Dynamic Mechanical and Morphological Studies on the Compatibility of Plasticized PVC/Thermoplastic Polyurethane Blends

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ABSTRACT: In this work, the compatibility of blends of plasticized poly(vinyl chloride) (p-PVC) and thermoplastic polyurethane (TPU) was investigated using a dynamic mechanical analyzer and scanning electron microscopy. Two kinds of TPU with different ratios of hard to soft segments, i.e., TPU90 and TPU70 were compared. p-PVC/TPU90 and p-PVC/TPU70 blends with variable weight ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) were prepared by melt blending. PVC was plasticized with 40 phr of dioctyl phthalate. It was found that TPU with a lower hard segment (i.e., TPU70) is more compatible with plasticized PVC than TPU with a higher hard segment (i.e., TPU90) in over the composition ranges examined. It was concluded that the compatibility of plasticized PVC and TPU are dependent on the ratio of hard to soft segments in TPU. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 415–422, 1999

INTRODUCTION

Polymer blends are one of the most investigated categories in the polymer sciences from both theoretical and practical points of view, because of the technical advantages to obtain a specified portfolio of physical properties, without the need to synthesize specialized polymer systems.^{1–7}

Thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics with elastomeric properties.^{8–13} The TPUs possess higher tensile modulus in comparison to rubber, high abrasion resistance, and resistance to oil and many solvents. TPUs are characterized by a two-phase morphology in which a soft phase containing either polyesters or polyethers is reinforced by condensation, with a hard domain consisting of an aromatic diisocyanate extended with a short-chain diol. By varying the amounts of the hard and soft segment, the properties can be varied over a wide range, and properties of blends also can be influenced. TPUs are used as nonmigrating plasticizer in poly(vinyl chloride) (PVC) without a decrease of physical properties.

Many polymers may be blended with TPUs to enhance physical properties and toughness. The good compatibility of TPU with polar thermoplastics such as polycarbonate, the acrylonitrile– butadiene–styrene copolymer (ABS) has opened the door to use TPU as a modifier to create new blends.^{14–19}

The blends of PVC and other polymers have been extensively studied for their commercial importance.^{1,2,20} The presence of chlorine in large quantities in PVC can effectively reinforce lack of flame retardance of TPUs, because TPUs are burnable as many organic materials; thus, in many application fields flame retardance is required. Important disadvantages of PVC is a limited thermal stability.²⁰ Therefore, improvement of thermal stability is required by blending. The practical purpose of studying PVC blends is to

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Materials	Source	Grade	Characteristics
TPU90	Sunkung Industry	SKYTHAN X590A	Thermoplastic polyurethane M_w = 3.0-3.5 × 10 ⁵ sheet type
TPU70	Sunkung Industry	SKYTHAN S770- A	Thermoplastic polyure than M_w = 3.0-3.5 × 10 ⁵
PVC	LG Chem.	LS100	straight PVC particle size: 100–150 μ m
DOP	Songwon Chem.		dioctyl phthalate (plasticizer)
KBC200	Kolon Chem.		Ca/Ba/Zn complex thermal stabilizer
KA699E	Kolon Chem.		epoxy oil (processing aids and wax)
CA-st	Songwon Chem.		internal and partially external wax
paraffin wax	Kangshin Chem.		external wax

Table I Materials and Their Characteristics

develop a permanently plasticized, high impactstrength material via incorporation of a low T_g polymer that is compatible with PVC. The flexible PVC softened with a plasticizer have been finding increasing utilization in plastic and rubber industries.

The objective of this work was to study the compatibility of plasticized PVC(p-PVC)/TPU blends. The blending of TPU with PVC allows a broader range of hardness and low-temperature flexibility. Although a few articles dealt with PVC/polyurethane or PVC/TPU blends, the compatibility of the blends have been very controversial, and the conclusions were not coincident, depending on the sample preparation methods and measuring techniques as well as the inherent characteristics of the components.²¹⁻²⁴ Furthermore, no articles have been published on the compatibility of plasticized p-PVC/TPU blends as yet. In this work, PVC was plasticized with dioctyl phthalate. The compatibility was investigated by using a Rheometrics dynamic analyzer and scanning electron microscopy.

