

Mechanical properties of simultaneous interpenetrating polymer networks of castor oil based polyurethane and polystyrene

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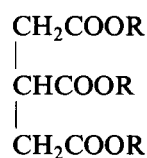
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Castor oil and 4,4'-diphenyl methane diisocyanate based polyurethane (PU)–polystyrene (PS) simultaneous interpenetrating polymer networks (IPNs) were synthesized with various PU/PS ratios (100/0, 90/10, 80/20, 75/25, 60/40 and 50/50). Mechanical properties (tensile strength, % elongation, elastic modulus, wear resistance, tear resistance and Shore-A hardness) of the IPNs showed a significant improvement beyond a critical styrene level (25% by weight). However, % elongation at break showed a maximum at 40% styrene. PU/PS IPNs of a fixed styrene level with varying amounts of styrene crosslinking agent, divinyl benzene (DVB), were also synthesized. These materials showed a significant improvement in the mechanical properties with increasing concentration of DVB. The observed behaviour is explained on the basis of results from swelling and Soxhlet extraction studies. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Castor oil is a relatively inexpensive source of secondary hydroxyl groups, and it has been used as a polyol to synthesize cost-effective polyurethane elastomers. Castor oil is a triglyceride of fatty acids with ricinoleic acid being the major constituent¹, and has the general structure.



with $R \equiv (\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CHOH}(\text{CH}_2)_5\text{CH}_3$ for ricinoleic acid. Its trihydroxyl structure helps in producing highly crosslinked urethane systems. The long pendant chains of the fatty-acid impart flexibility and hydrolysis-resistance to the network, and the double bonds present in the castor oil may serve as grafting centres. Urethane polymers exhibit excellent abrasion resistance. However, disadvantages with the use of castor oil include low hydroxyl number leading to inherently low modulus materials, a sluggish rate of curing of the secondary hydroxyl groups² and structural irregularity due to steric hindrance offered by the long pendant fatty acid chains during urethane formation, resulting in low tear strength³. In order to improve the overall mechanical strength, castor oil based polyurethane (COPU)

networks can be blended with polystyrene (PS) to form interpenetrating polymer networks. These encompass a wide range of novel polyblend materials in which at least one polymer is crosslinked in the immediate presence of the other. Depending on the route of synthesis they can be simultaneous IPNs, sequential IPNs, semi-IPNs, etc.⁴.

Castor oil polyurethane and polystyrene IPNs have been investigated in a number of previous studies. Sperling and coworkers^{5–9} carried out an exhaustive study of simultaneous IPNs based on TDI, castor oil and PS crosslinked with 1% divinyl benzene (DVB), and some of the results are reviewed below. Increasing PS content showed a transition from a stress–strain behaviour typical of reinforced elastomers to one typical of toughened plastics⁵. Increase in the isocyanate index from 0.75 to 0.95 gave a decrease in domain size and improved phase continuity, resulting in a higher tensile strength and lower elongation⁵. The time of mixing was found to have a significant effect on the morphology of the IPN⁶, particularly for determining the point of phase inversion. A separate study showed a complex morphology of the IPNs⁷. At a PU/PS ratio of 10/90, PU domains with a cellular (*salami*) PS structure were obtained, while at 40% PS, a bimodal distribution of PS domains was obtained.

The phase inversion point (indicated by a sharp increase in the tensile strength) was studied for a TDI, castor oil and sebacic acid PU–polyester and PS crosslinked with DVB IPNs of varying compositions⁹. The phase inversion point was found not to correlate well

