

Polyurethane–Polystyrene Interpenetrating Polymer Networks Synthesized at Low Temperature: Effect of Crosslinking Level

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SYNOPSIS

Interpenetrating polymer networks (IPNs) of polyurethane (PU)–polystyrene (PS) containing 50 wt % PU were synthesized at low temperature with varying crosslink density of each component. PU was polymerized first, followed by the photopolymerization of PS at low temperature (0 and 40°C). The theoretical molecular weight between crosslink (\bar{M}_c) of PU ranged from 8200 to 2050, and the \bar{M}_c of PS varied from linear to 2000. The degree of mixing of the components in these IPNs was investigated using dynamic mechanical analysis, electron microscopy, and density measurement. The degree of mixing increased with decreasing \bar{M}_c and/or synthesis temperature. The crosslink density variation at low synthesis temperature is more effective in enhancing the miscibility of IPN than at high synthesis temperature, because both the temperature and crosslink density can affect the polymer chain mobility during the synthesis. The variation of PU network crosslink density shows the better effect in increasing the miscibility of IPN than that of the PS network. The morphology and the density behavior agree well with the dynamic mechanical result.

INTRODUCTION

Interpenetrating polymer networks (IPNs) have been prepared by several synthetic methods.¹ These include materials called sequential IPNs, where the networks are made sequentially, and simultaneous interpenetrating networks (SINs), where both monomers or low molecular weight prepolymers are mixed with crosslinking agents of the component polymers and polymerized/crosslinked simultaneously via noninterfering reaction mechanisms (e.g., free radical polymerization vs. step polymerization).

It is known that the interpenetration plays a significant role in enhancing the miscibility of the polymer components because physical interlocking prohibits phase separation when the molecular

weight is built up during the IPN polymerization process.¹

We have illustrated that there are several factors in determining the miscibility of IPN, such as the onset point of phase separation (thermodynamic viewpoint), the rate of phase separation, and the rate of network formation (or chemical reaction rate). These factors are determined by the reaction condition (such as initiator concentration, catalyst, crosslink density, synthesis temperature, and synthesis pressure).^{2–6} The relative rate of the two competing kinetic processes of phase separation and network formation is the major factor of importance for controlling the morphology of the final product. When the relative rate of chemical reaction to the rate of phase separation is high, the interlocking of the two component polymers occurs earlier before the phase separation and the interlocked state prohibits further phase separation. Moreover, the fast chemical reaction reduces the time length in the kinetic process of phase separation. The resulting IPNs shows a highly miscible state. When the relative rate of chemical reaction to the rate of phase separation is low, IPNs with heterogeneous mor-

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phology are obtained where only partial interpenetration exists around the phase boundaries of the dispersed phases. Thus, the phase domain size and the degree of partial interpenetration are dependent on the rate of network formation and the rate of phase separation.

Lee and Kim have tried to enhance the miscibility of IPN by applying the reaction condition, such as synthesis pressure and temperature, during the polymerization process. They were able to increase the degree of interpenetration in the incompatible polyurethane-poly(methyl methacrylate)² and polyurethane-polystyrene³⁻⁵ SINs by applying pressure (up to 10,000 kg/cm²) during the simultaneous polymerization process and were able to obtain a transparent, nearly molecular level mixture of the two components. The synthesis pressure has direct and indirect effects on the onset point of phase separation, the rate of phase separation, and the rate of network formation. The synthesis temperature has a similar effect with the synthesis pressure. When we photopolymerized the PS component of the PU-PS IPN at low temperature (as low as 0°C), the enhanced miscibility of two components was shown.⁶ With low photosynthesis temperature, the chain mobility of the PS is reduced due to increased medium viscosity, and the rate of phase separation is lowered. But the rate of network formation is slightly decreased at low photosynthesis temperature. Thus the effects of reduced ratio of the rate of phase separation to the rate of network formation increases the degree of mixing of the two component polymers at the time of physical interlocking.

Donatelli et al. have reported that the crosslink density in the first formed network of a sequential IPN of styrene-butadiene rubber and polystyrene significantly influences its morphology and properties.⁷ Hourston and McCluskey have reported on the effect of crosslink density of each component of the polyurethane-polymethylacrylate IPN system.^{8,9} It was illustrated that the degree of mixing increased as increasing crosslink density. They prepared the IPN at high synthesis temperature (60–70°C) thermally.

