

SHORT COMMUNICATIONS

Thermal Properties of Ester Based Thermoplastic Polyurethane/ Polyester Ionomer Blends

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Thermoplastic polyurethane (TPU) has various applications. TPU is a linear segmented block copolymer composed of soft and hard segments which undergo phase separation.^{1–3} The properties of soft segment are determined by the types and molecular weights of polyols while properties of hard segments by the types of diisocyanate and chain extender. Thus, the properties of TPU may be adjusted by raw material and microphase separation of soft segments and hard segments. Another method to control the properties of polyurethane is the introduction of ionic groups into soft or hard segments. Polymers with ionic groups in the main chain or side chain are called ionomers and show interesting properties due to ionic groups.⁴ Ionomers are usually prepared *via* copolymerization of ionizable comonomers. There are many papers on the enhancement of compatibility of polymer blends using ionomers due to interactions of ion–ion or ion–dipole.^{5–8} For modification of TPU, blends of TPU, and polyester ionomer (PETI) were studied from view points of exchange reaction, miscibility between TPU and PETI, and ionic conductivity of the blends. To elucidate the characteristics of blends, morphology and thermal properties of the blends were investigated and the findings are reported in this paper.

EXPERIMENTAL

All polymers in this study were commercial products (Table I). Melt blends of an ester based TPU and a PETI (M-TPU/PETI) were prepared using single screw extruder (length-to-diameter ratio of 24 and barrel diameter of 40 mm) at 200 °C. TPU and PETI are sensitive to moistures and thus were dried in a vacuum oven at 40 °C for 12 h before melt mixing. PETI in the TPU/PETI blends was varied from 0 to 30% by weight. Solution blends of the TPU and the PETI (S-TPU/PETI) were prepared using a cosolvent, dimethyl formamide (DMF).

Cryogenically fractured surfaces of the blends were etched with water to dissolve water soluble PETI and coated with gold in vacuum after drying and observed with a scanning electron microscope (SEM, Hitachi X-650). Thermal properties of the blends were studied by a differential scanning calorimeter (DSC) (DSC 910 from DuPont Instruments equipped with TA2000). To control the thermal history, all samples were heated to 220 °C, maintained for 3 min, and cooled at -5 °C min^{-1} in DSC. The samples were quenched to -120 °C after exothermic peaks due to

Table I. Characteristics of raw materials

Material	Manufacturer	Grade	Characteristics
Ester based Thermoplastic polyurethane (TPU)	Hosung Chemex	5090A	M_w : 3.6×10^5 M_n : 1.4×10^5 Shore A hardness: 90
Ionomer containing sodiosulfo substituents attached to amorphous linear polyester (PETI)	Eastman Chemical	AQ-55	M_n : 1.5×10^4 Ion content (wt%): 10.7

