Hydrophilic–Hydrophobic Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 1. Morphology, Dynamic Mechanical Properties, and Swelling Behavior of Polyurethane–Polystyrene IPN's

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ABSTRACT: Hydrophilic–hydrophobic interpenetrating polymer networks (IPN's) of polyurethane (PU) and polystyrene (PS) were prepared by a simultaneous polymerization method under high pressure up to 10 000 kg/cm^2. The hydrophilic polyurethane networks were prepared by reacting hexamethylene diisocyanate (HDI) with a mixture of poly(tetramethylene ether glycol) (PTMEG) and polyethylene glycol (PEG) (50%/50% by weight) and with trimethylol propane (TMP) as the cross-linking agent. The morphology, dynamic mechanical properties, and swelling behavior of the IPN's prepared were analyzed to evaluate the effect of the synthesis pressure on the degree of intermixing of the component polymers. The morphology and the dynamic mechanical behavior showed that the degree of intermixing increased with increasing synthesis pressure. The domain size decreased from about 2000 Å at atmospheric pressure to 100 Å at 10 000 kg/cm^2, and the dynamic mechanical behavior also showed an inward shift in T_g's with increasing synthesis pressure. The swelling behavior showed that the swelling properties of the simultaneous interpenetrating polymer networks (SIN's) were influenced strongly by the morphology. The swelling ratios in water and ethanol, which were good solvents for the PU network, decreased with increasing degree of intermixing. The swelling ratios in toluene, a good solvent for both PU and PS networks, showed that the swelling behavior of the SIN's was not influenced by the morphology.

Introduction

The degree of intermixing of simultaneous interpenetrating polymer networks (SIN's) is mainly affected by the compatibility of the component polymers, the relative rate of network formation, and the mobility of the polymer chains at the time of phase separation. The effect of the relative rate of polymerization and the cross-link density of the component polymers has been evaluated on polyurethane–poly(styrene-*co*-acrylonitrile) SIN systems.[1] SIN's with similar network formation rates (similar gel time) and with the higher cross-link densities showed a higher degree of intermixing.

Synthesis pressure could be another factor in determining the morphology of SIN's. It has two competing effects, i.e., thermodynamic and kinetic. Thermodynamically, when the system shows a negative volume change of mixing, the enthalpy of mixing (ΔH_m) can be reduced by applying higher external pressure, and thus the Gibb's free energy of mixing (ΔG_m) can be reduced, which implies that phase separation occurs at a later stage of polymerization when polymerized under pressure. The pressure also reduces the rate of phase separation by reducing the mobility of the polymer chains. These combined effects of increased compatibility and reduced rate of phase separation increase the degree of intermixing at the time of interlocking, after which phase separation is prohibited by physical interlocking between the component polymers. Lee et al. were able to increase the degree of interpenetration in the incompatible polyurethane–poly(methyl methacrylate) and polyurethane–polystyrene SIN's by applying pressure during the simultaneous polymerization process and were able to obtain homogeneous, transparent SIN's with a nearly molecular level mixing of the two components.[2-4]

The polymer blends of the hydrophilic–hydrophobic component system have received a great deal of attention in view of their potential biomedical applications.[5-7] In general, these polymer blends, however, exhibit a large degree of phase separation due to incompatibility of the component polymers and poor mechanical properties owing to poor adhesion at the phase boundaries. Thus block or graft copolymers of hydrophilic–hydrophobic constituents have mainly been treated. If IPN's of hydrophilic–hydrophobic constituents can be prepared with controlled morphology by varying the synthesis pressure, their mechanical properties would be improved due to physical interlocking between the components at the phase boundary region.

In this paper, SIN's of hydrophilic polyurethane and hydrophobic polystyrene were prepared by applying pressure during the simultaneous polymerization process. The effect of the synthesis pressure on the morphology, dynamic mechanical properties, and the swelling behavior in water, ethanol, and toluene were analyzed.