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with the rheological criterion $(\eta_1\phi_2)/(\eta_2\phi_1) \approx 1$ where η_2 , η_1 and ϕ_1 , ϕ_2 are the viscosities and volume fractions of the two phases. Using a similar system as in ref. 5, but with 1.4% DVB, Kumar *et al.*¹⁰ found a sharp decrease in the tensile strength of the IPN with increasing PS content, when the rates of polymerization of the PU and PS networks were approximately matched. In a recent work, Ku *et al.*¹¹ studied simultaneous IPNs based on castor oil, MDI and PS for different PU/PS ratios. They found phase inversion to occur at 20–30% PU indicated by a sharp increase in the tensile strength with PS weight fraction. The elongation at break showed a maximum at 50% PU. Nuclear magnetic resonance (n.m.r.) studies indicated a domain size of about 100 Å, though scanning electron micrographs (SEMs) showed large domains. The n.m.r. studies also showed a monotonic decrease in styrene mobility with increasing PU fraction. Most recently, the mechanical properties and adhesive strength of semi-IPNs of polyurethane based on castor oil and TDI, and polystyrene have been reported¹².

The above review shows that material properties of PU–PS IPNs are sensitive to the composition, as well as to processing conditions. In particular, the phase inversion point changes significantly with the isocyanate used and the morphology depends on both composition and mixing. The studies show that the COPU–PS system is versatile and allows for control of product properties over a wide range. The main focus of the current study is the characterization of the mechanical properties of simultaneous IPNs of PU and PS, with the PU made from castor oil and crude diphenyl methane diisocyanate (MDI). Semi-IPNs and full IPNs, in which the styrene is crosslinked with DVB, are systematically studied over wide composition ranges. The main objective of the study is an understanding of the effect of the different factors on the mechanical properties of such IPNs, particularly in the context of the development of low cost shoe soling materials.

EXPERIMENTAL

Materials

The chemicals used for the study are listed in *Table 1*. Styrene and divinyl benzene were used freshly distilled after washing with 5–10% NaOH solution. Benzoyl peroxide (BPO) was used as the radical initiator for styrene.

Synthesis of COPU elastomers

The reactants, castor oil (1 equivalent) and MDI (1 equivalent) were weighed and mixed. Dibutyl tin dilaurate (DBTDL) catalyst (0.045% by weight of castor oil) was added to the reaction mixture and mixed using a

high speed stirrer for 2 min. The maximum reaction temperature was 40–45°C, due to the exothermic heat of reaction. The samples were first cured in closed moulds at room temperature for 12 h. Then they were post-cured at 90°C for another 6 h. COPU elastomers were also prepared with varying isocyanate indices (80–120) following the same procedure.

Synthesis of COPU–PS IPNs

Semi-IPNs of COPU–PS were prepared by first mixing all the reactants (castor oil, MDI, styrene, and BPO at a concentration of 0.5% by weight of styrene) at room temperature. The polyurethane network was synthesized in the presence of styrene at room temperature for 24 h, using closed moulds. In the next step styrene monomer was allowed to polymerize at 80°C for another 24 h. The COPU–PS ratios used were 50/50, 60/40, 75/25, 80/20, 90/10 and 100/0. Using the same procedure as above, full-IPNs with a 75/25 PU–PS ratio were obtained with varying percentage of DVB by weight of styrene (0%, 0.5%, 1%, 5% and 10%). The DVB was also mixed in at the initial stage with the rest of the components.

Physical characterization

Density. The density of the samples made was measured by the water displacement method at room temperature.

Swelling behaviour. The IPNs were cut into rectangular pieces, 2 cm × 3 cm × 0.3 cm, weighed accurately, and immersed in a solvent for 36 h to attain equilibrium swelling. The samples were then taken out from the solvent bath, wiped with tissue paper to remove the excess solvent, and weighed immediately. These were then dried in a vacuum oven at 100°C for 24 h, cooled in a desiccator, and then weighed again. The equilibrium swelling of the polymer (S) by the solvent (v/v) was calculated from ref. 14.

$$S = \frac{\rho_p(w_1 - w_2)}{\rho_s w_2}$$

where w_1 and w_2 are the weight of the swollen and dried polymer respectively, and ρ_s and ρ_p are the densities of the solvent and polymer respectively. The swelling behaviour of the IPNs was investigated in two solvents, ethyl acetate and toluene. Ethyl acetate is a polar solvent which can solvate COPU as well as PS, while toluene is a non-polar solvent and preferentially solvates PS¹³.

