Polyurethane Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 2. Morphology and T_g Behavior of Polyurethane–Polystyrene IPN's

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ABSTRACT: A series of interpenetrating polymer networks of polyurethane–polystyrene were synthesized under high pressure. The morphology, dynamic mechanical properties, and density behavior were analyzed to determine the effect of the synthesis pressure on the degree of interpenetration of the component polymers. The composition of the polyurethane and polystyrene was fixed at 50%/50% by weight. The dynamic mechanical behavior showed changes from the heterophase structure to the homogeneous single-phase IPN structure when the synthesis pressure was increased. IPN's with a theoretical molecular weight between cross-links ($\bar{M}_c$) of 2000 synthesized above 10000 kg/cm^2 showed one sharp glass transition, intermediate between the two component T_g's, and they were optically transparent. The morphology agreed well with the dynamic mechanical behavior, with dispersed domain sizes in the range of tens of angstroms. These results indicated that the IPN's formed were the completely interpenetrated networks of the polyurethane and polystyrene.

Introduction

Interpenetrating polymer networks (IPN's) have been prepared by three different methods: sequential polymerization,[1] latex blending,[2] and simultaneous polymerization.[3,4] The simultaneous polymerization method involves mixing of monomers or low molecular weight prepolymers and cross-linking agents of the component polymers and polymerizing/cross-linking them simultaneously via noninterfering reaction mechanisms (e.g., free radical polymerization vs. step polymerization). This method is expected to yield a higher degree of interpenetration since it is easy to obtain a homogeneous mixture when low molecular weight monomers are mixed.

There exist two competing kinetic processes of phase separation and network formation as the polymerization proceeds. The effect of the relative rate of polymerization of the component polymers has been evaluated on the polyurethane–poly(styrene-*co*-acrylonitrile) simultaneous interpenetrating polymer network (SIN) systems.[5] The SIN's with similar network formation rate (similar gel time) showed a higher degree of intermixing or interpenetration.

We were able to increase further the degree of interpenetration in the incompatible polyurethane–poly(methyl methacrylate) SIN's by applying pressure during the simultaneous polymerization process and were able to obtain a transparent, nearly molecular level mixture of the two components.[6]

It appears that the synthesis pressure has several direct and indirect effects in determining the morphology of the SIN's. During the process of simultaneous polymerization, there are two major events of importance to occur as the polymerization proceeds: phase separation and the interlocking of the two component networks (when the component polymers reach the gel point). The relative timing of the two determines the morphology; thus when the interlocking of the two component polymers occurs before the onset of phase separation, the interlocked state prohibits further phase separation, and the resulting SIN shows a homogeneous mixture of the two. When the interlocking occurs after the onset of phase separation, we obtain SIN's with heterogeneous morphology whereas only partial interpenetration exists around the phase boundaries of the dispersed phases. The domain size and the degree of partial interpenetration are dependent on the rate of phase separation and the timing of the interlocking.

The effect of pressure is shown schematically in Figure 1. The effect of pressure on the interaction parameter of the mixture is not known quantitatively, but it is generally accepted that the compatibility increases at high pressure, particularly when the system shows a negative volume change of mixing. The Gibb's free energy of mixing, ΔG_m, is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

The enthalpy of mixing, ΔH_m, can be expressed qualitatively as a function of external pressure P[7]

$$\Delta H_m \simeq V\phi_1\phi_1(\delta_1 - \delta_2)^2 + (P_i + P)\Delta V_m$$

where V is the molar volume of the mixture, δ_1 and δ_2 represent the solubility parameters of the two components, ϕ_1 and ϕ_2 represent their volume fractions, P_i is the internal pressure, and ΔV_m is the volume change of mixing. When the system shows a negative ΔV_m upon mixing, ΔH_m can be reduced by applying higher external pressure and thus decreasing ΔG_m. Thus at high synthesis pressure, the onset point of phase separation moves toward higher conversion and the mixture stays homogeneous at high molecular weight level. The synthesis pressure also affects the rate of phase separation by reducing the mobility of the polymer chains with reduced free volume. The combined effect of the increased compatibility and the reduced rate of phase separation increases the degree of mixing of the two component polymers at the time of interlocking. The time of interlocking (when both component networks reach the gel point and form an infinite structure), on the other hand, is dependent mostly on the cross-link density. Thus when the cross-link density is higher, each polymer component reaches the gel point at lower conversion and the mixture reaches the time of interlocking earlier.

