Characterization of Castor Oil–Based Interpenetrating Polymer Networks of PU/PS

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ABSTRACT: A series of interpenetrating polymer networks (IPNs) of polyurethane/polystyrene (PU/PS; 90/10, 75/25, 60/40, and 50/50) have been synthesized by condensation reaction of castor oil with methylene diisocyanate and styrene, employing benzoyl peroxide as initiator. Polystyrene is extracted from IPNs by the Soxhlet extraction method. The IPNs of PU/PS before and after PS extraction were characterized for physical, optical, and X-ray diffraction properties. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1739–1743, 1998

Key words: interpenetrating polymer network; physical property; optical property; microstructure

INTRODUCTION

Many plastics such as polystyrene (PS) are rather brittle as homopolymers. Such plastics may be toughened by incorporation of judicious quantities of an elastomeric materials. Polyurethane (PU)/ PS interpenetrating polymer networks (IPNs) have been extensively studied by many research workers.[1–5] Though castor oil, a renewable resource, has been a successful candidate in the formation of industrially useful materials, it is yet to be exploited for the modification of polymers.

A survey of literature reveals that some of the properties of these IPNs have not been studied systematically and extensively.[6–8] Here we employ X-ray profile broadening analysis to determine the microstructural parameters and hence to obtain the structure–property relationship on the basis of these parameters and physical measurements. The purpose of the X-ray analysis carried out here is to relate the changes in micro-structural parameters to the physical macro changes, such as hardness, done by earlier investigators in the case of manmade polymer fibers.[9] In this study we have not estimated the degree of crystallinity because the estimation of crystallite size and lattice strain are more fundamental as they determine the extent of broadening of the X-ray profiles in polymer samples. In most polymers the increase in hardness or tenacity is associated with increase in crystal size, and we have investigated this aspect for our samples using the wide angle X-ray scattering method.

EXPERIMENTAL

Materials

Castor oil was obtained from the local market (hydroxyl value 127, 2.12—OH groups/mol of castor oil), characterized according to literature.[10] Methylene diisocyanate (MDI) from Fluka, Switzerland, and benzoyl peroxide (Aldrich, Milwaukee, USA) and divinyl benzene (Schuchardt, Germany) were used as such. Styrene (Merck, Darm-

stadt, Germany) was freed from stabilizer prior to use.

Synthesis of IPNs

The IPNs were synthesized[11,12] by varying the PU/PS molar ratios. To the mixture of castor oil and MDI (NCO/OH ratio 1 : 2), styrene (monomer), 0.5% benzoyl peroxide (as initiator), and 1% divinyl benzene (crosslinking agent) were charged in different proportions into a round-bottom flask. The homogeneous mixture was poured into a mold, kept at room temperature for 28 h and then at 80°C for 12 h to initiate styrene polymerization. Linear PS was extracted from all IPNs using toluene as solvent by the Soxhlet extraction method, and the concentration of extractant was measured by DU 50 UV/Vis Beckman electron absorption spectrophotometry.

Techniques

Before and after PS extraction, IPNs were characterized according to the appropriate ASTM specifications. Density was determined by the displacement method according to ASTM D-792-86, ASTM D-676-58J for Shore A hardness, and ASTM D-1630 for abrasion resistance. The optical properties were measured using a Suga test instrument Haze Meter (Japan) using dust- and grease-free films of IPNs as per ASTM D-1003.

X-ray Profile Analysis

In generally adopted theories for X-ray profile analysis of polymer samples,[13,14] two kinds of structural line broadening are distinguished that can occur simultaneously: (1) size broadening, caused by a finite region size in the specimen diffracting incoherently with respect to other regions; and (2) strain broadening due to varying displacement of the atoms/molecules with respect to their reference positions. Normally, specimen size broadening is very small; it will be ignored here. X-ray powder data from the sample was recorded using a Stoe diffractometer with 25 ma and 30 kV specification. The data was collected in steps of 0.02 degrees. The pattern collected was corrected for Lorentz polarization and also for instrumental broadening.

A generally applicable one-dimensional model based on distortion of the lattice[15] was used to obtain average microstructural parameters, such as crystal size and strain, using the equatorial

Table I Microstructure Parameters of IPNs of PU/PS

Composition of IPNs (PU/PS)	N	g (%)	$\alpha^{\#}$
50/50 AE	9.6 ± 0.2	8.16 ± 0.05	0.098
50/50 BE	6.6 ± 0.1	4.93 ± 0.07	0.127
60/40 AE	7.9 ± 0.1	6.89 ± 0.06	0.170
60/40 BE	5.6 ± 0.1	2.04 ± 0.02	0.049
75/25 AE	7.4 ± 0.1	5.59 ± 0.09	0.152
75/25 BE	6.2 ± 0.1	3.83 ± 0.06	0.095
90/10 AE	7.2 ± 0.1	4.24 ± 0.07	0.114
90/10 BE	6.1 ± 0.1	2.76 ± 0.04	0.068
100 PU	6.1 ± 0.1	2.91 ± 0.06	0.072

