

Interpenetrating Polymer Networks Based on Hydrogenated Castor Oil–Isophorone Diisocyanate and Poly(butyl methacrylate)

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Hydrogenated castor oil was reacted with isophorone diisocyanate under different stoichiometric NCO/OH ratios to obtain polyurethanes. These polyurethanes were subsequently interpenetrated with butyl methacrylate monomer using ethylene glycol dimethacrylate as a crosslinker by radical polymerization using benzoyl peroxide as an initiator. Polyurethane/poly(butyl methacrylate) interpenetrating polymer networks (PU/PBMA IPNs) were obtained as tough films by casting in a glass mould. All IPNs were characterized for their resistance to thermal behavior, swelling (%), and mechanical properties. The morphology of the IPNs was studied by scanning electron microscopy. Enhanced mechanical properties were obtained with an increase in the NCO/OH ratios in addition to the regular trend obtained by increasing the polyurethane component in the blend.

Interpenetrating polymer networks (IPNs) were first synthesized by Miller in the 1960s. Since then, the jargon has been used to describe the combination of two or more different polymer networks, which consist of solely physical entanglements of the polymer chains synthesized either simultaneously or sequentially with respect to each other.[1–4] IPNs represent a new approach to the problem of mutual incompatibility of polymers.

Castor oil is a commercially important natural product containing unstauration and hydroxy functionality. The tri-functional castor-oil molecule gives opportunities to make renewable polymeric materials, which meet the needs to polymer industries. The conversion of castor oil into its urethane prepolymer, and then a sequential or simultaneous interpenetration of vinyl monomers into the urethane network to obtain high-strength polymers has been studied and reported on by many authors.[5–7] However, though scanty information is a available on the synthesis of hydrogenated castor-oil based polyurethanes,[8–9] their utilization in IPNs has not been explored. Hydrogenated castor oil is a modified oil with a saturated double bond in the castor-oil chains, which can be used to enhance the mechanical properties and thermal stability, and to increase the extent of interpenetration in the IPNs system.

Hence, our laboratory has undertaken a detailed research program for carrying out the synthesis of low-cost polyurethanes and their IPNs using hydrogenated castor oil, which can prove to be of immense importance to industry. The present artical deals with the synthesis and characterization of polyurethane/poly(butyl methacrylate) (PU/PBMA) IPNs. These IPNs were characterized with reference to the morphology as well as the mechanical, physical, and thermal properties.

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 (using Wij method), 2-5] was procured from M/s Jayant Oil Mill (Mumbai, India). Isophorone diisocyanate (IPDI) and benzoyl peroxide were obtained from E. Merck, (India) and triethanolamine [tris(2-hydroxy ethyl)amine] from Loba Chemie (Mumbai, India). The catalyst dibutyltin dilaurate (DBTL) was purchased from the local market. 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. Polyurethane Prepolymer (PU): Polyurethane prepolymer was prepared by reacting hydrogenated castor oil (50 wt% in xylene) and IPDI in various NCO/OH ratios, and along with the catalyst DBTL (0.01% w/w based on isocyanate) was taken in a reaction kettle equipped with a stirrer and a water condenser in a thermostated water bath. The reaction was carried out at 80 ± 2 °C with continuous stirring for 2 h. In order to facilitate crosslinking and chain extension, at the end of 2 h triethanolamine (1% w/w based on the total charge) was added to the charge and thoroughly mixed for 5 min. The resulting mixture was then poured into a mould, where it was initially kept at 80 °C for 24 h, and subsequently at 120 °C for 6 h to obtain polyurethane.

Formation of Interpenetrating Polymer Networks (IPNs): IPNs were synthesized sequentially using various proportions of polyurethane prepolymer and butyl methacrylate (BMA). Polyurethane prepolymer and BMA along with a benzoyl peroxide initiator (0.5% w/w based on BMA) were added to the reaction kettle and were intimately mixed for 3 min at 40 °C. The temperature was then raised to 80 ± 2 °C and the reaction was further continued for 1 h. Thereafter, the reaction mixture was poured into the mould and kept in an air-circulated oven, initially at 80 °C for 24 h, and finally at 120 °C for 6 h, to ensure complete crosslinking and polymerization. Finally, pale yellowish-colored films of the