Experimental Section

Synthesis. A series of hydrophilic PU and hydrophobic PS IPN's with varying compositions and synthesis pressures were prepared by the simultaneous polymerization method. The isocyanate-terminated polyurethane prepolymer was prepared by reacting 1 equiv of the polyol mixture with 2 equiv of HDI at 55 °C in a four-neck flask under dry nitrogen. The polyol mixture was composed of PTMEG (MW = 1000) and PEG (MW = 1000) in 1:1 ratio by weight. A catalyst, 0.01 wt % dibutyltin dilaurate (T-12), was added to the polyol mixture. PEG was dried at 60 °C for 24 h and PTMEG for 6 h under a 0.5 mmHg vacuum before use. The reaction was continued until the theoretical isocyanate contents were reached as determined by the di-*n*-butylamine method.[8] After mixing 1 equiv of the PU prepolymer with 1 equiv of dried trimethylolpropane (TMP), the cross-linking agent, and 0.02 wt % of T-12 using a high-torque stirrer, the air bubbles entrapped during mixing were removed by applying vacuum. The PU networks were prepared by casting the above mixture in a glass plate mold at 80 °C for 24 h. The PS networks were prepared by casting the purified styrene monomer mixtures containing 5.68 wt % of divinylbenzene (DVB) and 1 wt % of benzoyl peroxide (BPO) in a glass-plate mold at 80 °C for 24 h. IPN's of hydrophilic PU and hydrophobic PS were prepared by mixing PU prepolymer, TMP, T-12 (0.1 wt % based on the prepolymer and TMP mixture), styrene monomer, DVB, and BPO (1 wt % based on the monomer mixture of styrene and DVB). The mixture was charged into a reaction capsule for the high-pressure synthesis of the SIN's, and the capsule was then inserted into a high-pressure mold described in the previous paper.[2] The reaction mixture was polymerized at 80 °C for 24 h, and the synthesis pressures were increased to 10 000 kg/cm^2.

Dynamic Mechanical Analysis. The dynamic mechanical properties were obtained by Du Pont 981-990 dynamic mechanical analyzer (DMA) with a heating rate of 5 °C/min over a tem-

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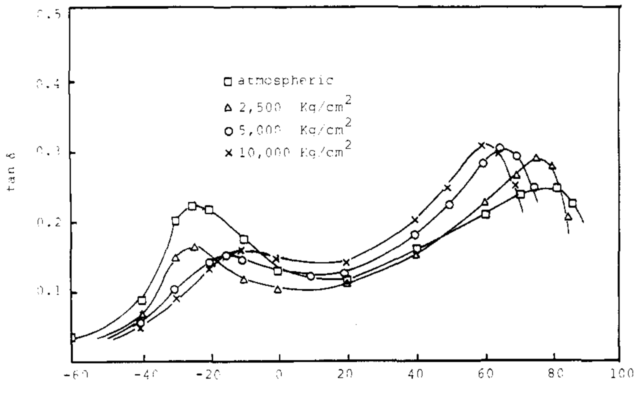


Figure 1. tan δ change with temperature of the SIN's of U50S50 synthesized at varying pressures.

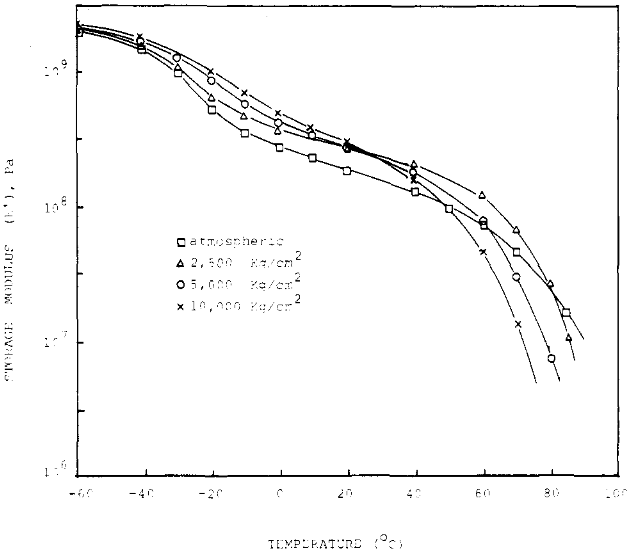


Figure 2. Storage modulus change with temperature of the SIN's of U50S50 synthesized at varying pressures.

perature range −70 to +140 °C. Rectangular (1.5 mm × 7 mm × 17 mm) test specimens were prepared and vacuum-dried at 40 °C for 7 days before testing. The DMA was a resonance frequency type, the oscillation amplitude was 0.2 mm, and the gap setting was 6.4 mm. The measured frequency range was 3–30 Hz.

