

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane-Polyacrylate Systems. VIII. The Influence of the Degree of Crosslinking of the Second Formed Network on the Morphology and Properties of Polyurethane-Polymethylacrylate Interpenetrating Polymer Networks

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Synopsis

A series of polyurethane-polymethylacrylate sequential interpenetrating polymer networks containing 40% by weight of polyurethane were prepared in which the levels of crosslinking in the second formed network—polymethylacrylate—was systematically altered over a wide range. The polymethylacrylate networks and the interpenetrating polymer networks were investigated using dynamic mechanical analysis, sonic velocity measurements, and tensile testing. In addition, the interpenetrating polymer networks were studied using transmission electron microscopy. The interpenetrating polymer networks showed high values of the Oberst damping factor. It was concluded that tightening the second formed network does not produce the dramatic effects associated with decreasing the average molecular weight between crosslinks of the first formed network.

INTRODUCTION

Sperling and Friedman¹ has defined an interpenetrating polymer network (IPN) as a polymer blend of two networks in which at least one of the networks has been synthesized and/or crosslinked in the intimate presence of the other. IPNs are subdivided into type² according to method of synthesis. Many such systems have now been synthesized and their properties investigated. For reviews of IPN synthesis, characterization, and properties, see Refs. 2 and 3. If only one polymer is crosslinked, the material is referred to as a semi-IPN. Earlier papers in the series⁴⁻⁹ have dealt with certain aspects of such systems.

Hourston and McCluskey have reported¹⁰ on the effect of decreasing the average molecular weight between crosslinks of the first formed network \overline{M}_c , for a similar polyurethane (PU)-polymethylacrylate (PMA) IPN system to the one which is the subject of this paper. It was found that as \overline{M}_c decreased the extent of mixing increased.

In this paper, the influence of increasing the level of crosslinking of the second formed network, PMA, is investigated.

EXPERIMENTAL

IPN Synthesis

The required amounts of the carefully dried PU precursors, Adiprene L-100 [Du Pont (U.K.) Ltd.] and trimethylol propane (Aldrich) were dissolved in the requisite amount of dry, destabilized methylacrylate (BDH Chemicals) containing 0.2% by weight of AIBN to initiate the vinyl polymerization and divinylbenzene (Cambrian Chemicals) which acts as crosslinker for the PMA network. The Adiprene L-100 prepolymer¹¹ had a number average molecular weight of 1900 g/mol. The mixture was thoroughly blended. Di-*n*-butyl tin dilaurate (BDH Chemicals) was then added at 2% w/w of PU to promote PU formation. The mixture was then carefully degassed and poured into a metal mold.⁴ The PU synthesis was allowed to proceed at room temperature for 24 h. Previously,¹⁰ the PMA network was then formed by heating to 65°C for 18 h and then to 90°C for a further 6 h. However, a modification of the method was necessary for systems containing more than 5% DVB. After the normal 24 h gelation period, the PMA network was formed by heating at 85°C for 12 h. On heating at 65°C for 18 h, "popcorn" polymerization¹² occurred. The samples heated for 12 h at 85°C were uniform and transparent.

Homonetwork Synthesis

To synthesize the PU sheet, the same procedure was used, but the PU precursors were dissolved in inhibited methylacrylate which was allowed to evaporate once the PU sheet had formed. The final stages of this process occurred in a vacuum oven.

Sheets of crosslinked PMA were prepared by placing a mixture of the monomer, the initiator, and the crosslinking agent directly into the mold. The polymerization was carried out at 85°C for 8 h. All resulting sheets were placed in a vacuum oven (30°C) for a minimum of one week to remove any residual monomer.

Characterization Properties

The \bar{M}_c values of the various PMA networks were determined as previously reported.¹⁰ (see Table I). Transmission electron micrographs were obtained with a Hitachi electron microscope (model HU-11 B). The samples were first stained using osmium tetroxide.

