Mechanical behaviour of sequential polyurethane–poly(methyl methacrylate) interpenetrating polymer networks

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Sequential pseudo-interpenetrating polymer network (IPN) preparations based on a polyurethane (PU) network and linear poly(methyl methacrylate) (PMMA), some containing particulate filler and titanium dioxide pigment, were evaluated in terms of dynamic and static behaviour. The dynamic technique was used to determine the damping behaviour across a temperature range. An explanation of the response is suggested. As might be expected the hardness, the elastic modulus and the tensile strength at ambient temperatures increased with increasing PMMA. Elongation to failure exhibited a peak value corresponding to the unique damping characteristics of an intermediate-level IPN. An improved low temperature impact strength was observed in IPNs compared with PMMA.

(Keywords: interpenetrating polymer networks; tan δ; glass transition; crosslink density; polyurethane; poly(methyl methacrylate))

INTRODUCTION

Interpenetrating polymer networks (IPNs) were first synthesized by Miller in the 1960s. Since that time the term has been used to describe the combination of two or more different polymer networks which consist of purely physical entanglements of the polymer chains synthesized either simultaneously or sequentially with respect to each other. These so-formed materials possess interesting characteristics compared with normal polyblends and are the only way in which crosslinked polymers may be intimately combined. IPNs are therefore closely related to the two-component polymer blends, grafts and block copolymers. However, due to their nature and method of synthesis, they permit a much greater molecular control over physical and mechanical behaviour.

It has been shown[1–5] that an enhancement of polymer properties may be brought about by the formation of heterogeneous systems in which one polymer exists above its glass transition temperature, T_g, whilst the other exists below its T_g at room temperature. This situation results in the composite at room temperature having one component being glassy whilst the other remains rubbery. By varying the relative amounts of each polymer in the IPN the properties may be altered, but these are mainly dependent upon which of the two materials forms the continuous phase. Thus, the produced material can range from a reinforced rubber to a high impact plastic. The ultimate goal is an understanding of the important factors in determining the properties exhibited by the resulting IPN so that materials with properties tuned to the required application may be produced.

IPNs may be prepared by several methods, including: (1) latex blending[6–10]; (2) sequential polymerization[6,7,11–14]; and (3) simultaneous polymerization[6,9,13,15–17,26,27].

It is generally believed that the simultaneous polymerization process, due to its nature, results in material with the smallest degree of phase separation and hence the highest degree of interpenetration. In sequential polymerization, however, the network first formed is likely to be the continuous network, the morphology of this system being dictated by its density of crosslinking. Crosslinking is responsible for control of the size of the phase domains of the second network and hence the properties exhibited by the material.

Two types of IPN may be formed, depending on whether the polymer components are crosslinked or not: a full-IPN is said to be formed when both of the components are crosslinked; a semi-[6] or pseudo-IPN[18] exists when only one of the components is crosslinked. The so-called pseudo-IPNs may be produced by the simultaneous or sequential methods discussed above and have, as expected, different properties to the full IPNs as reported in references 6, 9, 13, 28–31.

The present work examines the glass transition behaviour and the mechanical properties of pseudo-IPNs based on polyurethane (PU) and poly(methyl methacrylate) (PMMA). The aim is to elucidate the factors which determine the form of the transitions observed and, in turn, to formulate materials tuned to specific applications.

EXPERIMENTAL

Materials

The materials used are described in *Table 1*. Prior to IPN preparation the methyl methacrylate monomer was freed from inhibitor by washing first with aqueous sodium hydroxide, then with distilled water, followed by drying over anhydrous calcium chloride. The cast polyurethane

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Table 1 Raw materials

Designation	Description	Source
Unfilled PU	Base elastomer, consisting of 2000 and 400 molecular weight poly(oxypropylene glycol) mixture reacted with a semi-pure MDI of functionality 2.3	B&T Polymers Ltd
Filled PU	Filled with approximately 33% w/w inert particulate filler and pigmented with titanium dioxide	B&T Polymers Ltd
MMA	Methyl methacrylate	BDH Chemicals Ltd
AIBN	2,2'-azo-bis(2-methylproprionitrile) (azobisisobutyronitrile)	BDH Chemicals Ltd

sheets were dried prior to use by placing in a vacuum oven at 40°C for 24 h. All other chemicals were used as supplied.