Electron Microscopy. Transmission electronmicrographs were obtained on a JEM 100 CX (Jeol) electron microscope. The sample preparation technique used was based on Kato's osmium tetroxide staining technique[9] and Matsuo's two-step sectioning methods.[10]

Swelling Behavior. After the samples with dimensions of 6 mm × 2 mm were dried at 40 °C for 7 days under vacuum, they were immersed in distilled water, ethanol, toluene, or a mixture of water/ethanol with varying compositions and swollen in a vessel controlled at 25 °C. The swollen sample was taken off at regular intervals, and the excess solvent was removed by wiping with a filter paper. The sample was then weighed. Measurement was continued until there was no change in weight. The swelling ratio was calculated by the following equation:

$$\text{swelling ratio (\%)} = 100(W_s - W_d)/W_d$$

where W_s is the weight of swollen sample and W_d is the weight of dry sample.

Results and Discussion

Dynamic Mechanical Behavior. The dynamic mechanical behavior of the hydrophilic PU–hydrophobic PS SIN's prepared with varying synthesis pressure at a fixed composition of 50 wt % PU/50 wt % PS (U50S50) is shown in Figures 1 and 2. Samples are denoted as U50S50 (U and S represent polyurethane and polystyrene component, respectively, and the numbers represent the weight percent of the component). Figure 1 is the tan δ change with temperature. The SIN synthesized at atmospheric pressure exhibited two sharp transitions, each corresponding to the constituent polymer T_g's. As the synthesis pressure was increased, the peak shape became broader and the peak positions (T_g's) shifted inwardly. The inward shift of the T_g was interpreted as due to the effect of the mixed layers around the dispersed domains where the two polymer chains were molecularly mixed and physically interlocked; thus the large inward shift in T_g's could be interpreted as due to increased degree of intermixing (or interpenetration). Lee et al. observed a single glass transition temperature positioned intermediate of the constituent polymer T_g's in the other PU–PS SIN's synthesized at 10 000 kg/cm². Their PU networks were composed of PTMEG and MDI.[3] By introducing PEG instead of PTMEG and HDI instead of MDI, we did not observe a single glass transition temperature (i.e., a molecularly mixed SIN) in our PU–PS SIN's even at the same high synthesis pressure because of the reduced miscibility in the component polymers. As seen in Figure 1, as the synthesis pressure was increased, the peak height for the PU phase decreased and that for the PS phase increased, which implied that the PS phase became relatively more continuous. This effect is also shown in Figure 2. The SIN's showed a higher modulus as the synthesis pressure was increased.

Table I
Glass Transition Temperature of the SIN's of U50S50

synthesis pressure	T_g, °C low (PU)	T_g, °C high (PS)
atm	−25	78
1250 kg/cm²	−25	76
2500 kg/cm²	−25	75
5000 kg/cm²	−16	68
7500 kg/cm²	−15	65
10000 kg/cm²	−12	63

