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Sequential Interpenetrating Polymer Networks Synthesized from Polyester Based Polyurethane and Poly(butyl methacrylate)

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In this article we review the synthesis and morphology as well as the physical and mechanical properties of full- and semi-interpenetrating polymer networks (IPNs) obtained from polyester based polyurethane (PU) and poly(butyl methacrylate) (PBMA). The polyurethane was subsequently interpenetrated with butyl methacrylate monomer and ethylene glycol dimethacrylate as a crosslinker by radical polymerization using benzoyl peroxide as an initiator. Both full and semi IPNs (PU/PBMA IPNs) were obtained as soft films when cast in a glass mold. All PU/PBMA IPNs were characterized with respect to the swelling (%), apparent densities, thermal stability, morphology and mechanical properties. The morphology of the IPNs was studied by scanning electron microscopy. The effects of variations of the blend ratios on the above-mentioned properties were examined. Increasing the polyurethane component in the composite system notably increased the mechanical properties of all the IPNs. Full-IPNs exhibited higher apparent densities, mechanical properties and thermal stability than the corresponding semi-IPNs.

Interpenetrating polymer networks (IPNs) are materials containing two polymers, each in network form. IPNs are an inextricable combination of two polymers, at least one of which is sequentially or simultaneously synthesized and/or crosslinked in the immediate presence of the other. IPNs represent a new approach to the problem of the mutual the incompatibility of polymers. The thus obtained multi-component system displays a broad range of properties from elastomers to high impact plastics.[1,2] Castor oil is a commercially important natural product containing unsaturation and hydroxyl functionality. It is a renewable resource material abundantly available in India. It could be explored to make new polymeric materials in the event of the exhaustion of petroleum, on which many of today's polymer industries are based. The hydroxyl functionality of castor oil is widely used to make crosslinked polyesters and polyurethanes.[3]

Voluminous work has been carried out on IPNs based on castor oil.[4–7] However, there is only scanty information available on polyurethanes based on hydrogenated castor oil,[8,9] which could be further explored in order to meet end-use requirements using the IPN concept. Hydrogenated castor oil is a modified (saturated) form of castor oil, which can be used to enhance the overall mechanical properties and thermal stability, and also to increase the extent of interpenetration in the IPNs system, rather than the formation of accidental bonds between the constituent polymers, which are undesirable. The synthesis of polyurethanes and their IPNs using hydrogenated castor oil will certainly be of immense importance to industry.

Polyurethanes based on polyester polyol are well known for their coating and elastomeric properties, as compared to conventional polyesters. The polyurethane polymer provides a good span for the spectrum of properties that can be achieved by the mere selection of raw materials. The polyol backbone mainly contributes to the elongation properties, whereas the isocyanate component takes care of the tensile properties. This makes PU resins ideally suitable for IPN systems. Until now, there has been no work reported regarding the synthesis and characterization of IPNs using polyester based polyurethane, except for our own reported work.[10–13] Hence, our laboratory has undertaken a detailed research program for carrying out the synthesis of low cost polyurethanes using hydrogenated castor oil based polyester polyol and their IPNs using acrylic monomers. In our previous work[13] we studied IPNs based on low cost polyurethane synthesised from hydrogenated castor oil by varying the NCO/OH ratio along with poly(butyl methacrylate). The IPNs of the preceding and present paper mainly differ in terms of structural features of the PU building blocks. The preceding work used urethane oil based on hydrogenated castor oil and isophorone diisocyanate, while the present work used polyester made out of hydrogenated castor oil, trimethylol propane and sebacic acid.

Poly(butyl methacrylate) is soft and elastomeric and has only a limited field of applications. One of the successful methods used to enhance its strength is to incorporate a second phase consisting of dispersed particles of a hard polymer into the soft and flexible PBMA matrix.

The present article specifically deals with the synthesis and characterization of elastomeric IPNs using polyester based polyurethane and poly(butyl methacrylate). Although both the IPN component networks, PU and PBMA, are more or less soft in nature when considered singly, when taken together as PU/PBMA in different ratios, PU plays the role of a hard component compared to PBMA.