IPN preparation

The dried polyurethane sheets of dimensions 113 × 51 × 3 mm were weighed and then immersed in inhibitor-free methyl methacrylate (MMA) containing 0.5% (w/w) AIBN for various periods of time (15 min to 3 h). After the sheets had achieved the required percentage increase in weight, they were removed, blot dried and clamped between glass plates which were sprayed with silicone mould release agent. The whole assembly was then wrapped in polythene and left for 20 h at room temperature in order to facilitate uniform monomer diffusion. Subsequently the sheets were heated to 60°C for 23 h, followed by 2.5 h at 80°C and 1 h at 100°C for MMA polymerization. The polymerized sheets were allowed to cool down to room temperature prior to demoulding, wiped clean of release agent, and left for two weeks at room temperature to drive off any unreacted MMA.

The composition of the IPNs was estimated by substituting measured density values into the following rule of mixtures equation:

$$d_c = V_1 \cdot d_1 + V_2 \cdot d_2$$

where d_c = density of composite (IPN), V_1 = volume fraction of PU component, d_1 = density of PU component, $V_2 = (1 - V_1)$ = volume fraction of PMMA component and d_2 = density of PMMA.

The equation can be written as:

$$V_2 = (d_c - d_1)/(d_2 - d_1)$$

PMMA preparation

A methyl methacrylate prepolymer was formed by heating inhibitor-free monomer in a water-bath at 60°C until it had become noticeably viscous.

Following the removal of the reaction exotherm by immersion in an ice bath for 30 min, the prepolymer was cast in a glass cell consisting of two clean dry glass plates separated by a rubber gasket (cellulose dialysis tubing pulled over rubber tubing) and held together by means of spring clips. The PMMA polymerization was completed by applying the same reaction conditions as in IPN preparation.

Determination of crosslink density in polyurethanes

Polyurethane discs of diameter 16.1 mm and thickness 3.2 mm were punched out from original PU sheets using a Wadd punch. The discs were then placed in a conical flask (250 cm^3) and totally immersed in toluene (150 cm^3) for three weeks. The swollen discs were then removed individually, placed in fresh toluene and compression tested whilst still immersed using the apparatus and test method described by Cluff *et al.*[25] The loads applied to the disc under test ranged from 0.5 N to 5.0 N in 0.5 N increments, the compression being noted on the application of each mass.

The crosslink density was obtained by means of the following equation[25]:

$$v_e/V = h_0 S / 3 A_0 R T$$

where h_0 = the height of the undeformed unswollen disc (m), S = the slope of the linear portion (up to 5% compression) of the force vs. deflection graph (N m^{-1}), A_0 = the cross-sectional area of the unswollen disc (m^2), R = universal gas constant (J K^{-1} mol^{-1}), T = absolute temperature and v_e/V = the effective network chain concentration (i.e. crosslink density, mol m^{-3}).

Test methods

Dynamic mechanical data were obtained using a Du Pont 983 Dynamic Mechanical Analyser in resonant frequency mode over a temperature range from −80°C to 160°C at a heating rate of 4°C per min.

Tensile testing was performed at room temperature (23°C) using an Instron tensometer (Model No. 1026) in accordance with ASTM D 638M-84 at an elongation rate of 50 mm min^{-1}.

Hardness testing was performed according to ASTM D 2240-85 using Shore durometers of type A and D.

