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Dynamic Mechanical Properties of Interpenetrating Polymer Networks of Polyurethane and Poly(Styrene-co-Acrylonitrile)

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SUMMARY

Interpenetrating polymer networks (IPN's) of a combination of polyurethane (PU) and poly(styrene-co-acrylonitrile) (PSAN) were prepared by the simultaneous polymerization process. To observe the relative rate effect of the simultaneous polymerization, the polymerization kinetics of PU and PSAN were studied. The gel-times of PU and PSAN network were theoretically calculated, and three types of SIN's with different rates of network formation in each component were prepared for comparison. IPN's with $\overline{M}c$=3000 and $\overline{M}c$=4900 were prepared to observe the influence of the crosslink density. The glass transition behavior studied by the dynamic mechanical analysis showed larger shifts in Tg's in SIN's with similar gel-times and smaller $\overline{M}c$.

INTRODUCTION

Interpenetrating polymer networks (IPN's) in its broadest definition refer to any material containing two or more polymers which are in network form (KLEMPNER, 1978). They can be classified into two categories according to the synthetic mode. One is sequential IPN (SIPN) (HUELCK et al., 1972) and the other is simultaneous IPN (SIN) (KIM et al., 1976 ; TOUSAENT et al., 1974). The degree of intermixing of the SIN (simultaneous polymerization of the component monomers or oligomers) are mainly affected by the following factors.

(1) Compatibility of each component polymers
(2) Relative rate of reaction (network formation)
(3) Average molecular weight per crosslink
(4) Weight fraction of each component polymer networks
(5) Degree of polymerization at the time of gel
(6) Mobility of the polymer chain to phase separate

In the present work, the kinetics of polyurethane (PU) and poly(styrene-co-acrylonitrile) (PSAN) polymerization were studied. The gel-times of each component polymers of PU/PSAN SIN's were calculated theoretically by the simultaneous combination of the polymerization kinetics and the gelation theory of Flory-Stockmayer (FLORY, 1941 ; STOCKMAYER, 1943) for PU and that of Walling (WALLING, 1945) for PSAN. PU/PSAN SIN's were synthesized in varying weight ratios, with different $\overline{M}c$, and with different rate of reaction. The glass transition behavior and dynamic mechanical properties of PU/PSAN SIN's were studied.

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EXPERIMENTAL

Materials : Poly(tetramethylene ether) glycol (PTMG) ($\bar{M}n$=986), 1,4-butanediol (1,4-BD), and trimethylol propane (TMP) were dried at 60°C for 5 hours under a vacuum of 0.2 mmHg. Acrylonitrile (AN), styrene (ST), and divinylbenzene (DVB) were purified with standard laboratory techniques.

Kinetics : For PSAN polymerization, a 500 ml four-neck flask equipped with a nitrogen inlet, sleeve stirrer, thermometer, and reflux condenser was charged with 100 g of monomer mixture of SAN (AN/ST = 24.15/75.85 wt. ratio), 100 g of DMF, and varying amount of lauroyl peroxide (LPO). The reaction was carried out under dry nitrogen gas at different temperatures (50, 60, 70°C). A few grams of reaction mixture sampled at intervals of 15 min was precipitated in methanol and then dried at 50°C under vacuum to calculate extent of reaction by weighing the precipitates. For PU polymerization, the same flask used in the PSAN polymerization was charged with 100 g of isocyanate (NCO) terminated PU prepolymer (synthesis is described in the following section), 100 g of solvent mixture (cellosolve acetate : toluene : xylene = 2:1:1 wt. ratio), and 5.8 g of 1,4-BD and TMP mixture (1,4-BD/TMP = 2/9 eq. ratio). The concentration of catalyst (tetramethyl butanediamine) (TMBDA) and reaction temperatures (50, 60, 70°C) were varied. A few grams of reaction mixture was sampled at intervals of 10 min, and the unreacted NCO content was determined by the di-n-butyl amine titration method to calculate the conversion.

