a polyurethane and a poly(methyl acrylate) crosslinked with divinyl benzene were prepared and investigated using dynamic mechanical analysis, sonic velocity measurements, and electron microscopy. In the one series, the level of crosslinking was varied to give ultratight networks. In the other, the composition was altered, but the amount of the cross-linking agent used was kept constant. For the first series, it was concluded that the degree of crosslinking had a significant influence on the morphology and properties by controlling the amount of enforced mixing. The dynamic mechanical data for the second series fitted the Davies modulus–composition equation, indicating that both phases are continuous.

INTRODUCTION

An interpenetrating polymer network (IPN) may be defined as a material composed of a pair of polymeric networks which have been prepared in such a way that at least one of the networks has been synthesized and/or crosslinked in the presence of the other. As a result of the mutual incompatibility shown by most pairs of polymers, the usual situation is to generate a material showing phase separation, but having very small phases[1] as a result of the networks restricting the maximum phase size. For most IPNs it is very likely that extensive intermeshing of the component networks, often thought to be the definitive feature of an IPN, only occurs to any great extent at phase boundaries. Much has now been written, including several reviews,[2–5] about IPNs.

Semi-IPNs are materials intermediate between conventional polyblends of linear polymers and full IPNs. A semi-IPN results when one of the polymers is a network and the other is linear. If the first formed polymer is the crosslinked component, then the material is referred to as a semi-1-IPN. The converse situation yields a semi-2-IPN.

In earlier papers[6,7] the polyurethane used was described in detail[6] and certain properties of the analogous semi-1-IPN materials reported.[7] The materials discussed in this paper consist of a linear polyurethane synthesized in methyl acrylate which is then itself polymerized and crosslinked to yield semi-2-IPNs, which are not, in all cases, comparable to the semi-1-IPNs previously discussed.[7] The average molecular weights between crosslinks, $\overline{M}_c$, are very low, as a primary aim of this investigation is to ascertain the effect of tight networks on morphology and properties.

EXPERIMENTAL

Materials. The Adiprene L-100 precursor used in the polyurethane synthesis was kindly donated by DuPont Ltd. (U.K.). This isocyanate-terminated pre-polymer[8] had a number average molecular weight of 1990 g/mol and a weight average molecular weight of 3980 g/mol. The butane-1,4-diol and the methyl acrylate were supplied by BDH Ltd. Cambrian Chemicals provided the divinyl benzene crosslinking agent.

Polymerization. To prepare the semi-2-IPNs, all the reactants, including the crosslinking agent, were dissolved in the required amount of destabilized methyl acrylate. Dibutyl tin dilaurate (2 wt % polyurethane) was added to promote the reaction between Adiprene L-100 and butane-1,4-diol. The solutions were degassed and poured into molds[6] and maintained at 20°C for 24 h to allow polyurethane formation to occur. The temperature was then raised to 60°C for 18 h followed by a further 6 h at 90°C to polymerize the methyl acrylate network. AIBN (0.2 wt % methyl acrylate) was used as initiator. The polyurethane homopolymer was prepared in inhibited methyl acrylate as in the first stage of the semi-2-IPN synthesis. The methyl acrylate was then removed slowly under vacuum. The poly(methyl acrylate) homopolymer networks were prepared in the same molds and under the conditions detailed above. All the semi-2-IPNs and the homopolymers were placed under vacuum at 20°C for at least 10 days prior to use.

Techniques. The dynamic mechanical data were obtained using a Rheovibron Dynamic Viscoelastometer (Model DDV-II-B) at a heating rate of approximately 1°C/min. The longitudinal sonic velocities, V_L, were measured[9] with a Morgan Pulse Propagation Meter (Model PPM-5R). A Hitachi HU-11B electron microscope was used to obtain the transmission electron micrographs. Prior to microtomy the samples were hardened and stained with OsO_4 vapour.

RESULTS AND DISCUSSION

The first group of polyurethane–poly(methyl acrylate) semi-2-IPNs to be discussed were prepared so as to have a range of $\overline{M}_c$ values. For two of the samples the amounts of crosslinker used were very high, so that the effect on morphology and properties of very tight second-formed networks could be investigated.