Notched and un-notched specimens were impact tested in a three-point bending mode, 40 mm span, using an instrumented falling weight machine, fitted with a chisel shaped striker of angle 30° and tip radius 1.5 mm, at 1 m s^{-1} impact speed. The test-pieces were of dimensions 3.5 × 10 × 60 mm with some being notched to approximately 1 mm depth by milling using a cutter of angle 45° and tip radius 0.25 mm. The test pieces were then frozen to −40°C by immersion in liquid nitrogen and were allowed to reach −30°C immediately prior to impact. Impact tests were conducted at −30°C, i.e. below the T_g of the materials, where it was expected that any vulnerability would be indicated and hence the evaluation be more appropriate.

The crosslink density of the filled and unfilled PU homopolymers was determined by means of its equilibrium compression modulus.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The behaviour of a dynamic mechanical property (tan δ) over a range of temperature is shown in *Figures 1* and *2* for various IPN compositions and for the individual polymer components.

The striking features of the curves are: (1) the reductions in peak tan δ and (2) the less well defined peak for the intermediate composition IPNs. We propose that these phenomena emanate from the conformation of the

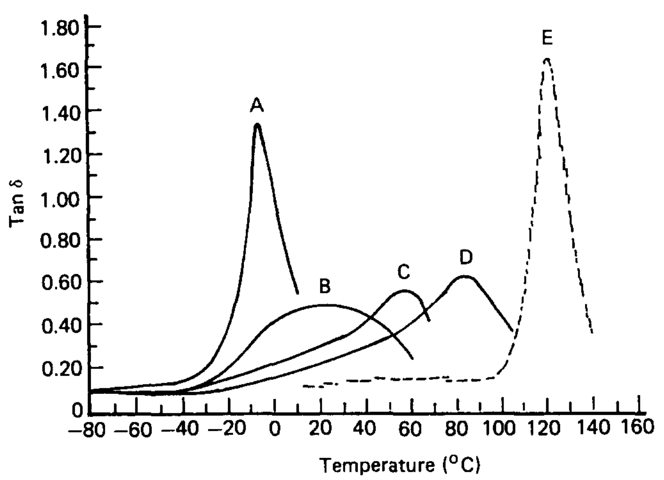

Figure 1 Tan δ–temperature plots for filled IPNs with PMMA/PU compositions (% vol.): A, 0/100; B, 12/88; C, 41/59; D, 54/46; E, 100/0

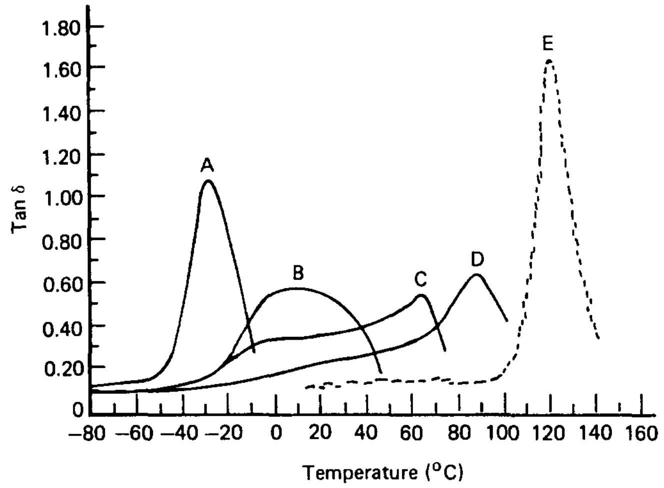

Figure 2 Tan δ–temperature plots for unfilled IPNs with PMMA/PU compositions (% vol.): A, 0/100; B, 29/71; C, 38/62; D, 52/48; E, 100/0

PU elastomers to the statistical theory of molecular networks, the molecular segments being considered as a Gaussian distribution of chains. The inclusion of a compatible glass polymer, viz. PMMA, inhibits segmental mobility by quasi-crosslinking and accordingly causes a reduction in the peak value of tan δ. In an intermediate level IPN a Gaussian-like spectrum of quasi-crosslink densities is generated as illustrated in *Figure 3* and undergoes juxtapositional glass transitions with temperature, resulting in the combined broad tan δ peak seen in *Figure 1*, curve B and *Figure 2*, curve B. Further increases in PMMA content shift the quasi-crosslink densities to the upper end of the distribution, giving a reduced damping response at ambient temperatures and a peak response earlier than that for 100% PMMA (as in *Figures 1* and *2*, curves C and D). Once the transition occurs in PU, it acts as an effective plasticizer in the matrix.