Synthesis : The NCO terminated PU prepolymer was prepared by reacting 2 equivalents of 4,4'-diphenylmethane diisocyanate (MDI) with 1 equivalent of PTMG. A 500 ml 4-neck flask described in the PSAN polymerization was charged with 2 equivalents of MDI. To this was added slowly with stirring 1 equivalent of PTMG. The reaction was carried out under dry nitrogen at 70°C until the theoretical NCO content determined by the di-n-butyl amine titration method was reached. PU network was prepared by reacting 1 equivalent of PU prepolymer and 1 equivalent of 1,4-BD and TMP mixture (2/9 eq. ratio for $\bar{M}c$=3000, 1/1 eq. ratio for $\bar{M}c$=4900). The PU prepolymer-1,4-BD-TMP mixture and 0.1 wt. % of TMBDA were homogeneously mixed for 5 min using a high torque stirrer. The mixture was cast in a closed glass mold (treated with PVA for the release in water) at 60°C for 12 hrs and 100°C for 4 hrs. PSAN network was synthesized by polymerizing monomer mixture composed of 75.85 g of styrene, 24.15 g of acrylonitrile, varying amount of DVB (4.53 g for $\bar{M}c$=3000, 2.72 g for $\bar{M}c$=4900), and 1 g of LPO. The monomer mixture was cast in the same mold used for the PU preparation and cured at 60°C for 12 hrs and 100°C for 4 hrs.

SIN's were prepared by simultaneous polymerization of PU and PSAN networks. One equivalent of 1,4-BD-TMP-TMBDA mixture was added to one equivalent of PU prepolymer at 60°C and then homogeneously mixed. The SAN-DVB-LPO monomer mixture was added in varying weight ratios (25, 50, and 75 wt. % PSAN) and homogeneously mixed for 3 min and degassed for 30 sec under vacuum to remove the air bubbles entrapped during mixing. The mixture was then cast in the same manner as described above.

Three kinds of pseudo-IPN (crosslinking agent in the PSAN network is omitted in the mixture, thus forming PSAN linear and PU network crosslinked) were prepared for 25/75, 50/50, and 75/25 wt. % PU/PSAN to measure the kinetic chain length, λ_n, of PSAN polymerized simultaneously with PU. They were prepared in the same manner as the SIN preparation.

Measurement : The average molecular weights of linear PSAN extracted from pseudo-IPN were measured with a GPC (Waters Associates) with RI detector. The column used was μ-STYRAGEL/10^4 Å. Monodispersed polystyrenes with molecular weights of 240000, 100000, 50000, 8500, and 4000 were used for calibration. DMF was used as a solvent, and the solvent flow rate was 1 ml/min.

Dynamic mechanical measurements were made with a du Pont 981 dynamic mechanical analyzer at a heating rate of 5^oC/min. Specimens were 1.7-2.0 mm in thickness, 9-11 mm in width, and 13-15 mm in length. All specimens were dried at 50^oC under 0.2 mmHg vacuum for 24 hrs to remove unreacted monomer.

RESULT AND DISCUSSION

1. Kinetics and Gel-time Prediction

The overall rate equation for PSAN polymerization was obtained as follows

$$\frac{dx}{dt} = K_s(1-x) \qquad (1)$$

where K_s is the rate constant for PSAN polymerization,

$$K_s = 8.69 \times 10^7 [I]_o^{0.79} \exp(-17200/RT) \ (\mathrm{min}^{-1}) \qquad (2)$$

$[I]_o$: the initiator concentration (mol/l)

Eq. (1) is integrated to give

$$K_s t = -\ln (1-x) \qquad (3)$$

The conversion at gel point (WALLING, 1945) is

$$X_c = 1 - (\frac{C_A}{C_{Ao}})_c = \frac{C_{Ao} + 2C_{Bo}}{4C_{Bo}(\lambda_n - 1)} \qquad (4)$$

where C_A is the concentration of monovinyl monomer and C_B the concentration of divinyl monomer. The gel-time of PSAN can be calculated by combining eq. (3) and (4).

$$t_{gel} = -\frac{1}{K_s} \ln [1 - \frac{C_{Ao} + 2C_{Bo}}{4C_{Bo}(\lambda_n - 1)}] \qquad (5)$$

The overall rate equation for PU polymerization was obtained as follows

$$K_u[NCO]_o t = \frac{x}{1-x} \qquad (6)$$

where K_u is the rate constant for PU polymerization,

$$K_u = 1.29 \times 10^{10}[\mathrm{Cat}]_\circ^{0.564} \exp(-11900/RT) \left(\frac{1}{\mathrm{mol \cdot min}}\right) \qquad (7)$$