Figure 1 shows tan δ–temperature plots for a linear and for three polymethyl acrylate homonetworks. Certain dynamic mechanical properties of these materials are presented in Table I, from which it is clear that, with increasing crosslinking agent, both the glass transition temperature, T_g, and the half-peak width increased and the maximum value of tan δ, tan δ_{max}, decreased. With these samples, not only is there an increase in the extent of crosslinking, but there is also a copolymer effect. The shift in Tg and the reduction in tan δ_{max} will both be influenced[10] by both factors, while the increase in half-peak width will be essentially the result of enhanced crosslinking.[11,12]

It has been suggested[13] that eq. (1) can be used to determine an approximate value of $\overline{M}_c$:

$$T_g - T_{g_0} = 3.9 \times 10^4 / \overline{M}_c \tag{1}$$

TABLE I
Dynamic Mechanical Properties (11 Hz) of the Linear and the Crosslinked Poly(methyl Acrylates)

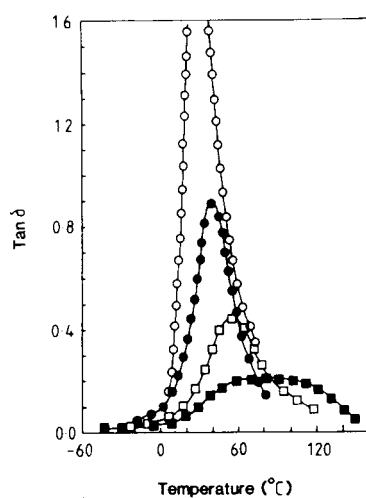| Divinyl benzene content (wt %)	T_g (°C)	Tan δ_{max}	Half-peak width (°C)
0	30	~2.0	31
5	40	0.9	36
15	55	0.45	51
25	80	0.22	107

Fig. 1. Tan δ–temperature plots (11 Hz) of a linear (O) and of three network polymethyl acrylates crosslinked with 5 (●), 15 (□), and 25 (■) wt % divinyl benzene.
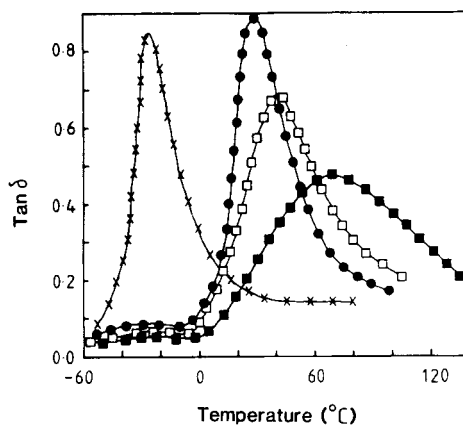

Fig. 2. Tan δ–temperature plots (11 Hz) of the linear polyurethane (X) and of three 40% poly-urethane–60% poly(methyl acrylate) semi-2-IPNs in which the network component has been crosslinked with 5 (●), 15 (□) and 25 (■) wt % divinyl benzene.

TABLE II
Glass Transition Temperatures[a] of Crosslinked Poly(methyl Acrylate) as Homopolymers and as
Components in the Semi-2-IPNs

Divinyl benzene content (wt %)	T_g homopolymer °C	T_g Semi-2-IPN °C	Difference in T_g (°C)
5	40	30	10
15	55	43	12
25	80	68	12

[a] Measured at 11 Hz.

T_{g0} is the glass transition temperature of the uncrosslinked polymer with the same chemical composition as the crosslinked one. T_g is the glass transition temperature of the crosslinked sample. Using this equation, an approximate measure of $\overline{M}_c$ (3900 g/mol) of the poly(methyl acrylate) sample crosslinked with 5% divinyl benzene was obtained.