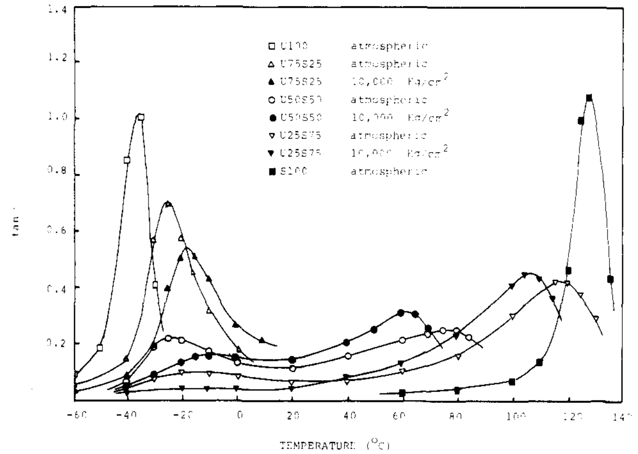


Figure 3. *tan δ change with temperature of SIN's with varying compositions.*

Table I shows the variation in T_g with synthesis pressure. At a synthesis pressure below 2500 kg/cm², the SIN's showed a very small shift in T_g's, whereas at a synthesis pressure above 5000 kg/cm², the SIN's revealed an inward shift in T_g for both the PU and the PS phase by 10–15 °C.

Figure 2 shows the dynamic tensile storage modulus change with temperature. SIN's synthesized at atmospheric pressure showed two distinct transitions corresponding to the constituent polymer transitions. As the

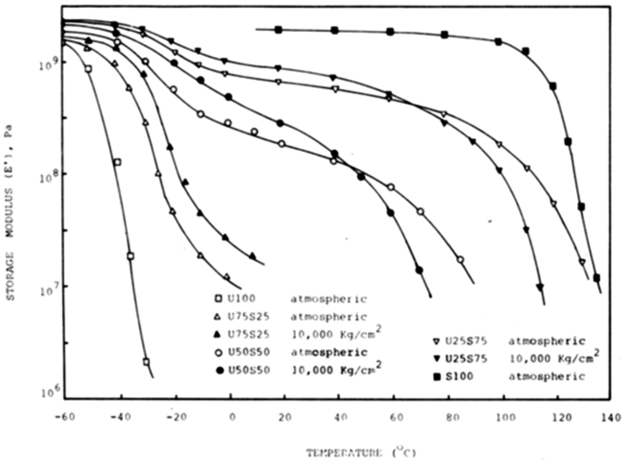
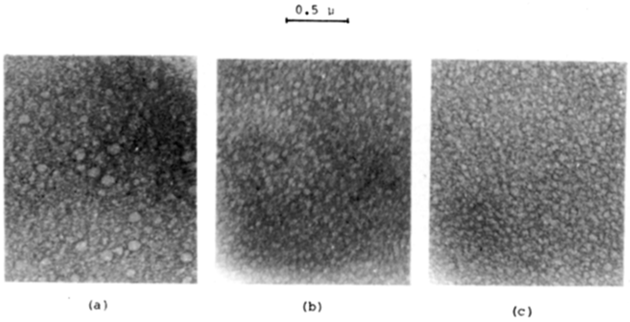


Figure 4. Storage modulus change with temperature of SIN's with varying compositions.



(a) (b) (c)

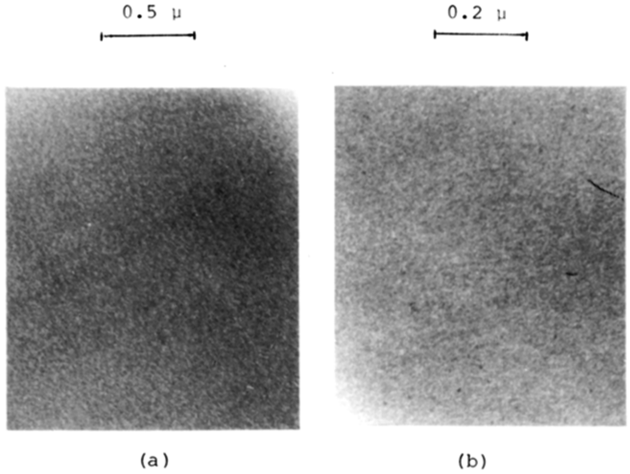
Figure 5. Electron micrographs of the SIN's of U50S50 synthesized at varying pressures: (a) atmospheric; (b) 1250 kg/cm^2; (c) 2500 kg/cm^2.

synthesis pressure was increased, the storage modulus decreased over a broad temperature range, which also implied the increased degree of intermixing.