The stress-strain measurements (20°C) were made with a Howden tensometer at a strain rate of 2.5 cm/min. Standard dumbbell specimens were pressed from the sheet. Strain was defined as change in length divided by original length. The dynamic mechanical analysis was conducted using a Rheovibron dynamic mechanical viscoelastometer (Model DDV-II-B) at a heating rate of approximately 1°C/min. V_L , the longitudinal sonic velocity, was measured at 20°C with a Model PPM-5R¹³ Morgan pulse propagation meter.

TABLE I
Average Molecular Weight Between Crosslinks in the PMA Networks

Divinylbenzene (wt %)	\bar{M}_c (g/mol)
1	7300
5	3800
10	1800
20	500
30	300

RESULTS AND DISCUSSION

The PMA Networks

Initial work involved varying the crosslink density of the PMA networks and investigating the effect of this on their mechanical properties. Then the crosslink densities of the PMA networks were changed in the IPN situation. PMA networks were prepared with divinylbenzene contents of 1, 5, 10, 20, and 30% (w/w). At high levels of divinylbenzene, some polydivinylbenzene will be formed. The 20% and 30% divinylbenzene samples showed increased opacity.

Figure 1 shows the stress-strain curves of the PMA networks. Table II summarizes the essential details. It is clear that with increasing crosslinking there is a decrease in the elongation to break, but the initial modulus

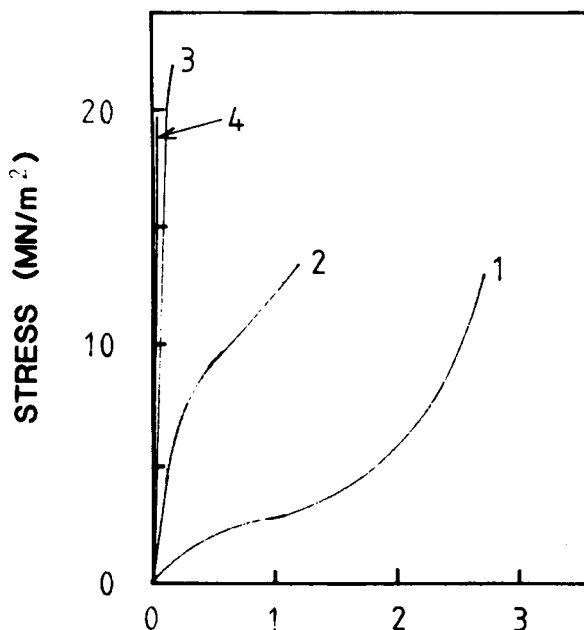


Fig. 1. Stress-strain curves (20°C) of the PMA networks with \bar{M}_c values of 3800 (1), 1800 (2), 500 (3), and 300 (4) g/mol, respectively.

TABLE II
Stress-Strain Data (20°C) of the PMA Networks

Divinylbenzene (wt %)	Tensile strength (MN/m ²)	100% modulus (MN/m ²)	Elongation at break (%)
5	13.0	2.7	276
10	13.1	12.1	120
20	21.8		20
30	19.8		3

increases. The network containing 30% divinylbenzene shows a decrease in tensile strength.

V_L for the PMA networks as a function of divinylbenzene content is shown in Figure 2. An increase in V_L is observed with increasing crosslinking levels, but at relatively high levels of crosslinker the rate of change decreases. $\tan \delta$ -temperature plots of the PMA networks are shown in Figure 3 with further details presented in Table III. There is a considerable shift in the position of the $\tan \delta$ maximum to higher temperatures with increasing crosslinking levels, accompanied by a considerable broadening of the transitions. Both are expected¹⁴ for a series of networks of increasing tightness.