$[\mathrm{Cat}]_\circ$: the concentration of catalyst (mol/l)

The conversion at the time of gel is related as,

$$\frac{1}{f-1} = \frac{X_c^2 \rho}{(1 - X_c^2(1-\rho))} \qquad (8)$$

where ρ is the ratio of hydroxyl groups belonging to branch units to the total number of hydroxyl groups in the mixture, and f ; the functionality of branch unit. The functionality of TMP is 3, and the value of ρ is varied by the ratio of 1,4-BD to TMP. Therefore, the gel-times of PU can be calculated from $[\mathrm{Cat}]_\circ$, $[\mathrm{NCO}]_\circ$, and ρ. The calculated gel-time values of PSAN and PU are shown in Table 1.

TABLE 1

Sample Description

Sample Code	$\overline{M}_c$	$[\mathrm{TMBDA}]_\circ$ (mol/l)	PU GEL Time(min)	$[\mathrm{LPO}]_\circ$ (mol/l)	PSAN GEL Time(min)	λ_n* (PSAN)
UC75SANC25** - ①***	3000	3.69×10^{-3}	75.3	2.20×10^{-2}	238.9	1785
UC75SANC25 - ②	3000	5.00×10^{-5}	238.9	2.20×10^{-2}	238.9	1785
UC75SANC25 - ③	3000	0	480.5	2.20×10^{-2}	238.9	1785
UC50SANC50 - ①	3000	1.25×10^{-3}	58.4	2.20×10^{-2}	136.2	3127
UC50SANC50 - ②	3000	2.78×10^{-4}	136.2	2.20×10^{-2}	136.2	3127
UC50SANC50 - ③	3000	4.85×10^{-5}	364.7	2.20×10^{-2}	136.2	3127
UC50SANC50 - ①	4900	1.19×10^{-3}	92.2	2.20×10^{-2}	220.0	3127
UC50SANC50 - ②	4900	2.56×10^{-4}	219.2	2.20×10^{-2}	220.0	3127
UC50SANC50 - ③	4900	1.78×10^{-5}	469.6	2.20×10^{-2}	220.0	3127
UC25SANC75 - ①	3000	2.93×10^{-2}	26.5	2.20×10^{-2}	93.2	4566
UC25SANC75 - ②	3000	1.86×10^{-3}	93.2	2.20×10^{-2}	93.2	4566
UC25SANC75 - ③	3000	2.18×10^{-4}	315.4	2.20×10^{-2}	93.2	4566

* λ_n : measured from GPC (PSAN polymerized without crosslinking agent and extracted from IPN)

** the weight percentage of the component polymers

*** ① represents an IPN with the PU gelation faster than PSAN gelation,

② with simultaneous PU and PSAN gelation,

③ with the PSAN gelation faster than PU gelation

2. Dynamic Mechanical Behavior

The glass transition temperatures (Tg's) determined from the damping ($\tan\delta$) peak on DMA thermograms are listed in Table 2. The low Tg corresponds to the PU glass transition and the high Tg corresponds to the PSAN glass transition. The PU/PSAN SIN's exhibit two distinct Tg's which are inwardly shifted from the Tg's of the component homopolymers. As the average molecular weight per crosslink, $\overline{M}c$, and the difference between the gelation times of each component polymers become smaller, the shift in the glass transition temperature increases. This means that the simultaneous gelation and high crosslink density would give higher probability of physical interlocking in SIN systems.

TABLE 2

Glass Transition Temperatures of Samples (^{o}C)

Sample Code	$\overline{M}_c$=3000		$\overline{M}_c$=4900	
	Low T_g	High T_g	Low T_g	High T_g
Homopolymer				
UC100	5	-	0	-
SANC100	-	135	-	131
IPN's				
UC75SANC25 - ①	9	130		
UC75SANC25 - ②	13	-		
UC75SANC25 - ③	9	128		
UC50SANC50 - ①	9	123	0	125
UC50SANC50 - ②	14	119	5	120
UC50SANC50 - ③	7	124	1	125
UC25SANC75 - ①	10	120		
UC25SANC75 - ②	10	119		
UC25SANC75 - ③	4	130		