Figure 3 shows the tan δ curve of SIN's synthesized at atmospheric and 10 000 kg/cm^2 with varying composition. For the SIN's of U75S25, it was difficult to obtain tan δ data at temperatures above 10 °C because of the low value of the storage modulus. The SIN of U75S25 synthesized at 10 000 kg/cm^2 showed that the PU tan δ peak shifted toward higher temperature by 7 °C compared to the SIN synthesized at atmospheric pressure. The SIN synthesized at atmospheric pressure also showed an 11 °C shift in the PU-component T_g when compared to the pure polyurethane. This indicated that the degree of intermixing increased when SIN's were synthesized at high pressure. SIN's of U50S50 and U25S75 also exhibited two separate but inwardly shifted transition behaviors, and SIN's synthesized at high pressure revealed a higher degree of intermixing.

Figure 4 shows the dynamic tensile storage modulus change with temperature of the same SIN's described in Figure 3. The storage modulus change also showed that there existed a higher degree of intermixing in SIN's when synthesized at higher pressure.

Morphology. Figures 5 and 6 show transmission electronmicrographs of the SIN's of U50S50 with varying synthesis pressure. The PU phase was stained by osmium tetroxide and appeared black and the unstained PS phase appeared white in the micrographs. Lee et al. reported that the U50S50 SIN's containing the PU phase of PTMEG and MDI exhibited the dispersed or somewhat cocontinuous PU domain.[2] However, distinctly dispersed and spherical PS domains were observed in these U50S50 SIN's, which might be due to the decrease in the compatibility between PU and PS by increasing the hydrophilicity in the PU phase. SIN's prepared at atmospheric pressure revealed the heterophase structure with a broad domain size distribution ranging from about 100 to 2000 Å. As the synthesis pressure was increased, the PS domain size decreased from about 500 Å at 1250 kg/cm^2 to 100 Å at 10 000 kg/cm^2, which indicated that the degree of intermixing increased with increasing synthesis pressure. Figure 7 shows the decrease in domain size with synthesis pressure, which was measured from the electronmicrographs. From close observation of the electronmicrographs, it was noticed that SIN's synthesized at below 2500 kg/cm^2 exhibited discrete PS domains, while SIN's synthesized at pressures above 5000 kg/cm^2 showed a degree of phase continuity among the PU and the PS phases.



(a) (b)

Figure 6. Electron micrographs of the SIN's of U50S50 synthesized at varying pressures: (a) 5000 kg/cm^2; (b) 10 000 kg/cm^2.

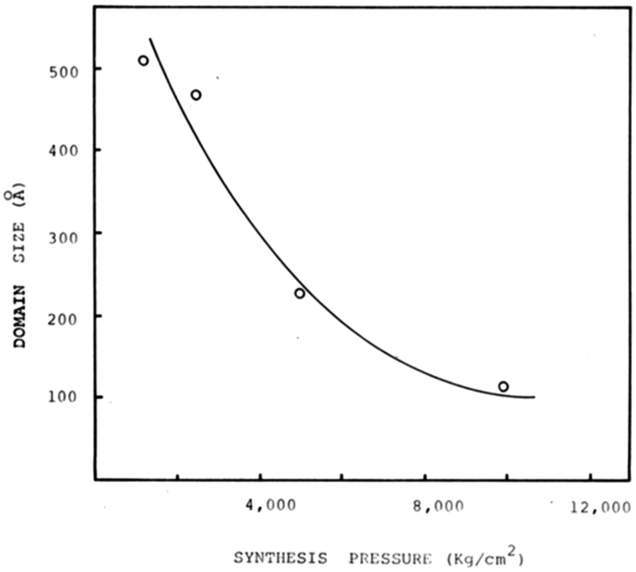


Figure 7. PS dispersed domain size change with synthesis pressure of the SIN's of U50S50.

