

# Semi- and Fully-Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. XII. The Influence of Polymerization Pressure on Morphology and Properties

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## SYNOPSIS

Polyurethane–poly(methyl acrylate) interpenetrating polymer networks (IPNs) of fixed composition (50/50) were prepared at 60°C and a range of pressures. Increased synthesis pressures generally resulted in improved mixing of the two networks. The physical properties of the IPNs initially improved as a result of the enhanced mixing, reaching a maximum for specimens synthesized at 250 MPa. The poorer properties for the IPNs, prepared at higher synthesis pressures, have been ascribed to decreased uniformity in the network.

## INTRODUCTION

Interpenetrating polymer networks (IPNs), like most other polymer/polymer systems, tend to phase separate as a result of the low entropy of mixing.<sup>1–3</sup> However, as a result of their interlocking phase configuration, the extent of separation is restricted. Some of the factors that control the morphology of IPNs are now reasonably clear and include compatibility of the polymer,<sup>4</sup> the level of crosslinking in each network,<sup>5–8</sup> composition,<sup>9,10</sup> interfacial tension,<sup>11,12</sup> as well as temperature,<sup>13,14</sup> and pressure<sup>15–19</sup> of synthesis.

In addition, the polymerization method can also play a vital role. Reversing the order of polymerization in a sequential IPN results in a changed morphology.<sup>4</sup> In simultaneous interpenetrating networks (SINs) the networks form during the same time period, although not necessarily at the same rate, leading to more complex morphologies. Touhsaent et al.<sup>20,21</sup> altered the relative reaction rates in an epoxy–polyacrylate SIN and found dramatic changes in morphology and in ultimate properties.

The effect of pressure on free radical polymeriza-

tion has been well documented.<sup>22,23</sup> The rate of polymerization ( $k$ ) varies with pressure ( $p$ ) according to the relationship,

$$\left[ \frac{\partial \ln k}{\partial p} \right]_T = \frac{-\Delta V^\ddagger}{RT}$$

where  $V^\ddagger$  is the volume of activation,  $R$  the gas constant, and  $T$  the absolute temperature.

For the dissociation of chemical initiators into free radicals, the activation volume is positive, leading to a retardation in the rate of initiation.<sup>22,24</sup> The volumes of activation for the propagation and termination reactions are strongly negative, however, leading to an increase in the overall rate of polymerization with an increase in pressure.

A number of authors have investigated the effect of pressure on the miscibility of both polymer/polymer systems,<sup>25–28</sup> as well as of oligomer pairs,<sup>29–31</sup> and of polymer/solvent systems.<sup>32,33</sup> For polymer blends, theoretical<sup>34,35</sup> as well as experimental<sup>25–28</sup> evidence indicates that the most likely behavior is an increase in the lower critical solution temperature with an increase in pressure, that is, increased miscibility of the component polymers.

This article reports on the effect of pressure applied during synthesis on the morphology and physical properties of polyurethane (PU)–poly(methyl acrylate) (PMA) IPNs.

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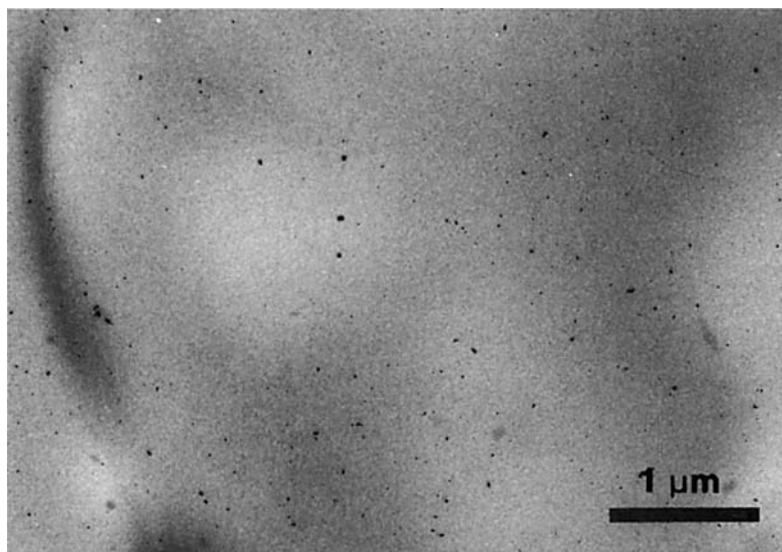


Figure 1 Transmission Electron Micrograph of the IPN synthesized at 25 MPa.