Storage modulus (E') and damping (tanδ) characteristics obtained from the dynamic mechanical analyzer (DMA) are shown in Fig. 1 - Fig. 4. The dynamic mechanical characteristics of the PU and PSAN homopolymers are shown in Fig. 1. As the $\overline{M}c$ becomes smaller, the Tg (the peak point of the tanδ curve) of the homopolymer network increases. The dynamic mechanical properties of PU50/PSAN50 SIN's (Fig. 2) clearly show the higher inward shift in Tg's of the simultaneously gelled SIN (UC50SANC50 - ②). This implies that although the SIN has two phase structure, the PSAN domain contains higher amount of the interlocked PU phase (lowering the PSAN Tg) and the PU domain contains higher amount of the interlocked PSAN phase (raising the PU Tg). The probability of forming the interlocked network is presumed to be higher when the two networks are crosslinked simultaneously than when there is large difference in the crosslink formation rates of each network (and thus allowing the second forming network the time to phase separate). The effect of the crosslink density on the degree of intermixing is shown in Table 2, Fig. 2 and Fig. 3. The SIN's with high crosslink density show larger shift

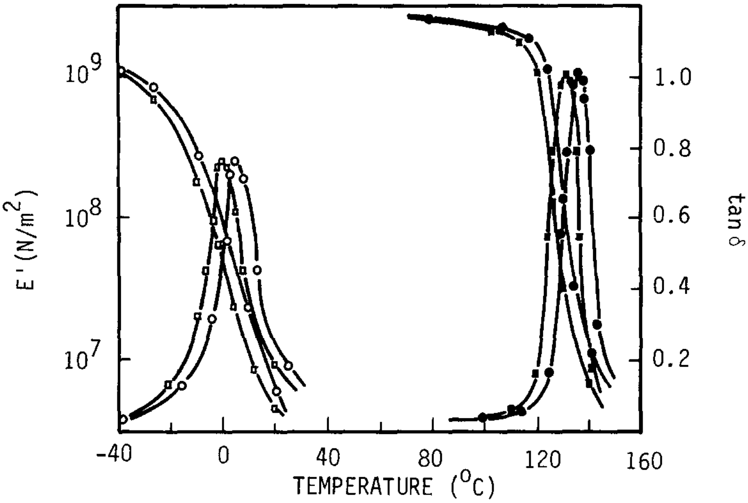

Fig. 1 Dynamic Mechanical Properties of PU and PSAN Homopolymers, ○ UC100($\overline{M}c$=3000), ● SANC100($\overline{M}c$=3000), □ UC100($\overline{M}c$=4900), ■ SANC100($\overline{M}c$=4900).

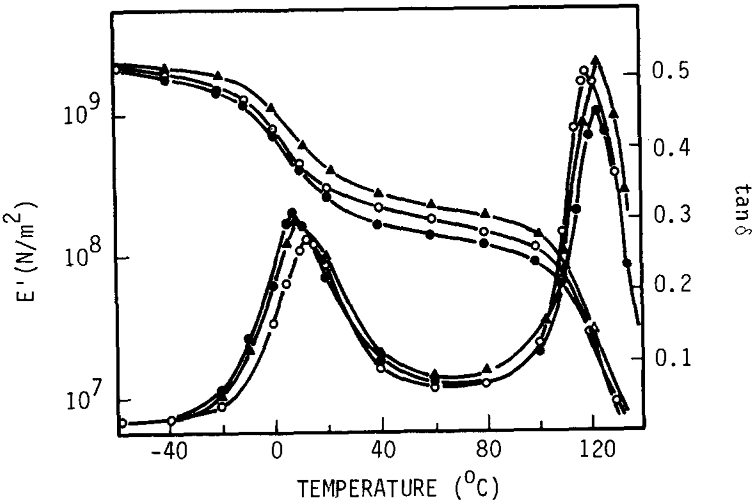

Fig. 2 Dynamic Mechanical Properties of PU50/PSAN50 SIN's($\overline{M}c$=3000) ● UC50SANC50 -①, ○ UC50SANC50 -②, ▲ UC50SANC50 -③.

