

Dynamic Mechanical Properties of Poly(vinyl Chloride) and Polyurethane Carboxylate Blends

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SYNOPSIS

The miscibility of thermoplastic polyurethane elastomers (TPUs) with poly(vinyl chloride) (PVC) was studied. PVC blends with TPUs, prepared from 4,4'-diphenylmethane diisocyanate as diisocyanate, hydroxy-terminated poly(butylene adipate) (PBA) as the soft segment, and dimethylolpropionic acid as the chain extender carrying a latent anionic site for neutralization by triethylamine, showed a single glass transition temperature (T_g), irrespective of neutralization of latent anionic sites of TPU. But in neutralized TPU/PVC blends, limited intimate segmental mixing was perceived from the mechanical properties observed. When hydroxy-terminated poly(propylene glycol) was used as the soft segment instead of hydroxy-terminated PBA, PVC/TPU blends showed two separate T_g 's of PVC and TPU, irrespective of neutralization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that poly(vinyl chloride) (PVC) is miscible with several aliphatic polyesters such as polycaprolactone or poly(butylene adipate) (PBA).^{1,2} The interaction between the polyester carbonyl and the PVC chlorine or the α -hydrogen has been suggested as the driving force for miscibility. Some multiblock or random copolymers with the repeating unit of caprolactone were also reported to be miscible with PVC,³⁻⁵ but their miscibility behavior depends on the content of this repeating unit in the copolymer. Thermoplastic polyurethane elastomers (TPUs) are linear multiblock copolymers composed of hard and soft segments.⁶ As a soft segment, hydroxy-terminated aliphatic polyester or polyol is commonly used for the synthesis of TPU, and some of these TPUs are miscible with PVC.^{3,5} TPUs with a carboxylic acid group show dramatic changes in physical properties upon neutralization.^{7,8} Great changes in miscibility with other polymers are also anticipated, because cohesion in hard domains increases upon neutralization.^{9,10}

In the present study, TPU was prepared from 4,4'-diphenylmethane diisocyanate (MDI) as diisocyanate, hydroxy-terminated PBA or poly(propylene glycol) (PPG) as the soft segment, and dimethylolpropionic acid (DMPA) as a latent anionic site for neutralization by triethylamine (TEA). The effect of neutralization and soft-segment structure on miscibility of this TPU with PVC was studied.

EXPERIMENTAL

Materials

Hydroxy-terminated PBA (Dongsung Chemical, South Korea) and PPG (Korea Polyol) used in this experiment were dried at 1–2 mmHg, 80°C for 2 h. The number-average molecular weight of these materials was 1000. MDI was filtered at 70°C in a N₂ atmosphere before use.

DMPA, a chain extender carrying a potential ionic center, was dried at 100°C over 2 h before use. TEA, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were dried over 3 Å molecular sieves before use. Suspension grade of PVC (Lucky, South Korea) was used without further purification.

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Preparation

TPU was prepared by the prepolymer method,¹¹⁻¹³ i.e., a weighed amount of hydroxy-terminated PBA or PPG was dissolved in THF with agitation in a four-necked flask. Then, MDI dissolved in THF was fed into the reactor, and the reaction proceeded for 2 h at 70°C under N₂ atmosphere to obtain the prepolymer. DMPA dissolved in a substantial amount of DMF was then fed into the prepolymer solution. The chain-extension reaction proceeded for over 3 h at 70°C. The viscosity increase with the progress of the reaction was controlled by adding additional THF to the solution, and the solid content upon completing the reaction was adjusted to about 10%. Neutralization was carried out with TEA at 50°C for 2 h.

Blends of TPU with PVC were prepared by solvent casting in THF at room temperature. Specimens for tensile and dynamic mechanical tests were obtained from film casting. Films were dried under vacuum for over 1 week.

Characterization

The dynamic mechanical properties of the film were determined using a Rheovibron (Toyo Baldwin DDV-II). With N₂ purging, measurements were done from -120 to 100°C. Mechanical properties at room temperature were measured on a tensile tester

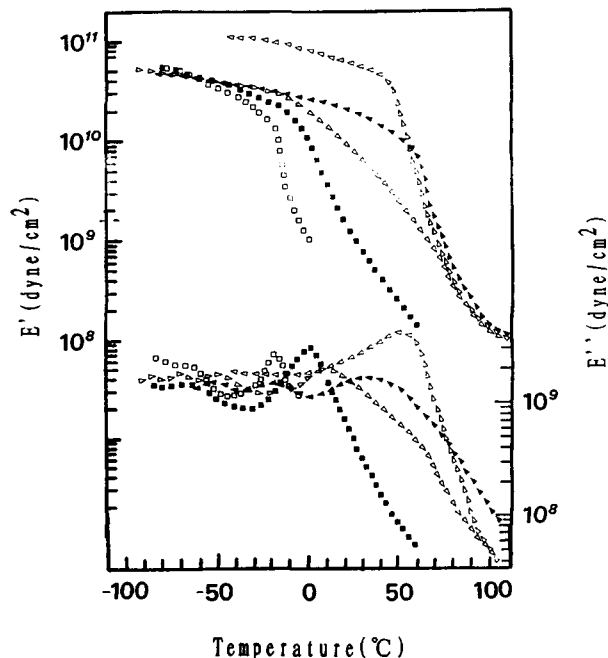


Figure 1 Temperature dependence of storage modulus and loss modulus for PVC/PU-1 blends: (□) 0/100; (■) 25/75; (▷) 50/50; (◄) 75/25; (◁) 100/0.