With low photosynthesis temperature (as low as 0°C), it could be estimated that the effect of crosslink density on the miscibility of IPN is very significant, because the T_g of PU is around synthesis temperature and the mobility difference of polymer chain is significant around its glass transition temperature. In this study, IPNs of polyurethane and polystyrene were prepared to study the effect of crosslink density variation at low synthesis temperature, of each component polymer, on the mis-

cibility resulting from the phase separation and the network interlocking process.

EXPERIMENTAL

Synthesis. The isocyanate-terminated polyurethane prepolymer was prepared by reacting 1 eq poly(tetramethylene ether) glycol (PTMG, molecular weight 1045) with 2 eq 4,4'-diphenylmethane diisocyanate (MDI) at 60°C. Mixtures of 1,4-butanediol (1,4-BD) and trimethylol propane (TMP) in 4 : 1, 1 : 1, and 1 : 4 equivalent ratios were used as the crosslinking and chain-extending agent for the polyurethane (PU) network. Divinylbenzene (DVB, 55% purity) was used as the crosslinking agent for the polystyrene (PS) network, its composition being 4, 2.5, and 0% by weight in styrene monomer.

The thoroughly mixed and degassed mixture of PU prepolymer, TMP/1,4-BD mixture (the amount being adjusted to give total NCO/OH ratio as 1), PU catalyst dibutyltin dilaurate (T-12, 0.01 wt % PU component mixture), styrene monomer, DVB, and benzoin (0.3 wt % PS component mixture) was charged between two glass plates sealed with a rubber O-ring and kept at 40°C for about 6 h for the polymerization of the component PU in the presence of styrene monomer mixture. Then the styrene monomer mixture was photopolymerized by exposure to UV light in the temperature-controlled refrigerated chamber. The photopolymerization of the styrene monomer mixture was carried out for 24 h at 0 and 40°C. The PU component was allowed to react almost to form the network earlier with the intention of observing the effect of temperature on the phase separation mainly during the photopolymerization of polystyrene component. The resulting theoretical molecular weight between crosslinks (\bar{M}_c) were 2000, 3300, and ∞ (linear) for polystyrene and 2050, 3300, and 8200 for polyurethane, respectively. Each of the homopolymers having above \bar{M}_c was also prepared. The composition of the polyurethane and polystyrene was fixed at 50/50% by weight. Samples were dried under vacuum at room temperature for more than 3 days before testing. The phase separation during drying can be excluded at room temperature.

Dynamic Mechanical Analysis. The dynamic mechanical properties were measured on a DuPont 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–+130°C.

Electron Microscopy. Transmission electron-micrographs were obtained on a JEM 100 CX (JEOL) electron microscope. The sample was stained with osmium tetroxide (OsO_4).

Density. The density was measured with a density gradient column with sodium bromide aqueous solution. All measurements were made at 25°C.

RESULTS AND DISCUSSION

Dynamic Mechanical Behavior

The $\tan \delta$ vs. temperature plot of the IPN synthesized at 0°C with varying \bar{M}_c of the PU component, when the \bar{M}_c of the PS component is fixed at 2000, is shown in Figure 1. The IPN of $\bar{M}_c = 3300$ shows two T_g 's but shifted inward 16°C for the PU phase and 51°C for the PS phase from the T_g 's of their homopolymers showing a semicompatible state (Table I). The semicompatible state means the state between the compatible state (homogeneous state) and incompatible state (heterogeneous state) which shows the broad $\tan \delta$ curve between the T_g 's of both the pure components. The IPN of $\bar{M}_c = 2050$ shows a broad transition across a wide temperature range and the T_g of PS phase is shifted 15°C more than the IPN of $\bar{M}_c = 8200$. Although there is a little T_g

increase of PU phase due to the increase of crosslink density of PU phase, it should be noted that the miscibility increases from the $\tan \delta$ curve. Figure 2 shows the $\tan \delta$ vs. temperature plot of the IPN synthesized at 40°C. There is less shift than that of the IPN synthesized at 0°C, but the increase of miscibility is also shown in this figure.

