

Interpenetrating Polymer Networks from Hydroxy-Terminated Polybutadiene-Based Polyurethanes and Poly(methyl methacrylate)

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SYNOPSIS

Isocyanate-terminated urethane prepolymer was prepared by reacting 2 mol of tolylene diisocyanate (TDI) with 1 mol of hydroxy-terminated polybutadiene (HTPB, mol. wt. = 3000) at room temperature ($30 \pm 1^\circ\text{C}$) in the presence of stannous octoate as the catalyst. Urethane prepolymer was subsequently mixed with 1,4-butane diol : glycerol (6 : 1 ratio), methyl methacrylate (MMA), and ethylene glycol dimethacrylate (EGDMA) to give an interpenetrating polymer network. Stannous octoate was used as a catalyst to give network I, and azobisisobutyronitrile (AIBN), as an initiator to give network II. Different proportions of MMA were added to the prepolymer for studying the effect of composition on mechanical properties, thermal behavior, and optical properties. The mechanothermal behavior was analyzed using a dynamic mechanical thermal analyzer. Tensile strength and modulus decreased with decreasing MMA content, whereas percent elongation at break increased. Thermal stability of the sample increased with increasing urethane content. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The chemical and physical combination methods and their properties of multipolymers have been of commercial and academic interest, since they provide a convenient route for the modification of properties to meet specific needs. Among these methods, interpenetrating polymer networks (IPNs) represent a new approach to the problem of mutual incompatibility of polymers. They possess excellent engineering properties because of the synergistic effect of individual polymers.

Considerable work has been reported by Sperling et al.,¹⁻⁴ Frisch et al.,⁵⁻⁸ Hourston and Zia,⁹⁻¹² and Patel et al.¹³⁻¹⁷ on the synthesis of IPNs based on polyurethanes (PU) obtained from castor oil, polyester, or poly(ether polyol) and diisocyanates. The effect of the isocyanate/hydroxyl ratio, cross-link

density, and vinyl monomer content on the various properties have been reported.¹⁵⁻¹⁷ Tough plastics or reinforced elastomers were obtained depending upon the composition. Although castor oil/polyester or poly(ether polyol) have been extensively used for the synthesis of PU however, no reports are available regarding the use of hydroxy-terminated polybutadiene (HTPB) for making polyurethane/poly(methyl methacrylate) (PU/PMMA) IPNs. In the present work, 1 mol of HTPB ($\bar{M}_n = 3000$) was reacted with 2 mol of 2,4/2,6-tolylene diisocyanate to prepare isocyanate-terminated prepolyurethane (PPU). One equivalent of PPU was then mixed with 1 equivalent of a 1,4-butane diol (BD): glycerol mixture (6 : 1 equivalent ratio) to form the PU network. The PMMA network was obtained using MMA as the monomer and ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent.

Various samples of PU/PMMA simultaneous interpenetrating polymer networks (SINs) were obtained by mixing PPU : BD : glycerol and MMA : EGDMA in different proportions. Samples having 10, 20, 30, 40, 60, and 80% (w/w) of MMA have

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been designated MB-1, MB-2, MB-3, MB-4, MB-6, and MB-8, respectively.

EXPERIMENTAL

Materials

An 80/20 mixture of 2,4/2,6-tolylene diisocyanate (TDI, E. Merck), stannous octoate (Sigma), methyl methacrylate (MMA) (Fluka), ethylene glycol dimethacrylate (EGDMA, E. Merck), glycerol (Qualigens), and butane diol (BD, Fluka) were used as such. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform. Hydroxy-terminated polybutadiene (HTPB, $\bar{M}_n = 3000$, viscosity = 6270 cps at 30°C, density = 0.9 g cm⁻³) was procured from Vikram Sarabhai Space Centre and was used as such.

Prepolymer Preparation

The prepolymer was prepared by reacting 1 mol of HTPB with two moles of TDI using stannous octoate as the catalyst. In a typical reaction, 60 g of HTPB (0.02 mol), 6.06 g of TDI (0.04 mol), along with few drops of stannous octoate was placed in a round-bottom flask fitted with a stirrer. The reaction was carried out at room temperature (30 ± 1°C) with continuous stirring. Stirring was carried out for 20–25 min to complete the reaction. Isocyanate-terminated prepolymer was obtained as a thick syrup.

PU Network

The PU network was obtained by mixing 1 equivalent of isocyanate-terminated prepolymer (PPU) with 1 equivalent of the BD : glycerol mixture (6 : 1 equivalent ratio) in the presence of stannous octoate as the catalyst. BD and glycerol were used as chain-extending and cross-linking agents.