Figure 2 shows tan δ–temperature plots for the linear polyurethane and for 40% polyurethane–60% poly(methyl acrylate) semi-2-IPNs with varying $\overline{M}_c$ values. It is clear that, when $\overline{M}_c$ of the poly(methyl acrylate) component is decreased, the polyurethane transition, in these tan δ–temperature plots at least, almost vanishes, indicating that the poly(methyl acrylate) component is present as an increasingly continuous phase. Also, compared with the corresponding homopolymers (Fig. 1), the poly(methyl acrylate) component transitions are shifted to lower temperatures. The magnitudes of these shifts are shown in Table II. Some part of these shifts may be attributed to enforced molecular mixing caused by the high degrees of crosslinking. However, it is also possible that the networks are looser when formed in the presence of polyurethane.

The dynamic loss modulus E''–temperature plots in Figure 3 show that as $\overline{M}_c$ of the poly(methyl acrylate) component decreases the corresponding transition becomes broader. The maxima of the poly(methyl acrylate) transitions also move progressively to higher temperatures as the divinyl benzene content is increased. If mixing alone were occurring, then the shift would be in the other direction, but both the copolymer effect and the decrease in $\overline{M}_c$ will lead to shifts
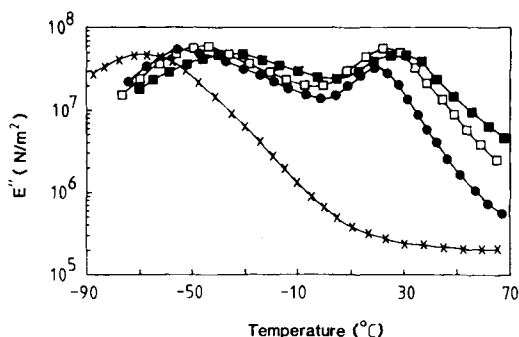

Fig. 3. E''-temperature plots (11 Hz) of the linear polyurethane (X) and of three 40% polyurethane–60% poly(methyl acrylate) semi-2-IPNs in which the network component has been crosslinked with 5 (●), 15 (□), and 25 (■) wt % divinyl benzene.
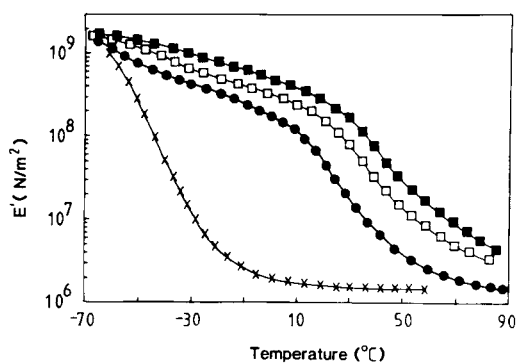
Fig. 4. E'-temperature plots (11 Hz) of the linear polyurethane (X) and of three 40% polyurethane–60% poly(methyl acrylate) semi-2-IPNs in which the network component has been crosslinked with 5 (●), 15 (□), and 25 (■) wt % divinyl benzene.

to higher temperatures. The lower transition, which is associated with the polyurethane-rich phase, is shifted dramatically to higher temperatures as the extent of crosslinking increases. This is a clear indication of an increasing degree of mixing.

In the dynamic storage modulus E'–temperature plots in Figure 4 both transitions are broad, again indicative of an increasing degree of mixing with increasing crosslinking.

Figures 5 and 6 are electron micrographs of 40% polyurethane–60% poly-(methyl acrylate) semi-2-IPNs crosslinked with 15 wt % and 25 wt % divinyl benzene, respectively. It is clear that the apparently discrete polyurethane (dark) phases are relatively small. The dark phases, however, have further internal structure indicating that the polyurethane is, very probably, also a continuous phase.

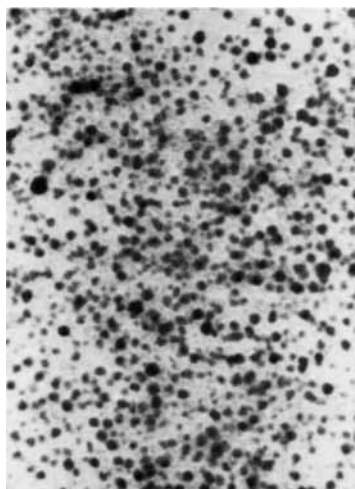Therefore, the molecular weight between crosslinks of the second formed