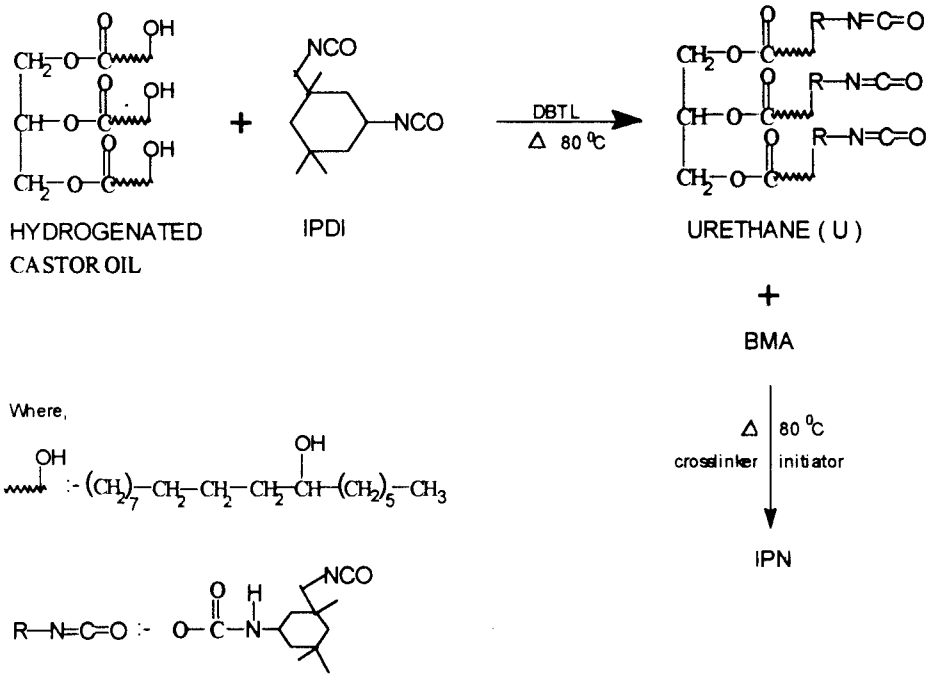


Fig. 1. Scheme for the synthesis of polyurethane prepolymer and IPN.

IPNs were obtained. The scheme for the synthesis of urethane and its IPNs with PBMA is shown in Fig. 1.

Characterization. The infrared spectra of the newly synthesized IPNs were obtained from a Shimadzu FTIR 4200 series spectrophotometer using KBr pellets, whereas in the case of urethane prepolymer, being in the liquid form, a thin film was cast over a NaCl block. The glass transition temperatures (Tgs) were determined by differential scanning calormetry (DSC) using a Du Pont 9000 thermal analyzer at a heating rate of 10 °C/min under a dry nitrogen atmosphere in the temperature range −50 °C to +150 °C. The tensile strength and elongation at the break point were measured at room temperature on a computerized tensile testing machine Tensilon (R & D Electronics, India), using the ASTM D 638 standard. The hardness was determined with a Shore A durometer using the ASTM D 2240-75 standard. Swelling studies of the samples were carried out in water, ethyl methyl ketone (MEK) and toluene.[10] Thermograms of the samples were obtained on a Mettler TA 4000 thermogravimetric analyser (TGA) at a heating rate of 10 °C/min in a nitrogen atmosphere, and the energy of activation was computed using Broido's method.[11] 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). The IR spectra of polyurethane prepolymer showed characteristic absorption bands at 1740 and 3400 cm^{-1}, corresponding to urethane and amide II (–NH stretching), respectively. As the prepolymer was isocyanate terminated, an intense, sharp band due to NCO was observed at 2270 cm^{-1}. The IR spectra of the IPNs showed all of the bands corresponding to the urethane and BMA network, and 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 representative IPNs (IPN 2, IPN 5, IPN 8) were scanned in the temperature range of −25 °C to +150 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. The DSC curves of both the homopolymer and the representative IPNs (IPN 2, IPN 5, IPN 8) are shown in Fig. 2. It exhibited the glass transition temperatures (Tgs) of both the PBMA homopolymer and the representative IPNs (IPN 2, IPN 5, IPN 8) at 30 °C and 23 °C, respectively. The inward shift of Tgs of representative IPNs (IPN 2, IPN 5, IPN 8) with respect to the Tg of PBMA homopolymer suggests that interpenetration had occurred between PU and PBMA to some extent.[3,12–13] Moreover, the appearance of a single Tg of the representative IPNs (IPN 2, IPN 5, IPN 8) confirmed the homogeneous phase morphology without any influence due to a variation in the NCO/OH ratio of the prepolymer polyurethanes in the PU/PBMA system.

