

Compatibility and Morphology in Polyurethane and Polystyrene Ionomeric Interpenetrating Polymer Networks

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ABSTRACT: Interpenetrating Polymer Networks (IPNs), composed of polyurethane (PU) and poly(styrene-acrylic acid) (PSAA), with containing mutual opposite charge groups, *i.e.*, tertiary amine group in PU and carboxyl groups in PSAA, were prepared in PU/PSAA ratio of 75/25 (PU-dominated), and 25/75 (PSAA-dominated). The compatibility and morphology of these IPNs were investigated through dynamic mechanical analysis and scanning electronic microscopy studies. Compatibility of IPNs was greatly enhanced through the introduction of charge groups into the system. There are different morphology and dynamic mechanical behaviours for PU/PSAA alloys between PU-dominated and PSAA-dominated alloys. PSAA in the PU-dominated alloys was found to aggregate to the hard segment of the PU matrix, resulting in heterogeneous distribution of hard/soft segments in morphology and having little effect on the shift of the temperature transition while PU in PSAA-dominated alloys was found to be distributed homogeneously in the PSAA matrix.

KEY WORDS Interpenetrating Polymer Network (IPN) / Morphology / Dynamic Mechanical Analysis / Polyurethane and Polystyrene Ionomer / Compatibility /

Interpenetrating Polymer Networks (IPNs) evolves permanent entanglements between polymers by virtue of interpenetrating effects rather than by covalent chemical bonds. Such entanglements will enhance the crosslinking density of the resultant IPNs. The IPNs will create characteristic properties suitable for special applications. The free volume of IPNs reduces as the interpenetrating networks increase and, as a result, the mechanical strength increases and exceeds that of the constituents.

IPNs from rubbery polyurethane (PU) and rigid polystyrene (PS) at different composition may promote compatibility between PS-reinforced PU or PU-toughened PS, since compatibility between PU and PS is poor due to the significant discrepancy in the solubility parameters between them.

From the viewpoint of thermodynamics, phase separation can be produced during po-

lymerization resulting from insignificant penetrating effects due to a positive value of the free energy of mixing.^{1,2)} By increasing intermolecular attractions through the introduction of opposite charge groups into the polymer components to improve compatibility, proposals³⁻¹⁰ have been proved successful.

In this paper, N-methyl diethanolamine (MDEA) was introduced into PU and AA to PSAA to impart attractions from tertiary amines and carboxyl groups in the polymer alloys. Through dynamic mechanical analysis and morphology studies, discussions have been given on the compatibilities of the polymer alloys containing opposite charge groups.

EXPERIMENTAL

Table I shows the materials with the designations used for the research. Polyol (PTMO

1000) was degassed at 70°C under vacuum overnight before being applied. Styrene monomer (S) was distilled under vacuum to remove the inhibitor. Other agents involved in Table I were used as received.

Preparation of Full-IPNs, Semi-IPNs and Linear Blends

PU prepolymers at 5.6% NCO determined by di-*n*-butylamine titration method,¹¹ were prepared by reacting 2 equivalent 4,4'-methylene bis(phenyl isocyanate) (MDI) with one equivalent poly(tetramethylene oxide) glycol (PTMO). PU prepolymer was mixed with a mixture of one equivalent MDEA or triethanolamine (TEA) with suitable composition of styrene monomer (S), acrylic acid (AA), divinyl benzene (DVB), and benzoyl peroxide (BPO). The mixture was agitated vigorously for three minutes at 80°C, and then degassed for 30 seconds. Afterwards, it was cast in an aluminum mold for reaction at 80°C for 24 hours, and postcured at 100°C for another 24 h. As for the preparation of the linear blends, the crosslinking agent, DVB, for

PSAA has to be removed and MDEA takes the place of TEA in the mixture. For Semi-IPNs preparation, either crosslinking agent has to be replaced by difunctional reactants. For this study, PU/PSAA alloys at ratios of 75/25 and 25/75 were prepared. Samples were kept in a desiccator at 50% R.H. for at least three days before being tested for physical and mechanical properties.

Testing Methods

Rheovibron Model DDV-IIC in the temperature range of -80°C to 160°C was used to determine the dynamic mechanical properties. Frequency was set at 110 Hz, heating rate kept at 1-2°C min⁻¹ in the transition regions, and 3-5°C min⁻¹ in the non-transition regions.