Nielsen¹⁵ proposed the following approximate empirical equation for relating T_g to the degree of crosslinking in networks:

$$T_g - T_g^0 \approx \frac{3.9 \times 10^4}{\bar{M}_c} \quad (1)$$

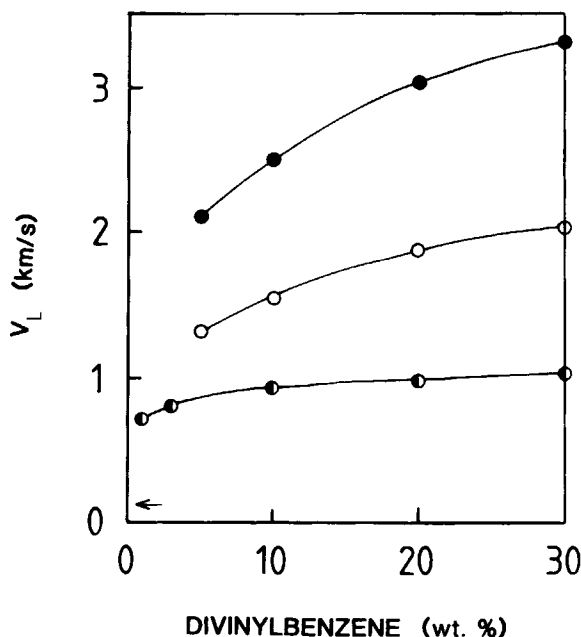


Fig. 2. V_L -divinylbenzene curves (20°C) of the PMA networks (●) and of the IPNs (○); (○) curve calculated using eq. (3). The arrow indicates the value (0.117 km/s) for the PU network.

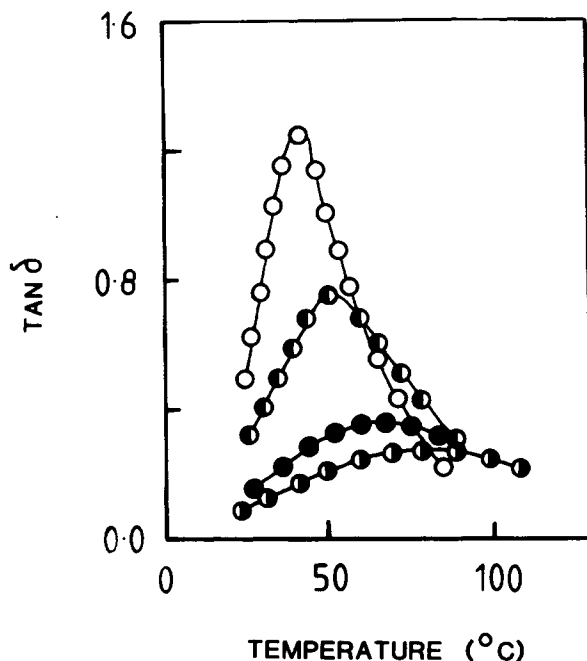


Fig. 3. $\tan \delta$ -temperature plots (11 Hz) of the PMA networks with \bar{M}_c values of 3800 (○), 1800 (◻), 500 (●), and 300 (◻) g/mol, respectively.

T_g^0 is the T_g of the uncrosslinked polymer. At divinylbenzene concentrations of 5 and 10% the predicted values are close to these experimentally determined (Table IV), but at 1 and 20% the values differ considerably.

Figures 4 and 5 show the dynamic storage modulus E' and the dynamic loss modulus E'' vs. temperature of selected PMA networks. Below the glass transition temperatures the dynamic storage moduli values are relatively insensitive to the crosslinking level, being of the order of 2.0×10^9 N/m². The corresponding E'' -temperature curves show considerable broadening as crosslinking increases. Crosslinking reduces the intensity of damping of a polymer but may greatly extend the temperature range over which effective damping is still possible.

The IPNs

What are the effects on mechanical behavior and morphology of these IPNs when the \bar{M}_c of the second formed network (PMA) is progressively reduced? IPNs of a constant composition (w/w) of 40 PU-60 PMA were

TABLE III
Dynamic Mechanical Data (11 Hz) for the PMA Networks

Divinylbenzene (wt %)	T_g (°C)	Half-peak width ^a (°C)
1	32	31
5	41	34
10	52	54
20	62	—
30	80	—

^a Width of peak ($\tan \delta$) at half-height.