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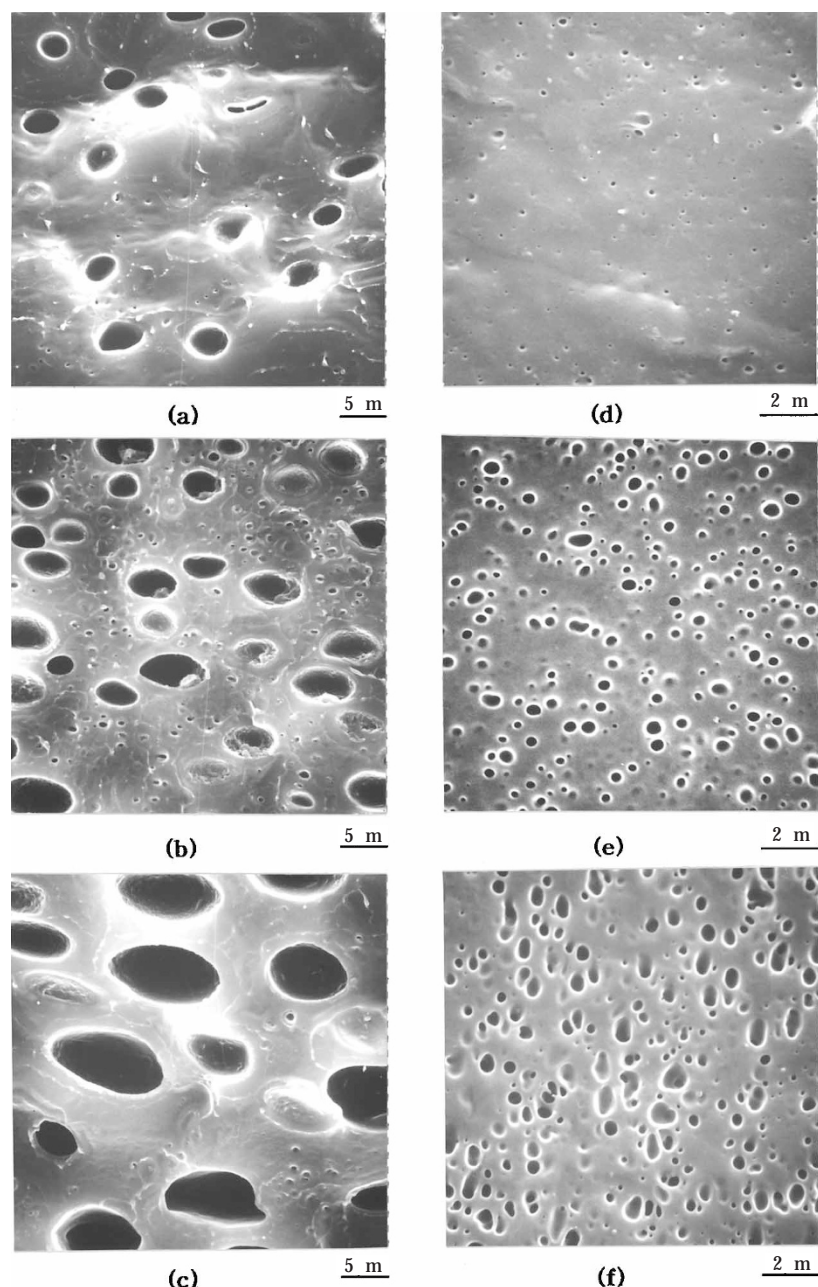


Figure 1. SEM of cryogenically fractured surfaces of various TPU/PETI blends: (a) S-TPU/PETI = 90/10; (b) S-TPU/PETI = 80/20; (c) S-TPU/PETI = 70/30; (d) M-TPU/PETI = 90/10; (e) M-TPU/PETI = 80/20; (f) M-TPU/PETI = 70/30.

crystallization of the blends leveled off, which were reheated from -100°C to 220°C at $10^{\circ}\text{C min}^{-1}$ to check thermal transition behavior in nitrogen gas flow. Ionic conductivities of the TPU/PETI blends were measured with a dielectric analyzer (DEA) (DEA 2980 equipped with TA2000). Temperature sweeps for the samples were made with a DEA from -100°C to 80°C at 0.1 Hz under nitrogen gas flow.

RESULTS AND DISCUSSION

Figure 1 shows SEM of cryogenically fractured surfaces of TPU/PETI blends. As specimens were etched with water to remove water soluble PETI in the fracture

surface, holes in the pictures are believed to represent the discrete phase of water soluble PETI. In a, b, and c of Figure 1, the particle sizes of the PETI in the S-TPU/PETI blends are $5\text{--}10\ \mu\text{m}$ while those for PETI of the M-TPU/PETI blends less than $2\ \mu\text{m}$ in Figure 1d, 1e, and 1f. There are many papers on exchange reactions in melts between condensation polymers such as polyester, polyamide, and polycarbonate.^{9–12} Products of exchange reactions usually improve compatibility of the polymer blends. According to Kricheldorf, monodisperse hard segment model compounds of TPU undergoes exchange reactions by thermal treatments and resulted in polydisperse compounds.¹³ Exchange reactions between the TPU and the PETI may occur