Synthesis of PU-PMMA Interpenetrating Polymer Networks

The required quantities of urethane prepolymer, the BD/glycerol mixture, MMA, EGDMA (1% based on MMA used), and AIBN (1%) were placed in a round-bottom flask fitted with a mechanical stirrer. The mixture was stirred at room temperature for 5–10 min to form a uniform mixture. Compositions having higher amounts of prepolymer were highly viscous and the air entrapped during mixing was removed by applying a vacuum. On the other hand, compositions rich in MMA were heated at 60°C (to initiate the polymerization of MMA) for different

intervals of time until an optimum viscosity was obtained. A Brookfield viscometer (RV TDV-II) was used for monitoring viscosity changes at 55, 60, and 65°C. Prepolymer syrup and MMA corresponding to compositions having 90, 80, and 70 wt % of MMA (samples MB-9, MB-8, and MB-7) were taken in a sample container and kept for 2 min to obtain the desired temperature. A shear rate of 10 rpm and a coaxial cylinder spindle (29BS) was used. The spindle was immersed up to the middle of the indentation in the shaft. The sample container was closed with cardboard containing a small cleft for the insertion of the spindle. This minimizes the loss of MMA during the curing studies. A chart speed of 1 or 3 cm per min was used. The percent viscosity was converted into viscosity in cps using a conversion table. Critical time (the minimum time after which viscosity increased drastically) was noted for each sample. This also gives an idea of how long one can heat the mixture for making it viscous before pouring it into the glass mold. If the mixture is heated for a longer period, then gelling takes place, and if for a shorter period, then the viscosity is so low that it leads to the formation of voids in the sheet.

Preparation of Mold

Two toughened glass plates of 215 × 290 mm² size were cleaned and sprayed with the releasing agent (silicone spray). A PVC gasket of diameter 3 mm was placed in between the plates that were held together using steel clamps. One side of the glass plate was kept open for pouring the syrup.

A small strip of mylar sheet was folded and was used as a funnel for pouring the syrup. Approximately 100 g of the syrup was added into the mold and the opening was closed using a metal plate followed by clamps.

The filled mold was then placed in a preheated water bath at 60°C for 6 h. The mold was then removed and placed in an air oven at 100°C for 4 h. After cooling, the clamps were removed and the sheet was taken out after passing a stream of water. The sheet was washed with water followed by wiping the excess water with a filter paper.

Characterization and Testing

Transmittance

Percent light transmittance of the sheet in the wavelength range of 200–800 nm was measured using a Perkin-Elmer Lambda 3B UV-visible spectropho-

tometer. Two specimens, each of size $30 \times 10 \times 2 \text{ mm}^3$, were used for testing and the average value is reported.

Tensile Properties

Tensile properties were determined according to ASTM D638 using the Instron Tensile Tester Model 1121 (at ambient conditions) and dumbbell-shaped specimens. The specimens from the flexible sheets were prepared with the help of a punching die, whereas from the rigid sheets, dumbbell-shaped specimens were prepared by first cutting 165 mm long and 14 mm wide rectangular pieces and then shaping them using a metal mold. The edges of the specimens were polished using a very fine sandpaper. The specimens were conditioned as per the standard before testing. A gauge length of 2.5 cm, full-scale load of 100 kg, and a crosshead speed of 1 cm/min was used. A minimum of five samples was tested for each composition and the average was taken.

Dynamic Mechanical Properties

Dynamic mechanical measurements of various IPN samples were carried out in the temperature range of -90 to $+100^\circ\text{C}$ using a Polymer Laboratory dynamic mechanical thermal analyzer (Model MKII) in a bending mode. A heating rate of $5^\circ\text{C}/\text{min}$, a frequency of 1 and 10 Hz, and a sample size of $12 \times 5 \times 3 \text{ mm}^3$ was used in each experiment. The equipment has built-in computerization facilities, and dynamic moduli (both storage and loss moduli) and damping (loss factor) were calculated by the built-in software and plotted by the plotter.

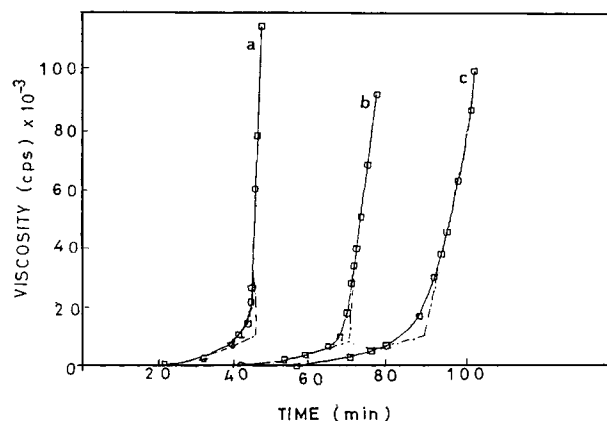


Figure 1 Plot of viscosity vs. time for IPN samples: (a) MB-7; (b) MB-8; (c) MB-9 containing 1% AIBN (w/w) at 60°C .