TABLE IV
Measured and Calculated [Eq (1)] Average Molecular Weights between Crosslinks

Divinylbenzene (wt %)	\bar{M}_c (g/mol)	\bar{M}_c [eq (1)] (g/mol)
1	7300	19,500
5	3800	3300
10	1800	1700
20	500	1100

chosen to study this effect. Evidence suggests¹⁶ that dual phase continuity exists at this composition.

Figure 6 shows the $\tan \delta$ -temperature dispersions of the IPNs. The samples containing 1 and 5% divinylbenzene are omitted from the figure in order to retain clarity. With increasing crosslinking, there is a slight shifting of the PMA relaxation to higher temperatures, accompanied by a marked broadening of the transition. On comparing the PMA relaxation of these IPNs with the corresponding PMA homonetwork relaxations, it is apparent that the PMA in the IPNs display T_g values at temperatures lower than those of the corresponding PMA networks (see Tables III and V). As the divinylbenzene content is increased in the PMA networks, a higher T_g is expected on the basis of increased crosslinking¹⁴ and also because of the copolymer effect. Polydivinylbenzene is a highly brittle material which has a considerably higher T_g than the PMA. However, the PU network into which the mixture of methyl acrylate and divinylbenzene is swollen prior

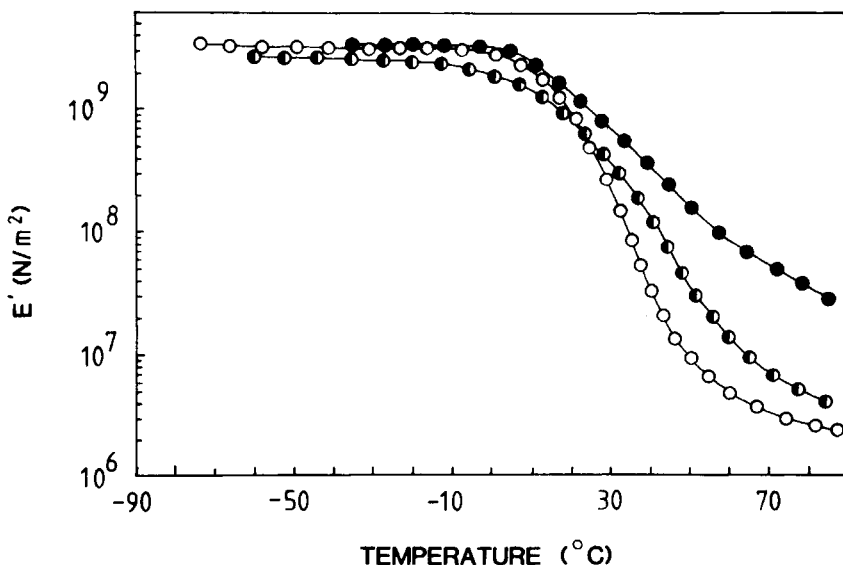


Fig. 4. E' -temperature plots (11 Hz) of the PMA networks with \bar{M}_c values of 3800 (○), 1800 (○), and 500 (●) g/mol, respectively.