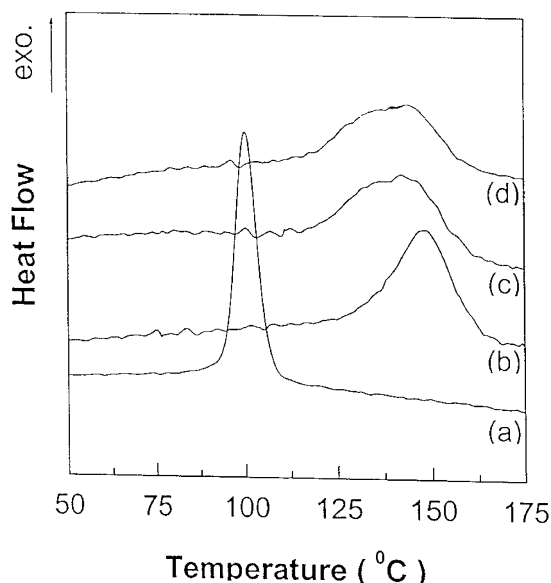


Figure 2. DSC thermograms of various TPU/PETI blends obtained by cooling from 220°C at 5°C min⁻¹: (a) TPU; (b) M-TPU/PETI = 90/10; (c) M-TPU/PETI = 80/20; (d) M-TPU/PETI = 70/30.

during melt mixing of the M-TPU/PETI blends. The finer dispersion of PETI in the melt blends compared with the PETI in the solution blends is attributable to compatibilizing effects of exchange reaction products. The morphology of polymer blend is generally determined by miscibility, thermal history, and shear force applied for the mixing to prepare blends.¹⁴ Thus decrease of particle size of discrete phase in the M-TPU/PETI blends may be attributable to different shear force as well as different thermal history of the blends to induce exchange reactions.

In Figure 2, DSC thermograms of the M-TPU/PETI blends obtained by cooling from 220°C at 5°C min⁻¹ are given. An exothermic peak due to the crystallization of hard segments of the TPU (T_{cc}), was observed at 100°C in Figure 2a and T_{cc} s of hard segments of the TPU in M-TPU/PETI blends were observed at 140°C in Figures 2b, 2c, and 2d. T_{cc} s of the hard segments of the TPU increased in the M-TPU/PETI blends compared with neat TPU. T_{cc} s of the TPU in M-TPU/PETI blends may possibly shift to higher temperature due to exchange reactions during mixing of TPU and PETI. Similar phenomenon in TPU/Polyamide-11 blends was reported by Kim *et al.*¹⁵ Figure 3 shows DSC thermograms of the S-TPU/PETI blends obtained by cooling from 220°C at 5°C min⁻¹. T_{cc} s of the hard segments of TPU's in the blends were observed at 96–99°C, nearly the same temperatures as for neat TPU. It is not clear why T_{cc} s in Figure 3 are scattered slightly depending on PETI content. According to Han, TPUs are not homogeneous at 110–190°C, but show characteristics of

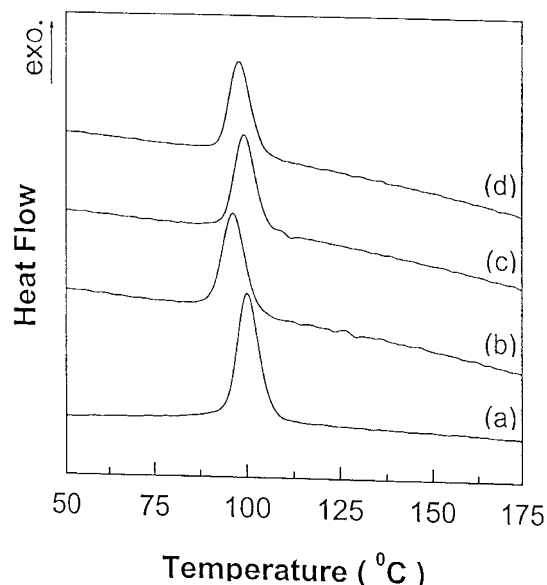


Figure 3. DSC thermograms of various TPU/PETI blends obtained by cooling from 220°C at 5°C min⁻¹: (a) TPU; (b) S-TPU/PETI = 90/10; (c) S-TPU/PETI = 80/20; (d) S-TPU/PETI = 70/30.