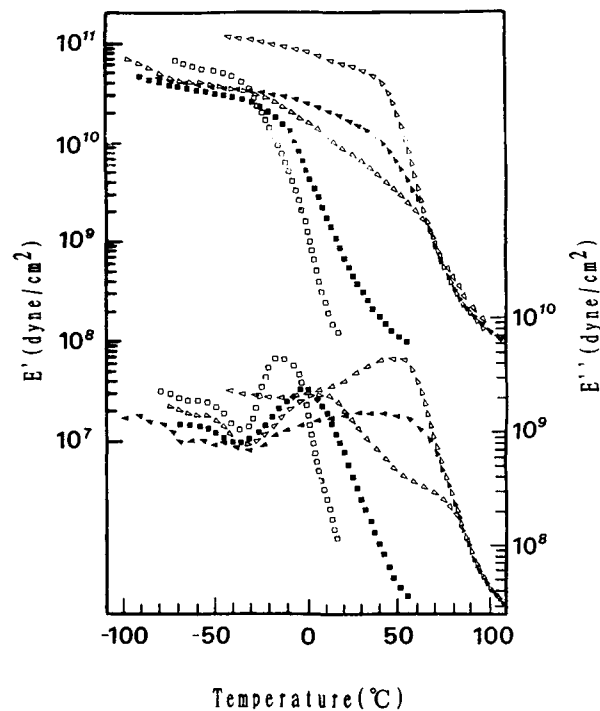


Figure 2 Temperature dependence of storage modulus and loss modulus for PVC/PU-II blends: (□) 0/100; (■) 25/75; (▷) 50/50; (◄) 75/25; (◁) 100/0.

(Tinus Olsen) following the standard procedure in ASTM D-412.

RESULTS AND DISCUSSION

The results from dynamic mechanical analysis by the Rheovibron are given in Figures 1-4 in terms of storage modulus E' and loss modulus E'' . For the blends of PVC with TPU from hydroxy-terminated PBA that is not neutralized by TEA (PU-1), the gradual shift of the single glass transition temperature (T_g), i.e., E''_{max} , and the gradually changed shape of the damping peak with composition indicate miscibility at the segmented level for all compositions.^{1,3} The neutralized PU-1, i.e., PU-II, has a larger damping peak area, probably due to the increased intermolecular cohesion by the Coulombic force of the ionic site (Fig. 2). PVC/PU-II blends also show a composition-dependent single damping peak, but the damping peaks of blends are broader and peak temperatures are situated nearer those of major components than in PVC/PU-1 blends (Fig. 2). This indicates larger composition fluctuations in the mixture, i.e., microheterogeneity.²

Increased cohesion of hard segment due to the strong Coulombic force of the ionic site in PU-II

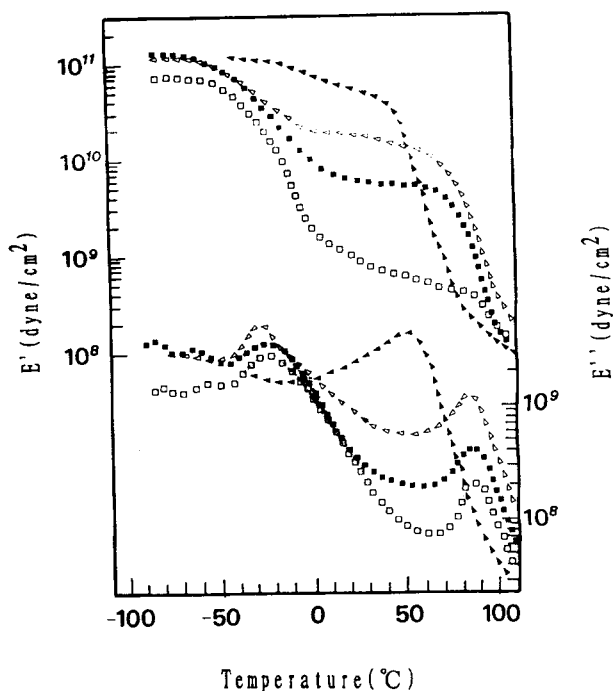


Figure 3 Temperature dependence of storage modulus and loss modulus for PVC/PU-2 blends: (■) 25/75; (▷) 50/50; (◄) 75/25; (◁) 100/0.