The $\tan \delta$ curve with varying crosslink densities of the PS component while the crosslink density of PU component remains the same ($\bar{M}_c = 2050$) was also measured for the IPNs synthesized at 0 and 40°C. The \bar{M}_c of PS phase was varied to 2000, 3200, and ∞ (linear PS). In this series of samples, it is also shown that the miscibility increase with increasing crosslink density of PS phase, and the miscibility of IPN synthesized at 0°C is better than that of samples synthesized at 40°C, as shown in Figures 1 and 2. The T_g was measured from the peak temperature of $\tan \delta$ curve (Table I). The low T_g was difficult to measure due to broad transition.

When the crosslink density of PS increases, the physical interlocking between two component polymers occurs earlier due to the fast gelation and the medium viscosity increases fast. Also, it brings more interpenetration of the component networks and the higher miscibility as illustrated in the previous paper.^{3,6} At low synthesis temperature, the mobility of PS polymer chain is reduced due to high medium

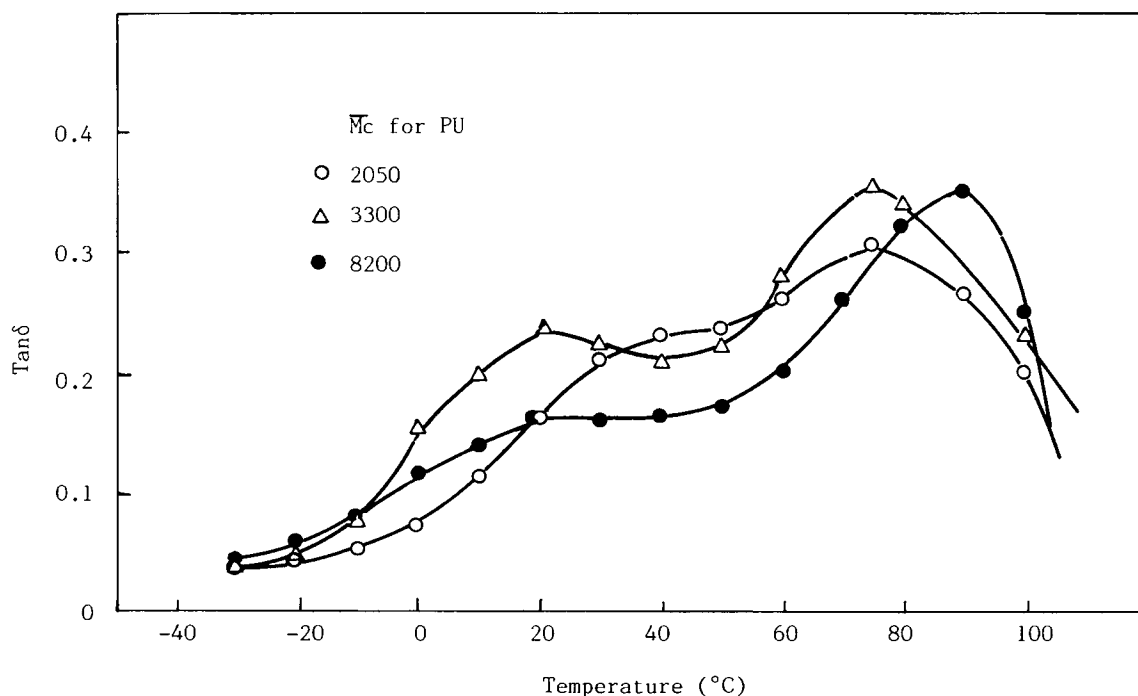


Figure 1 Dissipation factor ($\tan \delta$) vs. temperature of UC50SC50 IPNs synthesized at varying crosslink density of PU (synthesis temperature 0°C, $\bar{M}_c = 2000$ for PS).