The literature[16,19–22] indicates that only the compatible polymers produce IPNs with a broad transition at intermediate temperatures between the T_g of the components. Semicompatible polymers are said to produce a transition peak coincident with the T_g of one of the components, along with an indistinct shoulder overlapping with the second T_g. Effectively single-phase IPNs resulted in the present work from: (a) the comparable solubility parameters of the components (8.8, 9.1 and 9.2 cal$^{1/2}$ ml$^{-1/2}$ for MMA, PMMA and propylene oxide respectively[23,24]), (b) the use of solid PU as the start material and its inherent random spread of intermolecular interstices, themselves irregular. The occluded methyl methacrylate and, in turn, PMMA assumes a thorough intermingling with the host PU. The possibility of PMMA-rich regions will increase as the PMMA concentration increases. The crosslink density of the host polymer will also influence the composition levels where phase separation may occur. Work by Allen *et al.*[20–22] using a two-step polymerization process, high PMMA contents, as high as 90%, and PUs of high crosslink density showed clear phase separation and no grafting[22]. In this case the MMA polymerized under the isotropic pressure of the PU gel and accordingly assumes a globular dispersion. At high MMA concentrations neighbouring domains experience constraints and deform into polyhedra.

Hermant *et al.*[13] have employed tan δ peak width measurements at mid-height as an indicator of the degree of miscibility of the IPN component polymers. These measurements are a convenient way of quantifying the sharpness of the transitions and, as can be seen in *Table 2*, not only do the IPNs demonstrate broader transitions than their components, but also the transition width changes with composition for reasons outlined earlier.

It is also observed (*Table 2*) that the area under the tan δ curves remains about the same as the IPN composition varies, an indication perhaps that the polymer

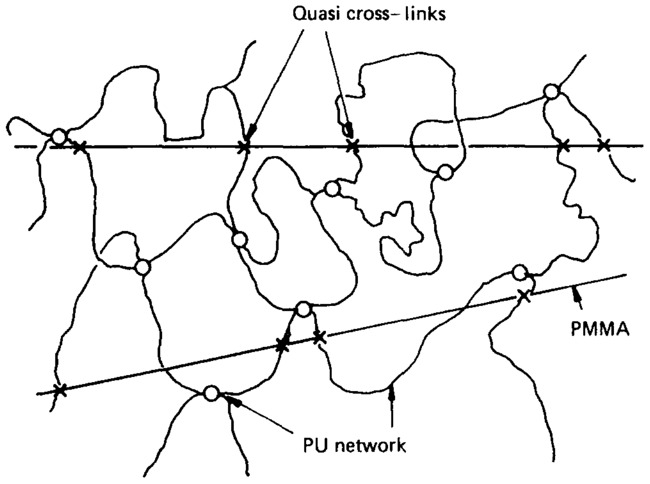

Figure 3 Diagrammatic representation of quasi-crosslinks in PU network/PMMA IPNs

Table 2 Glass transition data

	Composition (%PU/%PMMA)	T_g (°C)	Tan δ peak value	Transition width at half peak (°C)	Area under tan δ peak (tan δ × °C)
Filled	100/0	−7	1.34	18	26
	88/12	20	0.49	70	28
	59/41	58	0.55	47	28
	46/54	83	0.62	53	34
Unfilled	100/0	−16	1.09	22	24
	71/29	8	0.57	55	25
	62/38	64	0.53	–	30
	48/52	88	0.63	35	30
PMMA	0/100	121	1.64	16	29

components have a potential damping capacity exhibited in different forms over the temperature range.

