NOTE

Mechanical Behavior of Polyurethane and Polystyrene Ionomeric Blends

INTRODUCTION

Studies on the level of improvement of compatibility in polyblends were carried out by introducing the interactive groups into polymers.[1-3] In recent papers,[4-6] we studied the effect of the interaction between the tertiary amine group and carboxyl group, which have been introduced respectively into two incompatible polymers, on the compatibility, mechanical properties, and morphology of the resultant polyblends. Improvements in the level of compatibility and the mechanical properties of the polyblends were effectuated in proportion to increase of opposite charge groups. This paper presents the charge groups in the blends of polyurethane (PU) based on poly(caprolactone) glycol (PCL) and poly(oxytetramethylene) glycol (POTM) and styrene–acrylic acid copolymer [P(S–AA)]. The mechanical behavior, compatibility, and morphology have been investigated.

EXPERIMENTAL

PUs containing tertiary amine group were synthesized from 4,4'-methylene bis(phenyl isocyanate) (MDI), PCL of MW1238 or POTM of MW998 and N-methyl diethanolamine in two-step preparation method.

P(S–AA)s were synthesized at various ratios of styrene (S) to acrylic acid (AA) by means of bulk polymerization under a nitrogen atmosphere.

The PU/P(S–AA) blends were prepared in the solution. Both constituent polymers were separately dissolved in a solvent mixture of N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) with DMF/THF ratio of 10/90. The P(S–AA) solution was added in drops to the PU solution which was vigorously agitated with a mechanical stirrer in 6 h. Films of the polyblend were made by casting the blended solution on glass plates and allowing the solvent to evaporate in an oven at 70°C under vacuum for 48 h.

Testing Methods

The stress–strain properties were determined on an Instron Table Model 1130 testing machine according to ASTM D638.

The dynamic viscoelastic properties of the polyblends were measured by using a "Rheovibron" Model-II at the frequency of 110 Hz. The determination was made at a heating rate of 1°C/min in the transition region and of 3–5°C/min in the nontransition region, respectively.

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis of PU / P(S–AA) Blends

The temperature dependence of storage modulus (E') and loss modulus (E'') of the blends based on PCL and POTM in PU measured from the dynamic mechanical analysis (DMA) are shown in Figures 1–4. For the straight P(S–AA) with 15 mol% AA (Fig. 1, curve 0/100), a slight decrease of E' with increasing temperature as well as a broad peak of E'' between -20 and 60°C was observed in the region below T_g. It has been mentioned in the literature as the rotation of benzene ring around the backbone of the P(S–AA) structure.[7] Whereas for the straight P(S–AA) with 30 mol% AA in Figure 2 (curve 0/100), a lesser decrease of E' with increasing temperature and the corresponding flattened transition region of E'' were observed. These variations due to the increase of AA in P(S–AA) indicated that the rotational motion of benzene ring was reduced by the increase of AA content in P(S–AA), which promoted the intermolecular force through hydrogen bonding between the AA groups.

Due to the incompatibility between polyurethanes and polystyrene, the dynamic mechanical properties of PU/PS blends in the absence of any charge group were unable to be measured in
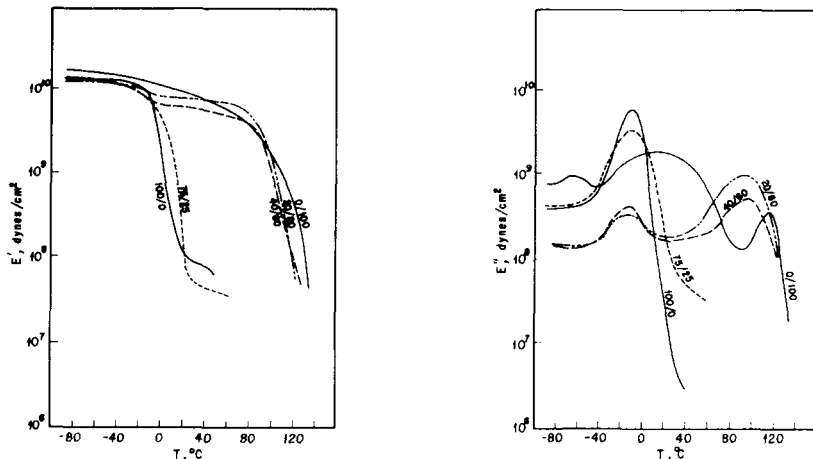
Fig. 1.   Temperature dependence of E' and E'' for the PU/P(S–AA) blends of various ratios indicated on the curves at the composition of PU = MDI/PCL/MDEA = 2/1/1 and P(S–AA) = S/AA = 85/15.