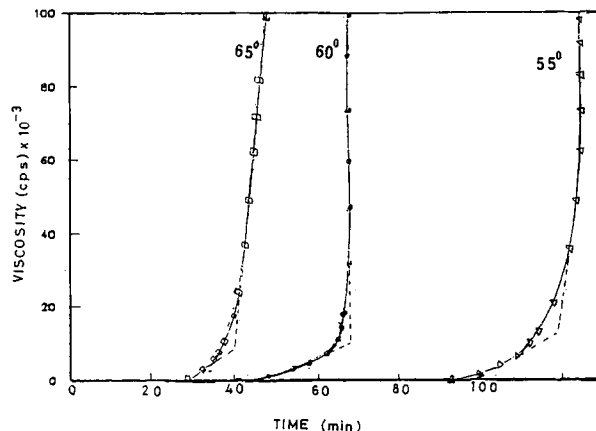


Figure 2 Plot of viscosity vs. time for MB-8 containing 1% AIBN (w/w) at 55, 60, and 65°C .

Thermal Behavior

Thermal stability of the samples was assessed using a DuPont 1090 thermal analyzer having 951 TG module. A heating rate of $10^\circ\text{C}/\text{min}$ and a sample size of $10 \pm 2 \text{ mg}$ was used in each experiment.

RESULTS AND DISCUSSION

Figures 1 and 2 show the effect of composition and temperature on the Brookfield viscosity. The temperature during this measurement was maintained constant by proper thermostating. At an early stage of the reaction, the viscosity increased slowly, but later it increased very rapidly, tending to reach a very high value as the reaction proceeds. The viscosity curve is characterized by a critical value of time and viscosity corresponding to the upturn point evaluated by extrapolation of the steep portion of

Table I Effect of PU/PMMA Composition on the Percent Transmittance of Various IPN Samples

Sample Designation	% Light Transmittance at Wavelength (nm)			
	500	600	700	800
MB-1	64.9	79.7	83.9	87.7
MB-2	77.5	85.9	88.5	91.5
MB-3	77.5	85.9	88.5	91.5
MB-4	40.9	63.7	74.3	81.6
MB-6	36.8	44.7	49.5	64.5
MB-8	33.6	51.9	61.6	70.3
PMMA	90.3	90.1	91.1	93.7

Table II Effect of PU/PMMA Composition on the Mechanical Properties of IPNs

Sample Designation	Tensile Strength (MN/m ²)	% Elongation	Tensile Modulus (kg/m ²)
MB-1	1.8	154	2,700
MB-2	2.5	114	4,500
MB-3	5.0	95	10,300
MB-6	17.8	76	70,000
MB-8	24.7	11	2,310,000

viscosity vs. time plot. η_c (critical viscosity) characterizes a given extent of growth of polymer chains. At any temperature, after a period of time equal to the critical time (T_c), the growth of the polymer chain is such that further polymerization cause a

significant increase in viscosity. Both η_c and T_c decrease with an increase in temperature (Fig. 2). The η_c 's of MB-7, MB-8, and MB-9 at 60°C were 1000, 850, and 700 poise, respectively. The T_c for MB-7, MB-8, and MB-9 at 60°C were 46, 70, and 86 min, respectively. T_c values increased with increasing MMA in the initial feed, whereas η_c decreased (Fig. 1).

The effect of composition on % transmittance was measured and the results are summarized in Table I. Percent transmittance decreased with increasing amounts of MMA in the feed. The mixture was clear before polymerization, whereas phase separation occurs, leading to turbidity, in the case of samples having a lower weight percent of polyurethane (PU). Nontransparent IPNs of PU-PMMA have been reported in the literature due to the incompatibility of PMMA with glycols.¹⁸