EXPERIMENTAL

Materials

Table I lists the polymers used in this study. PVC was supplied by LG Chem. Co, and two commercially available polyether-based TPUs—Skythan X590A and Skythan S770A—were kindly obtained from Sunkyong Industry Co. The basic difference between the two toluene diisocyanate (TDI)-based TPUs studied here is their hardness. The differences in hardness arise from different ratios of hard to soft segments, which in turn, leads to different soft segment molecular weights. The difference is shown in Table II.

Preparation of Blends

PVC lacks thermal stability at a processing temperature condition; thus, prepowder mixing with additives such as a thermal stabilizer was necessary before blending. The plasticized PVC compounds were formulated with the following ingredients before blending in a $3 \times 7''$ laboratory-made two-roll mill: 3 phr thermal stabilizer (KBC200), 2 phr polymeric processing aid (KA699E), 1 phr lubricant (CA-st), and 0.5 phr paraffin wax, as well as 40 phr dioctyl phthalate as a plasticizer. Then the plasticized PVC was blended with either of TPU90 and TPU70 (designated as p-PVC/TPU90 and p-PVC/ TPU70 blends, respectively) with variable weight ratio (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) in a laboratory-made table kneader at 60 rpm and 170°C for 8 min. The samples prepared are listed in Table III, and the sample notations are described therein.

Dynamic Mechanical Properties

The dynamic mechanical properties of the blends were determined using a RDA (Rheometric Dynamic Analyzer, RDAII) with a parallel-plate

Table II	The Comparison of TPU90 with
TPU70	

	Hard Segment/ Soft Segment	Hardness (Shore A)	
TPU90 TPU70	4.44 2.1	90 70	

Blend System	p-PVC (DOP40)	TPU 90	Blend System	p-PVC (DOP40)	TPU 70
PU90-0/10	100	0	PU70-0/10	100	0
PU90-1/9	90	10	PU70-1/9	90	10
PU90-2/8	80	20	PU70-2/8	80	20
PU90-3/7	70	30	PU70-3/7	70	30
PU90-4/6	60	40	PU70-4/6	60	40
PU90-5/5	50	50	PU70-5/5	50	50
PU90-10/0	0	100	PU70-10/0	0	100

Table IIIBlend Compositions

mode. With nitrogen purging, measurements were done from -100 to 100° C by temperature sweep type at a frequency of 1 rad/s. The complex viscosity of blends were measured at 190°C by frequency sweep type from 0.1 to 100 rad/s. The samples were compression molded into discs 20 mm in diameter and 2 mm thick. Strain was maintained to 10% for all of the samples.

Morphology

The morphology of the blends was observed with the Scanning Electron Microscope (JEOL JSM35CF). The samples were cryogenically fractured in liquid nitrogen. The fractured surface of the specimen was directly observed by gold coating.

RESULTS AND DISCUSSION

Dynamic Mechanical and Rheological Properties

Figure 1 shows the storage modulus (G') of p-PVC/TPU90 blends as a function of frequency. In the measured region, the storage modulus of plasticized PVC was higher than that of TPU90. The storage moduli of blends have intermediate value of plasticized PVC and TPU90 at all compositions.