Toluene extraction of polystyrene. The semi-IPN samples were cut into small pieces, and a weighed quantity (about 10 g) was packed in filter paper for each case. The

Table 1 Summary of raw materials used

| Raw material | Source | Technical data |
|-------------------------------------|---|--|
| Castor oil | Jayant Oil Mills, Bombay, India | OH No. 170 % water content = 0.46 |
| 4,4'-Diphenyl-methane di-isocyanate | Ashish Enterprises, India | NCO content = 30% |
| Dibutyl tin-dilaurate | Merck, Germany | |
| Styrene monomer | Polychem Ltd, Bombay | stabilized with <i>t</i> -butyl catechol |
| Divinyl benzene | Merck, Germany | stabilized with <i>t</i> -butyl catechol |
| Benzoyl peroxide | S. D. Fine Chemicals Ltd, Boisar, India | |

packets were kept in a Soxhlet extraction column and extracted with toluene for 24 h. The packets were dried at 80°C for 24 h in an oven, cooled in a desiccator, and weighed again to find the soluble content.

Mechanical properties

Hardness. The hardness of the IPNs was tested using Shore-A durometer, at a sample thickness of 6 mm.

Tensile properties. The tensile test specimens were cut from the IPN sheets in dumbbell shapes according to ASTM-412 specifications. All samples were of uniform thickness. The testing was done on an Instron Tensile Tester-1195 at a deformation rate of 10 mm min⁻¹ (i.e. at 25% elongation per minute, for a gauge length of 40 mm). All measurements were made at room temperature.

Wear index. This property of the IPNs was measured as per ASTM D-1630, by cutting the samples as square pieces of 2.0 cm × 2.0 cm × 1.3 cm, which were then abraded by pressing the samples under a frictional load of 0.6 kg against a rotating abrasive wheel. The weight loss in grams for 1000 cycles was reported as the wear index.

Tear testing. The specimens were cut according to the specified dimensions of Die C given in ASTM-624. The notched specimens were made with a sharp and smooth V-edged notch of 90° angle at the centre. The samples were clamped in the grips of the testing machine and deformed at fixed rate of 10 mm min⁻¹, and the maximum force applied to tear the sample was noted. The tear resistance was calculated as $T = F/d$, where F is the maximum force to tear the sample and d is the sample thickness.

RESULTS AND DISCUSSION

The effect of variation in isocyanate index (NCO/OH ratio), on the various mechanical properties of the COPU network formulations is shown in Figure 1. The tensile strength and % elongation at break show a steep rate of increase beyond an index of 100. In contrast, the modulus of elasticity, tear strength, hardness and wear index nearly level off beyond an index of 110. Stoichiometrically, in order for every hydroxyl group to react with an isocyanate group, an index of 100 is required. Increasing the index increases the crosslink density by the reaction of the isocyanate to form allophanate links, resulting in an improvement in the properties. Toluene extraction shows a sol component of 5.27% for the COPU with an index of 100 indicating incomplete network formation (Table 2). Increasing the amount of isocyanate alone thus does not provide a sufficient improvement in properties for the application under consideration.

Figure 2 shows the mechanical properties of semi-IPNs with varying amounts of styrene. There is little change in the tensile strength, % elongation at break, elastic modulus and tear resistance up to 25 wt% of styrene in the formulations (Figure 2a). Beyond styrene levels of 25%, there is a sharp increase in these properties. However, % elongation at break shows a maximum at about 40 wt% styrene and then decreases with increase in styrene fraction. The wear index decreases

monotonically, and by a significant extent, with an increasing styrene fraction (Figure 2b). The small change in the properties below 25% styrene indicates that there is little intermixing between the two polymers, and that styrene is dispersed in the polyurethane continuous phase. The steep rate of increase in the properties beyond styrene concentrations of 25% implies a higher degree of physical entanglement between the COPU network and PS. This would result in an effective stress transfer between the two polymer components of the IPN upon deformation leading to an enhancement in the mechanical strength and improvement in the % elongation