The effect of synthesis pressure, synthesis temperature, and cross-link density on phase separation and the network interlocking process were studied in this paper on polyurethane–polystyrene IPN's.

Experimental Section

Synthesis. The isocyanate-terminated polyurethane prepolymer was prepared with the same materials and same procedure as described in the previous paper of this series[6] except no catalyst was used. The molecular weight of poly(tetra-

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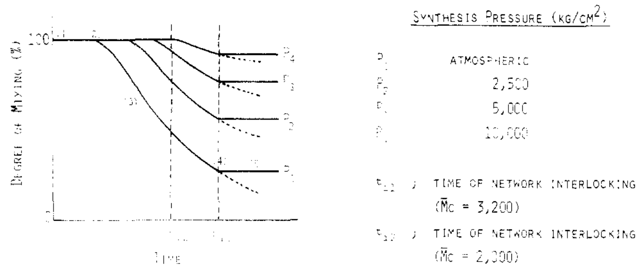

Figure 1. Schematic diagram showing the qualitative effect of pressure and cross-link density on the phase separation and network interlocking process during the simultaneous polymerization of the component polymers: (1) mixture stays homogeneous at low conversion; (2) onset of phase separation; (3) phase separation process (rate is dependent on pressure); (4) time of network interlocking (interlocking prohibits further phase separation; degree of interpenetration determined at this point); (5) time-independent morphology.

methylene ether) glycol was 986. Mixtures of 1,4-butanediol (1,4-BD) and trimethylolpropane (TMP), the chain-extending and cross-linking agent for the PU network, in 1:4 and 1:1 equivalent ratios were used to obtain two different levels of $\bar{M}_c$. The resulting theoretical molecular weights between cross-links ($\bar{M}_c$) were 2000 and 3200, respectively. Styrene monomers used for the PS polymerization were purified before use.[8] Divinylbenzene (DVB) was used as the cross-linking agent for the PS network, its composition being 4% and 2.5% by weight in styrene monomer for $\bar{M}_c$ of 2000 and 3200. The thoroughly mixed and degassed mixture of PU prepolymer, TMP/1,4-BD mixture, PU catalyst dibutyltin dilaurate (0.03 wt % PU), styrene monomer, DVB, and benzoyl peroxide (one part per hundred styrene by weight) was charged into a reaction capsule and kept at room temperature for about 24 h for the partial polymerization of PU.

This capsule was inserted into a reaction mold as described in the previous paper[6] and polymerized at 80 °C for 24 h and 110 °C for 4 h. The PU component was allowed to partially react at room temperature to reach the gel point earlier with the intention of increasing the viscosity at high-temperature molding. The reaction was carried out with varying pressures up to 10000 kg/cm^2.

Samples prepared were coded as follows: the first letter denotes the polymer component (U for polyurethane and S for polystyrene), the second letter C denotes the cross-linked network, and the third numeral denotes the weight percentage of the component polymer.

To evaluate the effect of synthesis temperature, IPN's were also synthesized at 120 and 140 °C for 28 h; the synthesis pressure was 5000 kg/cm^2 and the $\bar{M}_c$ was 3200.