The complex viscosities of the p-PVC/TPU90 blends are shown over 3 decades of frequencies in Figure 2. The blends show non-Newtonian behaviors. In the measured frequency region, the complex viscosity of the plasticized PVC was higher than that of TPU90. It is of interest that the TPU90 exhibits almost Newtonian behavior over the high-frequency ranges above a few rad/s. The result will be discussed later in more detail. At 90/10 and 80/20 compositions, the blends have relatively high complex viscosity values, while the complex viscosities of 50/50 composition as well as 70/30 and 60/40 compositions were lower than those of TPU90 at high frequency around hundreds rad/s. It is indicated that phase separation in the blends having these compositions takes place, due to the weakness of shear planes at the interfaces between phases. The viscosity of blends may be less than that of either of the pure component in a mixture when the adhesion between the phases is poor.⁴

Figures 3 and 4 show storage modulus and complex viscosity of the p-PVC/TPU70 blends, respectively. In a measured region, the storage modulus and complex viscosity of the plasticized PVC were higher than that of TPU70. The differences between Figures 1 and 3 or Figures 2 and 4 seem to be small. Careful inspection of the four figures indicate, however, that for the p-PVC/



Figure 1 Storage modulus as a function of frequency for the p-PVC/TPU90 blends with different compositions.



Figure 2 Complex viscosity as a function of frequency for the p-PVC/TPU90 blends with different compositions.

TPU70 blends the storage moduli as well as the complex viscosities of 90/10 and 80/20 blends were higher than the respective values of both plasticized PVC and TPU70, whereas for the p-PVC/TPU90 blends, the storage moduli and the complex viscosities were decreased with increasing TPU90 contents. The differences may come



Figure 3 Storage modulus as a function of frequency for the p-PVC/TPU70 blends with different compositions.



Figure 4 Complex viscosity as a function of frequency for the p-PVC/TPU70 blends with different compositions.

from the different compatibility of p-PVC with TPU70 or TPU90. The results imply that the TPU70 exhibits better compatibility with p-PVC than the TPU90 at lower TPU contents. The TPU70 also did not show a noticeable decrease of complex viscosity as a function of frequency over the high-frequency ranges above a few rad/s, as in the case of TPU90.



Figure 5 Storage modulus as a function of temperature for the p-PVC/TPU90 blends with different compositions.



Figure 6 Storage modulus as a function of temperature for the p-PVC/TPU70 blends with different compositions.

Figures 5 and 6 show the storage moduli (G') of the p-PVC/TPU90 and p-PVC/TPU70 blends as a function of temperature, respectively. A proportional decrease in G' is observed with TPU content in the transition region $(-40-20^{\circ}C)$. In both the p-PVC/TPU90 and p-PVC/TPU70 blends at higher temperature, a rubber plateau region appears. This is typical elastomer behavior due to TPU characteristics. Therefore, G' becomes larger with increasing the TPU content at a higher temperature. For the TPU90, the gradual decrease of G' after the glass transition is reminiscent of the almost-Newtonian viscosity behavior of TPU at a high frequency. The results were reported to indicate that microphase separation of the hard segments takes place and provides a self-reinforcement of the elastomer, leading to the usually high modulus and high viscosity behaviors.²¹ Similar behavior was also observed for **TPU70**.

In Figures 7 and 8, the loss tangent (tan δ) of the p-PVC/TPU90 and p-PVC/TPU70 blends are shown as a function of temperature. The p-PVC/ TPU90 blends showed two distinct transition representing the T_g of each component at all compositions. The plasticized PVC exhibits a maximum peak temperature at 30°C, indicating the glass transition temperature. TPU70 also exhibits a maximum at -37° C, representing the glass transition of soft segments of TPU. Another peak around -90° C of the TPU90 is due to the local motion of the polyether group.²¹ The result in



Figure 7 Tan δ as a function of temperature for the p-PVC/TPU90 blends with different compositions.

Figure 7 is evidence of incompatible behavior of the blends. In addition, for the p-PVC/TPU90 blends of 90/10, 80/20, and 70/30 compositions, the combination of transition broadening and depression in the glass transition temperature of PVC and the T_g elevation of the soft segment exhibited that the system is partially compatible. At 60/40 and 50/50 compositions, the difference



Figure 8 Tan δ as a function of temperature for the p-PVC/TPU70 blends with different compositions.



90/10

80/20



70/30





Figure 9 SEM micrographs of p-PVC/TPU90 blends.

between two T_g 's of polymers was increased, and two glass transitions coinciding the component T_g 's with those of the unblended polymers are indicative of macrophase separation. It is noted that at this composition, the phase separation was clearly observed due to the reduced interfacial tension.