Swelling Behavior. Figure 8 shows the swelling ratio at 25 °C for the SIN's of U50S50 as a function of synthesis pressure. Generally it has been known that the swelling behavior of the polymer blend is strongly influenced by the heterophase structure. For the homo-IPN's in which networks I and II are identical in chemical composition, Thiele and Cohen derived a swelling equation,[11] and Siegfried et al. modified the original equation by the insertion of the thermoelastic front factor term to account for internal changes on swelling.[12] However, their equations are

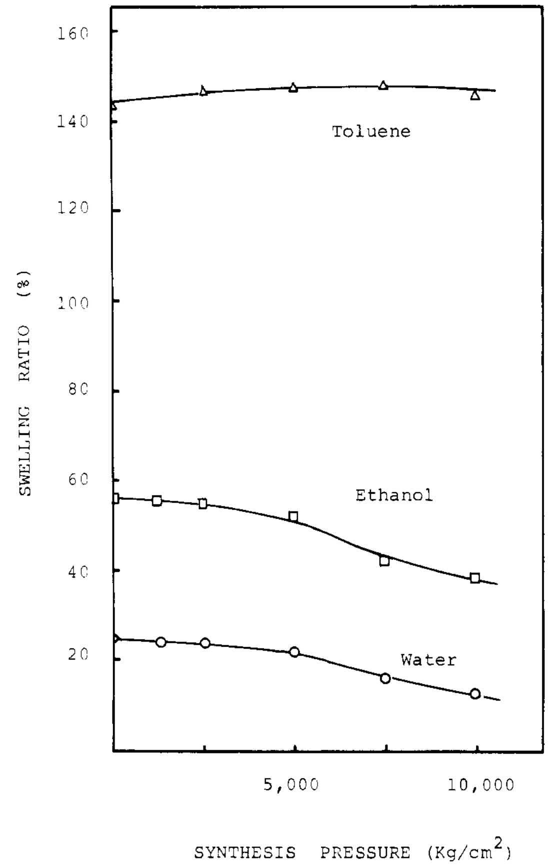


Figure 8. Equilibrium swelling ratio vs. synthesis pressure for the SIN's of U50S50 in water (○), ethanol (□), and toluene (△).

limited to IPN's in which a solvent swells both networks.

Particularly polymer blends containing hydrophilic and hydrophobic microdomains reveal that the hydrophobic domains act as physical cross-links when swollen in water and can thus control the swelling ratio. It is expected that as the number of the physical cross-links (hydrophobic domains) increases, the swelling ratio decreases. The phase continuity and the domain size thus play an important role in determining the swelling behavior of the SIN's of hydrophilic and hydrophobic component polymers. When SIN's of hydrophilic and hydrophobic microdomains are swollen in water or ethanol (the swelling agent for the hydrophilic phase), the swelling agent diffuses through the hydrophilic phases. At fixed composition, SIN's containing hydrophilic and hydrophobic microdomains give decreased swelling ratios in water as the number of the dispersed hydrophobic domains increases, as well as increasing the degree of intermixing. The swelling ratio in water of the SIN's synthesized at atmospheric pressure showed somewhat low values of 25% compared to those of 35% based on the linear additivity of the swelling ratios of pure PU (70%) and pure PS (0%), indicating that the hydrophobic PS domains could affect the swelling behavior of the hydrophilic PU polymer when the degree of intermixing was changed due to the compressive effects of the unswollen network. The swelling ratio for the SIN's in water and ethanol decreased slightly as the synthesis pressure increased from atmospheric to 5000 kg/cm^2, above which they showed a somewhat abrupt decrease. However, the swelling ratio in toluene remained nearly constant. The rapid decrease in swelling ratio in water and ethanol may be due to the decreased domain size and the change from the distinctly dispersed domain to some degree of cocontinuous structure of the PS phase, as seen in the electronmicrographs. However, the swelling ratios in toluene,