Dynamic Mechanical Analysis. The dynamic mechanical properties were measured on a Du Pont 981-990 dynamic mechanical analyzer (DMA). The oscillation amplitude was 0.2 mm and the gap setting was 6.4 mm. The scanning rate was 5 °C/min over a temperature range of −50 to +130 °C. Rectangular (1.5 mm thick × 6 mm wide × 16 mm long) test specimens were prepared. The DMA was a resonant frequency type, and the frequency range was 3-35 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 tetraoxide staining technique[9] and Matsuo's two-step sectioning method.[10]

Density. The density was measured with a density gradient column with sodium bromide aqueous solution. All measurements were made at 23 °C.

Results and Discussion

Dynamic Mechanical Behavior. The dynamic mechanical properties of the UC50SC50 IPN's (with a theoretical $\bar{M}_c$ of 2000) synthesized under different pressures are shown in Figure 2. IPN's prepared at atmospheric pressure distinctly show the T_g's of the polyurethane and polystyrene phases. At a synthesis pressure of 2500 kg/cm^2, the PU and PS T_g's both move inwardly and the PU transition appears as a shoulder in the broad transition. At higher pressure, a single glass transition is exhibited, but the peak temperature of the PS dominant phase moves toward lower temperature as the intermixing of the polyurethane component is increased. Also the shape of the tan δ curve changes from a broad to a sharp transition, which indicates that the mixture becomes homogeneous when synthesized above 10000 kg/cm^2 pressure. The effect of changing the cross-link density is shown in Figure 3. IPN's with a theoretical $\bar{M}_c$ of 3200 also show similar behavior as those of $\bar{M}_c$ of 2000, but the phase separation is more enhanced in this case. The degree of intermixing of the two-component polymer is lower compared to IPN's with high cross-link density as evidenced with the more distinct PU transition shown in IPN's synthesized at 2500 kg/cm^2. Also the broader tan δ transition curve indicates a lower degree of intermixing. This cross-link density effect is related to the shift of the point of interlocking shown in Figure 1 as discussed previously.

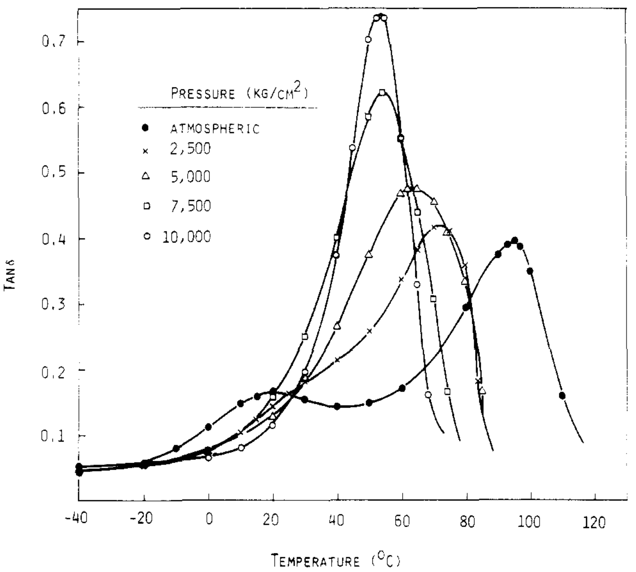

Figure 2. Dissipation factor (tan δ) vs. temperature of UC50SC50 IPN's ($\bar{M}_c$ = 2000) synthesized at varying pressures.