A morphological study was performed with the aid of a scanning electronic microscope (SEM). Microphotographs were taken of the surface of the samples, which were fractured in liquid nitrogen and coated with gold powder.

Table I. Materials

Designation	Composition	Supplier
MDI	4,4'-methylene bis(phenyl isocyanate)	Bayer Chemical Co.
PTMO 1000	Poly(tetramethylene oxide) glycol M.W. = 1002	Union Carbide Chemical Co.
MDEA	Methyl diethanol amine	Merck Chemical Co.
TEA	Triethanolamine	Wako Pure Chemical Co.
S	Styrene	Hayashi Pure Chemical Co.
AA	Acrylic acid	Merck Chemical Co.
DVB	Divinyl benzene	Merck Chemical Co.
BPO	Benzoyl peroxide	Merck Chemical Co.
DBA	Di- <i>n</i> -butylamine	Hayashi Pure Chemical Co.
PU	PTMO 1000/MDI/MDEA (or TEA) = 1/2/1 (equivalence)	
PS (or PSAA)	S (or S/AA)/DVB/BPO = 28.5/1.5/0.6 (weight fraction)	
LPU/LPSAA15	Linear blend of PU and PSAA with 15 mol% AA	
CPU/CPSAA15	IPN of crosslinked PU and PSAA with 15 mol% AA	
LPU/CPSAA15	IPN of linear PU and crosslinked PSAA with 15 mol% AA	

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis

From Figures 1 and 2, we observed that the E' curves have two declining stages for either Full-IPNs (Figure 1) or linear blends (Figure 2) in the absence of AA in PSAA at PU/PSAA ratio of 25/75. One declining stage which emerged as 15 or 30 mol% AA was introduced into PSAA, meaning that the introduction of AA serves to impart a homogeneous property of the resultant alloys.

From the E'' curves in Figures 1 and 2, two separating transition peaks in the absence of AA in PSAA were observed with one at low temperature representing the transition of the PU phase, and the other at high temperature indicating the PSAA phase. These separating transitions resulting from the poor compatibility between both components were caused by the rather significant difference in the solubility parameter falling between them.¹²⁻¹⁴

Introduction of 15 mol% AA into PSAA increased its compatibility through intermolecular attractions by the tertiary amine and

carboxyl group in the system, thus forming a combined broad transition peak between two transition peaks of the polymer components. As the AA content was increased up to 30 mol%, the transition peak turned narrower in peak shape. This indicates that the compatibility can be further improved with continual increase of AA content. The transition peak for the presence of AA in the linear blend system is even broader than that in the case of Full-IPN system. This shows that compatibility has been improved in linear blends, though not so satisfactorily as that in the Full-IPNs, since Full-IPNs possess permanent entanglements which force polymer chains to hold together during polymerization and thus increase its compatibility.¹⁵

Figure 3 shows the temperature dependence of E' and E'' for polymer alloys at PU/PSAA at 25/75 and with 15 mol% AA in PSAA. E'' curves have broad transitions at high temperatures near that of the crosslinked PSAA. Transition peaks emerged at different temperatures with different heights indicate the various degrees of compatibility as follows:

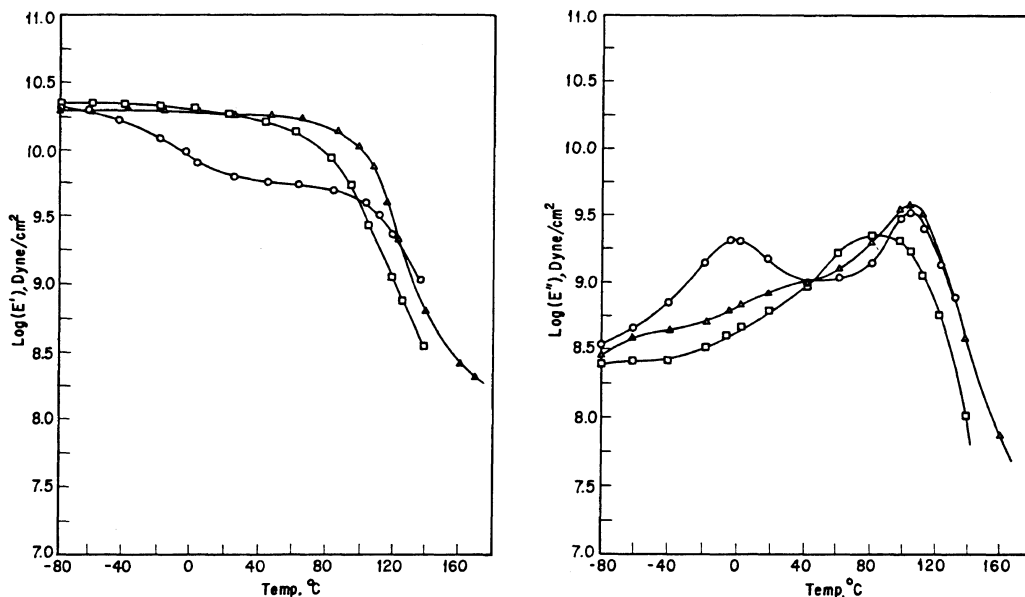


Figure 1. Temperature dependence of E' , E'' of CPU/CPSAA Full-IPNs at a ratio of 25/75 with CPSAA containing various AA content (mol%): —○—, 0; —□—, 15; —△—, 30.

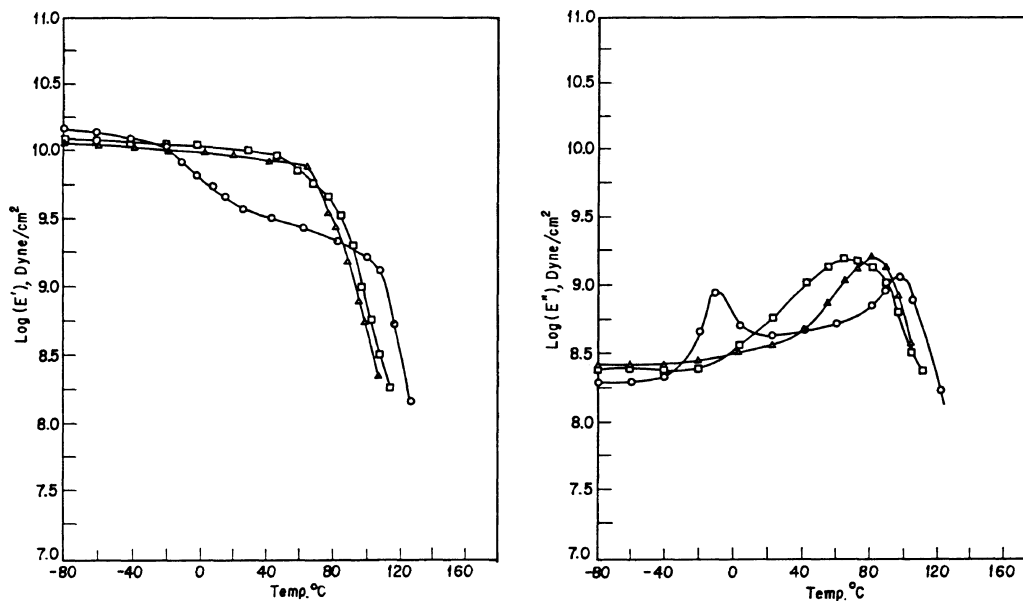


Figure 2. Temperature dependence of E' , E'' of LPU/LPSAA linear blends at a ratio of 25/75 with LPSAA containing various AA content (mol%): —○—, 0; —□—, 15; —△—, 30.