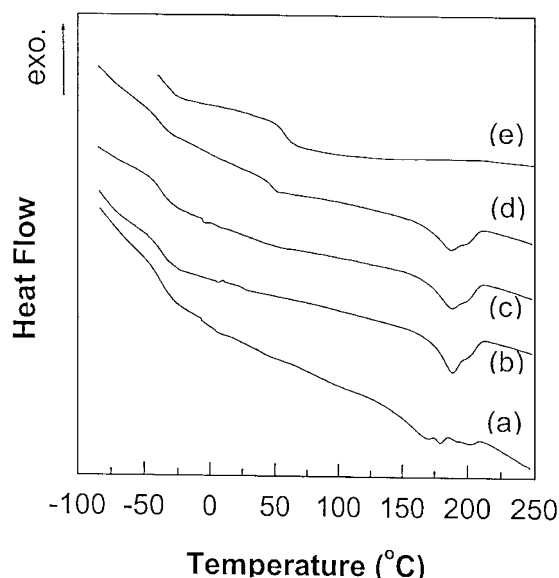


Figure 4. DSC thermograms of various TPU/PETI blends obtained by heating from -100°C at 10°C min⁻¹: (a) TPU; (b) M-TPU/PETI = 90/10; (c) M-TPU/PETI = 80/20; (d) M-TPU/PETI = 70/30; (e) PETI.

temperature dependent morphology.¹⁶ The slight scattering of T_{cc} s in Figure 3 may result from slight different morphologies of TPUs depending on PETI contents during cooling crystallization.

Figure 4 shows DSC thermograms obtained by heating M-TPU/PETI blends after cooling crystallization. Enthalpy change due to glass transition of the soft segments of TPU in the blends (T_{gs}) was observed around -47°C and endothermic peaks due to melting of the hard segments of the TPU (T_{mh}) were observed from

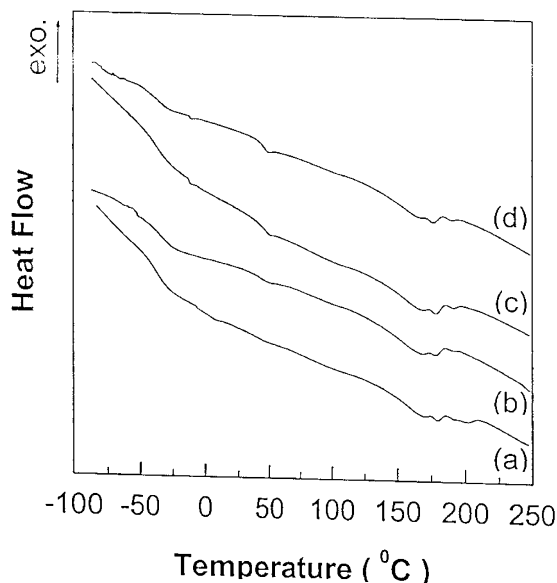


Figure 5. DSC thermograms of various TPU/PETI blends obtained by heating from -100°C at $10^{\circ}\text{C min}^{-1}$: (a) TPU; (b) S-TPU/PETI = 90/10; (c) S-TPU/PETI = 80/20; (d) S-TPU/PETI = 70/30.