In the p-PVC/TPU70 blends, as shown in Figure 8, single glass transition temperatures (T_g) between two components are exhibited, indicating some sense of compatibility over the entire compositions examined. The maximum peaks of blends are, however, broader, and peak temperatures are shifted inward to those of each component. Comparison of Figures 7 and 8 strongly suggests that the compat-

ibility between plasticized PVC and TPU70 are better than that with TPU90.

Most of polymer blends known so far are found to be incompatible. But some polymer blends show compatible behavior due to various reasons such as specific interactions between the blend components. The compatibility is, however, characterized by the occurrence of a negative free-energy change during mixing, which is very rare in the case of high molecular-weight polymers. However, this is more or less exhibited by binary blends having specific interactions between the blend components such as dipole–dipole interaction, hydrogen bonding, ion– dipole interaction, ion–ion complex formation, and repulsive interaction.^{5,6}



90/10







60/40



Figure 10 SEM micrographs of p-PVC/TPU70 blends.

PVC is also polar due to C—Cl dipole. This dipole cause interaction with many polar polymers.^{17–19} PVC, by virtue of the weakly "acidic" or proton-donating α -hydrogen, has been shown to exhibit compatibility with a considerable number of polymers. The polymers that are compatible with PVC include butadiene–acrylonitrile copolymers, segmented polyether ester copolymers, poly(ε -caprolactone), and others.

The compatibility between plasticized PVC and TPU may be due to the presence of weak hydrogen bonds between the carbonyl groups of the TPU soft segment and the methine protons of PVC, resulting in the heterochain association.^{22,23}

Morphology

The phase morphology of the p-PVC/TPU90 blend systems of various compositions are shown in Figure 9. The micrographs show that plasticized PVC and soft segment of TPU are the continuous phase, and TPU is the dispersed phase. The dynamic mechanical studies showed that plasticized PVC has some compatibility with soft segment of TPU. Therefore, the hard segment is a major domain. The PU90-1/9 (i.e., p-PVC/TPU90 of 90/10 composition) shows fine phase morphology but the PU90-2/8 (i.e., p-PVC/TPU90 of 80/20 composition) exhibits a small domain of the hard segment of TPU, where domain size ranges from 1–2 μ m in diameter. The domains are regularly distributed throughout the specimen. With the increase of TPU content, the domain size increases from 0.1–0.3 μ m to 3 μ m in diameter.

Figure 10 shows the SEM micrographs of the fractured surfaces of the p-PVC/TPU70 blends of various compositions. It is expected that the micrographs show nearly the same tendency as those of the p-PVC/TPU90 blends. But careful inspection of Figure 9 and Figure 10 indicates that the domain sizes are quite a bit smaller than for the p-PVC/TPU90 blends. The domain was remarkably finer compared to that of the p-PVC/ TPU90 blends. Therefore, the morphology results is in accord with the dynamic mechanical behavior described above. The complex viscosity is governed by the state of dispersion and the size of dispersed phase, as well as particle-particle interaction. It is of no doubt that the morphology of Figures 9 and 10 implies that the compatibility of the p-PVC/TPU70 blends was much better than that of the p-PVC/TPU90 blends.

CONCLUSIONS

In this work, the dynamic mechanical properties and morphology of blends of plasticized poly(vinyl chloride) (PVC) and thermoplastic polyurethane (TPU) were investigated. PVC was plasticized with dioctyl phthalate. Two kinds of TPU, i.e., TPU90 and TPU70, were compared. The p-PVC/TPU90 and p-PVC/TPU70 blends with variable weight ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) were prepared by melt blending. It was observed that the p-PVC/TPU70 blends shows much better compatibility than the p-PVC/TPU90 blends, based on the morphology and dynamic mechanical behavior. It was concluded that the compatibility of plasticized PVC and TPU are dependent on the ratio of the hard to soft segment in TPU.

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