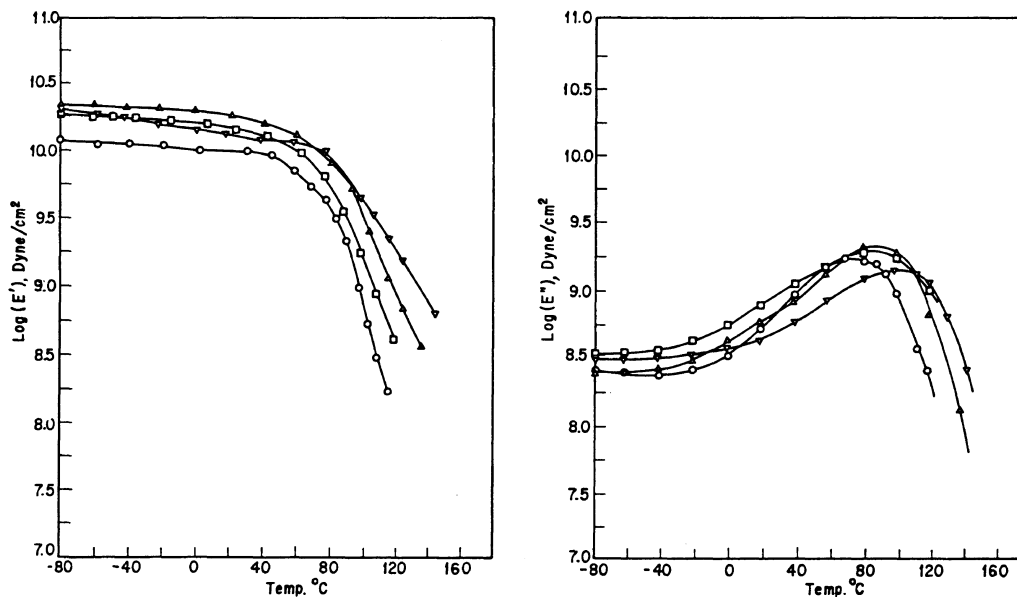


Figure 3. Temperature dependence of E' , E'' of PU/PSAA alloys at a ratio of 25/75 with 15 mol% AA in PSAA: —△—, CPU/CPSAA15; —□—, CPU/LPSAA15; —▽—, LPU/CPSAA15; —○—, LPU/LPSAA15.

Full-IPN > PSAA-crosslinked Semi-IPN > PU-crosslinked Semi-IPN > Linear blend. The reasons why the degree of compatibility of

PSAA-crosslinked polymer alloys is higher than that in the case of PU-crosslinked alloys can be explained by the molecular chain dif-

fusion theory.^{16,17} In early stage of polymerization, the viscosity of PU prepolymer is so high that both the linear and crosslinking PU reactions failed to change drastically in the viscosity and diffusion speed of PU chains during the polymerization. However, the viscosity of S-AA in crosslinking reactions increases faster than in linear reactions. As a result, PSAA in crosslinking reaction was not given sufficient time to diffuse because of higher viscosity building up, making PSAA-crosslinking alloys allow more interpenetrating structures than PU-crosslinking systems, leading to better compatibility.

Similar phenomena as mentioned above were observed for alloys at PU/PSAA at 75/25 as shown in Figures 4 to 6. Two transition peaks for polymer alloys without AA in the system converged to one transition peak as the AA was incorporated, and the shift of E'' transition peak to a higher temperature increased with increasing AA content but was not so significant as that of PU/PSAA alloys at 25/75 ratio. This is attributed to the transition peak of PU-dominated alloys showing mainly

the transition of the soft segment of PU rather than that of the hard one. While PSAA was incorporated in the system, it was attracted by the tertiary amine group in the hard segment of PU and therefore PSAA agglomerated in PU hard segment, instead of in PU soft segment. This results in less effect on the shift of transition peaks of PU-dominated alloys.

Scanning Electron Microscopy

Microphotographs taken of PU/PSAA polymer alloys are shown in Figures 7 and 8, and we can see that the polymer alloys without AA in the system are dispersed phases scattered in the matrix in the form of round particles, (Figures 7(a), 7(c) and Figures 8(a), 8(c)).

Looking at the average diameter of the particles and their occupied area fractions listed in Table II, once the introduction of AA into PSAA is made, particle disappears. It becomes clear that the phase separation diminishes as AA is introduced. From Table II, the particle in Full-IPNs is invariably larger than that in the linear blends. This is probably due to the lesser degree of compatibility as a result