Mechanical properties

The mechanical properties of the constituent materials as well as the IPNs are given in *Figures 4–6*.

The elastic modulus and the ultimate tensile strength of the IPNs, (*Figures 4* and *5*) increase, as expected, with increasing PMMA content. The figures also show the contribution of the filler to the materials' stiffness and strength.

The behaviour of the percentage elongation to failure (*Figure 6*) highlights the possibilities of improvements in mechanical performance with appropriate formulation. Contrary to expectations the elongation increases and goes through a maximum with increasing PMMA content. This demonstration of improved ductility corresponds to the higher damping (as in *Figures 1* and *2*) of the IPNs at ambient temperatures. The occurrence of the percentage elongation maximum at different regions along the composition scale for the filled and unfilled systems results mainly from expressing the PMMA content based on PU plus filler.

However, the attainment of higher percentage elongation to failure with the filled system may be due to

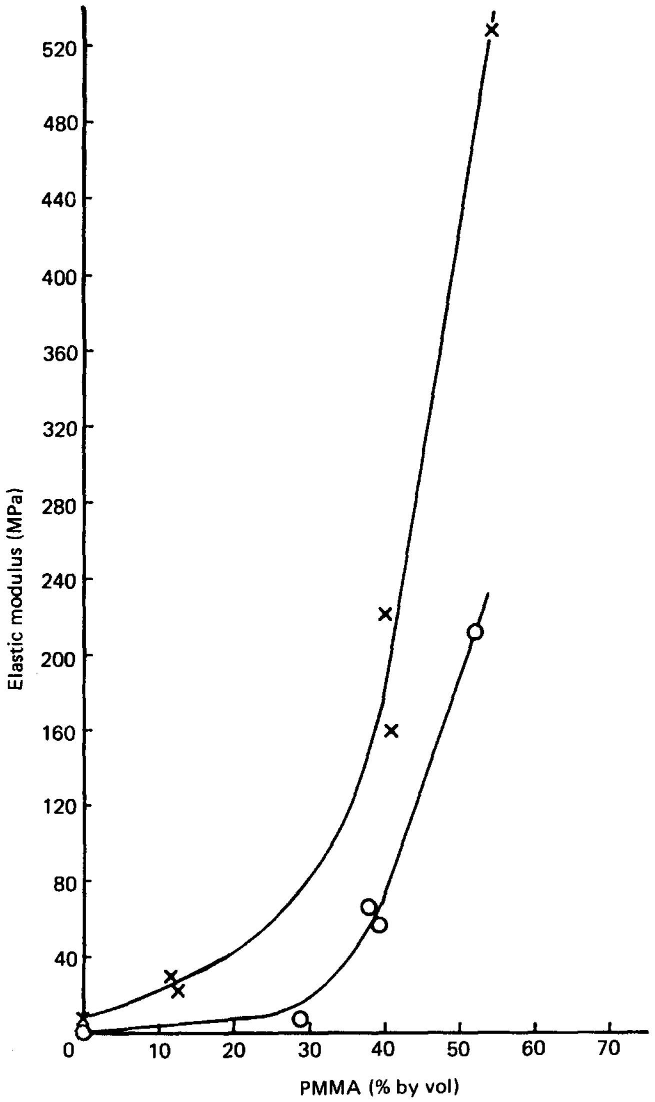

Figure 4 Elastic modulus vs. % PMMA for filled (×) and unfilled (○) IPN systems

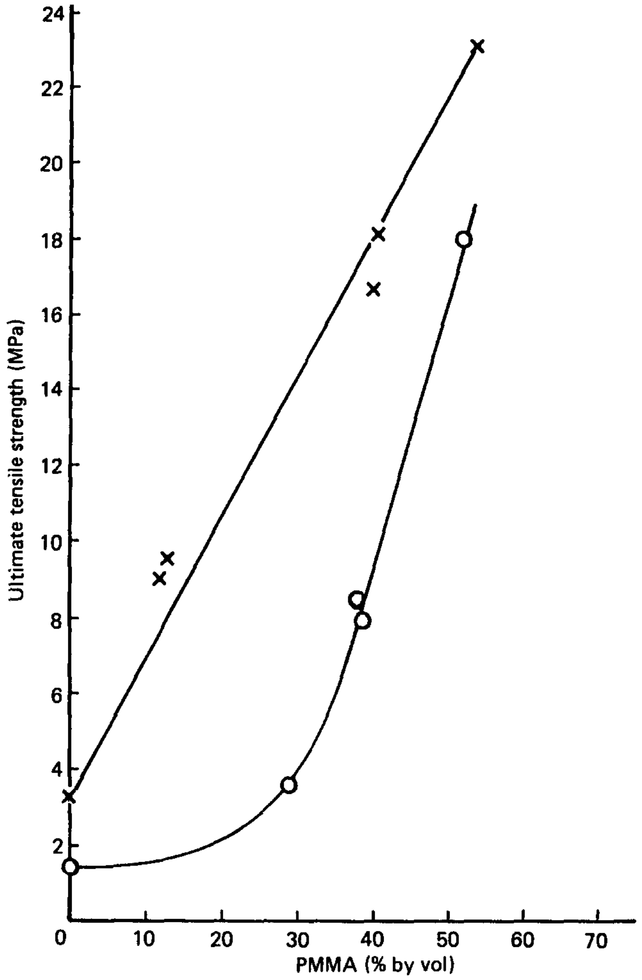

Figure 5 Ultimate tensile strength vs. % PMMA for filled (×) and unfilled (○) IPN systems

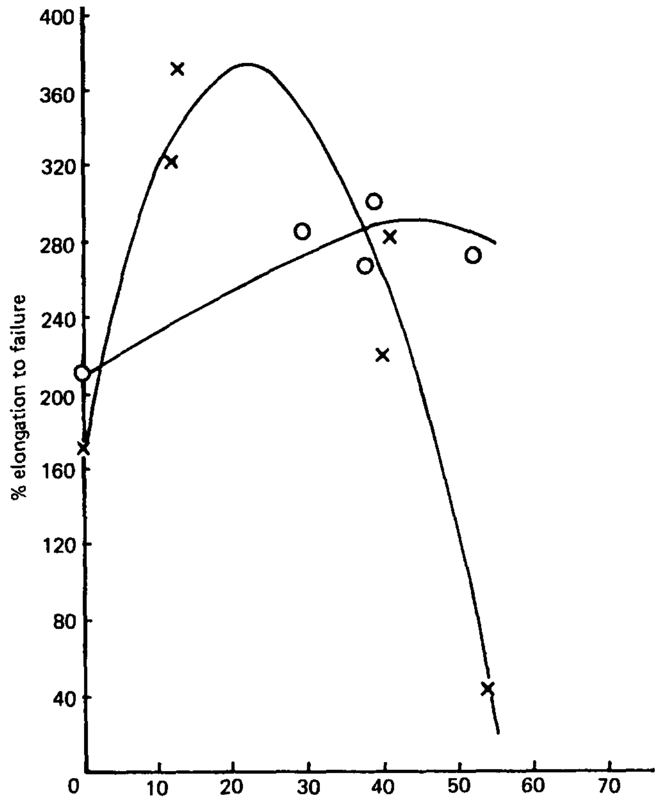

Figure 6 Per cent elongation vs. % PMMA for filled (×) and unfilled (○) IPN systems

the presence of titanium dioxide pigment which, depending on its surface treatment, can offer an active site for polymerization.

At low temperatures, about −30°C, the IPNs exhibit a higher impact strength than the PMMA, even in the presence of normally impact reducing rigid particulate fillers, as shown in *Figures 7* and *8*.