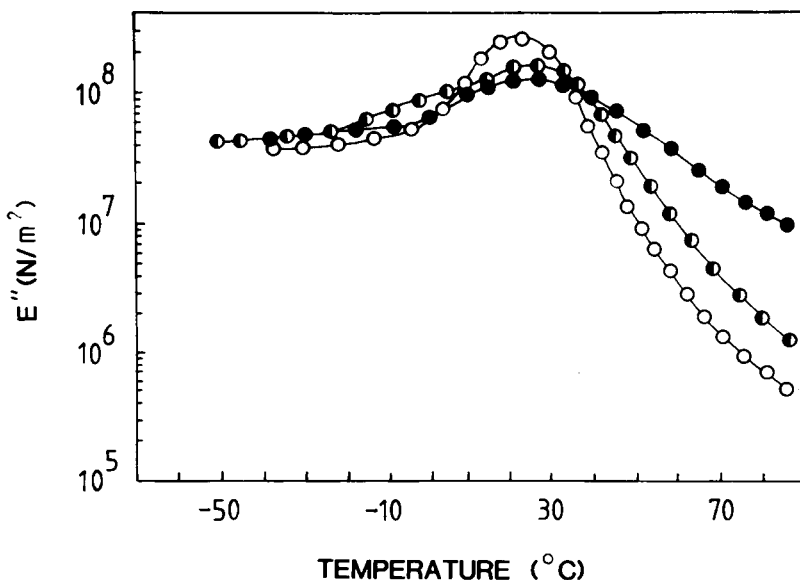


Fig. 5. E'' -temperature plots (11 Hz) of the PMA networks with \overline{M}_w values of 3800 (○), 1800 (○), and 500 (●) g/mol, respectively.

to polymerization may exert a significant restriction on the formation of the PMA network, resulting in a reduction in the crosslink density of the PMA component and a consequent lowering of the temperature at which the PMA relaxation occurs. Greater mixing between the two components will also favor a lowering in temperature of the PMA relaxation.

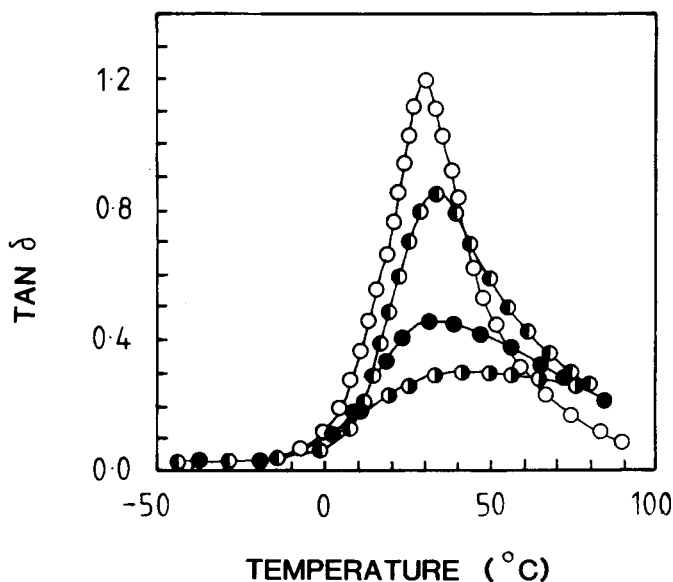


Fig. 6. $\text{TAN } \delta$ -temperature plots (11 Hz) of the PU-PMA IPNs (40 wt % PU) in which the PMA network was formed using 3% (○), 10% (○), 20% (●), and 30% (○) divinylbenzene, respectively.

TABLE V
Dynamic Mechanical Data (11 Hz) for the IPNs

Divinylbenzene (wt %)	T_g (°C)	K [eq. (2)] (°C)
1	25	10
3	30	11
5	33	13
10	34	11
20	35	21
30	38	10

At 1 and 5% divinylbenzene, it is reasonable to assume that the copolymer effect is negligible. For these two IPNs, the PMA transition is lowered by around 7–8°C compared with the corresponding PMA networks. Whether the lower IPN PMA T_g 's are the result of some mixing or the consequence of a lower degree of crosslinking in the presence of the PU network is not possible to resolve.

At high divinylbenzene levels, it is likely that the latter predominates, because the PU T_g 's (Figs. 7 and 8) are not shifted. Figure 7 shows the E' data as a function of temperature for the IPNs. At low temperatures the crosslinking does not have a significant effect on the storage modulus. At higher temperatures, as expected, the degree of crosslinking does play a significant role. Two transitions are apparent. The one around -40°C is the glass transition of the predominantly PU phase. Figure 8 shows the E'' vs. temperature curves. Again, two relaxations are evident. Increasing the