Fig. 5. Electron micrograph of a 40% polyurethane–60% poly(methyl acrylate) semi-2-IPN in which the network component has been crosslinked with 15 wt % divinyl benzene.
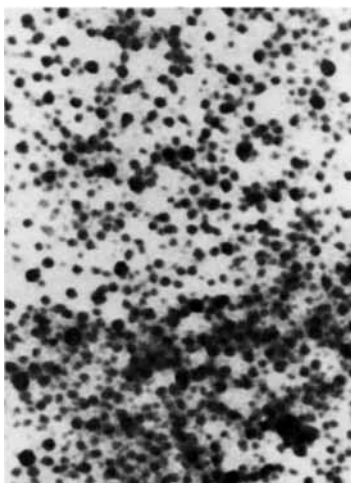
Fig. 6. Electron micrograph of a 40% polyurethane–60% poly(methyl acrylate) semi-2-IPN in which the network component has been crosslinked with 25 wt % divinyl benzene.

component of this semi-2-IPN does have a significant influence on morphology, and, hence, properties. Other investigators[14,15] have also shown a decrease in domain size of the linear component when the $\overline{M}_c$ value of the crosslinked component was decreased.

To study the effect of changing composition, semi-2-IPNs with varying amounts of the linear polyurethane were prepared. The divinyl benzene concentration was kept constant at 25% (w/w) of the methyl acrylate in any particular composition. Tan δ–temperature plots of these materials are presented in Figure 7. Even when the polyurethane content is 60 wt %, tan δ_{max} of the polyurethane-rich phase is only around 0.1. This suppression from an approximately *pro rata* magnitude is again clear evidence that the poly(methyl acrylate) component is a continuous phase. The tan δ_{max} values for the poly(methyl acrylate)
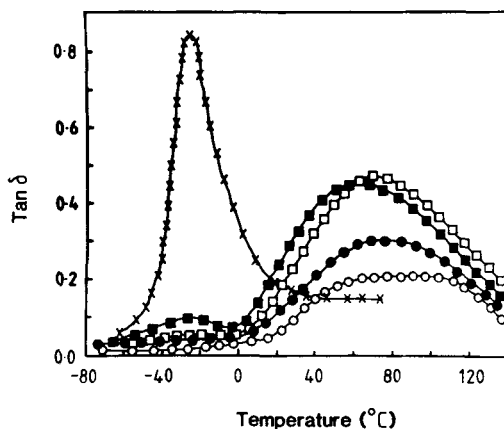

Fig. 7. Tan δ–temperature plots (11 Hz) of the linear polyurethane (X), a poly(methyl acrylate) network crosslinked with 25 wt % divinyl benzene (O) and the semi-2-IPNs containing 20 (●), 40 (□), and 60 (■) wt % of polyurethane.
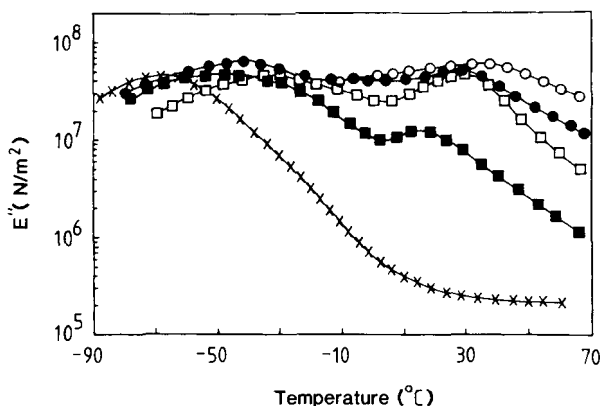
Fig. 8. E''-temperature plots (11 Hz) of the linear polyurethane (X), a poly(methyl acrylate) network crosslinked with 25 wt % divinyl benzene (O) and the semi-2-IPNs containing 20 (●), 40 (□), and 60 (■) wt % polyurethane.

transitions are not in order of composition. This is not surprising as $\overline{M}_c$ is very likely to be influenced by the amount of polyurethane present during cross-linking.