Mechanical Properties. From the data of the mechanical properties of IPNs (Table 1) it can be revealed that as the composition of PU in the PU/PBMA IPNs increased, the mechanical properties, such as the tensile strength and hardness, increased, and the % elongation decreased. It was interesting to find that PU/PBMA IPNs followed the same trend with a change in the NCO/OH ratio of prepolymer polyurethane. The PU/PBMA IPNs with the same composition, but different NCO/OH ratios, showed an increase in the tensile strength and hardness along with a decrease in the % elongation. Because the PU is a hard component compared to PBMA, there is no wonder why the properties of IPNs, such as hardness and tensile strength, increased, and the % elongation decreased with increasing proportion of PU. But, surprisingly, the same trend was also observed while playing with the NCO/OH ratio. This can be attributed to the fact that, as the NCO/OH ratio in-

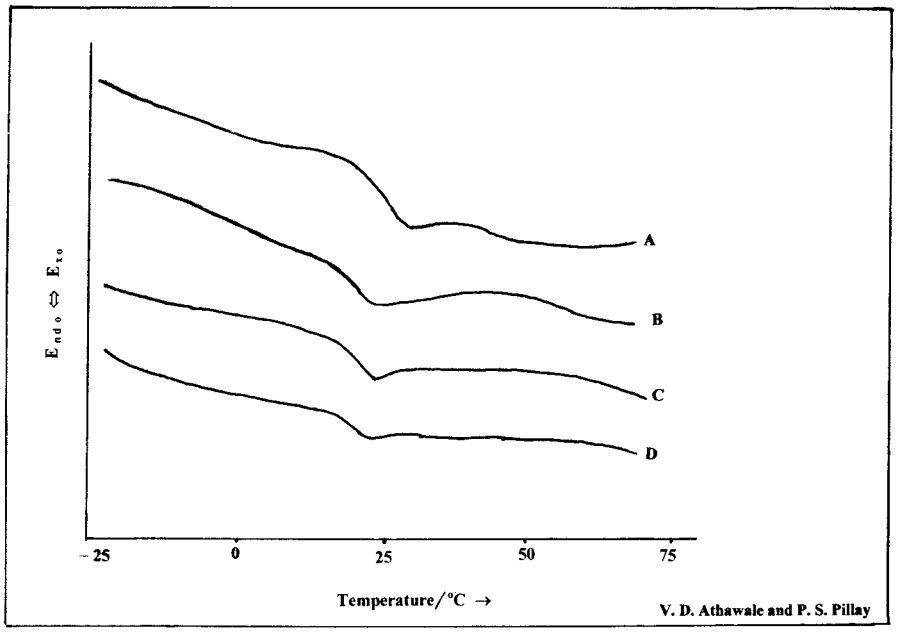


Fig. 2. DSC curves of homopolymer and representative IPNs. (A) PBMA-homopolymer, (B) IPN 2, (C) IPN 5, (D) IPN 8.

Table 1. Mechanical Properties of Homopolymer and IPNs

Sample code	NCO/OH ratio	Composition PU/PBMA wt%	Tensile strength MPa	Elongation %	Hardness Shore A
IPN 1	1.8	25/75	0.2	88.0	75
IPN 2	1.8	50/50	1.1	82.2	78
IPN 3	1.8	75/25	2.3	74.0	80
IPN 4	2.0	25/75	0.9	78.3	79
IPN 5	2.0	50/50	1.7	69.4	82
IPN 6	2.0	75/25	2.8	62.0	85
IPN 7	2.2	25/75	1.4	73.5	84
IPN 8	2.2	50/50	2.5	65.4	87
IPN 9	2.2	75/25	3.6	58.7	91
PBMA	—	0/100	6.9	230	70

creased, the number of free NCO groups of the PU component increased, which might have worked as an active site for further crosslinking of the PU component during the curing of the IPNs. This extra crosslinking of the PU would have been reflected as an increase in the tensile strength and hardness, while undergoing a decrease in the % elongation.