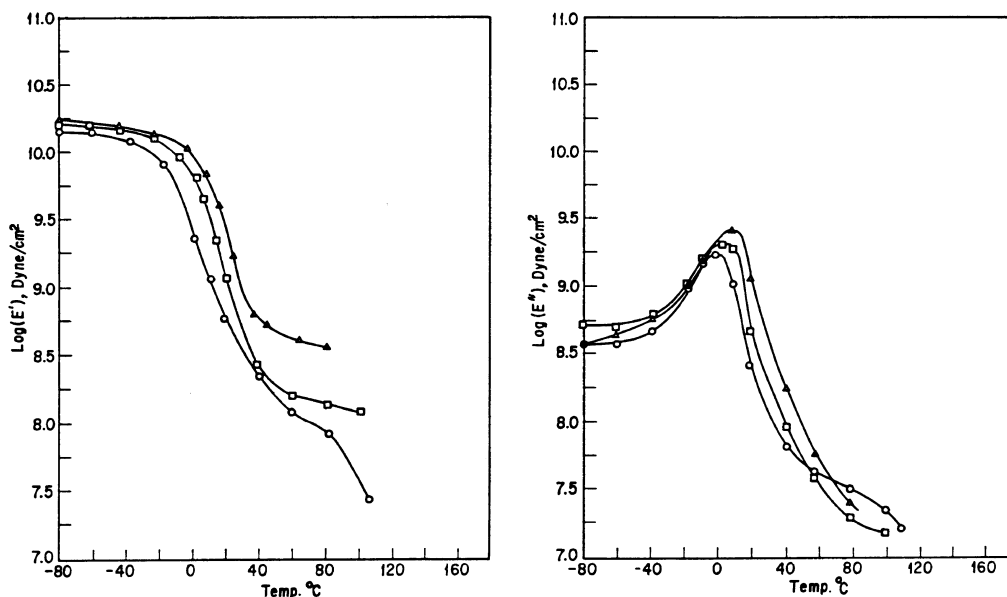


Figure 4. Temperature dependence of E' , E'' of CPU/CPSAA Full-IPN at a ratio of 75/25 with CPSAA containing various AA content (mol%): —○—, 0; —□—, 15; —△—, 30.

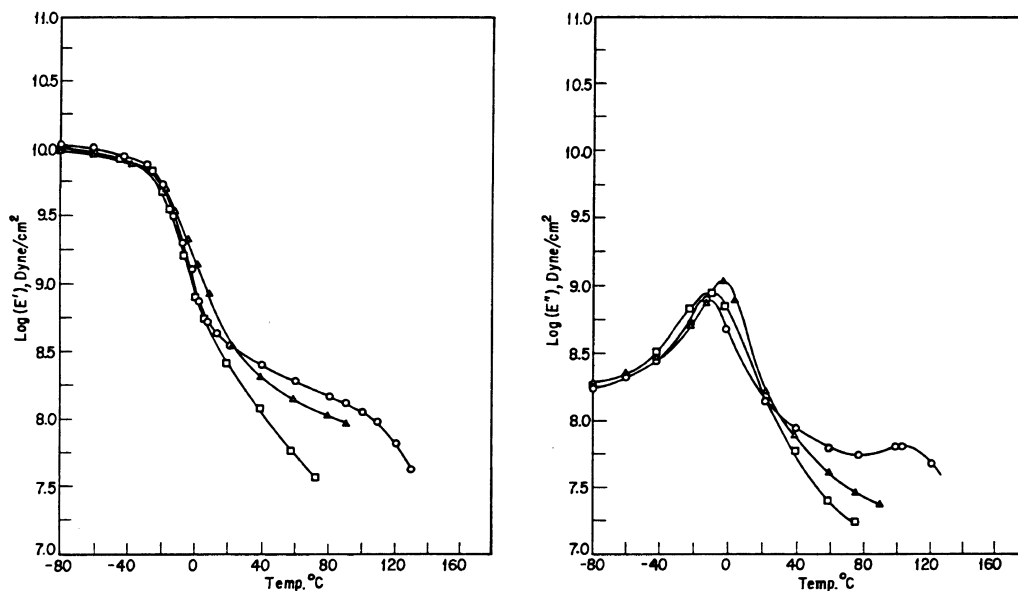


Figure 5. Temperature dependence of E' , E'' of LPU/LPSAA linear blends at a ratio of 75/25 with LPSAA containing various AA content (mol%): —○—, 0; —□—, 15; —△—, 30.