AE, after extraction; BE, before extraction; N, number of unit cells counted in a direction perpendicular to the reflecting (hkl) plane; g, lattice strain; $\alpha^{\#}$, enthalpy (see text).

reflection. The corrected experimental X-ray profile was matched with the simulated profile using the equations

$$I(s) = I_{N-1}(s) + I'_N(s) \qquad (1)$$

where $I'_N(s)$ is the modified intensity for the probability peak centered at D ($=Nd_{hkl}$), the crystal size. It has been shown that[16]

$$I'_N(s) = 2a_N/D\pi^{1/2}\exp/idns\{1 \\ - a_Ns[2D(a_Ns + i\pi^{1/2}\exp(-a_N^2s^2)]\} \quad (2)$$

where $a_N^2 = Nw^2/2$, w is the standard deviation of the nearest-neighbor probability function,[16] and (a_Ns) is Dawson's integral on the error function with purely complex argument and can be easily computed. N is the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane. The experimental profile between s_0 and $s_0 + s_0/2$ (or s_0 and $s_0 + B/2d$, if there is truncation of the profile $B < 1$) is matched with the corresponding simulated order of reflection between s_0 and $s_0 + s_0/2$ (or s_0 and $s_0 + B/2d$) for various values of N and g to minimize the difference between calculated and experimental normalized intensity values. SIMPLEX, a multidimensional algorithm,[17] is used for minimization. Table I lists the values of N and g (lattice distortion or strain) and, along with these, standard deviations obtained for a reflection in all these samples.

Table II   Properties of PU/PS IPNs

Composition of IPNs (PU/PS)	Density (g/mL)	Abrasion Resistance	Surface Hardness (Shore A)	Molecular Weight ($\bar{M}_v \times 10^{-4}$)
100 (PU)	0.965	—	80	—
90/10	0.960	0.0118	80	cannot be determined
75/25	0.980	0.0134	82	12.40
60/40	0.991	0.0187	85	1.85
50/50	1.072	0.0180	88	7.77

RESULTS AND DISCUSSION

Our earlier communication[18] reported on a detailed study of the engineering properties such as tensile strength, modulus, elongation at break, and thermal properties of PU/PS systems. The tensile strength and modulus increased with increase in the plastic (PS) component, whereas percent of elongation decreased.[19] The values of tensile strength, modulus, and percent elongation lie between 1.8 and 10 MPa, 3.1 and 25.6 MPa, and 129 and 64 MPa (PU/PS 90/10 to 50/50), respectively. Thermal properties, such as decomposition temperature, at various percent weight losses and integral procedural decomposition temperature values increased with increase in urethane content in IPNs.[18,20]

Density, surface hardness values and abrasion resistance values lie in the range of 0.960–1.072 g/mL, 80 to 88 Shore A, and 0.0118–0.0187, respectively (Table II). Abrasion resistance and surface hardness increase with increase in PS percentage, because PS is plastic and PU is rubbery in nature.

Densities of IPNs increase with increase in PS content (because PS density is greater than 1). A slight reduction in densities was observed for PS-extracted IPNs. The extracted IPNs became brittle and lost their elasticity.[12] This may be due to an increase in surface hardness. Densities of extracted IPNs fall in the same range, but abrasion resistance was not measured because PS-extracted IPNs were brittle.

Optical Properties

Results of diffuse light, total light transmittance, and haze measurements are given in Table III. These are in the expected ranges.[12] Results indicate that the percentage of transmittance of light was very good in all IPN films and in the range of 40.8 to 68.2%. The difference is attributed to the variation in PU content of IPNs. Increase in the PS content of the IPNs decreases the transmittance and increases percent haze.[12] Comparison of optical properties of 100% PU, as well as 100% PS, component polymers indicated that PS is a transparent film with 99% transmittance while PU (castor oil + MDI) has transmittance around 43%, depending on the levels of NCO/OH ratios. Thus IPNs containing a low PU content are good transparent films with minimum haze percentage.

Electron Absorption Spectra

PS extracted from different IPNs using toluene solvent and the extractant were analyzed by ultraviolet (UV) spectrophotometry. Two peaks[21] were obtained due to PS, the first peak in the