The main objective of the present work was to produce elastomeric IPNs, and to investigate whether the combination of the two relatively elastomeric components can provide the desirable physical/mechanical properties, to comply with the requirements of industrially important elastomers, which could be substituted for natural and semi-synthetic elastomers.

Experimental

Materials. British standard specifications (BSS) grade hydrogenated castor oil [Acid value, 2.0 mg KOH/g; hydroxyl value, 162 mg KOH/g; and iodine value 2–5 (using Wij method)] was procured from M/s Jayant Oil Mill (Mumbai, India). Trimethylolpropane, [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] and sebacic acid were purchased from s.d. fine chem. Ltd., (Mumbai, India). Isophorone diisocyanate (IPDI) and benzoyl peroxide were obtained from E. Merck. (India) and triethanolamine [tris(2-hydroxyethyl)amine] from Loba Chemie (Mumbai, India). The catalyst dibutyltin dilaurate (DBTL) was purchased from SRL (India). Butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from E. Merck (India) and Fluka (Switzerland), respectively, and were freed from any stabilizer, initially by washing with aqueous NaOH (0.5%), followed by washing with water. Vinyl monomers were dried over anhydrous sodium sulfate and distilled under reduced pressure prior to use. All other reagents were of analytical grade and used without further purification.

Syntheses. HCO based Polyester Prepolymer:[6] Hydrogenated castor oil, sebacic acid and trimethylolpropane in a ratio of 1:1:1 gram equivalent along with dibutyltin dilaurate (as a catalyst) were taken in a reaction kettle equipped with a thermometer, a water condenser, a stirrer and a nitrogen inlet (Fig. 1, Step 1–3). This reaction mixture was heated and maintained at 180–200 °C in an atmosphere of nitrogen. The reaction was continued until an acid value < 5 mg KOH/g of polyester polyol was obtained. Water formed during the course of the reaction was removed by adding a small amount of xylene to the reaction kettle to form an azeotropic mixture, and distilling it with the aid of a Dean–Stark apparatus. The reaction mixture was treated with an excess of methanol in order to remove any unreacted starting materials. The thus obtained hydrogenated castor oil alkyd resin had a hydroxyl value and acid value of 211 mg of KOH/g and 4.6 mg of KOH/g on resin solids, respectively.[14] The overall yield at the end of the reaction was found to be 96.4% (approximately), as calculated experimentally.

Polyurethane Network (PU): Polyurethane was prepared by reacting one equivalent of polyester polyol based on hydrogenated castor oil (50 wt% in xylene) and two equivalents of IPDI along with catalyst DBTL (0.01% w/w based on isocyanate) in a reaction kettle equipped with a stirrer and a water condenser in a thermostated water bath. The reaction was carried out at 40 ± 2 °C, with continuous stirring for 2 h (Fig. 1, Step 4). After a period of 2 h, for effective crosslinking and chain extension, triethanolamine (1% w/w based on the total charge) was added to the reaction mixture and was thoroughly mixed for 5 min. The resulting mixture was then poured into the mold, where it was kept initially at 80 °C for 24 h and subsequently at 120 °C for 6 h to obtain homopolymer polyurethane.

Formation of Interpenetrating Polymer Networks (IPNs). Full-IPNs: IPNs were synthesized sequentially using various proportions of polyurethane (PU) and butyl methacrylate (BMA). The reaction kettle containing isocyanate terminated prepolymer polyurethane along with 1 wt% triethanolamine (for chain extension and curing) was added with a predetermined amount of BMA, 0.5 wt% EGDMA (based on BMA) as a crosslinker and 0.5 wt% benzoyl peroxide (based on BMA) as an initiator. The reaction mixture was thoroughly mixed for 3 min at 40 °C. The temperature was then subsequently raised to 80 °C to initiate PBMA polymerization. After stirring for 1 h and 30 min the reaction mixture was poured into the mold and kept in an air circulated oven, initially at 80 °C for 24 h, and finally at 120 °C for 6 h to facilitate complete network formation. Finally, pale yellowish-colored films of the IPNs were obtained.

Semi IPNs: The semi-IPNs were synthesized in the same way as the full-IPNs with the only difference being that the crosslinker for PBMA, i.e. EGDMA, was not added, thereby maintaining PBMA as a linear polymer. The scheme for the synthesis of polyurethane and its IPNs with PBMA is shown in Figs. 1a and 1b.