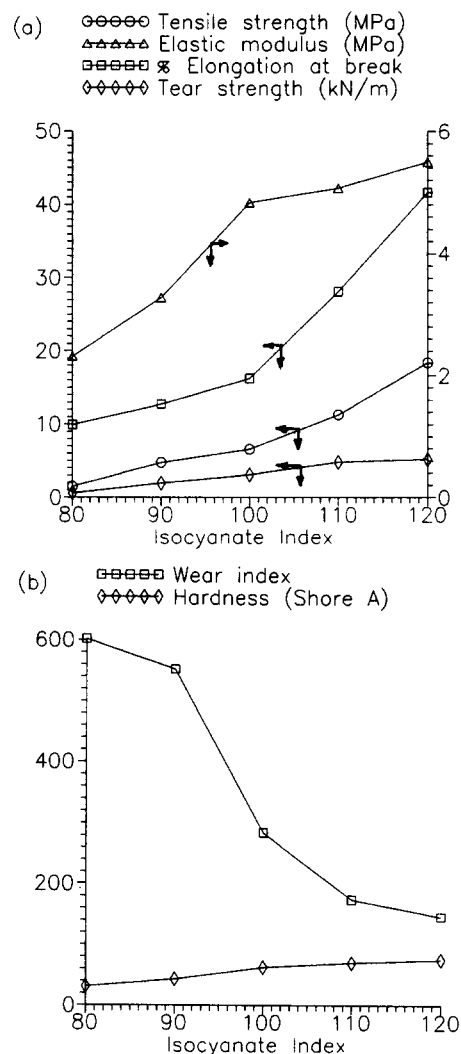


Figure 1 Variation of mechanical properties of COPU elastomers with isocyanate index. (a) Tensile properties, and tear resistance. (b) Wear index and Shore-A hardness

Table 2 Vol% swelling of semi-IPNs in different solvents for different styrene fractions. The fraction of styrene extracted by Soxhlet extraction with toluene is also given

| PU/PS% | % swelling | | Wt% toluene extract |
|--------|------------|---------------|---------------------|
| | Toluene | Ethyl acetate | |
| 100/0 | 61 | 100 | 5.3 |
| 90/10 | 60 | 98 | 6.0 |
| 80/20 | 68 | 99 | 8.0 |
| 75/25 | 72 | 100 | 9.0 |
| 60/40 | 95 | 108 | 12.8 |
| 50/50 | 80 | 105 | 8.9 |

upon tensile deformation. The physical entanglement is most likely due to the formation of a bicontinuous phase structure at a critical styrene composition. Such a transition has been reported previously for COPU-PS systems, but in these studies the PS was also crosslinked as discussed above. The critical styrene concentration obtained here is also somewhat lower than reported previously. The fall in % elongation at break after a maximum at 40% styrene concentrations indicates that there might be intrapolyurethane network crosslinking taking place through the PS chains. The grafting of the PS chains in this case would occur at the double bonds of the castor oil. The tensile properties obtained are lower than those reported by Yenwo *et al.*⁵ and Ku *et al.*¹¹ for 50% PS. This may be because of crosslinking of the PS network by 1% DVB in these studies.