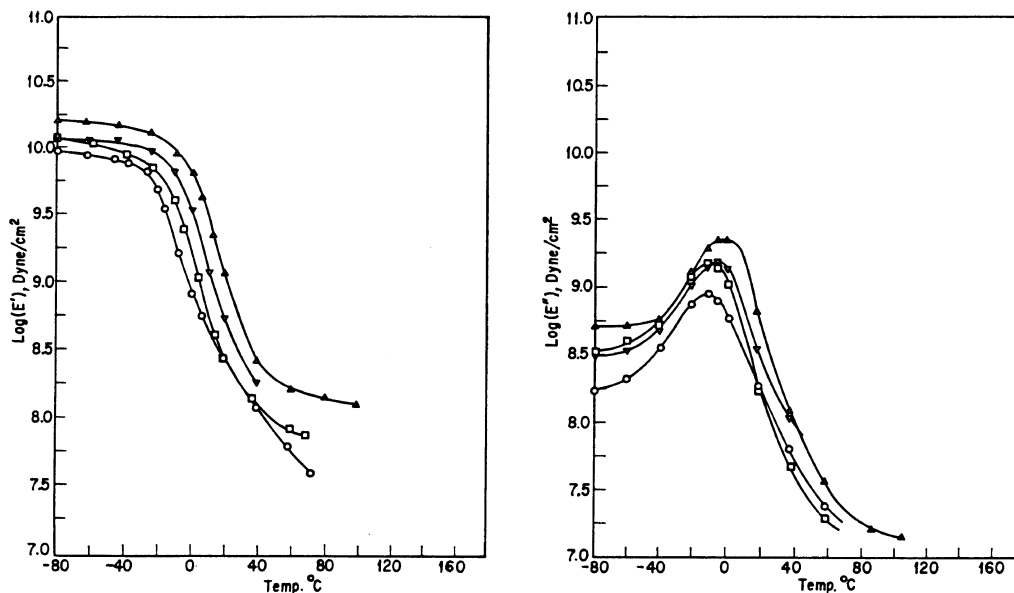


Figure 6. Temperature dependence of E' , E'' of PU/PSAA alloys at a ratio of 75/25 with 15 mol% AA in PSAA: —△—, CPU/CPSAA15; —□—, CPU/LPSAA15; —▽—, LPU/CPSAA15; —○—, LPU/LPSAA15.

of the crosslinking effect.

Furthermore, the dispersed particles in PU-dominated alloys is larger than that in PS-

dominated alloys. We also see 57.2% for the CPU/CPS alloys at 25/75 in Table II showing the occupied area fraction of the dispersed