Hardness tests were performed to corroborate the trend of the compositions in the IPNs and, as seen in *Figure 9*, there is a linear increase in hardness as the percentage of PMMA increases, up to perhaps a saturation level. The contribution of fillers to the hardness is obvious at low PMMA concentrations.

Crosslink density in PUs

The compressive force-deflection data, *Figure 10*, have two distinct linear regions for both the filled and the unfilled PUs. The change in the slope occurs at about 5% compression, which is the maximum recommended for the crosslink density measurements[21]. Therefore, by substituting the slope of the initial linear region into the equation given above, the crosslink densities of the filled and unfilled PUs were found to be 2.758×10^{-5} and 2.997×10^{-5} mol cm^{-3}, respectively. These low values reflect the employment of low functionality polyols in PU preparation. The small difference in the crosslink densities of filled and unfilled PUs is attributed to the presence of an active pigment such as titanium dioxide, which may affect the distribution of crosslinking by, for example, localization of crosslinking in network systems[32,33].

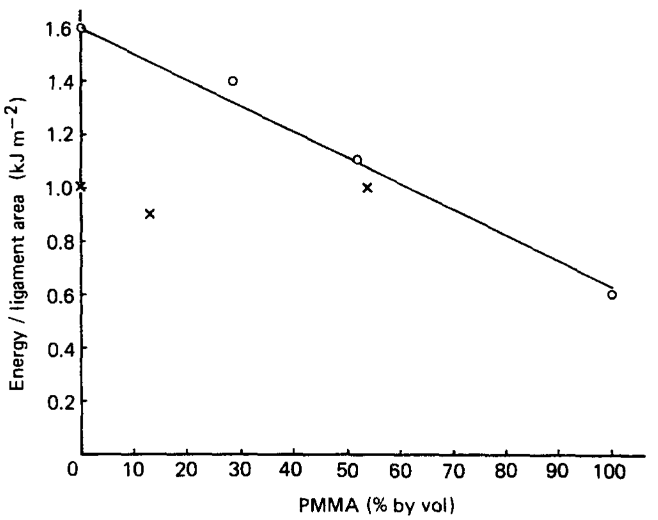

Figure 7 Notched impact energy at failure per ligament area vs. PMMA content for filled (×) and unfilled (○) IPN systems

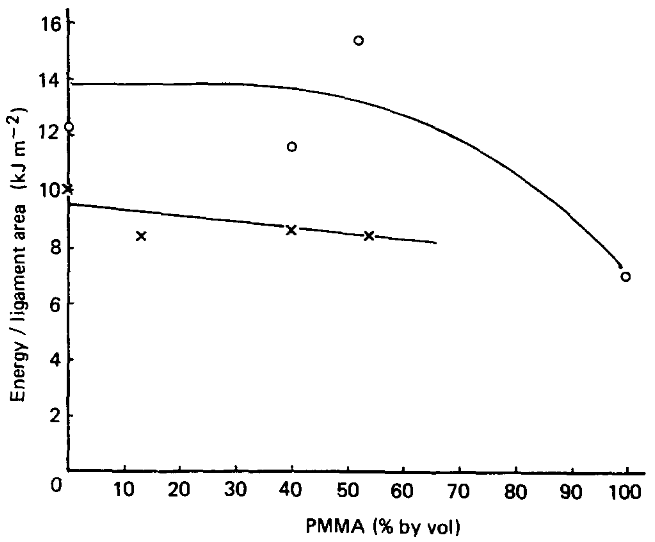

Figure 8 Un-notched impact energy at failure per ligament area vs. PMMA content for filled (×) and unfilled (○) IPN systems