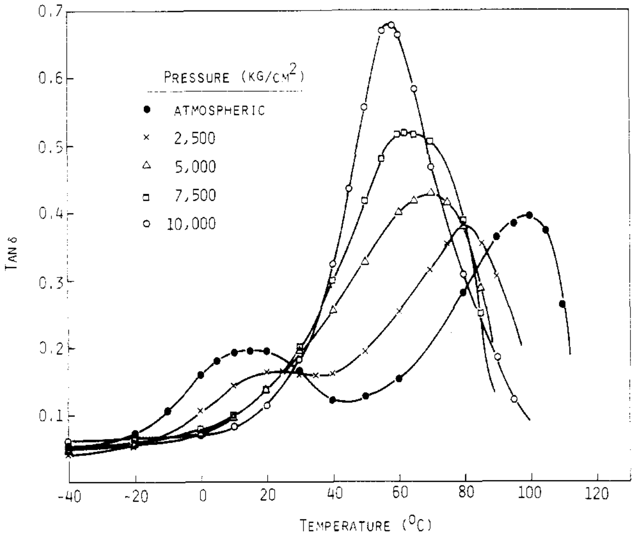

Figure 3. Dissipation factor (tan δ) vs. temperature of UC50SC50 IPN's ($\bar{M}_c$ = 3200) synthesized at varying pressures.

The shift of the T_g of the PS dominant phase is plotted in Figure 4. The higher degree of intermixing with the PU network is shown as a lowering of the T_g of the PS dominant phase. The IPN's with an $\bar{M}_c$ of 2000 all show increased degree of interpenetration with PU when com-

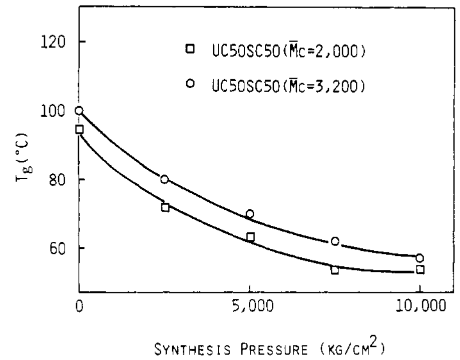

Figure 4. Glass transition temperature (T_g) of the PS dominant phase in IPN's synthesized under different pressures.

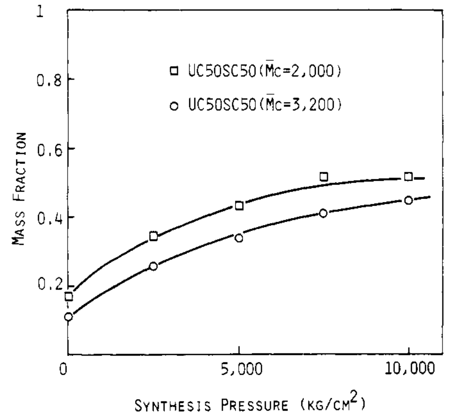

Figure 5. Calculated mass fraction of PU in the PS dominant phase in IPN's synthesized under different pressures (from the Fox equation).

Table I
T_g and Polymer Composition (Calculated from the Fox Equation) of the PS Dominant Phase

sample	synthesis press, kg/cm^2	T_g, K	composition PU	composition PS
UC50SC50 ($\bar{M}_c$ = 2000)	atmos	368	0.17	0.83
	2500	345	0.35	0.65
	5000	336	0.43	0.57
	7500	327	0.51	0.49
	10000	327	0.51	0.49
UC50SC50 ($\bar{M}_c$ = 3200)	atmos	373	0.11	0.89
	2500	353	0.26	0.74
	5000	343	0.34	0.66
	7500	335	0.41	0.59
	10000	330	0.45	0.55

pared with IPN's with an $\bar{M}_c$ of 3200. The effect of increased synthesis pressure is similar in both IPN's.

This T_g shift is converted to the mass fraction of the PS and PU component polymers in the PS dominant phase by assuming that the Fox equation is valid in this system:[11]

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

where T_{g_1} and T_{g_2} represent homopolymer T_g's of the PU and PS and w_1 and w_2 represent weight fractions. The PU homopolymer T_g obtained was 278 K when $\bar{M}_c$ was 3200 and 283 K when $\bar{M}_c$ was 2000. PS T_g's were 390 K ($\bar{M}_c$ = 3200) and 392 K ($\bar{M}_c$ = 2000). All homopolymers were synthesized at atmospheric pressure.