## EXPERIMENTAL

### Materials

The isocyanate-terminated polyurethane prepolymer, Adiprene L-100, supplied by Du Pont, had a  $\bar{M}_n$  value of 2000 g/mol and a polydispersity of 2.1. Trimethylolpropane (TMP), supplied by Aldrich Chemicals, was used as the crosslinking agent giving a theoretical mass between crosslinks ( $\bar{M}_c$ ) of 2090 g/mol. In practice,  $\bar{M}_c$  was likely to be higher as a result of the diluting effect of the methyl acrylate.<sup>36</sup> The NCO : OH ratio was 1.1, since this gives a network with the lowest  $\bar{M}_c$  and the best properties.<sup>6</sup> Dibutyl tin dilaurate (1.04% w/w of Adiprene L-100) was added as a urethane catalyst. The methyl acrylate contained 1 mol % of ethyleneglycol di-

methacrylate as a network former, yielding a theoretical  $\bar{M}_c$  of 8600 g/mol.

Azobisisobutyronitrile (AIBN) (0.2% w/w of methyl acrylate) was used to initiate the free radical polymerization.

### Synthesis

The requisite amounts of Adiprene L-100 and TMP were dissolved in methyl acrylate in order to give an IPN containing 50% by weight of PU. The solution was carefully degassed and any volatilized methyl acrylate was replaced. The remaining ingredients were added and mixed before final degassing. The mixture was carefully poured into an aluminium foil bag lined with polyethylene. This bag contained

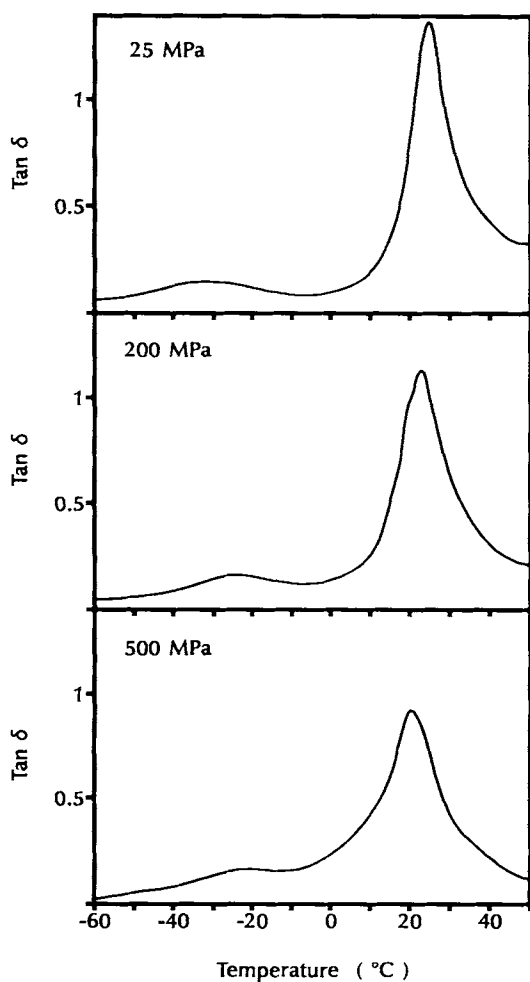
Table I Dynamic Mechanical Data for the IPNs Synthesized at a Range of Pressures

Synthesis Pressure (MPa)	PU Transition			PMA Transition			
	Tan $\delta$ max		$E''$ max Temperature (°C)	Tan $\delta$ max		Half-Peak Width (°C)	$E'$ (20°C) (MPa)
	Temperature (°C)	Magnitude		Temperature (°C)	Magnitude		
25	-29	0.14	-37	25	1.36	27	52.9
150	-27	0.14	-35	25	1.49	27	61.8
200	-24	0.16	-32	23	1.12	32	26.6
250	-17	0.19	-29	22	0.98	34	23.0
350	-22	0.17	-30	23	1.13	32	20.6
500	-17	0.17	-28	21	0.92	37	15.6