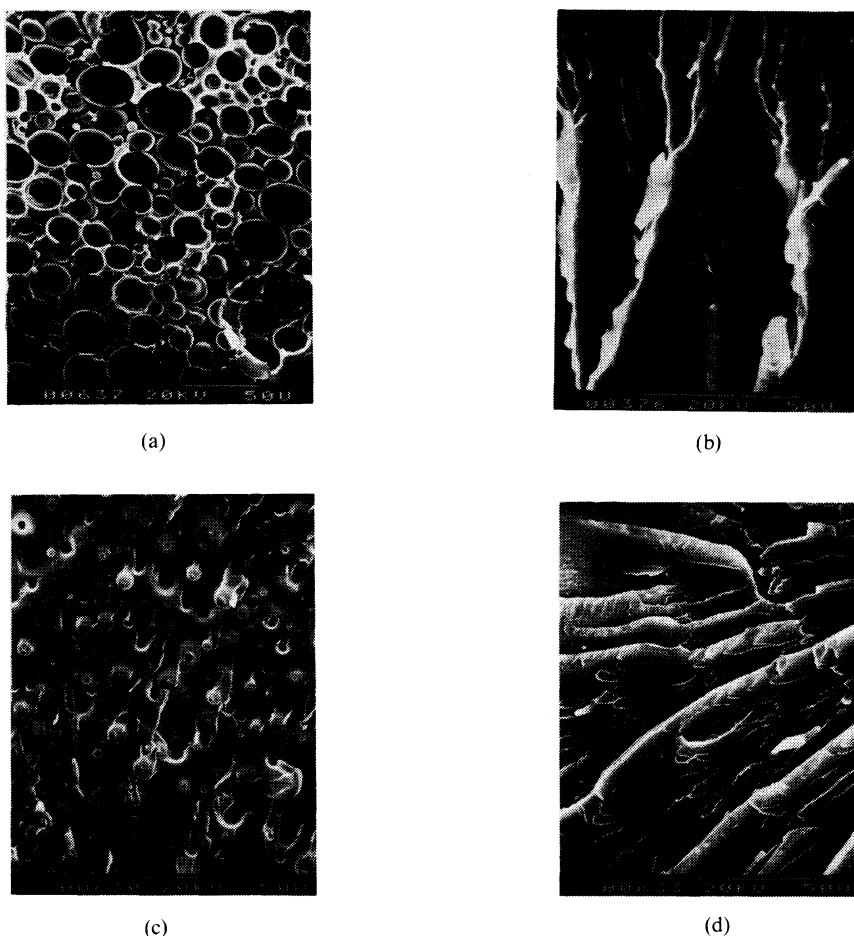


Figure 7. Microphotographs of SEM for PU/PSAA=25/75 polymer alloys: (a) CPU/CPS; (b) CPU/CPSAA15; (c) LPU/LPS; (d) LPU/LPSAA15.

Table II. The average particle size and occupied area of dispersed phase of PU/PSAA Full-IPNs and linear blends in the matrix

Sample	PU/PSAA weight ratio	Average particle size/ μm	Particle occupied area/unit area/%
CPU/CPS	75/25	71.9	25.5
LPU/LPS	75/25	10.7	7.8
CPU/CPS	25/75	17.2	57.2
LPU/LPS	25/75	4.4	15.3

particles. Assuming the cross-sectional area of the dispersed phase is proportional to its volume,¹⁸ it becomes obvious that the dispersed

particles are composed of PU and PSAA altogether.

The microphotographs of SEM of CPU/CPS and LPU/LPS ratios of 75/25 in Figures 8(a) and 8(c) indicate clearly that there is stress rupture on the dispersed particles. This indicates that the PS would be the dispersed phase in the PU matrix. This was not noted for the CPU/CPS and LPU/LPS ratios of 25/75 in Figures 7(a) and 7(c) respectively, and PU thus appears to be the dispersed phase in the PS continuous phase. Tiny grains which exist in Figure 7(a) seen in white color and different from PU particles, may be particles of PS.