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

$$\text{Swelling}\% = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer.}}$$

The percentage swelling data of all the IPNs were determined by non-polar solvet toluene, polar solvent MEK (ethyl methyl ketone), and water, which are represented in Table 2. The IPNs did not dissolve in solvents because of high crosslinking between their components. Marginal swelling of all the IPNs was observed in toluene and MEK, whereas, no swelling was observed in water. It is known that along with an increase in the NCO/OH ratio, the chemical and solvent resistance of polyurethane is improved.[14] In contrast, the IPNs synthesized in the present study did not show much change in the swelling percentage with varying the NCO/OH ratio of prepolymer

Table 2. Swelling Percentage of Homopolymer and IPNs

Sample code	Composition UA/PBMA wt%	NCO/OH ratio	Swelling/%		
			Toluene	MEK	Water
IPN 1	25/75	1.8	88	102	1
IPN 2	50/50	1.8	95	112	1
IPN 3	75/25	1.8	104	130	1
IPN 4	25/75	2.0	95	114	1
IPN 5	50/50	2.0	116	128	1
IPN 6	75/25	2.0	124	145	1
IPN 7	25/75	2.2	98	120	1
IPN 8	50/50	2.2	126	132	1
IPN 9	75/25	2.2	144	148	1
PBMA	0/100	—	190	179	1

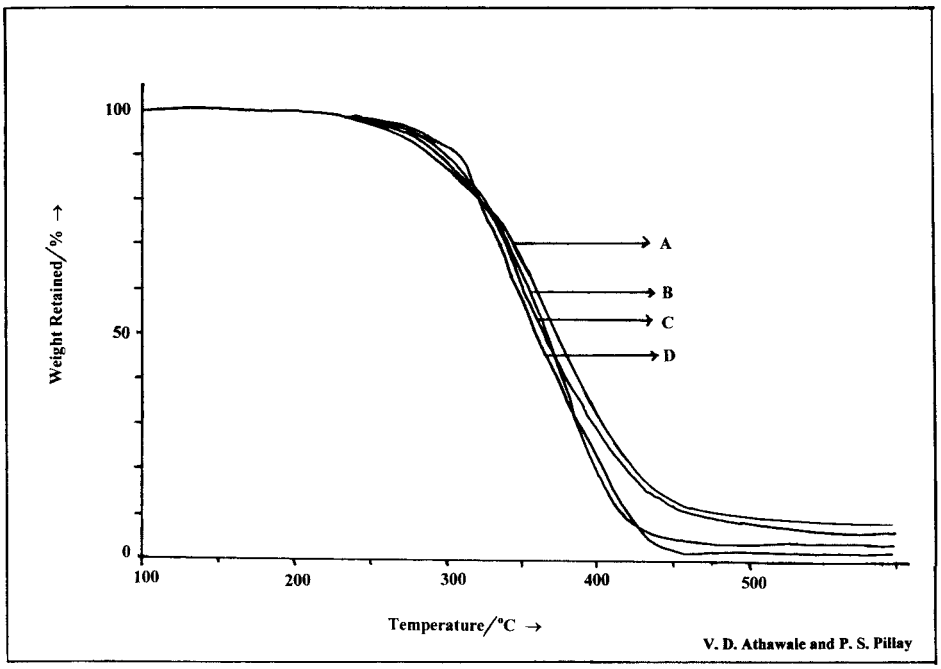


Fig. 3. TGA curves of homopolymer and representative IPNs. (A) PBMA-homopolymer, (B) IPN 2, (C) IPN 5, (D) IPN 8.

Table 3. Thermal Decomposition of Homopolymer and IPNs

Sample code	NCO/OH ratio	Decomposition stage/°C		Activation energy kJ mol^{-1}	
		Stage 1	Stage 2	Stage 1	Stage 2
PBMA	—	275–450	—	155	—
F-IPN 2	1.8	200–360	360–500	126	139
F-IPN 5	2.0	200–360	360–500	118	134
F-IPN 8	2.2	200–360	360–500	105	134

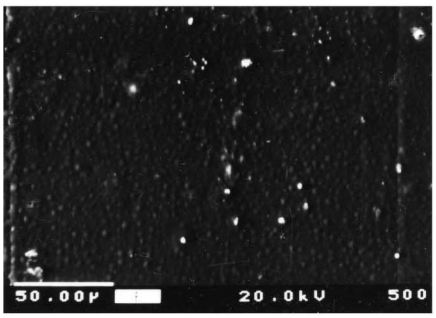
polyurethane and the PU/PBMA composition in the PU/PBMA IPNs. This may have been due to the formation of a closely packed interpenetrating network system between prepolymer polyurethane and PBMA, thus limiting the swelling of any one of the components in the PU/PBMA IPN system. Moreover, a perusal of Table 2 also revealed that the PU/PBMA IPNs, irrespective of the NCO/OH ratio of prepolymer polyurethane and various PU/PBMA compositions, showed an increase in the swelling percentage along with an increase in the PBMA content, and was more prominent in MEK than in toluene, because of the polarity of MEK.