The results of the equilibrium swelling studies carried out in a polar solvent (ethyl acetate) and a non-polar solvent (toluene) are given in Table 2. There is a slow increase in the % equilibrium swelling by volume in both solvents with increase in styrene concentration at low styrene concentrations. However, a marked rise in % swelling occurs between 25-40% styrene, which then decreases with a further increase in styrene fraction. The extent of swelling in ethyl acetate is much greater, as

expected. The swelling behaviour is thus very similar to that of the elongation at break, and results from the same causes as discussed above, namely formation of a bicontinuous structure and intranetwork crosslinking of the PU by the PS. Studies on PU-PS semi-IPNs using polypropylene glycol (which has no double bonds for possible grafting of the PS chains) instead of castor oil, but with all other conditions remaining the same, do not show the decrease at 50% styrene¹⁵. Results of Soxhlet extraction studies of the COPU and semi-IPNs are also given in Table 2. The small fraction of the styrene extracted indicates grafting of the PS onto the PU network. Significantly larger amounts of styrene were extracted from PU-PS IPNs made with polypropylene glycol¹⁵. Both the above results support the conclusion that intranetwork crosslinking of the PU by the PS chains might be occurring at higher PS concentrations.

The variation in the mechanical properties of the 75/25 IPNs with varying amounts of the styrene crosslinking agent, DVB, are shown in Figure 3. As noted above, semi-IPNs with 25% styrene exhibit an insignificant increase in the mechanical properties as compared to COPU (Figure 2). However, with increasing concentrations of % DVB at constant styrene levels, there is a significant improvement in the tensile properties, wear

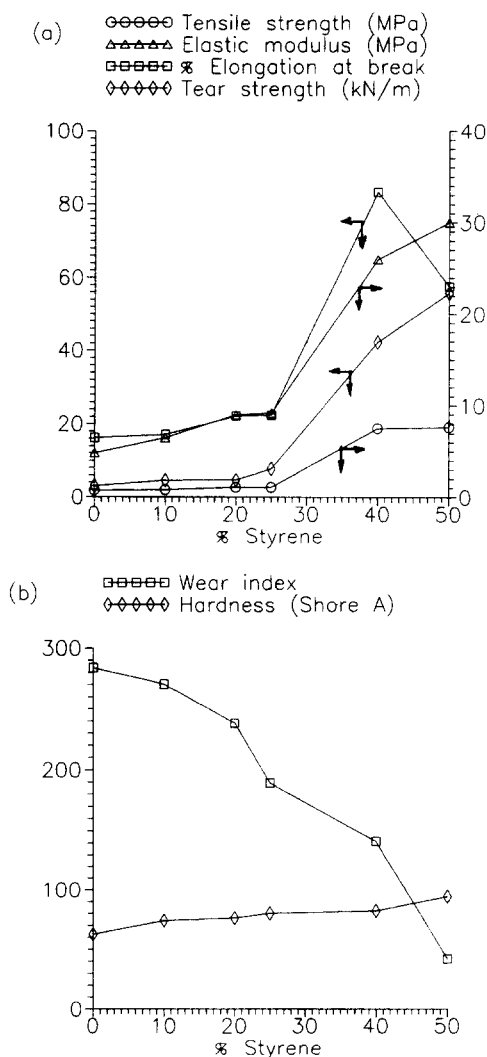


Figure 2 Variation of mechanical properties of semi-IPNs with styrene %. (a) Tensile properties, and tear resistance. (b) Wear index and Shore-A hardness