Table I T_g and Polymer Composition (Calculated from the Fox Equation) of the PS-Dominant Phase for UC50SC50^a

\bar{M}_c (PU Phase)	\bar{M}_c (PS Phase)	Synthesis Temp (°C)	T_g (K)	Composition	
				PU	PS
2050	2000	0	348	0.36	0.64
		40	369	0.20	0.80
3300	2000	0	348	0.34	0.66
		40	372	0.17	0.83
8200	2000	0	363	0.20	0.80
		40	374	0.14	0.86
2050	3200	0	356	0.29	0.71
		40	368	0.20	0.80
2050	∞	0	368	0.18	0.82
		40	378	0.11	0.89

^a T_g of the homopolymer:

UC100 ($\bar{M}_c = 2050$) 284 K,	SC100 ($\bar{M}_c = 2000$) 399 K
UC100 ($\bar{M}_c = 3300$) 278 K,	SC100 ($\bar{M}_c = 3200$) 397 K
UC100 ($\bar{M}_c = 8200$) 268 K,	SL100 ($\bar{M}_c = \infty$) 394 K

The T_g 's of the PS homopolymers synthesized at 0 and 40°C are in the experimental error range.

viscosity, and the rate of phase separation becomes slow. On the other hand, the rate of network formation is slightly decreased at low synthesis temperature because of photopolymerization. Therefore,

the effects of the reduced ratio of the rate of phase separation to the rate of network formation increases the miscibility of the two component polymers.

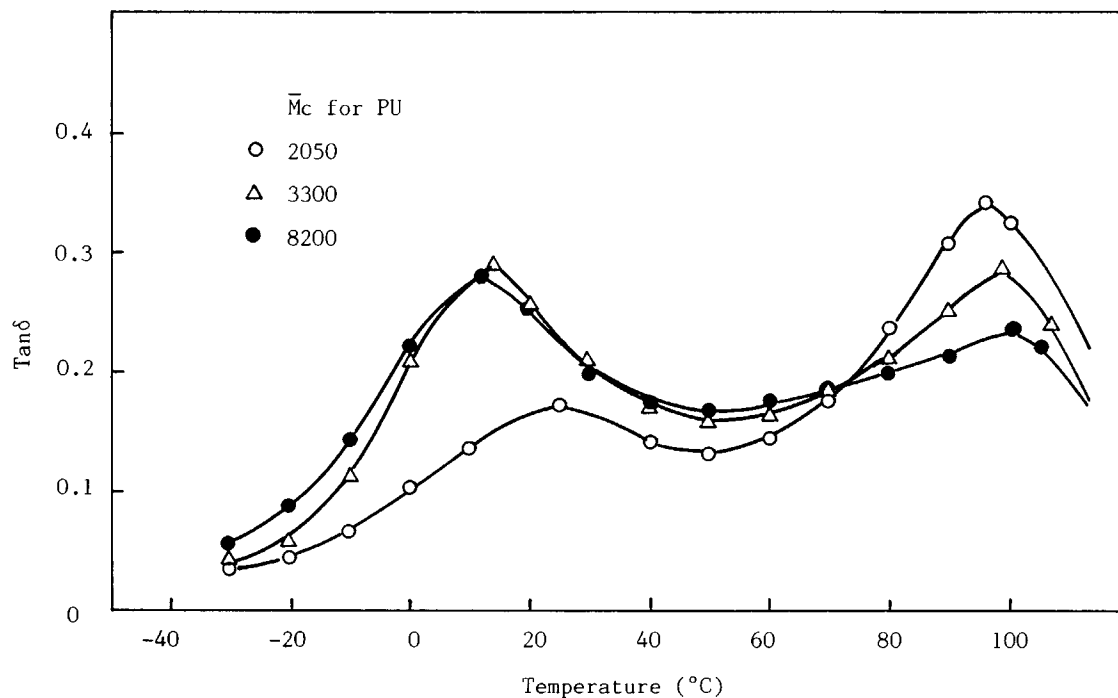


Figure 2 Dissipation factor ($\tan \delta$) vs. temperature of UC50SC50 IPNs synthesized at varying crosslink density of PU (synthesis temperature 40°C, $\bar{M}_c = 2000$ for PS).