Characterization. The infrared spectra of the IPNs and the homopolymers were obtained from a Shimadzu FTIR 4200 series spectrophotometer using KBr pellets. The glass transition temperatures (T_{gs}) were determined by using a differential scanning calorimeter (DSC) on a Du Pont 9000 thermal analyzer at a heating rate of 10 °C/min under a dry nitrogen atmosphere in the temperature range -75 °C to $+100$ °C. The tensile strength and elongation at the breakpoint were measured at room temperature on a computerized tensile testing machine, Tensilon (R & D Electronics, India), using the ASTM D 638 method. Hardness measurements were made on a Shore A hardness tester using the ASTM D 2240 method. Swelling studies of the samples were carried out in water, ethyl methyl ketone (MEK) and toluene.[15] Using weighed strips of films of measured volumes, the apparent density of the films was obtained.[16] Thermograms of the samples were obtained on a Mettler TA 4000 (TG-50) thermogravimetric analyser (TGA) at a heating rate of 10 °C/min in a nitrogen atmosphere; and the energy of activation was computed using the Broido method.[17] The sample morphology was studied by scanning electron microscopy (SEM). The samples were prepared by freeze fracturing them in liquid nitrogen, and then applying a gold coating of approximately 200 Angstrom units. The gold-coated samples were mounted on SEM stubs with a silver adhesive paste.

Results and Discussion

Infrared Spectroscopy (IR). Figures 2(a), (b) and (c) exhibit the IR spectra of polyurethane, full-IPN (F-IPN2) and semi-IPN (S-IPN2), respectively. The IR spectra of polyurethane showed the characteristic absorption bands at 1740 and 3400 cm^{-1}, corresponding to urethane and amide II (–NH stretching), respectively. Because the prepolymer was isocyanate terminated, an intense and sharp band due to NCO was observed at 2270 cm^{-1}, and other bands related to various groups present in the polyester polyol. Moreover, the IR spectra of both the full- and semi-IPNs were similar to that of the polyurethane. The IR spectra of the IPNs showed that all of the bands corresponding to the urethane and BMA network (1100–1300 cm^{-1} characteristics of $\rangle$C=O stretching) were merged with each other, which made the spectra difficult to differentiate from each other. However, the full- and semi-IPNs were distinguished based on the of sharpness of the $\rangle$C=O stretching band, which is very sharp in semi-IPNs as compared to that exhibited in case of the full-IPNs. Further, the IR spectra of homopolymer and IPNs did not show the appearance of any additional bands, thereby ruling out the possibility of any chemical interaction between the component networks.