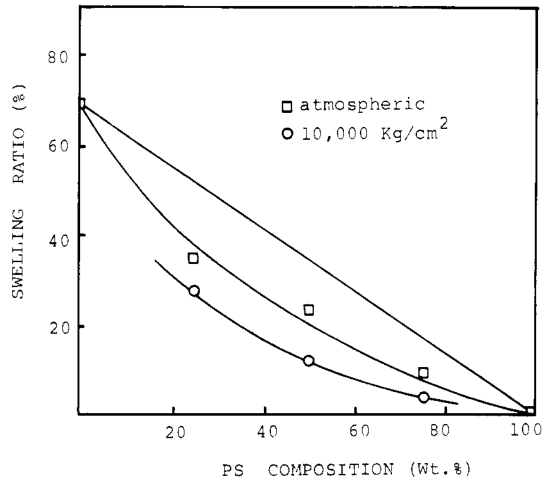


Figure 9. Equilibrium swelling ratio in water vs. composition for SIN's synthesized at atmospheric pressure (□) and 10 000 kg/cm^2 (○).

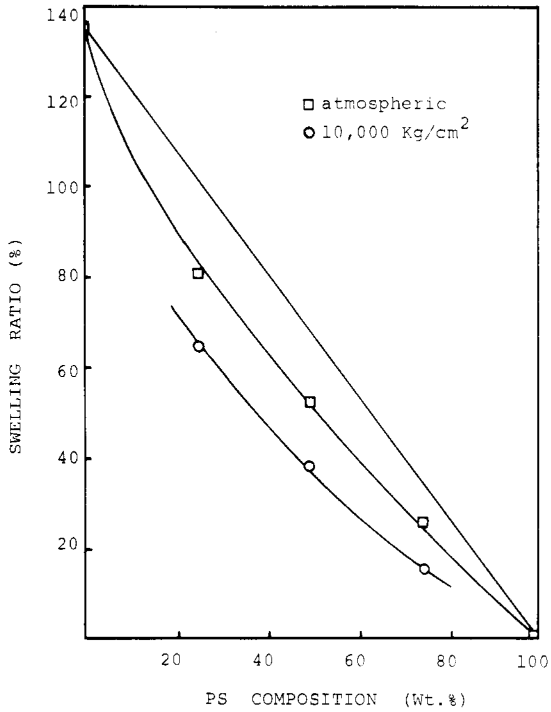


Figure 10. Equilibrium swelling ratio in ethanol vs. composition for SIN's synthesized at atmospheric pressure (□) and 10 000 kg/cm^2 (○).

a good swelling agent for both PU and PS, were not seriously influenced by the morphology change.

Figures 9 and 10 show the effect of the synthesis pressure of SIN's in water and ethanol. The solid line represents the value based on the linear additivity rule. For both water and ethanol, SIN's synthesized at higher pressure exhibited lower swelling ratios over the whole composition range, indicating that the increased degree of intermixing as well as the phase structure change affect the swelling behavior of SIN's.

Figure 11 shows the swelling behavior of U50S50 SIN's in water/ethanol mixtures with varying ethanol concentration. The SIN's synthesized at atmospheric pressure and 10 000 kg/cm^2 both showed a maximum value in swelling around 75–85% ethanol content. It was presumed that the solubility parameter of the hydrophilic PU phase was in the same range as that of the 80% ethanol mixture.

In conclusion, the swelling behavior of the SIN's con-

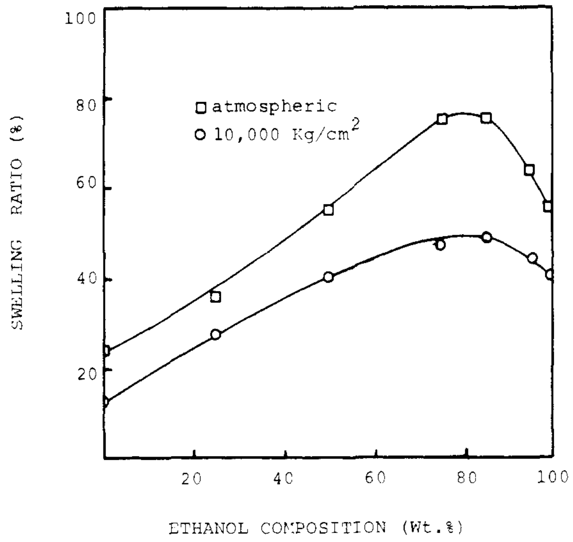


Figure 11. Equilibrium swelling ratio vs. solvent composition for the SIN's of U50S50 synthesized at atmospheric pressure (□) and 10 000 kg/cm^2 (○) (solvent: water/ethanol).

taining hydrophilic and hydrophobic microdomains in water or ethanol is influenced strongly by the degree of intermixing as well as the phase structure.