The resulting mass compositions in the PS dominant phase are shown in Table I and Figure 5. When IPN's are synthesized at atmospheric pressure, there exists only partial interpenetration of the two component polymers, presumably because the interlocking occurs after the onset of phase separation. Thus the IPN's have a two-phase structure with a predominantly PS phase and a predominantly PU phase. The degree of intermixing of the PU component in the PS dominant phase was shown to be 17% by weight when the cross-link density was high ($\bar{M}_c$ = 2000) and 11% by weight when the cross-link density was low ($\bar{M}_c$ = 3200).

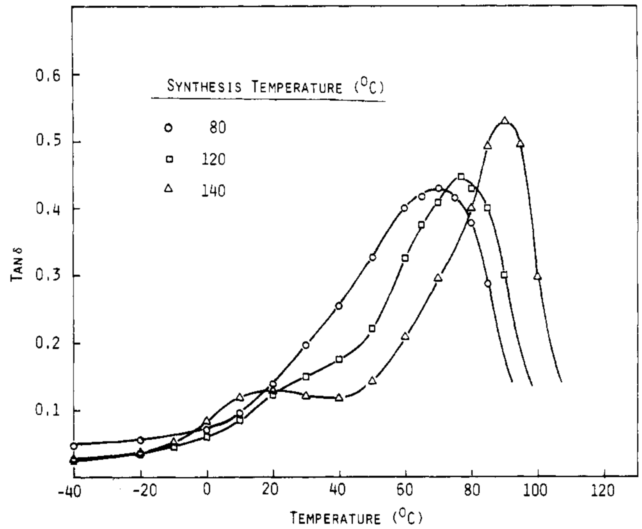

Figure 6. Effect of synthesis temperature on the tan δ curve of IPN's synthesized at 5000 kg/cm^2 pressure ($\bar{M}_c$ = 3200).

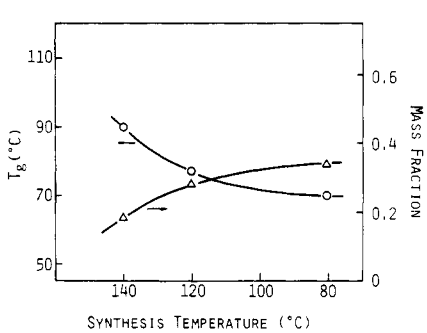

Figure 7. Effect of synthesis temperature on T_g and PU mass fraction (calculated) in the PS dominant phase of IPN's synthesized at 5000 kg/cm^2 ($\bar{M}_c$ = 3200).

As the synthesis pressure is increased, the mass fraction of PU component in the PS dominant phase increases and reaches as high as 51%, which means that the network is composed of a perfectly homogeneous phase structure. The deviation of 1% from the mixture composition of 50% by weight can be considered as an error. Thus UC50SC50 IPN's with an $\bar{M}_c$ of 2000 synthesized at 10 000 kg/cm^2 are completely interpenetrated polymer networks, which have not been synthesized before. It is also shown that for IPN's with an $\bar{M}_c$ of 3200, the homogeneous structure can be reached at synthesis pressures higher than 10 000 kg/cm^2.

The effect of the synthesis temperature is shown in Figure 6. As the synthesis temperature is increased, the degree of interpenetration decreases. This seems to be due to the increased rate of phase separation, mainly because the mobility of polymer chain increases at high synthesis temperature. The corresponding T_g shift and the PU mass fraction change in the PS dominant phase are shown in Figure 7. The PU mass fraction decreased from 34% to 19% when the synthesis temperature was changed from 80 to 140 °C (IPN's with an $\bar{M}_c$ of 3200 synthesized at 5000 kg/cm^2).