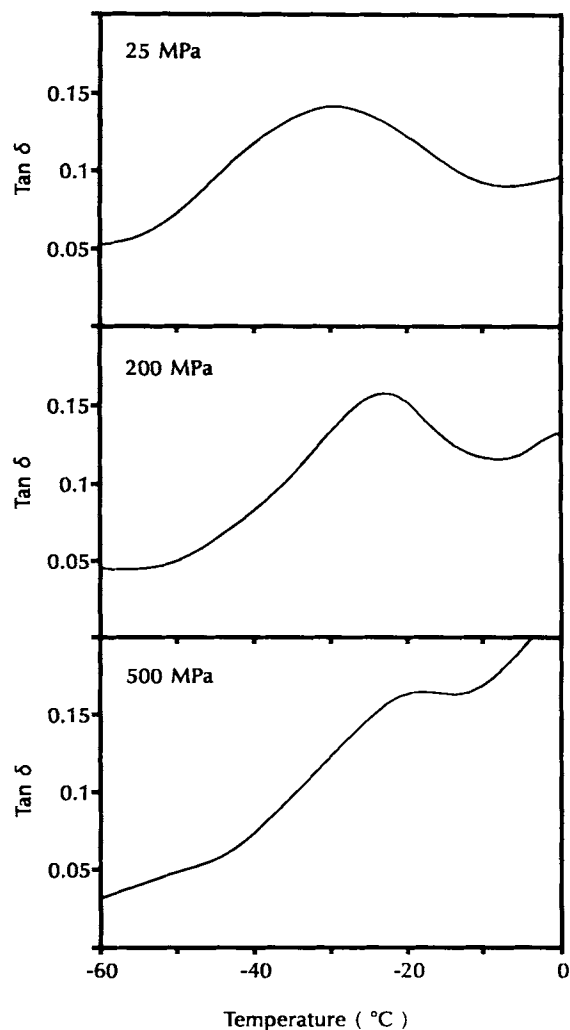
two parallel glass plates, separated at the corners by silicone rubber spacers. The bag had previously been flushed with nitrogen. The bag was then sealed and placed in the chamber of an hydraulically operated high pressure vessel. Heating was effected by submersing the vessel in a thermostatted oil bath.

Samples were polymerized for 18 h at 60°C, followed by 6 h at 90°C in an attempt to drive the reaction to completion. The initial pressure was varied from 25 to 500 ( $\pm 10$ ) MPa, but as a result of shrinkage, dropped by between 25 and 40 MPa during the course of the polymerization. Temperatures between the glass plates may have exceeded 60°C for short periods because of the reaction exotherm and the insulating power of the surrounding polymeric material.<sup>13</sup>

After polymerization, the bag was cut open and the sheet of material was recovered from between the glass plates by freezing the glass/IPN/glass



**Figure 2**  $\tan \delta$  vs. temperature plots for samples synthesized at 25, 200, and 500 MPa.



**Figure 3**  $\tan \delta$  vs. temperature plots for samples synthesized at 25, 200, and 500 MPa showing a more detailed view of the PU transition.

sandwich in liquid nitrogen. All samples were dried to constant mass at 20°C under vacuum.

Since the addition polymerization does not go to completion, 3% (by wt) excess methyl acrylate was added. Mass loss studies on drying indicated a decrease in PU content from 51.6 to 49.7% as the pressure was increased. The decrease is the result of the increased rate of free radical polymerization at higher pressures.<sup>22,24</sup>

### Characterization

Transmission electron micrographs were obtained using an Hitachi electron microscope (Model HU-11B). The samples were hardened and stained using osmium tetroxide.

Dynamic mechanical analysis was performed with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer in the dual cantilever mode. The frequency was 1 Hz and the heating rate was 2°C/min.