in the component polymer transition temperatures. In PU transition, SIN with $\overline{M}c$ = 3000 (UC50SANC50 -②) shows Tg shift of 9^{o}C while the equivalent SIN with $\overline{M}c$ = 4900 shows Tg shift of 5^{o}C. In PSAN transition, also SIN with $\overline{M}c$ = 3000 shows shift of 16^{o}C while that with $\overline{M}c$ = 4900 shows shift of 11^{o}C. The modulus of the SIN with fast PSAN network formation (denoted as ③) is higher than the modulus

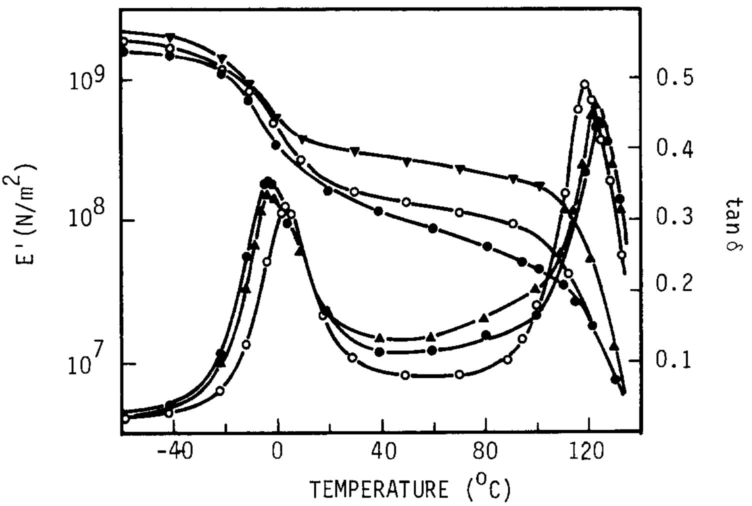

Fig. 3 Dynamic Mechanical Properties of PU50/PSAN50 SIN's ($\overline{M}c$=4900)
● UC50SANC50 - ①, ○ UC50SANC50 - ②, ▲UC50SANC50 - ③.

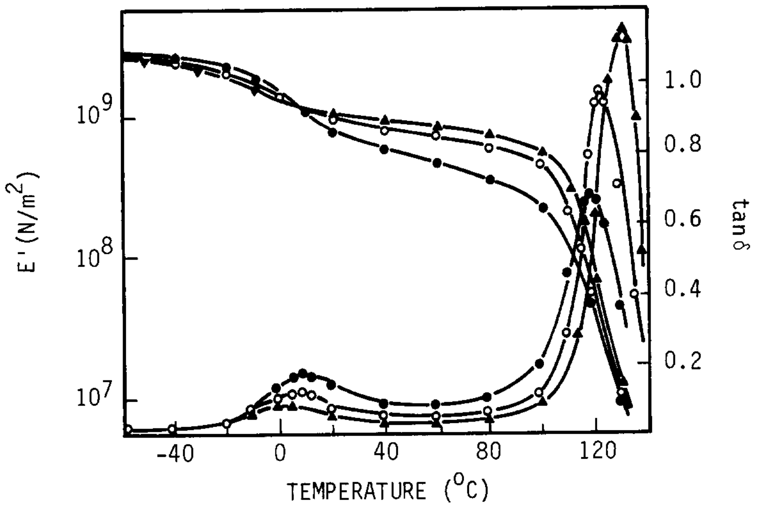

Fig. 4 Dynamic Mechanical Properties of PU25/PSAN75 SIN's ($\overline{M}c$=3000)
● UC25SANC75 - ①, ○ UC25SANC75 - ②, ▲UC25SANC75 - ③.

of the SIN with fast PU network formation (denoted as ①). The modulus of the simultaneously gelled SIN (denoted as ②) is in between the modulus of the two (Fig. 2, 3, and 4). In the tan δ curve, the ③ SIN shows highest damping at the PSAN transition temperature while the ① SIN shows highest damping at the PU transition temperature (Fig. 2 and 4). The above modulus and tan δ behavior implies the morphology difference in ③ and ① SIN. It seems that the ③ SIN has PSAN phase continuous and PU phase dispersed, while ① SIN has the reverse morphology. The simultaneously gelled SIN (②) may have cocontinuous morphology.

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