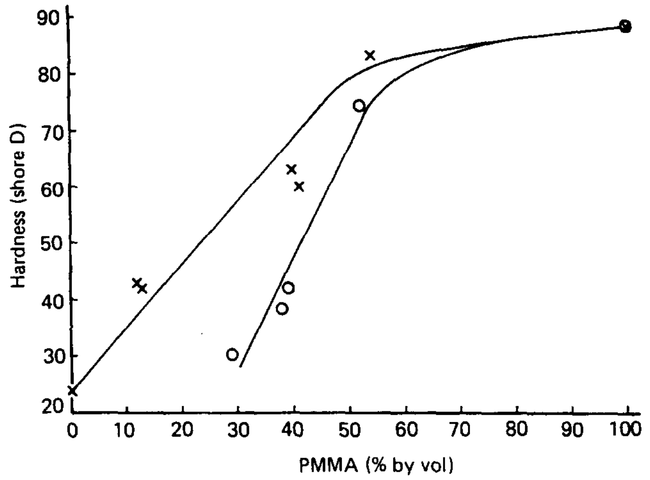

Figure 9 Shore hardness vs. % PMMA for filled (×) and unfilled (○) IPN systems

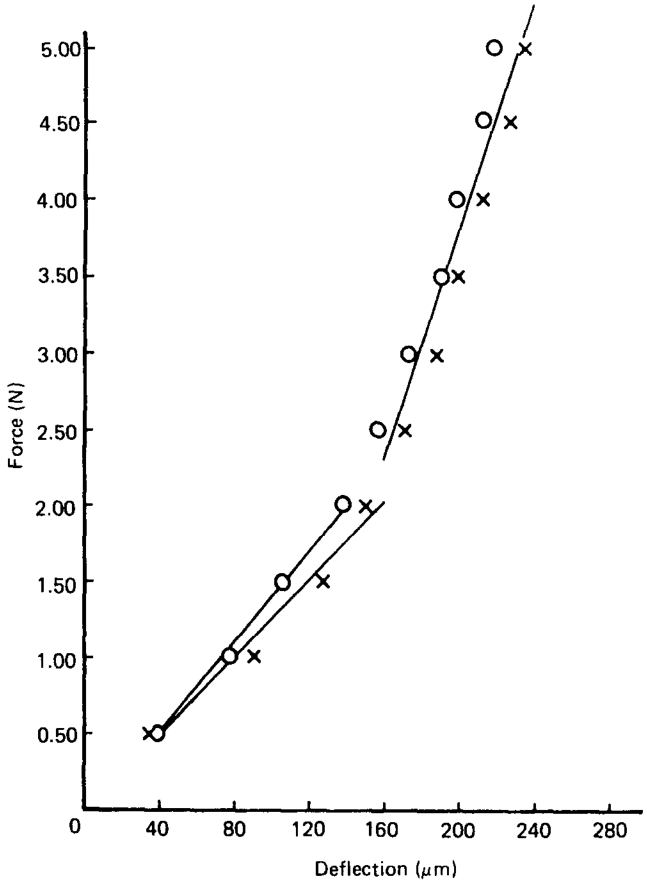

Figure 10 Compressive force vs. deflection for filled (×) and unfilled (○) IPN systems

CONCLUSIONS

The introduction of the glassy polymer PMMA into PU elastomers at some intermediate level of incorporation produced an IPN with a broad glass transition. It is suggested that this is a compound transition generated by a spectrum of quasi-crosslink densities which are a manifestation of the restriction imposed by the rigid polymer component on the segmental mobility of the elastomer. Besides the broadening of tan δ-peak in IPNs, a reduction in the peak value of tan δ, and a fixed magnitude of damping (expressed as the area under tan δ-temperature trace) are also readily observable.

The increase in the PMMA content of the IPNs produced the expected trends in mechanical behaviour: an increase in hardness, the elastic modulus and the tensile strength, and a decrease in impact strength. However, the percentage elongation to failure at ambient temperatures went through a maximum with the increasing PMMA content.

The presence of filler resulted in an increase in the static mechanical properties and a decrease in impact strength, without affecting the trends observed in these properties over the IPN composition range.

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