A J. J. Lloyd tensile tester (type T5002) was used to obtain stress-strain data on samples of gauge length 25 mm. The crosshead speed was 20 mm/min and the temperature was 20°C.

## RESULTS AND DISCUSSION

Figure 1 is a transmission electron micrograph of the PU-PMA IPN, synthesized at 25 MPa. It shows a very fine structure in which dark, OsO<sub>4</sub> stained PU regions are evenly distributed throughout the PMA matrix. Close inspection indicates that both phases are continuous, in accordance with the model of interpenetration proposed by Huelck et al.<sup>4</sup>

Dynamic mechanical analysis showed that the PU and PMA components were clearly present as distinct phases. All the results are presented in Table I, while selected curves have been used in Figures 2-5. This has been done in order to avoid clouding the general trends with too much detail. The tan  $\delta$ -temperature data (Figs. 2 and 3, plus Table I) show that increasing the pressure from 25 to 500 MPa causes a slight (4°C) shift to lower temperatures of the PMA transition while at the same time, the PU transition is shifted from -29°C to about -17°C. The temperature of the PU transition in the sample synthesized at 500 MPa has been estimated, since at this pressure the PU transition appears as a shoulder on the PMA peak.

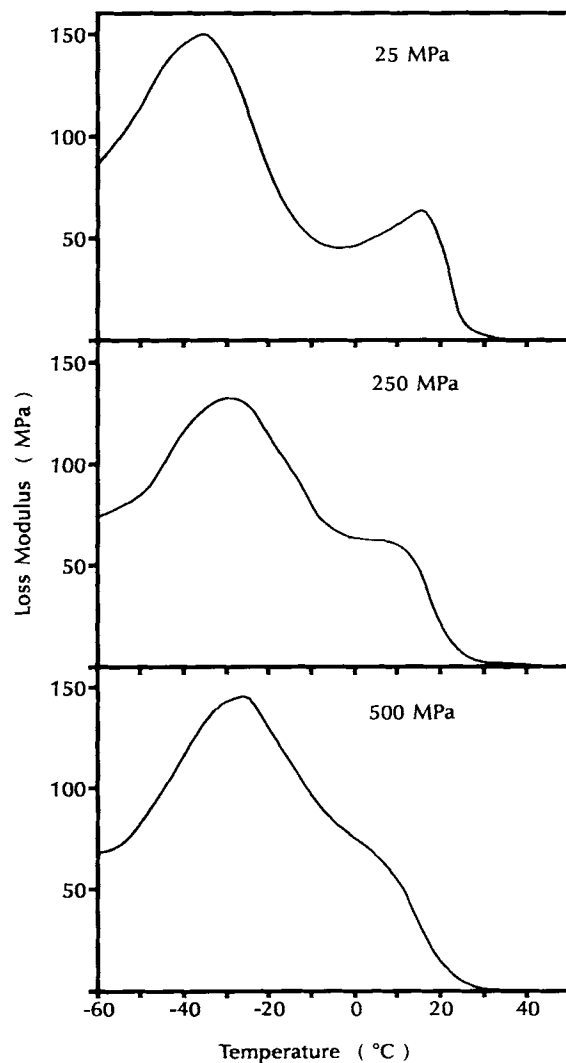
The increase in  $T_g$  for the PU phase implies a delay in the onset of free rotation about backbone bonds, most likely as a result of the still glassy PMA being more closely associated with the PU and thus restricting the motion of its segments. In contrast, PU would act as a diluent for the PMA, and more intimate contact would result in a decrease in  $T_g$ . Clearly, increasing the pressure during synthesis leads to changes in  $T_g$ , which suggest improved mixing of the two components of this IPN system.