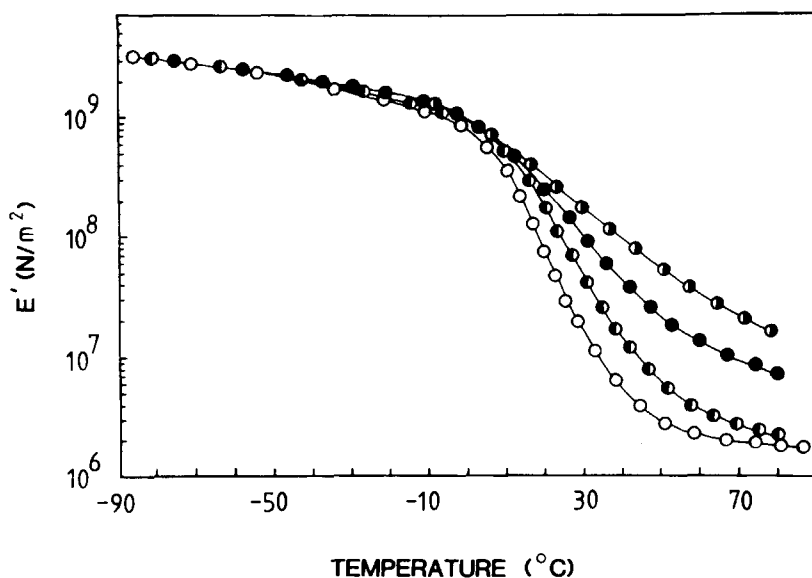


Fig. 7. E' -temperature plots (11 Hz) of the PU-PMA IPNs (40 wt % PU) in which the PMA network was formed using 3% (○), 10% (○), 20% (●), and 30% (○) divinylbenzene, respectively.

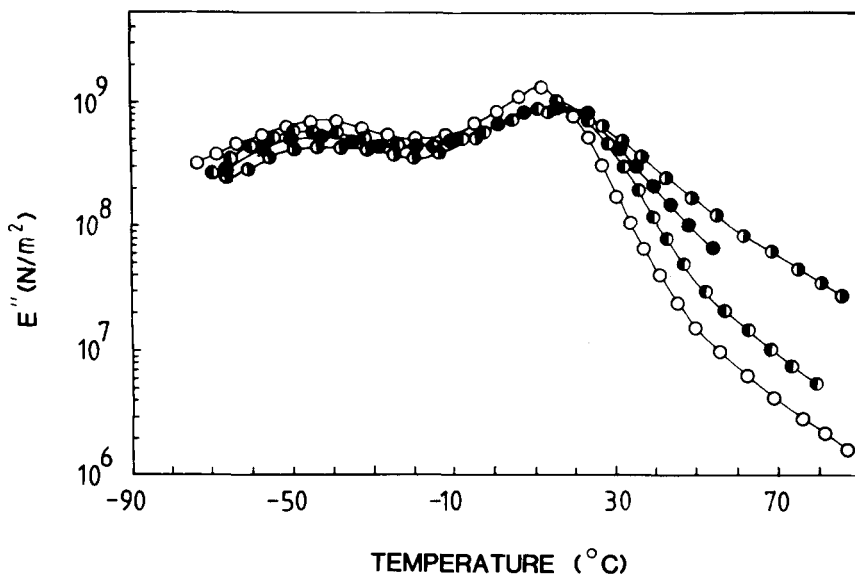


Fig. 8. E'' -temperature plots (11 Hz) of the PU-PMA IPNs (40 wt % PU) in which the PMA network was formed using 3% (○), 10% (□), 20% (●), and 30% (○) divinylbenzene, respectively.

crosslinking level up to 10% DVB shifts and broadens the PMA E'' transition, but above 10% DVB, the position of the E'' maximum is approximately static, although further broadening occurs. With increased crosslinking of the PMA network, the PU transition is progressively suppressed.