The PS-rich phase T_g 's of the samples prepared which were taken from the peak temperature in the $\tan \delta$ vs. temperature plot are listed in Table I. The T_g of homopolymers having the same \bar{M}_c were also listed. The T_g was rather high due to the instrument and the experimental condition. To compare the degree of mixing as the compositions change, the T_g shift converted to the mass fraction of the PS and PU component polymers within PS dominant phase by assuming that the Fox equation is valid in this system¹:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} represent homopolymer T_g 's of PU and PS and w_1 and w_2 represent weight fractions. The resulting mass compositions in the PS dominant phase are shown in Table I and Figures 3 and 4. Many of the PU-rich phase T_g 's of the IPNs were difficult to measure due to broad transition.

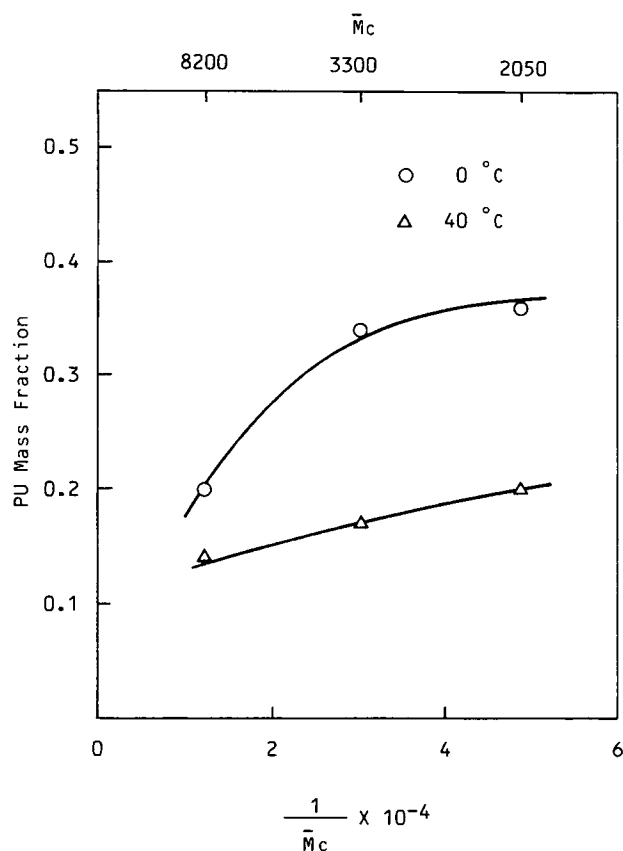


Figure 3 Calculated mass fraction of PU in the PS-dominant phase of IPNs with varying crosslink density of PU ($\bar{M}_c = 2000$ for PS).

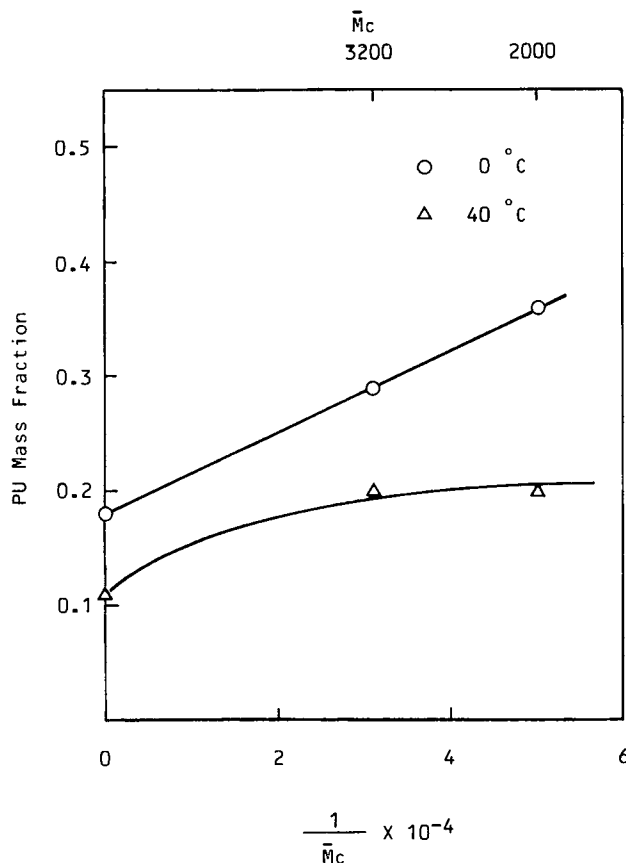


Figure 4 Calculated mass fraction of PU in the PS-dominant phase of IPNs with varying crosslink density of PS ($\bar{M}_c = 2050$ for PU).