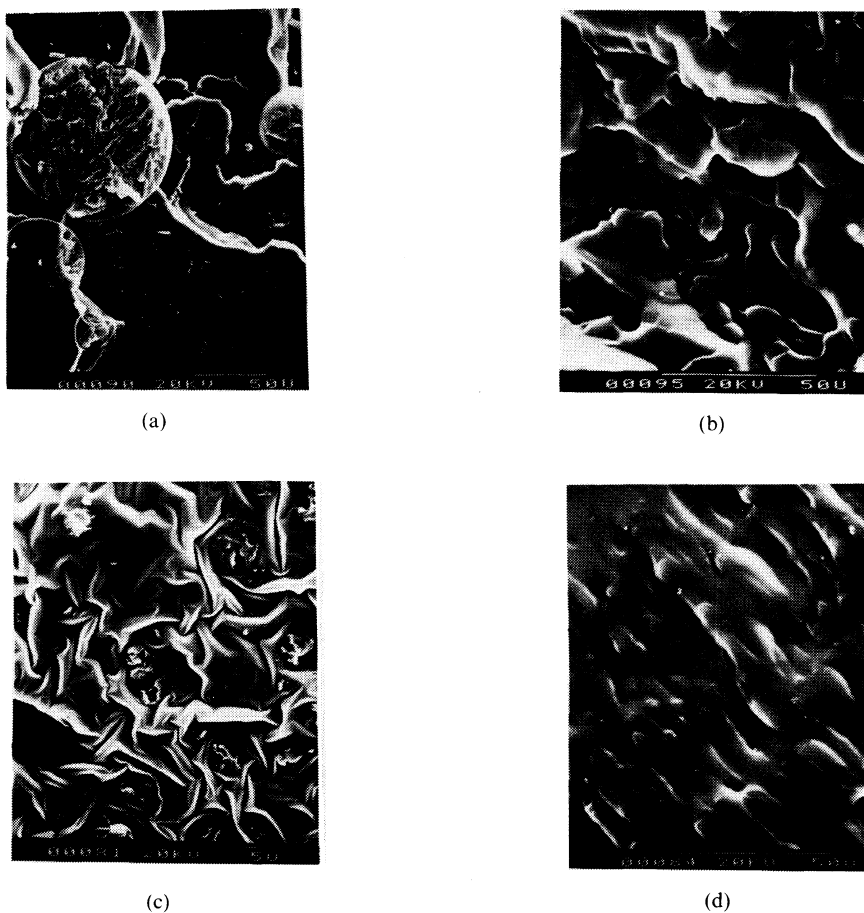


Figure 8. Microphotographs of SEM for PU/PSAA = 75/25 polymer alloys: (a) CPU/CPS; (b) CPU/CPSAA15; (c) LPU/LPS; (d) LPU/LPSAA15.

Glass Transition Temperature

The transition temperatures of PU/PSAA alloys in Full-IPNs, Semi-IPNs and Linear blends are listed in Table III. Two transition temperatures can be observed in Full-IPNs and Linear blends without the presence of a charge group in the system. However, one transition temperature is observed for the alloys containing a charge group. This single transition temperature (T_g) will rise with increase of AA content in the system.

In regard to differences between the observed T_g s and those calculated, we found that the difference (ΔT_g) at PU/PSAA ratio of 25/75 is much smaller than that at 75/25. This indicates

that the transition peak at low temperature (T_{g1}) is in fact the transition temperature of the PU soft segment. PSAA introduced is concentrated on the tertiary amine group in the hard segment of PU as mentioned before, and thus the non-uniform fractured surface can be observed from the SEM micrographs as shown in Figures 8(b) and 8(d) with PU/PSAA alloys at 75/25.

In other words, T_{g1} is not appreciably affected by the introduction of PSAA into PU-dominated alloys. Therefore, the calculated value of T_g under such a condition differs noticeably from the value determined by dynamic mechanical analysis.

Table III. Glass transition temperatures of PU/PSAA Full-IPNs, Semi-IPNs, and linear blends

Sample	PU/PSAA weight ratio	T_{g1}/K (from E'')	T_{g2}/K (from E'')	T_{gcal}^*/K	$\Delta T_g/K$ $= T_{gcal} - T_g$
CPS	0/100	—	383	—	—
CPSAA15	0/100	—	407	—	—
CPSAA30	0/100	—	423	—	—
LPS	0/100	—	375	—	—
LPSAA15	0/100	—	393	—	—
LPSAA30	0/100	—	413	—	—
CPU	100/0	270	—	—	—
LPU	100/0	261	—	—	—
CPU/CPS	75/25	273	355	—	—
CPU/CPSAA15	75/25	271	—	304	33
CPU/CPSAA30	75/25	284	—	308	24
CPU/LPSAA15	75/25	258	—	300.75	43
LPU/CPSAA15	75/25	265	—	297.5	32
LPU/LPSAA15	75/25	262	—	294	32
LPU/LPSAA30	75/25	280	—	299	19
CPU/CPS	25/75	272	376	—	—
CPU/CPSAA15	25/75	—	365	372.75	8
CPU/CPSAA30	25/75	—	378	384.75	7
CPU/LPSAA15	25/75	—	351	362.25	11
LPU/CPSAA15	25/75	—	376	370.5	-6
LPU/LPSAA15	25/75	—	349	360	11
LPU/LPSAA30	25/75	—	355	375	20
LPU/LPS	25/75	262	377	—	—
LPUS/LPS	75/25	262	377	—	—

* $T_{gcal} = W_{PU}T_{gPU} + W_{PSAA}T_{gPSAA}$ where T_{gPU} , T_{gPSAA} , and W_{PU} , W_{PSAA} are glass transition temperatures and weight fractions of PU and PSAA, respectively.

CONCLUSIONS

Owing to the ionic interaction between the tertiary amine in PU and the carboxyl group in PSAA, the introduction of AA into the system increases the compatibility for the IPNs composed of PU and PSAA.

SEM micrographs indicated the introduction of AA into PSAA to eliminate the dispersed phase in the alloys resulting in homogeneous morphology.

The dynamic mechanical analysis of such alloys in the presence of AA in PSAA shows a single transition peak consistent with SEM observation.

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