Morphology. The morphology agrees well with the dynamic mechanical behavior. Transmission electron

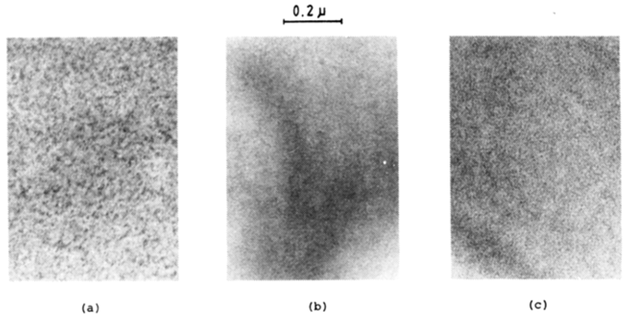

Figure 8. Electron micrographs of UC50SC50 IPN's ($\bar{M}_c = 2000$) synthesized at (a) atmospheric, (b) 5000 kg/cm^2, and (c) 10 000 kg/cm^2.

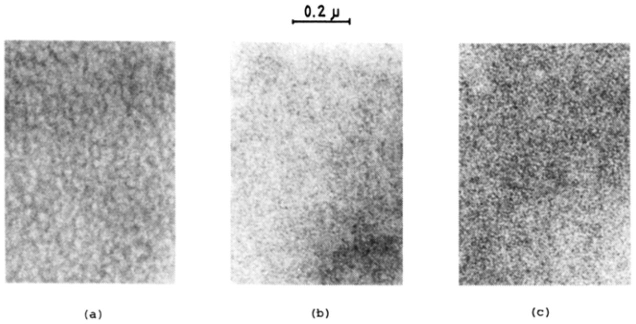

Figure 9. Electron micrographs of UC50SC50 IPN's ($\bar{M}_c = 3200$) synthesized at (a) atmospheric, (b) 5000 kg/cm^2, and (c) 10 000 kg/cm^2.

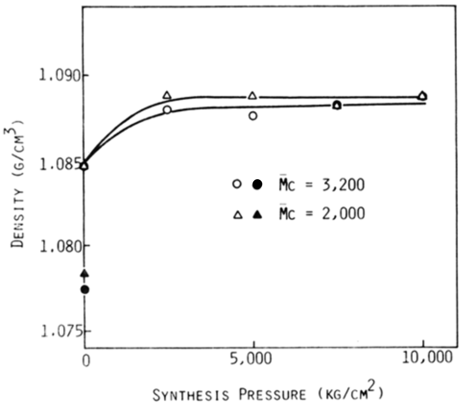

Figure 10. Density vs. synthesis pressure of IPN's; (○, △) experimental data; (●, ▲) calculated values based on volume additivity rule.

micrographs of IPN's with an $\bar{M}_c$ of 2000 are shown in Figure 8. The morphology of IPN's synthesized at atmospheric pressure shows a somewhat co-continuous structure of the PU and PS phases. As the synthesis pressure increases, the PU phase forms completely dispersed domains and the PU phase domain size decreases as the intermixing increases. The IPN synthesized at 10 000 kg/cm^2 shows domain sizes in the range of tens of angstroms (about 30–50 Å), which can be considered as the molecular level of mixing. IPN's with a low cross-link density ($\bar{M}_c = 3200$) show similar behavior (Figure 9) but the PU domain size of IPN synthesized at 10 000 kg/cm^2 is in the range 50–100 Å, larger than that of the IPN with an $\bar{M}_c$ of 2000.

Density. The densities of the IPN's prepared are shown in Figure 10. There is an abrupt change in densities when the synthesis pressure is changed from atmospheric to 2500 kg/cm^2. Above 2500 kg/cm^2, there is no significant difference in density. The difference in densities of IPN's with different cross-link density also falls within experimental error. It seems that IPN's synthesized above 2500 kg/cm^2 have nearly constant densities of about 1.088.

The calculated density averages based on volume additivity of the component homopolymers are 1.077 ($\bar{M}_c = 2000$) and 1.078 ($\bar{M}_c = 3200$). Thus it is clear that there is a negative volume change of mixing due to the interpenetration of the component polymers. A similar behavior was also reported for IPN's synthesized at atmospheric conditions.[12]

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Registry No. (Styrene)·(divinylbenzene) (copolymer), 9003-70-7.

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