Figures 8 and 9 are plots of E'' and E' against temperature. Both figures show that the transitions are broad and that the lower temperature one, associated with the predominantly polyurethane phase, is, again, shifted to higher temperatures relative to pure polyurethane. The other transition is shifted to lower temperatures with respect to the pure network. This is particularly clear in Figure 8. It is concluded that all three semi-2-IPNs show substantial mixing.

Modulus-composition theories have previously been applied[16,17] to IPNs and to semi-IPNs. Two such relations have been tested for these polyurethane–poly(methyl acrylate) semi-2-IPNs. The logarithmic rule of mixtures[18,19] is shown in

$$\log E' = \phi_1 \log E'_1 + \phi_2 \log E'_2 \qquad (2)$$

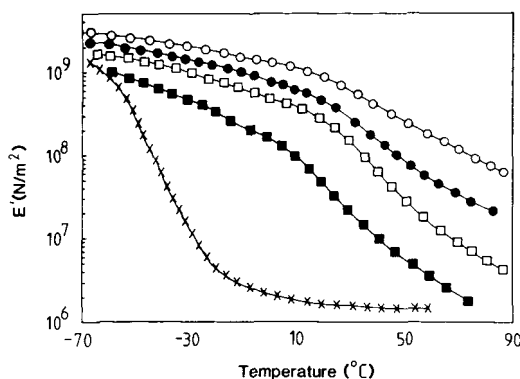ϕ is the volume fraction and the subscripts 1 and 2 refer to the pure components.

Fig. 9. E'-temperature plots (11 Hz) of the linear polyurethane (X), a poly(methyl acrylate) network crosslinked with 25% wt % divinyl benzene (O) and the semi-2-IPNs containing 20 (●), 40 (□), and 60 (■) wt % of polyurethane.
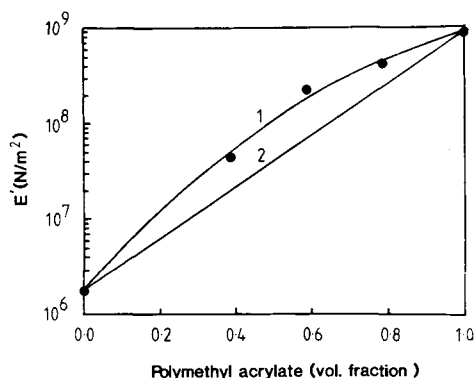
Fig. 10. E'–composition data (20°C, 11 Hz): (1) Davies equation; (2) logarithmic rule of mixtures.

Davies[20,21] has suggested the following relation, which is designed[22] to be applicable to two component materials in which both components are present as continuous phases:

$$E'^{1/5} = \phi_1 E_1'^{1/5} + \phi_2 E_2'^{1/5} \qquad (3)$$

The dynamic storage moduli (20°C) of the semi-IPNs and of the homopolymers are plotted against composition in Figure 10. Clearly, the logarithmic rule of mixtures does not fit the experimental data, but the Davies equation fits well, as expected,[22] for composite materials in which both phases are continuous.

The V_L–composition plot of these semi-2-IPNs is given in Figure 11. A straight line can be drawn through the points representing the crosslinked homopolymer and all the semi-2-IPNs, confirming the earlier conclusion that the poly(methyl acrylate) component is present as a continuous phase in all the semi-IPNs investigated.

It can be concluded that, for all these polyurethane–poly(methyl acrylate) semi-2-IPNs, $\overline{M}_c$ is a very important factor in controlling morphology and properties.
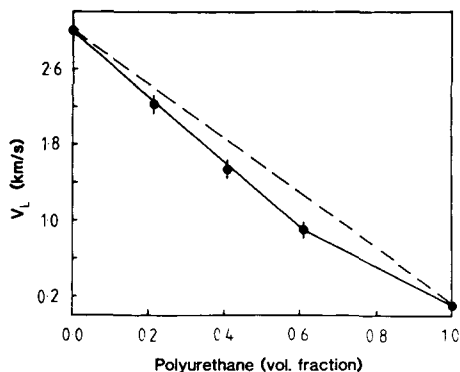

Fig. 11. V_L–composition plot (20°C).

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