Figure 3 shows the plot for \bar{M}_c variation of the PU phase. When the synthesis temperature is 0°C , the mass fraction of PU in the PS dominant phase is 0.2 and it increases gradually with decreasing \bar{M}_c ; finally the mass fraction of PU increases up to 0.36 when the \bar{M}_c of PU phase is 2050. The mass fraction 0.5 means perfect mixing, so that 0.36 means 72% of the degree of mixing of the component polymers. This means the fairly miscible state. When the synthesis temperature is 40°C , the miscibility increases also with decreasing \bar{M}_c of PU phase. But the degree of mixing in the entire range of \bar{M}_c is lower than that of the 0°C case and the increasing pattern is moderate with decreasing \bar{M}_c of the PU phase. This is because that the medium viscosity and the mobility of polymer chain is affected significantly by the temperature, and thus the rate of phase separation is reduced in the case of the low mobile polymer chain. The crosslink density also has the same effect on the medium viscosity and the mobility of polymer chain during the synthesis and miscibility of the IPN after the synthesis.

When the IPN was synthesized at 0°C, the abrupt increase of mass fraction, i.e., degree of mixing, between $\bar{M}_c = 8200$ and $\bar{M}_c = 3300$ was shown. The T_g of PU homopolymer is -5 and +5°C for $\bar{M}_c = 8200$ and $\bar{M}_c = 3300$, respectively. The synthesis temperature of 0°C is sited between the two T_g 's. Thus, the mobility of PU network is very low when $\bar{M}_c = 3300$ and 2050 and is relatively high when $\bar{M}_c = 8200$. This mobility difference makes the abrupt change of miscibility to be shown in the above range. Although the T_g value can be varied a little according to the instrument used, it makes little difference because the glass transition has some temperature range and the mobility change around T_g is very large.

Figure 4 shows the \bar{M}_c of PS network vs. PU mass fraction plot. With increasing crosslink density of PS phase, the gelation of PS phase occurs earlier and it increases the network interpenetration and the miscibility as described before. The monotonic increase is shown in an IPN of 0°C in contrast to the case of crosslink density variation of the PU network. The synthesis temperature effect on the miscibility is similar with Figure 3.

The crosslink density variation of the PU network, which has a low T_g around the synthesis tem-

perature, is more effective in controlling the miscibility than that of the PS network, which has a high T_g . Also, the crosslink density variation is more effective at low temperature than at high temperature in controlling the miscibility due to the combined effect of temperature and crosslink density on the polymer chain mobility.

Morphology

The morphology via transmission electron microscopy also shows the crosslink density effect on the miscibility and phase structure. The morphology of IPNs synthesized at 0°C with varying crosslink densities of the PU component when the \bar{M}_c of PS is 2000 is shown in Figure 5.

In the IPN synthesis, the phase separation is thought to take place earlier in the polymerization, forming a relatively large domain size. A secondary phase separation follows, showing fine structure around the large domain size.¹ In our system, the medium viscosity increases as the polymerization of styrene monomer proceeds. At a certain conversion, the medium viscosity becomes very high, so that the primary phase separation cannot be maintained any more. Also, the phase domain size is somewhat re-