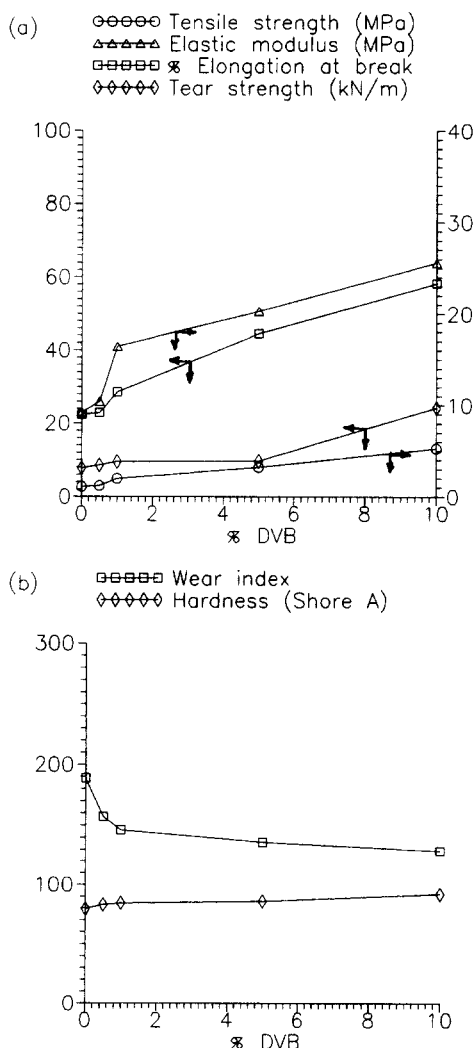


Figure 3 Variation of mechanical properties of full-IPNs with DVB %. (a) Tensile properties, and tear resistance. (b) Wear index and Shore-A hardness

resistance, Shore-A hardness and tear resistance. The increase in the degree of crosslinking of PS at constant styrene levels, as evident from the decrease in the % equilibrium swelling values shown in Table 3, enhances the degree of entanglement of the two polymer network components of the full-IPNs and results in improved mechanical properties. While the hardness, elastic modulus, tensile strength, and elongation at break for the highest DVB % are comparable to the semi-IPN values for 50% styrene, the tear resistance is higher and wear index is significantly lower for the semi-IPNs. The properties obtained satisfy the requirements for shoe soles, with the exception of elongation at break which is lower than required¹⁶.

Comparison of the variation of the wear index for the different polymers discussed above, shows the best correlation of the property with the tear resistance (Figure 4). The wear index decreases sharply with increase in tear resistance and then levels off at high values of the tear resistance. The data for all the materials falls on a single curve, to a very good approximation. There is also a correlation between the wear index and the elastic modulus, but it is not as good. The above result indicates that changing the formulation composition to increase the tear resistance would also reduce the wear index.

CONCLUSIONS

Castor oil has been used for synthesizing COPU and simultaneous COPU-PS IPNs. Properties are found to increase monotonically with isocyanate index for the COPU. In case of semi-IPNs, the mechanical properties were found nearly unchanged, below the critical styrene level of 25%, when compared to COPU. Above this styrene fraction significant improvements in the properties were observed due to the formation of a bicontinuous phase structure. Styrene levels higher than 40% gave a lower % elongation at break due to intranetwork crosslinking of the COPU by the PS chains. This result is supported by swelling and extraction studies. Although a styrene fraction of 25% showed no significant change in properties, using the styrene crosslinking agent (DVB) in small amounts brought about significant improvement in the mechanical properties of 75/25 semi-IPN. The semi-IPNs and full IPNs have material properties which make them promising

Table 3 Vol% swelling of full-IPNs with 25% PS, in different solvents for different DVB fractions

| DVB % | % swelling | |
|-------|------------|---------------|
| | Toluene | Ethyl acetate |
| 0.0 | 100 | 72 |
| 0.5 | 94 | 70 |
| 1.0 | 90 | 68 |
| 5.0 | 83 | 66 |
| 10.0 | 76 | 63 |

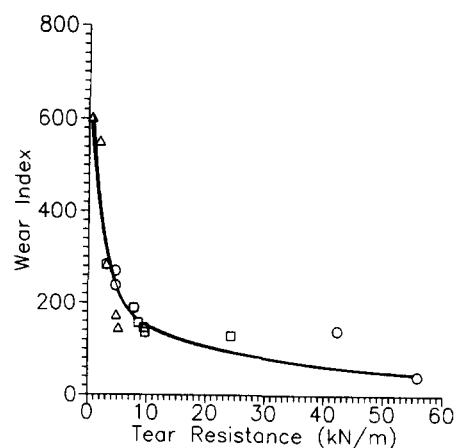


Figure 4 Variation of wear index with tear strength for all the materials. Δ , COPU elastomers; \circ , semi-IPNs; \square , full-IPNs

candidates for shoe soling applications. The wear index for the different polymers is found to correlate well with the tear strength.

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