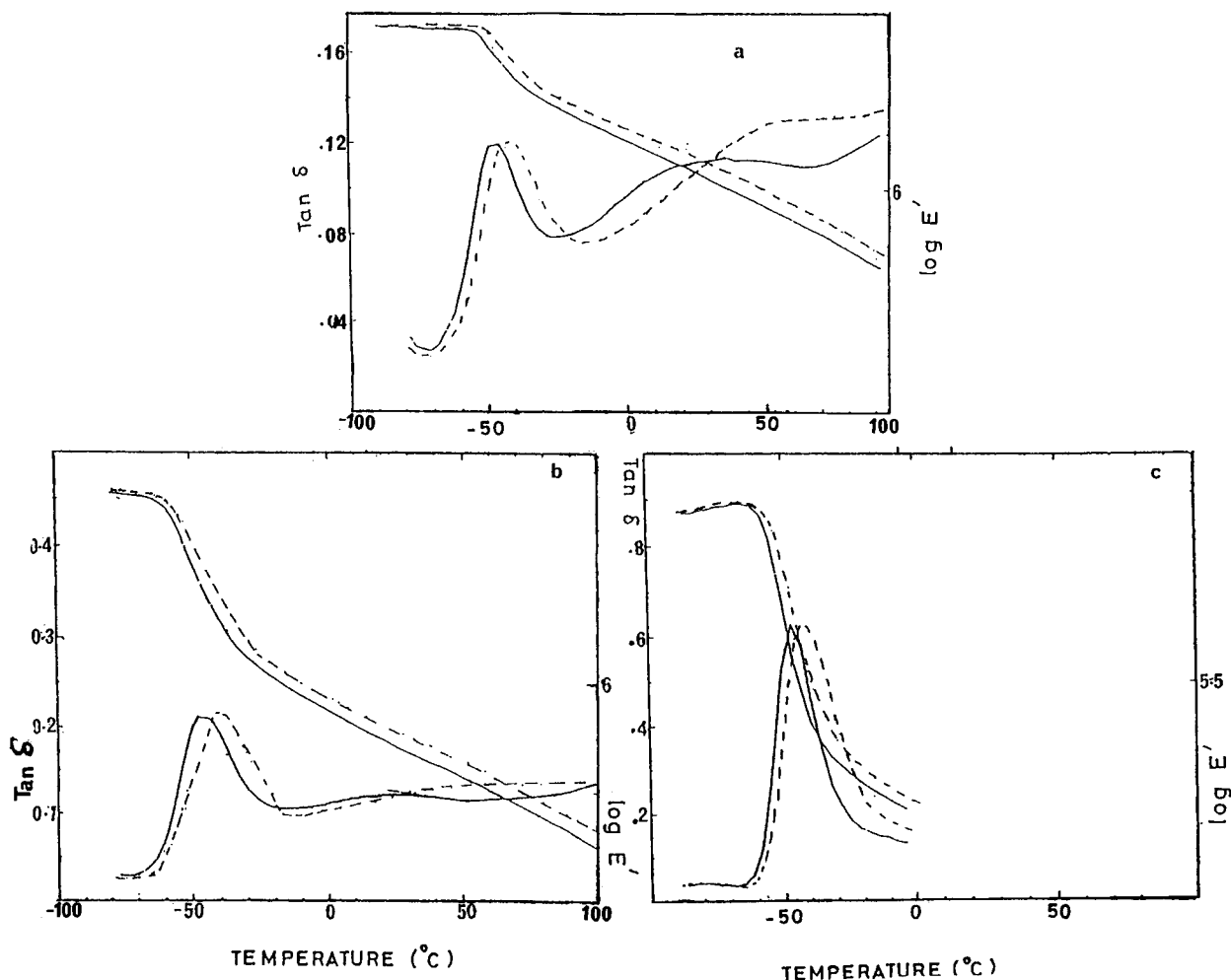


Figure 3 DMTA traces of various IPN samples at frequency of (—) 1 Hz and (---) 10 Hz: (a) MB-8; (b) MB-6; (c) MB-2.