this study. As the charge group AA was increased to 15 mol% in P(S–AA), the shifts of E' with various PU/P(S–AA) ratios on the temperature scale in Figures 1 and 3 were still similar to the behavior of incompatible system[8] but for the blends at high P(S–AA) content only a slight decrease of the storage modulus below T_g took place. While for the AA content raised up to 30 mol% in P(S–AA), the behaviors of E' curves of the blends for various PU/P(S–AA) ratios in Figures 2 and 4 acted in a manner similar to those of compatible polyblends.[8] On the contrary, the E'' of these ionomeric blends at high P(S–AA) content always exhibited two transitional peaks on the temperature scale in spite of the AA content which was increased up to 30 mol% in P(S–AA). One of the two peaks of E'' in Figures 1–4, which showed at a low temperature, represented the transition of PU phase and the other one at a high temperature was for the blend of P(S–AA)-dominated phase. As the P(S–AA) content increased in the PU/P(S–AA) blends, the low-temperature peak of E'' remained at the same temperature as that of straight PU except that of the blend at 20/80 ratio in Figures 2 and 4, and the high-temperature one shifted to a low temperature with PU content increased in the blends. These behaviors indicated the low-temperature transition phase was still representative of PU by itself, and the one with high-temperature
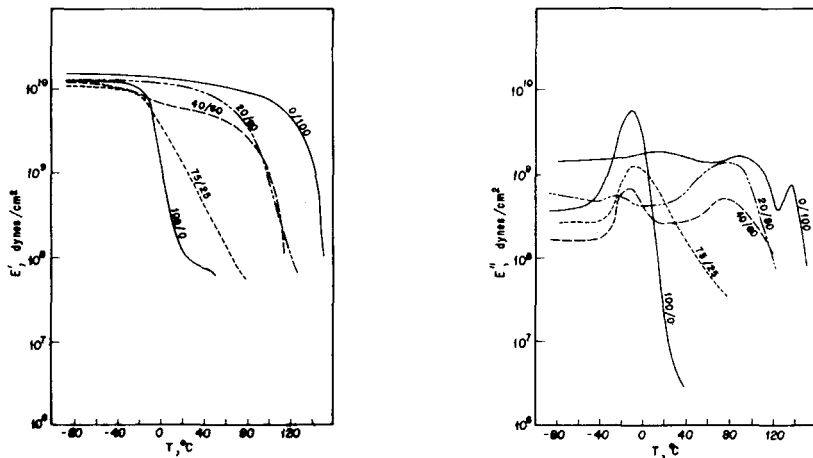