The loss modulus ( $E''$ ) vs. temperature curve (Fig. 4) shows the PU shift even more clearly while the peak arising from the PMA transition disappears in the higher pressure samples where mixing is improved. Figure 6 shows the PU transition temperatures, as defined by the loss modulus maximum, and by  $\tan \delta_{(\max)}$ , as a function of the pressure applied during synthesis of the IPNs. Higher synthesis

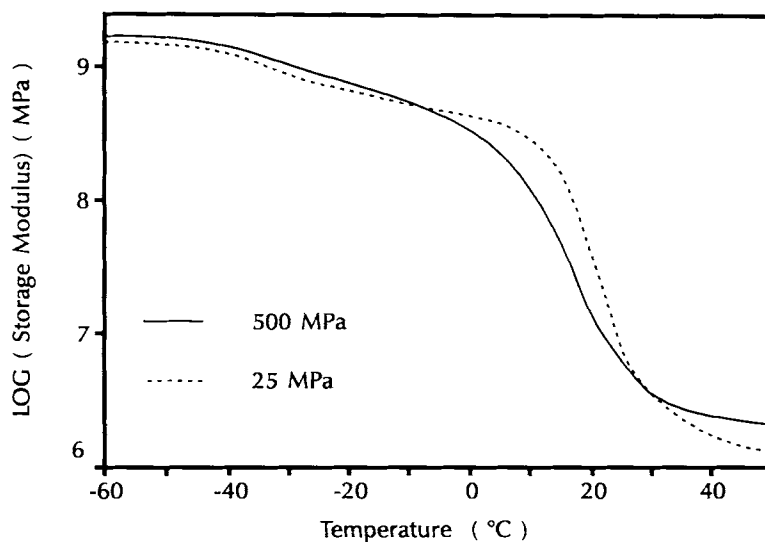
pressures result in a shift of the PU transition to higher temperatures.

The storage modulus ( $E'$ ) (Fig. 5) of the IPN prepared at 25 MPa shows two distinct steps as the temperature increases, associated with the transitions in the PU component, and, at higher temperatures, in the PMA component. Although the IPN synthesized at 500 MPa also shows two steps, they are less accentuated, reflecting the enhanced level of mixing when IPNs are synthesized at elevated pressures. The storage modulus at 20°C decreases steadily with increased synthesis pressure, as a result of the glass transition shifting to lower temperatures.

The improved mixing at elevated pressures is further confirmed by the half-peak widths of the



**Figure 4** Loss modulus vs. temperature plots for samples synthesized at 25, 250, and 500 MPa.



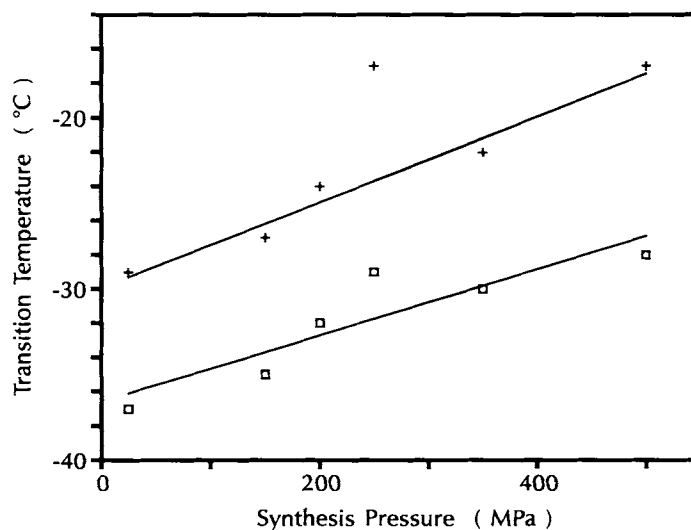
**Figure 5** The storage modulus vs. temperature plots for samples synthesized at 25 (----) and 500 (—) Mpa.

PMA  $\tan \delta$  peak (Table I). Improved mixing is accompanied by an increase in the half-peak width up to the point where the two transitions merge.

All the above results are consistent with those of Lee and Kim,<sup>15-18</sup> who investigated PU-polystyrene as well as PU-poly(methyl methacrylate) IPNs synthesized under high pressure. The magnitude of the shift they found in the  $T_g$  of the less rubbery component was, however, far greater than in this work. This is possibly the result of the fact that they used synthesis temperatures close to, or below, the

glass transition temperature of the less rubbery component, whereas the PMA in the IPNs described in this article was formed at a temperature well above its glass transition temperature. Thus, the forming PMA network would be more mobile, and, hence, be able to phase separate more at elevated pressures. Decreased mixing at elevated temperatures of synthesis has been shown previously.<sup>13,14,16</sup>

It should be noted that the glass transition temperature is, itself, a function of pressure.<sup>37</sup> Increasing the pressure decreases the free volume, thus in-



**Figure 6** Temperature of Loss Modulus Maximum ( $\square$ ) and  $\tan \delta_{(max)}$  (+) for the PU transition as a function of synthesis pressure.