seems to restrict the intimate segmental mixing in PVC/PU-1I blends. In Figure 5, the initial modulus of PVC decreases as PU-1 is added, but this decrease is diminished in the PVC/PU-1I blend, i.e., the

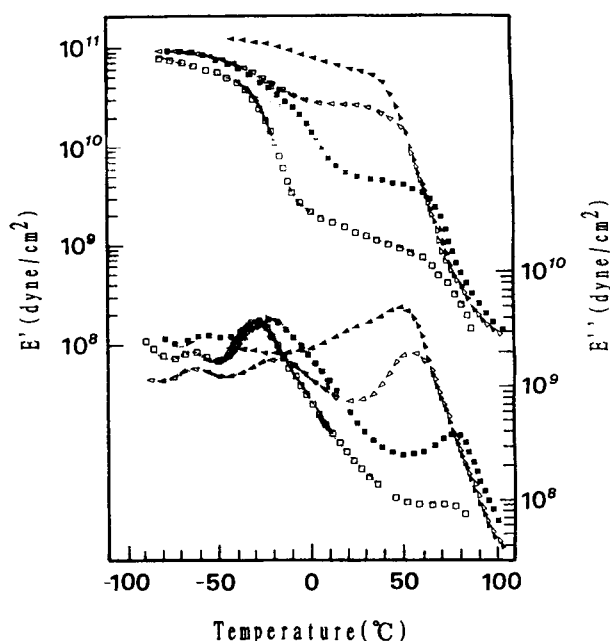


Figure 4 Temperature dependence of storage modulus and loss modulus for PVC/PU-2I blends: (■) 25/75; (▷) 50/50; (◄) 75/25; (◁) 100/0.

PVC/PU-1I blend shows an *s*-shaped composition-initial modulus curve. This result also suggests some heterogeneity in PVC/PU1I blends because, in order to retain the initial modulus of the major component in the presence of some minor component, some heterogeneity will be necessary.¹⁴

PVC blends with TPUs from hydroxy-terminated PPG, before and after neutralization by TEA (PU-2 and PU-2I), show two well-separated damping peaks of PVC and TPU (Figs. 3 and 4). This confirms limited mixing of PVC with polyether-based TPUs as reported before.³ In blends, the damping peak of PVC moves to a higher temperature (Figs. 3 and 4) probably due to the selective dissolution of low molecular weight PVC or some additives such as suspending agents into TPU domains. The gradual shift in PVC/PU-2I blends compared with that of PVC/PU-2 blends shows that this dissolution is limited when there exists strong intermolecular interaction in the TPU domain. In Figures 3–5, measured values of TPUs are not shown, because these TPUs were too weak to measure values accurately. Assuming that the initial moduli of PU-2 and PU-2I are near zero, the initial moduli of PVC/PU-2 and PVC/PU-2I blends generally show negative deviation from the single additive rule. Limited segmental mixing seems a cause of this minus deviation.¹⁵

CONCLUSIONS

TPUs prepared from MDI, hydroxy-terminated PBA, and DMPA have enough miscibility with PVC to show a single T_g in blends, irrespective of neu-

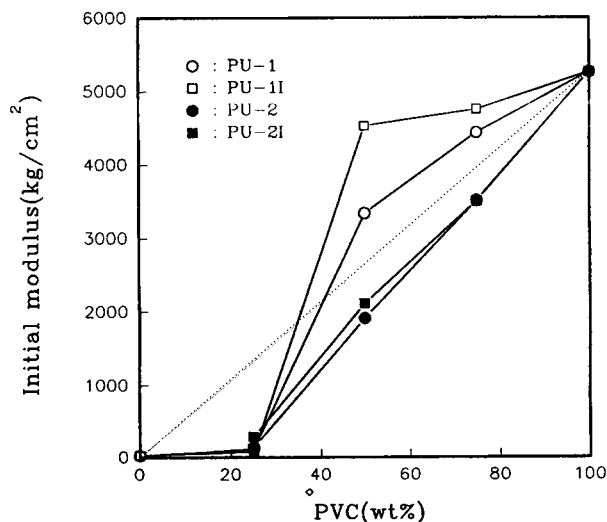


Figure 5 Initial modulus of PVC blends with (○) PU-1, (□) PU-1I, (●) PU-2, and (■) PU-2I.

tralization of carboxylic acid groups of the DMPA unit in TPU by TEA. But after neutralization, increased cohesion of hard segments, due to the strong Coulombic force of ionic sites in the TPU ionomer, restricted the intimate segmental mixing. When hydroxy-terminated PPG was used as the soft segment, two separate T_g 's of PVC and TPU were observed, irrespective of neutralization.

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