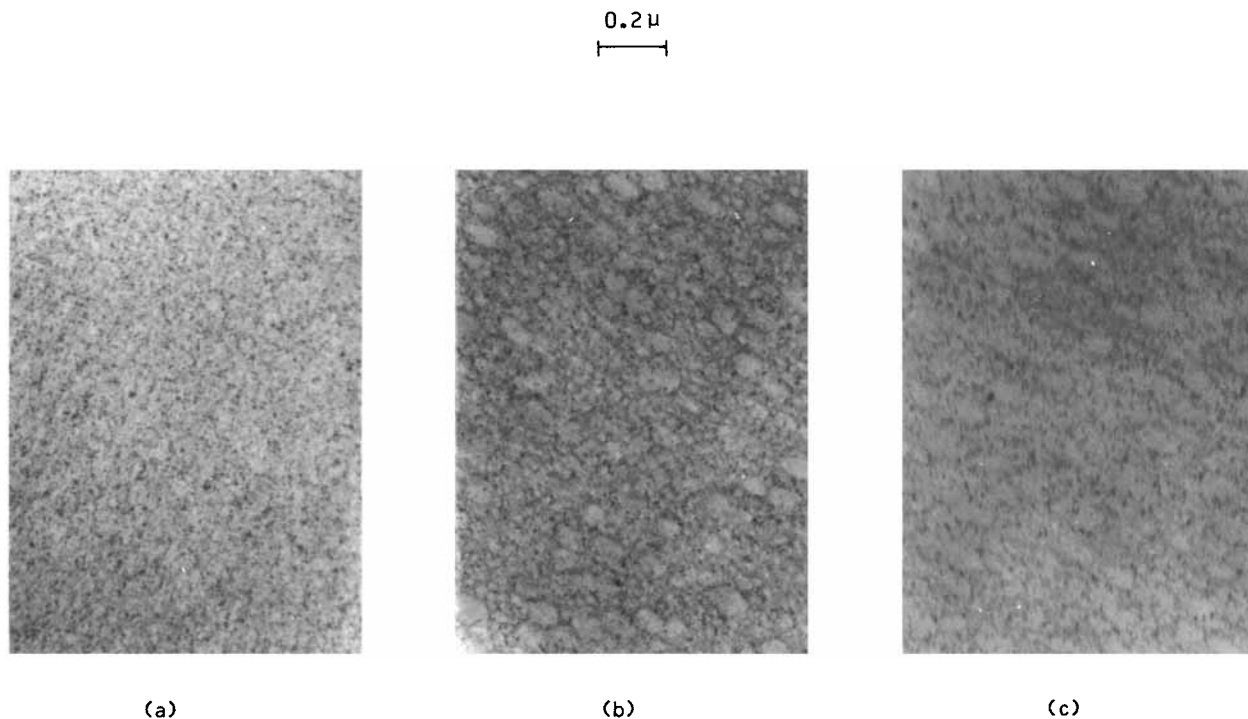


Figure 5 Transmission electron micrographs of the UC50SC50 IPNs synthesized at 0°C with varying crosslink densities of PU ($\bar{M}_c = 2000$ for PS): (a) $\bar{M}_c = 2050$; (b) $\bar{M}_c = 3300$; (c) $\bar{M}_c = 8200$.

stricted according to the size of \bar{M}_c . In some case, the vitrification prohibits further phase separation. The secondary phase separation occurs when the medium viscosity is high and the mobility of the polymer chain is low. The IPN with $\bar{M}_c = 2050$ of PU shows dual phase continuity and domain sizes in the range of hundreds of angstroms (200–300 Å) [Fig. 5(a)]. It is thought that secondary phase separation mainly occurs due to the low synthesis temperature and the high crosslink density.^{6,10} There are two kinds of domain structures when \bar{M}_c is 3300 and 8200. Figure 5(b) shows a somewhat irregular phase structure, having a large domain size of about 1000 Å, and a secondary phase separated fine structure. At high \bar{M}_c (= 8200), primary phase separation mainly occurs and secondary phase separation occurs at a later stage of synthesis. It can be noted that the miscibility increase with increasing crosslink density.

Density

The density vs. crosslink density ($1/\bar{M}_c$) of PU and PS phase synthesized at 0 and 40°C is shown in Figures 6 and 7. The density was measured at 25°C.