Thermal Degradation. The clustering of the TGA curves in Fig. 3 indicates that there was no significant difference in the degradation behavior of the IPNs. Thus, the NCO/OH ratio of prepolymer polyurethane in the PU/PBMA IPN system does not have any influence on the thermal stability of the IPNs.

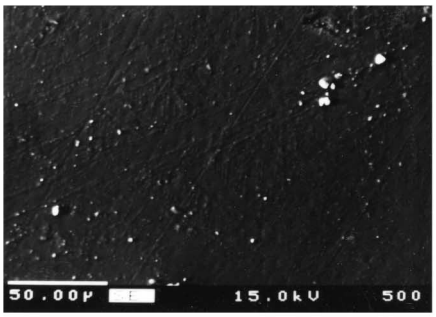
The PBMA homopolymer showed a single-stage thermal decomposition curve, which indicated an unzipping of the butly methacrylate (PBMA) monomer. However, the representative IPNs (IPN 2, IPN 5, IPN 8) exhibited two stages during the process of thermal degradation. Stage I corresponded to urethane bond breaking at between 200 °C to 360 °C. Stage II is the decomposition of polyol at 360 °C to 500 °C. Moreover, it also indicated complete decrosslinking and thermal degradation of the IPNs. It is clear from the activation–energy (E^*) data, (Table 3) that the IPNs showed an enhancement in the thermal stability over that of the PBMA homopolymer. The relatively lower activation energy for stage I compared to stage II for each of the representative IPNs (IPN 2, IPN 5, IPN 8) indicated that the first degradation step was very fast and less stable, whereas the second step was delayed, but relatively more stable.

Morphology. The scanning electron micrographs reveal the morphology of the representative IPNs (IPN 2, IPN 5, IPN 8), respectively, in Fig. 4 (a, b, c). In the micrographs, the polyurethane is present as the continuous phase dispersed with small white dots of PBMA, which indicated a phase separation. The domains of the dispersed phase were clearly regular, and spherical in shape. The PBMA domain size of the representative IPNs (IPN 2, IPN 5, IPN 8) in Fig. 4 (a, b, c) were 2–8 μm, 1–7μm, and 1–5μm, respecti vely, which showed that the IPNs derived from prepolymer polyurethanes with a higher NCO/OH ratio exhibited a decrease in the phase separation, indicating a homogeneous phase morphology. This can be attributed to an improved compatibility between the constituent polymers caused by the short chain length of the PU prepolymer having a higher NCO/OH ratio.

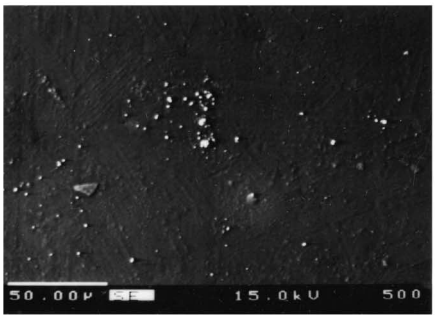
Conclusions. Based on the above investigation, it is clear that the decomposition process of the IPNs was hardly affected



4(a)



4(b)



4(c)

Fig. 4. SEM micrographs of the representative IPNs. 4(a) IPN 2, 4(b) IPN 5, 4(c) IPN 8.

by the NCO/OH ratio of prepolymer polyurethane. The IPNs showed good thermal stability, solvent resistance, and enhanced mechanical properties, as compared to that of PBMA component networks. The micrographs of the IPNs exhibited an enhanced homogeneous phase morphology along with an increase in the NCO/OH ratio of prepolymer polyurethane. The slight shift in the T_g value of the IPNs compared to the T_g value of PBMA homopolymer revealed that some extent of the interpenetration occurred in the PU/PBMA system. Moreover, the single T_g value of the IPNs with PU component having a different NCO/OH ratio indicated the homogeneous nature of the PU/PBMA IPN system and better compatibility within the system, itself. Hence, it can be concluded using the IPN concept, that it is possible to design the most desirable material for specific end-use requirements.

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