Fig. 2.   Temperature dependence of E' and E'' for the PU/P(S–AA) blends of various ratios indicated on the curves at the composition of PU = MDI/PCL/MDEA = 2/1/1 and P(S–AA) = S/AA = 70/30.
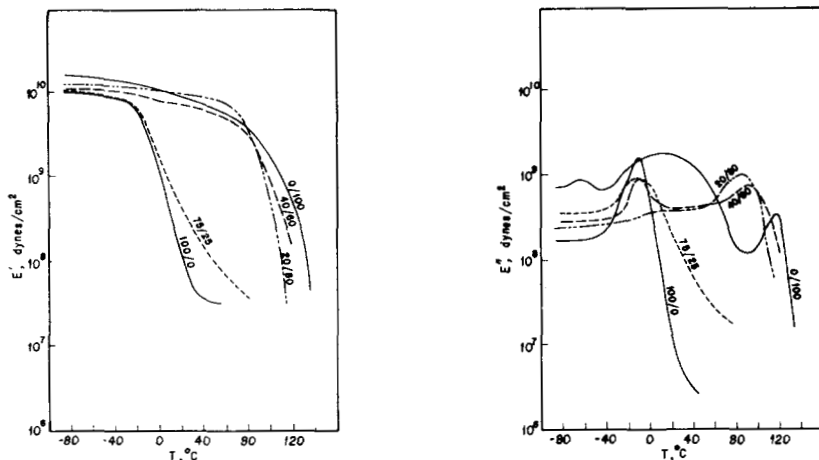
Fig. 3. Temperature dependence of E' and E'' for the PU/P(S–AA) blends of various ratios indicated on the curves at the composition of PU = MDI/POTM/MDEA = 2/1/1 and P(S–AA) = S/AA = 85/15.
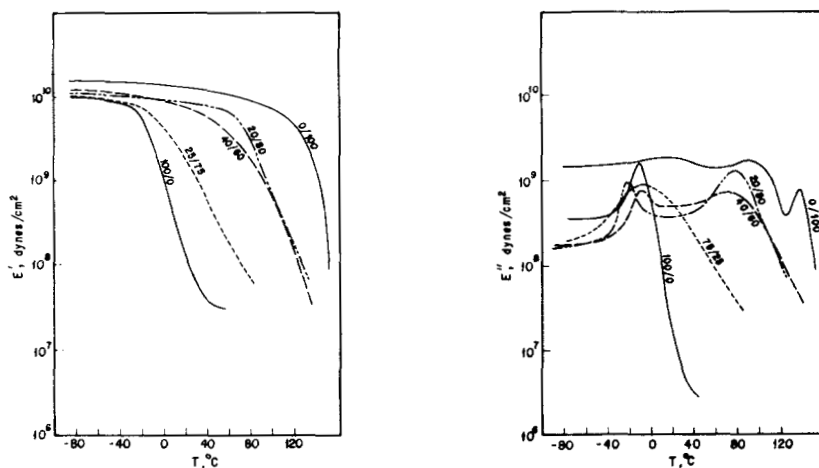

Fig. 4. Temperature dependence of E' and E'' for the PU/P(S–AA) blends of various ratios indicated on the curves at the composition of PU = MDI/POTM/MDEA = 2/1/1 and P(S–AA) = S/AA = 70/30.

transition was composed of PU and P(S–AA) at different PU/P(S–AA) ratios. While the exceptional shift of the low-temperature peak to a lower temperature for the blends at 20/80 ratio and with 30 mol% AA in P(S–AA) as shown in Figures 2 and 4 revealed more "pure" soft segments of PU existed in this phase due to the MDEA-containing hard segments of PU attracted out of the soft/hard segment-mixed phases of PU by the AA in P(S–AA) through the interaction of the opposite charge groups in the blends.[1-3] For the PU/P(S–AA) blends at 75/25 ratio, the broadened transition peaks of E'' curves in Figures 1–4 indicated that the PU-dominated PU/P(S–AA) blends were one-phase blends of a semicompatible system.