Glass Transition Temperature. The DSC curves of both

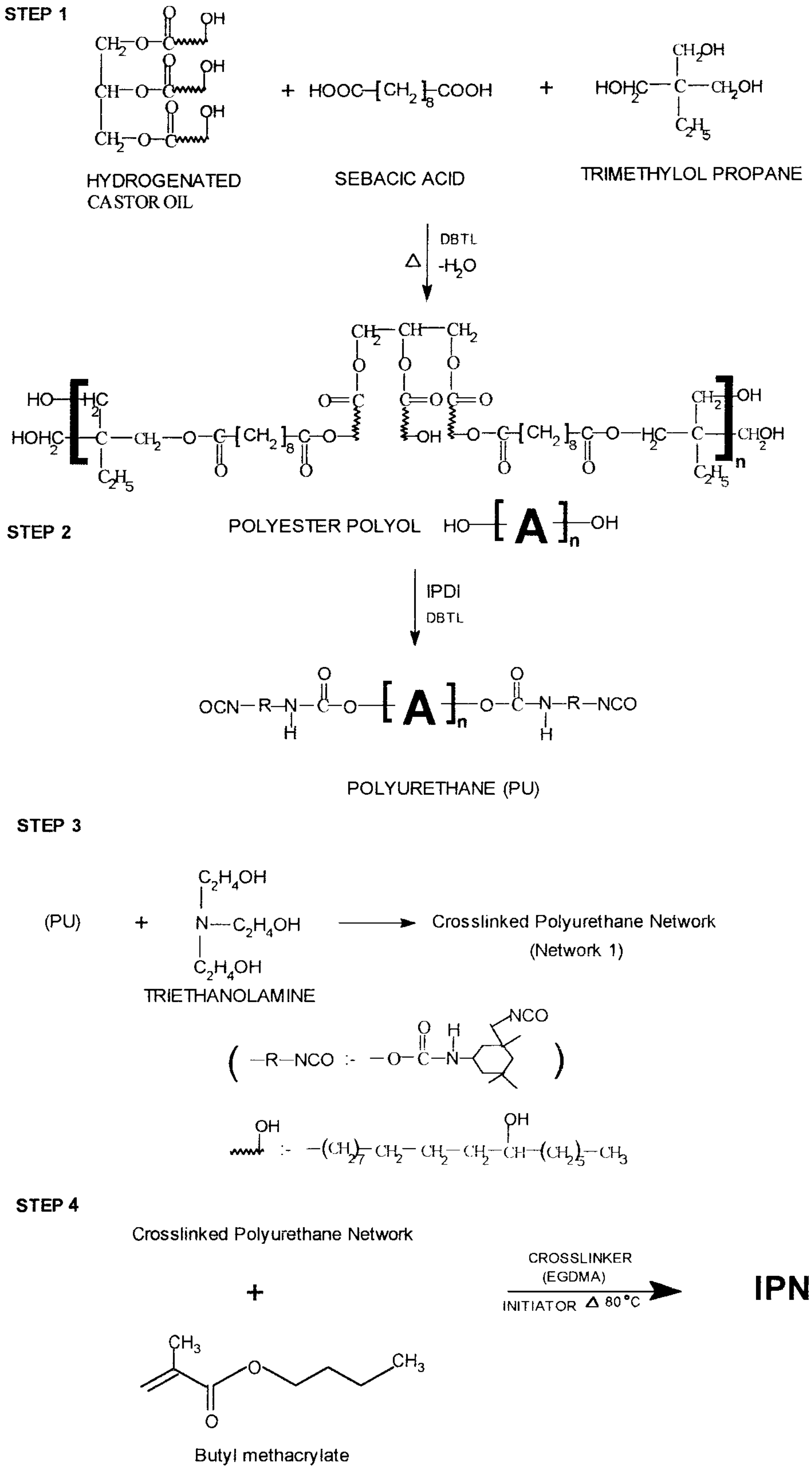


Fig. 1. Scheme for the synthesis of polyurethane and IPN.

the homopolymer and the representative IPNs (F-IPN2 and S-IPN2) shown in Fig. 3 exhibited the glass transition temperatures (T_{gs}) of both the PU (curve A) and PBMA (curve B) homopolymers at −16 °C and 30 °C, respectively. The full and semi-IPNs showed an inward shift, in T_{gs}, which indicated that some extent of interpenetration had occurred between PU