**Table II** Tensile, Hardness, and Swelling Data for the IPNs Synthesized at a Range of Pressures

Synthesis Pressure (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	200% Secant Modulus (MPa)	Hardness (Shore A)	Volume Fraction of Rubber (%)
25	2.2	340	0.55	66	31
150	2.4	390	0.41	61	28
200	3.9	390	0.55	61	27
250	5.4	430	0.72	59	29
350	4.5	375	0.77	62	31
500	2.1	250	0.76	58	33

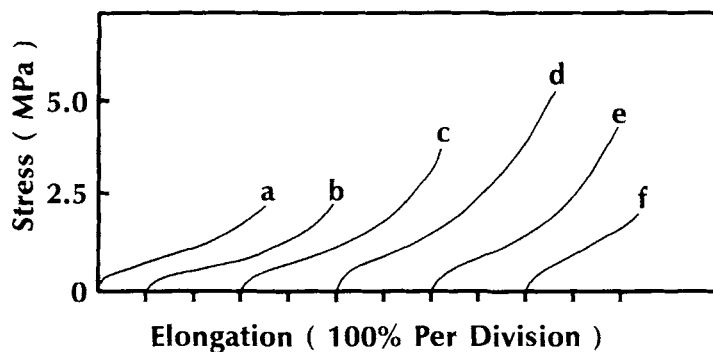
creasing  $T_g$ . This shift in  $T_g$  is of the order of  $16^\circ\text{C}$  per 100 MPa, although in some instances values closer to  $30^\circ\text{C}$  per 100 MPa have been recorded.<sup>37</sup> In addition, the forming polymer is often swollen in the second monomer or in its own as yet unreacted monomer, further complicating the issue. It is clear, therefore, that comparisons between the mobilities of different systems should be made with extreme caution.

The physical properties of the IPNs are shown in Table II, while typical stress-strain curves are given in Figure 7. For the purpose of clarity, the curves have been shifted along the horizontal axis. As the pressure of synthesis was increased, the tensile strength improved, as expected, with improved mixing. However, at higher pressures, tensile strength started to decrease. The elongation at break followed a similar pattern, while the 200% secant modulus showed a gradual increase.

It has been shown<sup>22</sup> that the volume of activation of a number of chemically initiated vinyl radical polymerizations is in the range  $-17$  to  $-20$   $\text{cm}^3/\text{mol}$ . This leads to relative increases in the rate of reaction of 7–8 times at 300 MPa. This increase in the rate of network formation will obviously assist in the

prevention of phase separation by allowing less time for that separation to occur, but may also be responsible for a less uniform network. Such a network in the IPN would not alter the improved mixing, as shown by dynamic mechanical analysis, nor would it be inconsistent with a lower storage modulus at  $20^\circ\text{C}$  (Table II), since the small strain imposed during dynamic mechanical analysis would not be influenced by this nonuniformity. However, in a tensile test the network segments will be strained in a nonuniform manner, leading to a higher 200% modulus and premature failure. The increased modulus is not the result of any overall increase in crosslink density, since, within experimental limits, swelling studies show a constant equilibrium volume fraction of rubber when swollen in toluene (Table II).

Furthermore, hardness values (Table II), which are related to crosslink density, are relatively constant. If anything, they indicate a slight decrease in crosslink density for the IPN prepared at the highest pressure. A nonuniform distribution of crosslinks has previously been proposed<sup>38</sup> to explain the decrease in tensile strength in rubbers when the crosslink density exceeds some critical value.



**Figure 7** Typical stress-strain curves for IPNs synthesized at (a) 25, (b) 150, (c) 200, (d) 250, (e) 350, and (f) 500 MPa.

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