An approximate measure of the damping ability of a material is given by the Oberst¹⁷ equation

$$K = \frac{\Delta T \cdot E''_{\max}}{E'_{T_g}} \quad (2)$$

This defines a measure of damping, K . ΔT is the width of the E'' vs. temperature transition at half-peak height, E''_{\max} is the maximum value of E'' , and E'_{T_g} is the storage modulus at T_g . The K values for these IPNs are given in Table V. They have K values of about 10 except for the IPN crosslinked with 20% divinylbenzene which has a value of 21. Most homopolymers have K values of around 6.

Figure 9 shows the stress-strain curves of the IPNs. With increasing divinylbenzene levels, the elongation to break is reduced, but this is accompanied by an increase in the tensile strength. The stress at break values do approximately conform to the envelope fracture pattern proposed by Smith and Chu.¹⁸ The 5% divinylbenzene IPN is the toughest material. Table VI presents the essential details of the tensile experiments. Tables II and VI show that the elongation at break is increased, but tensile strength is decreased if the IPN systems are compared with the respective PMA networks.

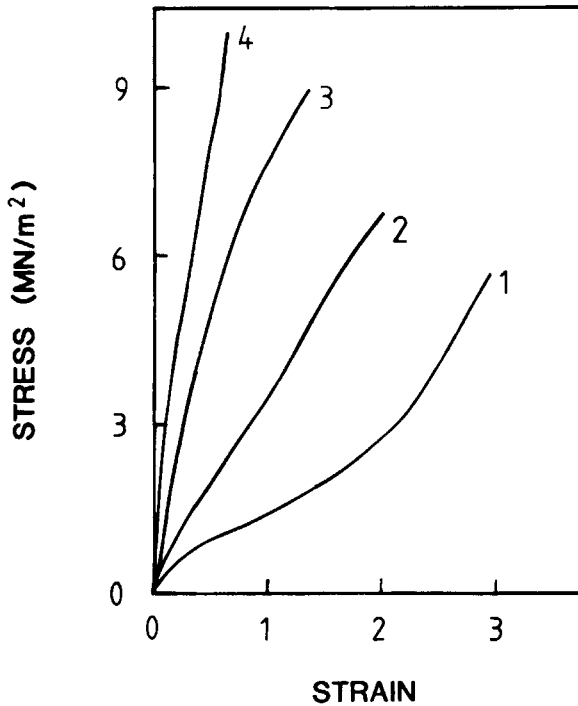


Fig. 9. Stress-strain curves (20°C) of the PU-PMA IPNs (40 wt % PU) in which the PMA network was formed using 5% (1), 10% (2), 20% (3), and 30% (4) divinylbenzene, respectively.

Figure 2 shows V_L of these IPNs as a function of divinylbenzene content. As the divinylbenzene is increased, there is initially a significant increase in V_L . However, above 10% divinylbenzene there is only a gradual change. This figure also shows that the IPN line lies significantly below that predicted using

$$V_L = \omega_1 V_{L1} + \omega_2 V_{L2} \quad (3)$$

V_{L1} and V_{L2} are the longitudinal sonic velocities of the PU network (0.117 km/s) and those of the PMA networks, respectively. ω_1 and ω_2 are the weight fractions of the PU and PMA components, respectively. This is taken to mean that the PU component is the more continuous at all levels of divinylbenzene.

TABLE VI
Stress-Strain Data (20°C) for the IPNs

Divinylbenzene (wt %)	Tensile strength (MN/m ²)	100% modulus (MN/m ²)	Elongation at break (%)
3	3.6	0.9	310
5	5.7	1.4	300
10	6.8	3.5	200
20	8.9	7.6	135
30	10.1	—	62

As the rise in V_L of the IPNs with increasing divinylbenzene content could occur because of enhanced mixing and/or because of the increasing modulus of the PMA component, it is not possible to deduce more from these results than to say that it is clear that the PU component is significantly more continuous than is the PMA network.

From electron micrographs, it was clear that there was phase separation in all the IPNs reported here. The PU component was present as a continuous phase, and, as the divinylbenzene content was increased, the PMA domains were only marginally reduced in size. There was some evidence in the micrographs to suggest that the PMA component became more continuous as the crosslinking level was increased.

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