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Registry No. (HDI)·(PTMEG)·(PEG)·(TMP) (copolymer), 99809-28-6; (DVB)·(styrene) (copolymer), 9003-70-7.

References and Notes

(1) Park, I. H.; Lee, J. H.; Kim, S. C. *Polym. Bull. (Berlin)* **1983,** *10,* 126.
(2) Lee, D. S.; Kim, S. C. *Macromolecules* **1984,** *17,* 268.
(3) Lee, D. S.; Kim, S. C. *Macromolecules* **1984,** *17,* 2193.
(4) Lee, D. S.; Kim, S. C. *Macromolecules* **1984,** *17,* 2222.
(5) Shimada, M.; Miyahara, M.; Tahara, H.; Shinohara, I.; Okano, T.; Kataoka, K.; Sakura, Y. *Polym. J. (Tokyo)* **1983,** *15,* 649.
(6) Nakashima, K.; Takakura, K.; Komoto, Y. *J. Biomed. Mater. Res.* **1977,** *11,* 787.
(7) Okano, T.; Nishiyama, S.; Shinohara, I.; Akaike, T.; Sakurai, Y.; Kataoka, K.; Tsuruta, T. *J. Biomed. Mater. Res.* **1981,** *15,* 393.
(8) Malec, E. J.; David, D. J. In "Analytical Chemistry of Polyurethanes"; David, D. J., Stanley, H. B., Eds.; Wiley: New York, 1969; p 87.
(9) Kato, K. *J. Polym. Sci., Part B* **1966,** *4,* 35.
(10) Matsuo, M.; Kwei, J. K.; Klempner, D.; Frisch, H. L. *Polym. Eng. Sci.* **1970,** *10,* 327.
(11) Thiele, J. L.; Cohen, R. E. *Polym. Eng. Sci.* **1979,** *19,* 284.
(12) Siegfried, D. L.; Thomas, D. A.; Sperling, L. H. *Macromolecules* **1979,** *12,* 586.

Studies of Surface Composition and Morphology in Polymers. 2. Bisphenol A Polycarbonate and Poly(dimethylsiloxane) Blends

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ABSTRACT: Results from X-ray photoelectron spectroscopy and ion scattering spectroscopy analyses are presented for blends of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS). Analysis of these results shows surface enrichment of the lower surface energy DMS component. A model is presented describing the morphology of the top 50 Å of the sample surface. A structural comparison to earlier work on copolymers of BPAC/DMS is also presented. Results show that all blends of less than 11% bulk DMS reach a surface concentration of approximately 85% DMS over the topmost 50 Å. All results show that no gradient exists over this depth, unlike the results for block copolymers. In addition, comparisons to previous work on other two-component block/blend systems show that surface energy differences alone cannot predict the degree of segregation in such polymers. Scanning electron micrographs allow confirmation of composition/morphology relationships.

Introduction

In a previous paper,[1] the near-surface region of block copolymers consisting of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS) were examined, via X-ray photoelectron spectroscopy (XPS or ESCA) and low-energy ion scattering spectroscopy (ISS), in order to quantify the degree of surface segregation of the DMS segments present in these materials. The results showed a dramatic increase of the DMS segment at the air/polymer interface that was in agreement with previous work[2,3] on other concentrations of DMS/BPAC block copolymers. In our work segregation was quantified in order to give the weight percent of BPAC and DMS present in the surface region, which can be compared to that of the bulk. The ability to predict the amount of each component of the block copolymer present at the surface for a given bulk concentration should greatly aid in the development of engineering materials that require specific surface properties.

This work also demonstrated the usefulness of ISS as a complement to ESCA for the study of polymers. By combining these techniques it was possible to study the surface of the polymers at different depths in a "nondestructive" way and also gain quantitative infor-