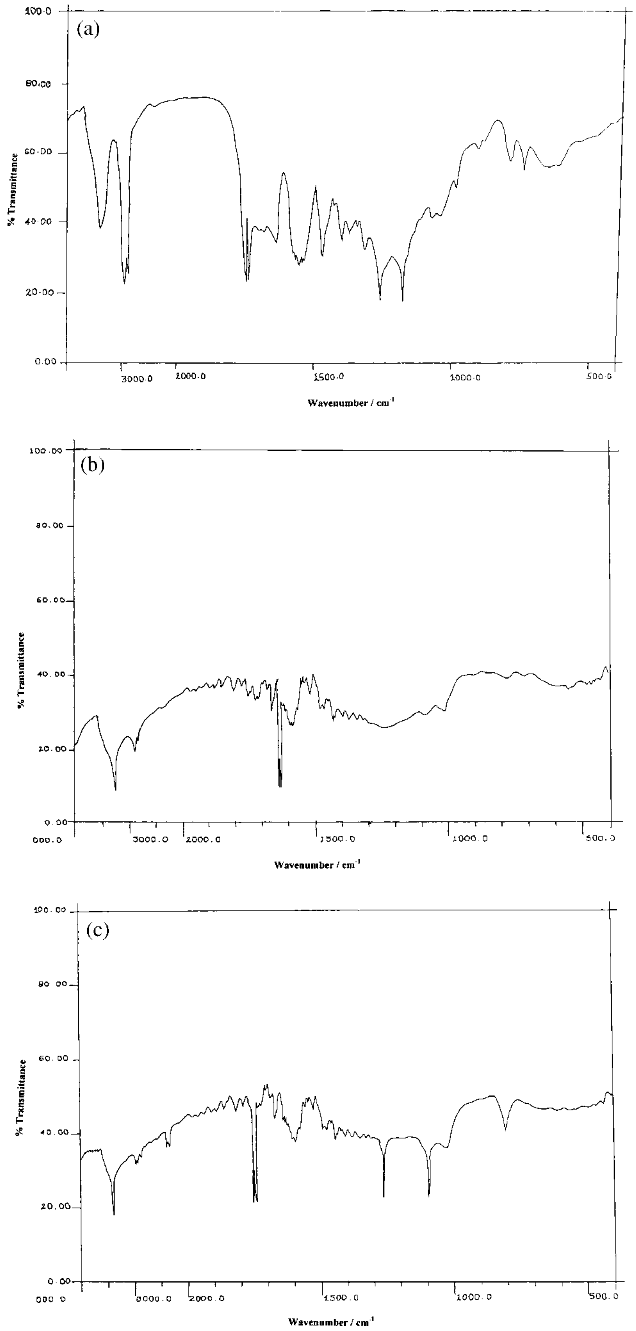


Fig. 2. IR spectra of PU-homopolymer (a), F-IPN 2 (b), and S-IPN 2 (c).

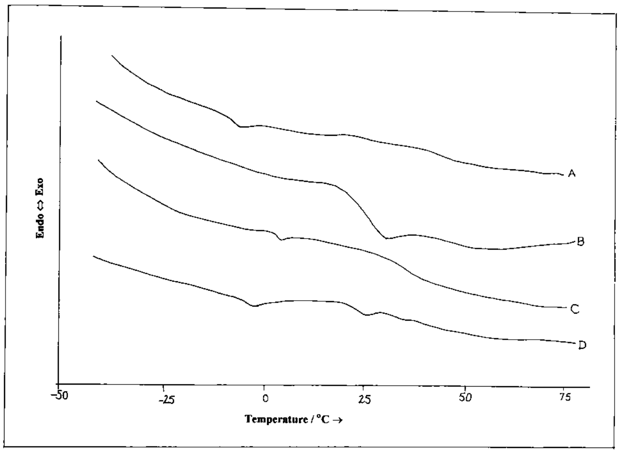
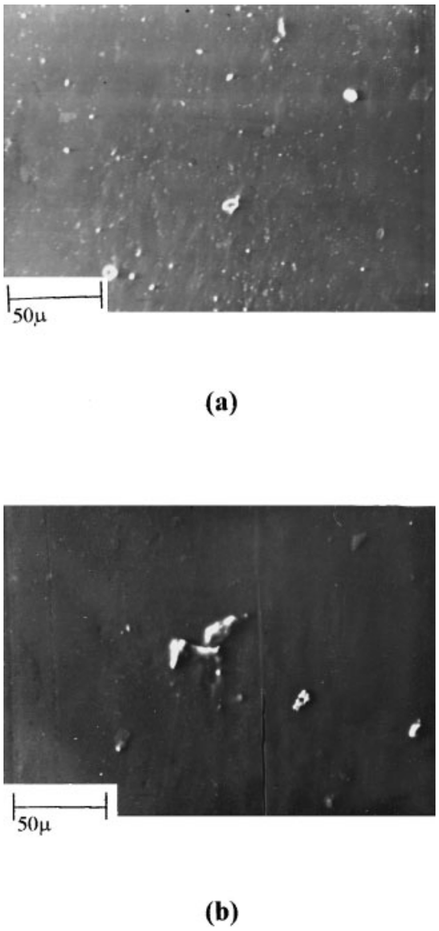


Fig. 3. DSC curves of homopolymer and representative IPNs, (A) PU-homopolymer, (B) PBMA-homopolymer, (C) F-IPN 2, and (D) S-IPN 2.