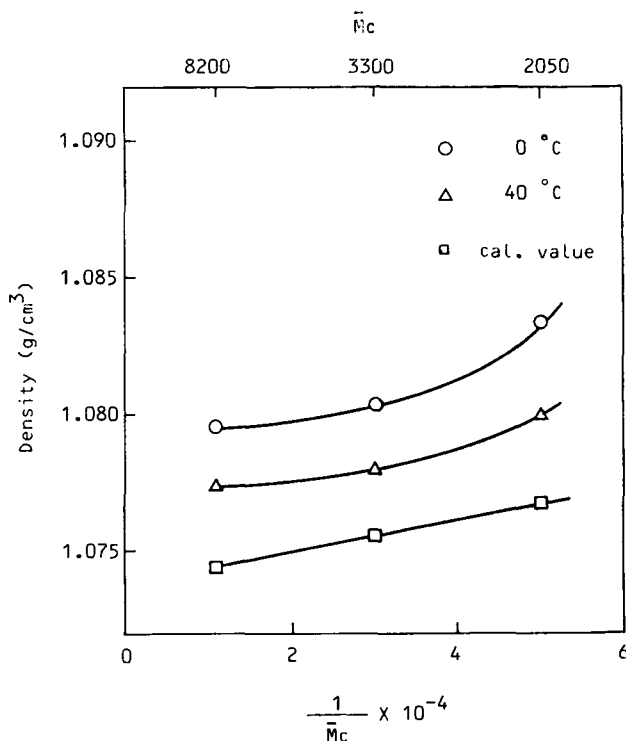


Figure 6 Density vs. crosslink density ($1/\bar{M}_c$) of PU in the IPNs synthesized at 0 and 40°C. [$\bar{M}_c = 2000$ for PS; (□) calculated values based on the volume additivity rule.]

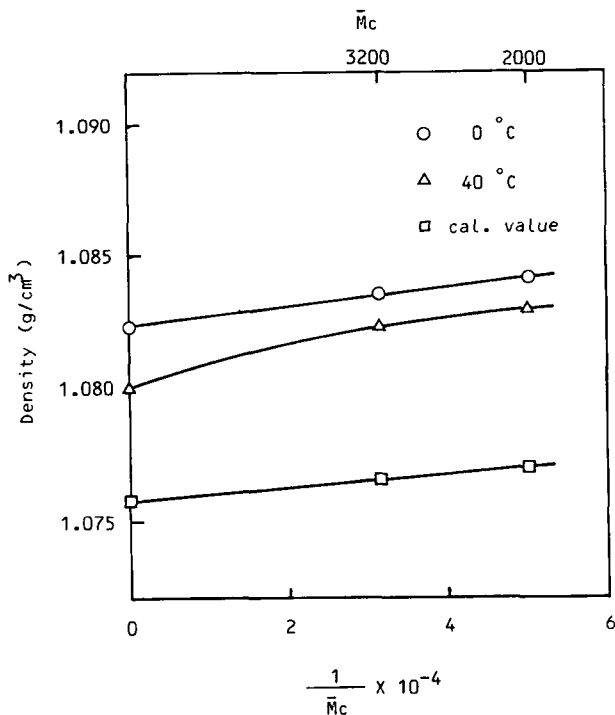


Figure 7 Density vs. crosslink density ($1/\bar{M}_c$) of PS in the IPNs synthesized at 0 and 40°C. [$\bar{M}_c = 2050$ for PU; (□) calculated values based on the volume additivity rule.]

The densities of each homopolymer were also measured. The densities of PU homopolymers were 1.1027, 1.0997, and 1.0972 g/cm³ for $\bar{M}_c = 2050, 3300,$ and 8200, respectively. The densities of PS homopolymers were 1.0525, 1.0517, and 1.0502 g/cm³ for $\bar{M}_c = 2000, 3200,$ and ∞ (linear PS), respectively. The PUs were prepared at 40°C and the densities of PS prepared at 0 and 40°C were within experimental error range. The density of the IPNs synthesized at both temperatures show increased densities over the calculated densities based on the volume additivity of the components; this increase seems to be due to the increase of the degree of mixing. Although there is some difference in the increasing pattern between the density behavior and the mass fraction of PU in the PS-dominant phase with varying crosslink density and synthesis temperature, the relative magnitude of the density of IPNs agrees well with the degree of mixing.

CONCLUSION

This study extends an earlier study⁶ on low temperature synthesis of the polyurethane–polystyrene IPN and shows the effect of crosslinking level of

each components during low temperature synthesis. The miscibility increases with decreasing synthesis temperature and increasing crosslink density of each component, as can be estimated.^{1,6-9} The crosslink density variation of PU network which has a low T_g around the synthesis temperature is more effective in controlling the miscibility than that of the PS network which has a high T_g . The crosslink density variation is more effective at low temperature than at high temperature in controlling the miscibility due to the combined effect of temperature and crosslink density on the polymer chain mobility.

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