Stress–Strain Properties of PU / P(S–AA) Blends

The stress–strain properties of the polyblends were very much influenced by the introduction of charge groups into the blend constituents. The PU/PS blends in the absence of any charge group were known as an incompatible system and exhibited very poor stress–strain properties
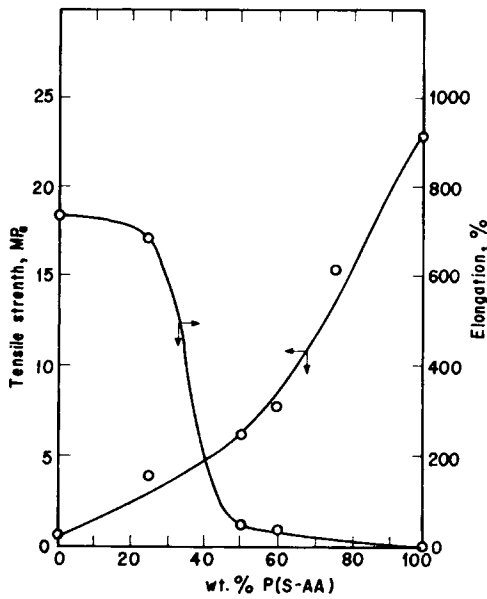
Fig. 5. Tensile strength and elongation of the PU/P(S–AA) blends vs. blending ratios at the P(S–AA) containing 15 mol% AA: (O) PU (MDI/POTM/MDEA = 2/1/1)/P(S–AA).
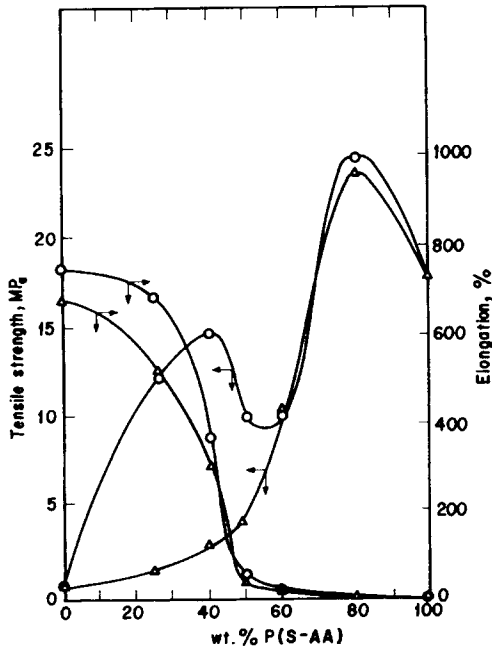

Fig. 6. Tensile strength and elongation of the PU/P(S–AA) blends vs. blending ratios at the P(S–AA) containing 30 mol% AA: (O)PU (MDI/POTM/MDEA = 2/1/1)/P(S–AA); (△) PU (MDI/PCL/MDEA = 2/1/1)/P(S–AA).

which were unable to be measured due to the grossly separated phase and poor cohesiveness between two phases in the blends. However, as the charge groups were introduced into the blends, the stress–strain properties had drastic changes as shown in Figures 5 and 6. For the blends in which the P(S–AA) contained 15 mol% AA, the curve of tensile strength vs. various PU/P(S–AA) ratio in Figure 5 was in a concave shape for the blends in which PU was based on POTM; however, that of the blends in which PU was based on PCL was still too low to be shown in the figure. The higher tensile strength of the blend generally comes as a result of better compatibility between the two constituents. Therefore, the compatibility between the POTM-based PU and P(S–AA) was obviously better than that between the PCL-based PU and P(S–AA) at the blend in which the P(S–AA) contained 15 mol% AA. While the AA content was increased up to 30 mol% in P(S–AA), the curves of tensile strength vs. PU/P(S–AA) ratio had shifted upwards to become a double-peaked curve for the blends in which PU was based on POTM and a S-shaped curve for the blends in which PU was based on PCL as shown in Figure 6. These values of tensile strength no longer followed those calculated from the additive rule of the blends. A maximum value of tensile strength observed at the PU/P(S–AA) ratio of 20/80 was discovered for the ionomeric blends. It was also found that the density of these blends initially increased with increases in the P(S–AA) content in blends and, of which the maximum value emerged at the same PU/P(S–AA) ratio of 20/80.[6] The corresponding E'' curves (i.e., 20/80 curves shown in Figures 2 and 4) always exhibited a microphase of more "pure" soft segments of PU as mentioned before. These informations implied that the increase of tensile strength of the blends came as a result of reduction in the free volume of the blends and the toughening effect due to the soft microphase of PU separated from the rigid matrix. Whereas for the blends at low P(S–AA) content [less than 50 wt% P(S–AA)] in Figure 6, the tensile strength curves varying in shape was largely owing to varying degree of compatibility of P(S–AA) with the different polyol-based PU matrices as well as the stability of the phase mixing which took place in the phase inversion region.

CONCLUSION

The polyblends from the polyurethane and polystyrene ionomers considered in the present study achieved not only in the improvement of compatibility between them both but also in wholesome mechanical properties by increasing the content of charge group in the polymers. Thus, this ionomeric blending thanks to its utilization of strong interaction between the two opposite charged polymers, will be a potential method for the preparation of a polyblend of various degrees of compatibility from two polymers of incompatible system.

References

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