(a)

(b)

Fig. 4. SEM micrographs of the representative IPNs, (a) F-IPN 2, and (b) S-IPN 2.

and the PBMA homopolymer.[18,19] A single T_g was displayed by the representative full IPN (F-IPN2) (curve C), which lay between those of their constituent homopolymers, indicating a single-phase morphology. In contrast, the representative semi-IPN (S-IPN2) (curve D) exhibited two T_{gs} at -5 °C and 26 °C, shifted inwardly from those of the respective homopolymers, suggesting a heterophase morphology. The lower and higher T_g values exhibited by the semi-IPNs (S-IPN 2) were due to polyurethane and the PBMA transition, respectively. Further, the fact that only one T_g was obtained for full IPNs as against two T_{gs} in the case of semi-IPNs indicated that there was a better interpenetration in full-IPNs as compared to that in the semi-IPNs.

Morphology. The properties of the IPNs are dependent on the two-phase morphology that develops during the polymerization process. Most multicomponent systems under-go phase separation, yielding various morphologies according to their thermodynamic and kinetic environments. Studies of their morphological features have been central in multicomponent system research because the domain shapes and interfacial characteristics determine the key mechanical properties together with the glass transition temperature, etc.

The morphology of IPNs is revealed by electron micrographs of the representative 50% PU/50% PBMA IPNs (S-IPN2 and F-IPN2). Both of the representative IPNs showed microphase dispersion of the PBMA phase in the polyurethane matrix (Fig 4(a), (b)). In Fig 4(a) the size of the PBMA domains in F-IPN2 ranges from 3–12 µm, compared to the domain size of 5–23 µm, for S-IPN2 in Fig 4(b). The smaller domain size of the dispersed PBMA in the polyurethane matrix in Fig 4(a) compared to that in Fig 4(b), gives an indication that there is better interpenetration resulting in an improved compatibility between the two polymer systems in the case of the F-IPNs, and caused a decrease in the degree of phase separation compared to that of the semi-IPNs.

Mechanical Properties. The tensile strength, elongation at break and the Shore A hardness data of the IPNs and their component networks are given in Table 1. PBMA is characterized by the highest tensile strength and elongation compared to urethane networks. In all cases, a minimum in the tensile strength was observed at 25% polyurethane, and a maximum at 75% polyurethane. The lowering of the tensile strength, as observed at a larger fraction as high as 75% of PBMA in the IPN system, even though PBMA has a high strength compared to PU, can be attributed to the individual effect of the components present in the IPN system. PU is densely crosslinked as compared to PBMA, due to which the interpenetration of PBMA chains in the PU network is restricted up to some extent, causing a less extent of interpenetration in the IPN system.[20] However, the IPN system with 75% PU/25% PBMA composition has a high extent of interpenetration, because most of the PBMA chains became interpenetrated in the PU network, exhibiting a high tensile strength compared to IPN with a 25% PU/75% PBMA composition.

Table 1. Mechanical Properties of Homopolymers and Interpenetrating Polymer Networks (IPNs) of PU/PBMA

Sample code	Composition PU/PBMA	Tensile strength	Elongation /% at break	Hardness Shore A
	wt%	MPa		
		Homopolymers		
PU	100/0	1.08	104	82
PBMA	0/100	6.9	230	70
		Full-IPNs		
F-IPN 1	25/75	0.62	124	74
F-IPN 2	50/50	0.85	114	77
F-IPN 3	75/25	0.99	106	80
		Semi-IPNs		
S-IPN 1	25/75	0.45	133	72
S-IPN 2	50/50	0.79	121	77
S-IPN 3	75/25	0.92	110	79

Thus, the tensile strength increased along with an increase in the extent of interpenetration in the IPNs, which is because of increasing the PU content in the IPN system. Moreover, it can be noted from Table 1 that the elongation at break decreased with a corresponding increase in the polyurethane content in the PU/PBMA IPNs.

Furthermore, it was found that the semi-IPNs exhibited higher values of percentage elongation for all proportions compared to the corresponding full-IPNs. This can be explained by considering the fact that in the semi-IPNs, because one of the constituent polymers (PBMA) remains linear, it exhibits a higher mobility, whereas in the case of full-IPNs the higher degree of crosslinking restricts the mobility of the PBMA chains, because even they are crosslinked. It was observed that as the proportion of polyurethane in the blend was increased, the hardness (Shore A) also increased, because the soft and flexible PBMA was being substituted by more and more of polyurethane.