135°C to 205°C . Figure 4 shows the glass transition of PETI (T_{gp}) only in M-TPU/PETI(70/30) blend. In Figure 5, DSC thermograms obtained by heating the S-TPU/PETI after cooling crystallization are given. Enthalpy change due to glass transition temperatures of the TPU in the blends was observed at -47°C and endothermic peaks were observed from 135°C to 205°C due to melting of the hard segments of the TPU in the blends. T_{gs} and T_{mhs} in Figures 4 and 5 are similar although there are slight differences. Compositions of soft and hard segment domains of the TPU may thus change little even though exchange reactions at the interface of TPU and PETI during melt mixing result in finer dispersion of PETI. Glass transition temperatures of PETIs, T_{gps} , were observed at $31\text{--}42^{\circ}\text{C}$ for all S-TPU/PETI blends. The compatibility of TPU and PETI in solution blends may have been lower than that of melt blends in which exchange reactions between TPU and PETI enhance compatibility. This is why the glass transition temperatures of PETI in the S-TPU/PETI blends are observed clearly compared with those of PETI in M-TPU/PETI blends.

In Figure 6, Arrhenius plots for ionic conductivities of the M-TPU/PETI blends are given. TPU and PETI show change in slope in ionic conductivity around 257 K and 293 K respectively. This change for TPU, PETI, and TPU/PETI blends seems related to glass transitions of soft segments of TPU and PETI respectively. Ionic conductivity of M-TPU/PETI blends was higher than for TPU and PETI. This was observed also in S-TPU/PETI blends. According to Okamoto, ionic conductivity of rigid polyelectrolytes increases by

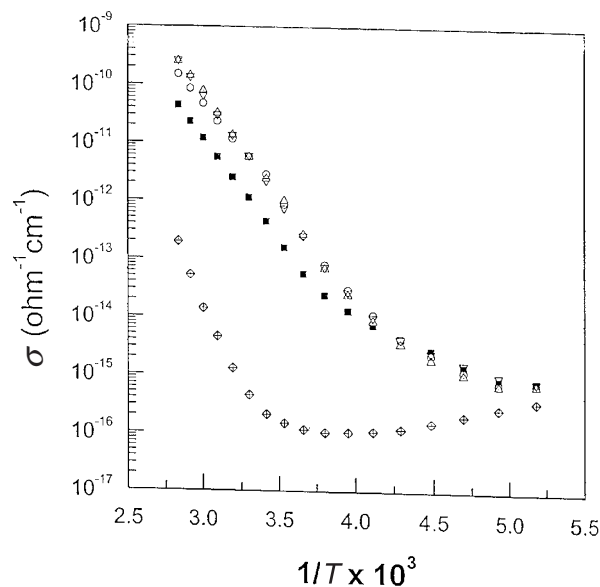


Figure 6. Arrhenius plots of ionic conductivity of M-TPU/PETI blends: (■) TPU; (○) M-TPU/PETI = 90/10; (△) M-TPU/PETI = 80/20; (▽) M-TPU/PETI = 70/30; (◇) PETI.

blending of polyelectrolytes and plasticizers.¹⁷ T_{gps} of the blends were lower compared with neat PETI in Figure 4, implying of dissolution soft segments of TPU into PETI due to partial miscibility. Even though T_{gs} s of TPU in the blends change hardly, a small amount of PETI may have dissolved in the soft segment domain of TPU due to partial miscibility. Increase of ionic conductivity of the TPU/PETI blends compared with TPU or PETI is attributable to dissolution of PETI in soft segments of TPU which imparts plasticizing effect on ionic PETI.

CONCLUSION

Melt blends of ester based TPU and PETI showed finer dispersion of PETI than corresponding solution blends due to exchange reactions during melt mixing. T_{cc} s of the TPU in M-TPU/PETI blends increased while those of S-TPU/PETI blends hardly changed. Exchange products may affect crystallization of hard segments of TPU. Increase of ionic conductivity of TPU/PETI blends compared with TPU or PETI was observed in M-TPU/PETI and S-TPU/PETI blends. Increase of ionic conductivity of the blends may be attributable to PETI dissolved in the TPU rich phase due to partial miscibility, especially in the soft segment rich phase, and glass transition temperature much lower than that of PETI.

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