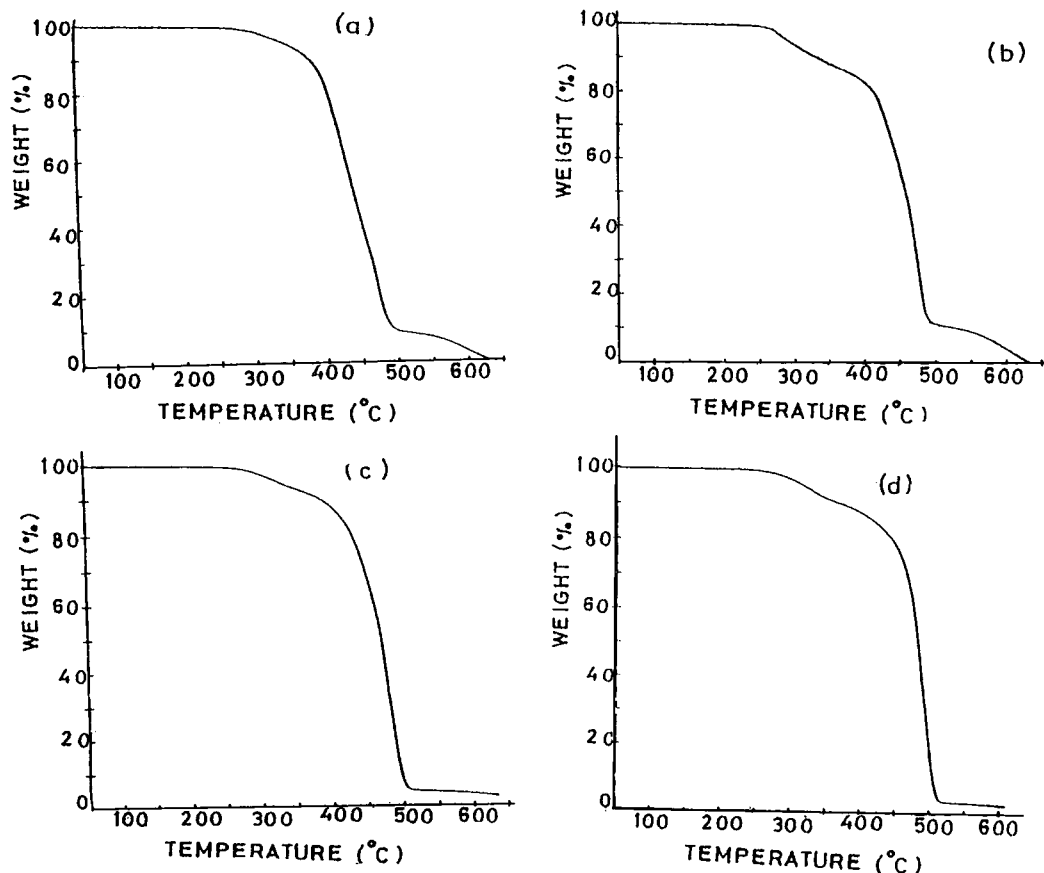


Figure 4 TG traces of (a) MB-8, (b) MB-6, (c) MB-4, and (d) MB-2.

From the stress-strain curve, tensile strength (MPa), percent elongation at break, and initial modulus were calculated and the results are summarized in Table II. Tensile strength and modulus increased with increasing the plastic (PMMA) component, whereas percent elongation decreased.

Figure 3 shows the variation in storage modulus (E') and $\tan \delta$ with temperature for various samples at 1 and 10 Hz. α -Relaxation (T_g) due to the PU component was observed as a sharp transition in the damping curve at a temperature of -46°C at 1 Hz. A broad transition was observed in the temperature range of 0 – 50°C , with a peak temperature at 20°C in all samples. This transition could be assigned to the β -relaxation temperature of PMMA. The β -relaxation at 20°C (1 Hz) due to the torsional liberation of the ester group has been reported in PMMA.¹⁹ The position of the α -relaxation peak of PU and the β -relaxation peak of PMMA remains unaffected with changing composition. Therefore, it can be concluded from these results that the PU/PMMA IPNs remain incompatible over the whole composition range studied.

Figure 4 shows the TG traces for various samples. A two-step degradation was observed in all the samples. The relative thermal stability of the various samples was evaluated by comparing decomposition temperature at various percent weight losses (% DT) and integral procedural decomposition tem-

Table III Thermal Behavior of PU/PMMA IPNs in Nitrogen Atmosphere

Sample Designation	Decomposition Temperatures ($^\circ\text{C}$) at Various % Weight Losses				IPDT ($^\circ\text{C}$)
	20	30	40	50	
MB-1	460	475	485	490	479
MB-2	450	470	480	485	460
MB-3	435	455	465	475	458
MB-4	435	450	465	470	454
MB-6	415	435	450	460	452
MB-8	410	425	435	445	447

perature (IPDT). IPDT was calculated in the temperature range of 50–500°C for all the samples using Doyle's method.²⁰

All the samples were stable up to 250°C, followed by a rapid weight loss around 400°C. Almost complete decomposition was observed beyond 500°C. Decomposition temperature at various percent weight losses and IPDT values increased with increasing urethane content in IPNs (see Table III). Higher thermal stability of IPNs could be explained on the basis that the MMA formed during degradation may act as a radical scavenger for PU degradation products. Lee and Kim also reported an enhancement in thermal stability of PU-PMMA and PU-PS IPNs.²¹

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