Thermogravimetric Analysis. The thermal behavior of the representative semi and full IPNs (S-IPN2 and F-IPN2) and those of the urethane and PBMA homopolymers are in close approximation to each other (Table 2). The clustering of the PU/PBMA curves in Fig. 5 indicates that there was no significant difference in the degradation behavior of the IPNs. As expected, in the case of a PU homopolymer and the representative semi and full IPNs (S-IPN2 and F-IPN2) two-stage decomposition was observed, whereas, only one-stage decomposition was observed during the degradation process of the PBMA homopolymer. Both the S-IPN2 and F-IPN2 were stable up to 240 °C, followed by a substantial loss in weight at around 290–500 °C. A weight loss of about 50% in the temperature range of 290–390 °C can be attributed to the breaking of a –NH bond in the polyurethane and de-cross-linking of the two network forms of the IPNs. In this temperature range, the monomer attached to the backbone of the PU network is most probably detached by a free radical mechanism from the trunk of the main constituent polymer. The final weight loss that occurred in the range of 390–500 °C can be ascribed to a breakage of the bonds of the homopolymer PBMA and polyol decomposition of polyurethane, which is bound to be a slow process.[21] For IPNs and the PU homopol-

Table 2. Thermal Decomposition of Homopolymers and Interpenetrating Polymer Networks (IPNs) of PU/ PBMA

Sample code	Decomposition stage/ °C		Activation energy/kJ mol^{-1}	
	Stage 1	Stage 2	Stage 1	Stage 2
PU	290–390 °C	390–500 °C	123	159
PBMA	275–450 °C	—	155	—
F-IPN 2	240–390 °C	390–500 °C	123	141
S-IPN 2	240–390 °C	390–500 °C	117	140

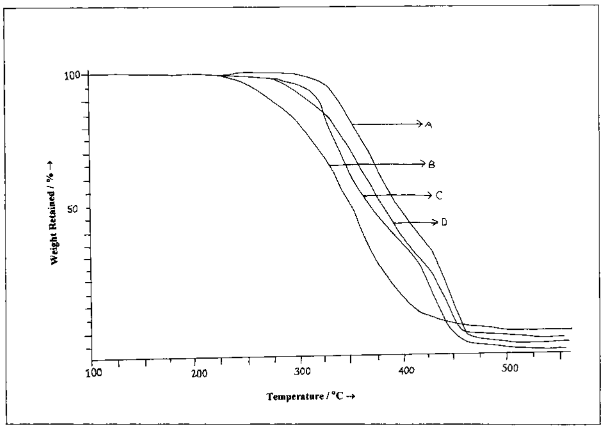


Fig. 5. TGA curves of homopolymer and representative IPNs, (A) PU-homopolymer, (B) PBMA-homopolymer, (C) F-IPN 2, and (D) S-IPN 2.

Table 3. Swelling Properties of Homopolymers and Interpenetrating Polymer Networks (IPNs) of PU/ PBMA

Sample code	Composition PU/PBMA	Swelling/%		
	wt%	Toluene	MEK	Water
		Homopolymers		
PU	100/0	40	58	1
PBMA	0/100	190	179	1
		Full-IPNs		
F-IPN 1	25/75	116	121	1
F-IPN 2	50/50	102	108	1
F-IPN 3	75/25	82	94	1
		Semi-IPNs		
S-IPN 1	25/75	128	136	1
S-IPN 2	50/50	114	129	1
S-IPN 3	75/25	98	99	1

ymer, the activation energy values (Table 2) are considerably higher in the temperature range of 390–500 °C than in the range of 290–390 °C, indicating that the degradation process is relatively faster in the first stage compared to the second stage.