Table III   Optical Properties of PU/PS IPNs

| Composition of IPNs (PU/PS)	Percentage of Diffuse	Percent Parallel	Total Percentage of Transmittance	Percentage of Haze
90/10	20.5	20.3	40.8	42.3
75/25	17.9	26.1	44.0	37.4
60/40	14.6	37.9	52.5	30.0
50/50	9.1	59.1	68.2	17.8
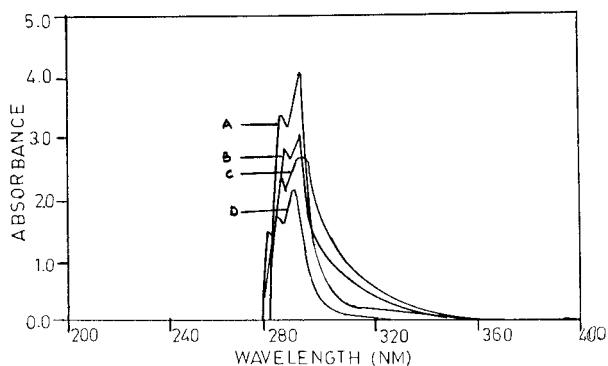
Figure 1 UV spectra of PS extracted from different IPNs using toluene: (A) 90/10; (B) 75/25; (C) 60/40; (D) 50/50.

wavelength range of 272–284 nm and second peak around 291 nm. The viscosity average molecular weight ($\bar{M}_v$) of extracted PS was also determined and values fell in range of 1.8×10^4 to 12×10^4 (Table II). The highest $\bar{M}_v$ of 12×10^4 was obtained for PU/PS 75/25. This is due to the high percentage of linear and uncrosslinked PS in 75/25 IPN. UV spectra of PS extracted from different IPNs are shown in Figure 1. From the area under the curve of UV spectra it is evident that the amount of PS extracted increases from 90/10 to 50/50 and the values are in the expected range.

X-ray Results

Sample X-ray spectra for PU/PS 75/25 and 50/50 IPNs are given in Figures 2 and 3, respectively. Each figure has two curves, one for before extrac-
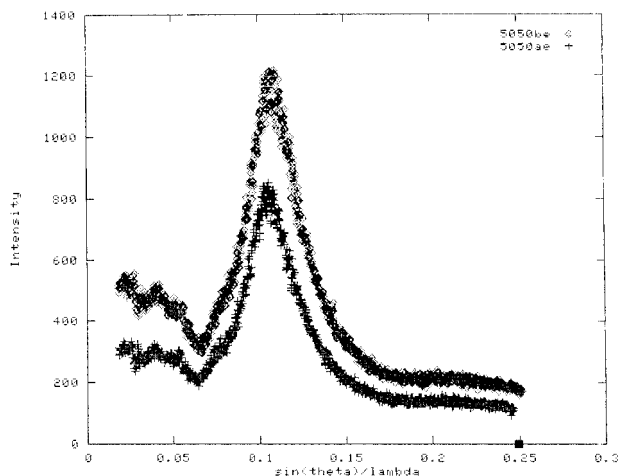
Figure 2 X-ray diffractometer recordings for 50/50 PU/PS IPNs: ($\diamond$) before extraction; ($+$) after extraction of PS.
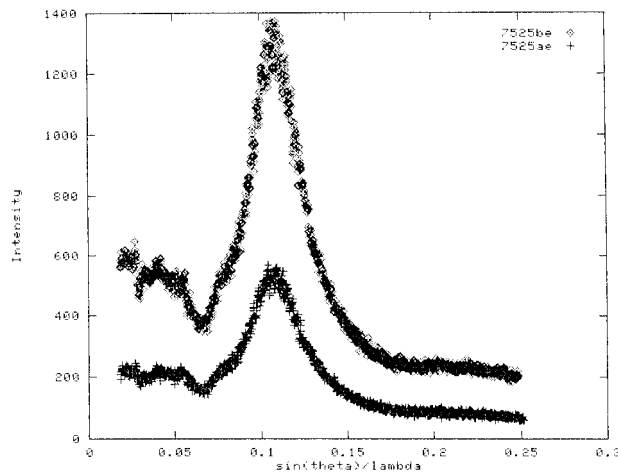
Figure 3 X-ray diffractometer recordings for 75/25 PU/PS IPNs: ($\diamond$) before extraction; ($+$) after extraction of PS.

tion and the other for after extraction of PS. It is evident from Table I that with increase in PS concentration the crystal size and strain increase; this is also reflected in hardness data. The increase in the transparency with increase in the percentage of PS is due to the increase in crystal size and, to some extent, the increase in strain present in these samples.

Another important fact to be noted from Table I is that the crystal size and strain increase after extraction of PS. Using these parameters one can calculate the enthalpy ($\alpha^{\#}$) using Hosemann's paracrystalline disorder, where

$$\alpha^{\#} = (N)^{1/2} g \qquad (3)$$

It is found that both enthalpy and size increase with increase in percentage of PS, i.e., there is reordering of molecules within these samples. Here $\alpha^{\#}$ values imply physically that the growth of paracrystals in a particular material is appreciably controlled by the level of g in the net plane structure. We can conclude from these studies that with incorporation of PS more energy is consumed in order to build up the crystal network compared with the pure sample.

CONCLUSIONS

Independent physical, optical, and X-ray studies of PU film in the presence of additional PS give consistent results regarding significant changes such as increase in transparency and hardness

which are due to increases in crystal size and strain in these samples, thereby establishing the structure–property relation in these materials.

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