Swelling Percentage. The percentage of swelling was calculated for each IPN by using a procedure given Sperling and Mihalakis, which is written as

$$\text{Swelling\%} = [(\text{Weight of swollen polymer} - \text{Weight of dry polymer}) / \text{Weight of dry polymer}] \times 100$$

The percentage swelling data of all IPNs were determined using a non-polar solvent (toluene), polar solvents (ethyl methyl ketone) and water, which are represented in Table 3. The IPNs did not dissolve in solvents because of high crosslinking between their components. The data (Table 3) show that the PBMA homopolymer exhibits a very high swelling percentage, as compared to the PU homopolymer. It was observed that the percentage of swelling was greater for semi IPNs than for full IPNs. A possible reason for this is that in the case of semi IPNs the crosslinking density is low because one of the constiuent polymer (PBMA) is linear, and hence the solvent can penetrate to the core of the IPN matrix with ease, thereby increasing its swellability. Further, it was observed that the swelling percentage in the case of semi- as well as the full-IPNs, went on decreasing with an increase of the polyurethane content in the IPNs. This can be attributed to the fact that the PU homopolymer forms a very tight network, as compared to the PBMA homopolymer; hence, and the proportion of the PU homopolymer increased in the blend, more and more highly swellable PBMA homopolymer was being replaced by the PU homopolymer. Moreover, it was observed that in semi- and full-IPNs the extent of swelling was greater in MEK than in toluene. This can be attributed to the polar nature of MEK.

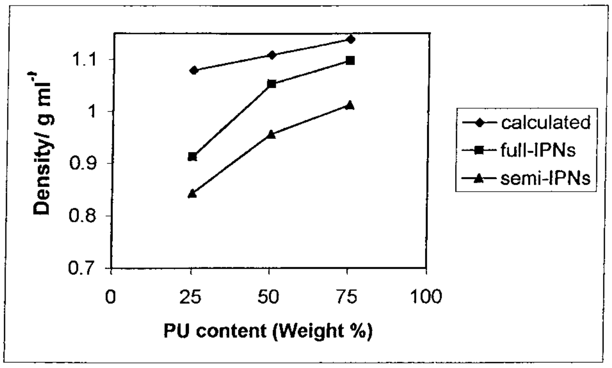


Fig. 6. Graph of density versus PU contents (wt%) of the IPNs.

Apparent Density. Figure 6 shows the trends of changes in the density for the semi- and full IPNs of the PU/PBMA system. The calculated densities, based on the volume additive principle, which states that [$d = w_1d_1 + w_2d_2$], where d is the density of the IPN sample, w_1 and w_2 are the weight fractions of the constituents, and d_1 and d_2 are the corresponding densities, respectively. The density of the polyurethane homopolymer (1.168 g/cm^3) is higher than that of the PBMA homopolymer (1.050 g/cm^3); hence, it can be logically appreciated that the density value of the IPN system should increase proportionately when PU substituted more and more PBMA. Moreover, the density curves of the full IPNs and semi IPNs lay below the curve, representing the calculated densities. Comparing the densities of full and semi IPNs, it was observed that the actual and calculated densities do not match with each other, which implies that there seems to be a low-density amorphous region. The deviation between the calculated and observed densities is dependent on the amount of such an interpenetrating layer in the blend.[22] Further, it is apparent from the Fig. 6 that the full IPNs exhibited higher density values than their corresponding semi IPNs. On the contrary, in the case of full-IPNs, the higher degree of crosslinking restricts the statistical probability of threading, and thereby precludes the reinforcing effect of interpenetration; therefore, the density curve of full-IPNs lies below the density curve of semi-IPNs. Finally, it can be noted that the densities of all the IPNs in each case lay between the densities of the parent networks.

Conclusion

Both the semi- as well as the full-IPNs were highly transparent, indicating a good compatibility between the constiuent polymers. The full-IPNs exhibited better compatibility because of an enhanced interpenetration, as revealed by SEM. The slight shift in T_{gs} of the constituent polymers indicated some extent of interpenetration in the PU/PBMA IPN system. All of the IPNs of the PU/PBMA system showed phase separation, good thermal stability, solvent resistance, hardness and the mechanical properties over and above those of the component networks. The elastomeric properties are attributed to the phase separation of PU and PBMA. The above study has demonstrated that the bulk properties of these PU/PBMA IPNs depend upon the nature and extent of the phase separation of the constituent polymers (PU and PBMA) in the PU/PBMA IPN system.

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