

Mechanical Properties and Morphology of Thermoplastic Polyurethane Elastomer with Poly(vinylidene fluoride) Blends

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SYNOPSIS

A study on blends of thermoplastic polyurethane elastomer (TPU)/poly(vinylidene fluoride) (PVDF) is described. This investigation focused on the effects that PVDF has on the mechanical behaviors and morphological characteristics of the blends. Basic thermodynamic and structural considerations were applied to predict the blend miscibility. It was found that addition of PVDF disrupted the intermolecular chain interactions in TPU, resulting in lowering of mechanical properties in the blends. Our results showed that the 50/50 blend has the lowest mechanical strength. At higher levels of PVDF (>50%), the mechanical strength increased proportionally to PVDF. It was also found that both the breaking strain and the energy at break of these blends decreased with increased PVDF content. The lowering of the mechanical properties in the blends could be attributed to the formation of layered structures caused by the immiscibility of the polymers. It was concluded that TPU/PVDF blends were incompatible at all compositions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have emerged as an important group of polymeric materials since the late 1970s and have been experiencing substantial growth since the 1980s. Interest in polymer blending is reflected in the numbers of patent applications and research publications by both industry and academia.[†] Blending of polymeric materials has been shown to be an useful and cost-effective route, in comparison with the synthesis of new polymers, for enhancing material properties and/or developing materials with desired performance.¹ Current developments in polymer blends are directed toward specific applications and the interest in alloys is widespread with frequent commercial product introductions. There are varieties of commercial polymer blends whose properties are engineered for specific applications and these blends are often classified as either compatible or incompatible systems. In spite of the vo-

luminous publications on polymer blend systems, there are no research citations on blends of thermoplastic polyurethane (TPU) with poly(vinylidene fluoride) (PVDF). This article reports on our study on the mechanical behavior and morphology of TPU/PVDF blends.

Thermoplastic Polyurethanes

The thermoplastic polyurethane (TPU) group of elastomers is an important class of polymers which have found many novel and specialized applications where high mechanical and chemical performances are important material prerequisites. TPUs are known for their good mechanical strengths, wear and tear resistance, and low-temperature elasticities.² These unique properties of TPUs are attributed to the unique molecular structure of the polymer chains. TPUs have molecular structures that consist of relatively long and flexible polyether or polyester chain segments which are covalently bonded end-to-end by rigid segments of urethane blocks. The flexible polyol chain segments (known as the soft segments) constitute the amorphous and rubbery phase, while the rigid segments (known as the hard segments), composed of short-chain diol extenders

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[†] Recent Rapra databases have produced 7224 items which have been classified under polymer blends or a multicomponent keyword. The figures include 216 reviews and 10 books.

and diisocyanates, constitute the *para*-crystalline phase.³ These hard segments are generally dispersed in the amorphous phase.⁴ The result of this unique molecular configuration gives TPUs the superficial property of an elastomer with the processability of thermoplastics. Combination of these two material properties and the presence of polar chemical groups in the polymer chains make TPUs excellent candidates for polymer blending.⁵⁻⁷

Poly(vinylidene fluoride)

PVDF is a partially crystalline polymer known for its excellent resistance to solvent, thermooxidative degradation, and exceptional hydrolytic stability. It has also high mechanical strength, stiffness, and toughness.²

EXPERIMENTAL

Materials

The TPU used in this study was Estane 5714-F1 (B. F. Goodrich), a polyether polyurethane based on poly(tetramethylene-ether glycol), and diphenylmethane diisocyanate (MDI). Estane 5714-F1 is a thermoplastic elastomer known for its low-temperature flexibility and excellent resistance to abrasion and tear. It is also very resistant to hydrolysis and fungi attacks and is widely used as coatings in life jackets and tarpaulins and, more recently, in medical devices.

The PVDF used in this study was Kynar™ Ex-1000 (Pennwalt). It is commonly used in surface coatings, as seals in pump and valve components, membranes, pipes, vessels and autoclaves, films for packaging pharmaceutical products, medical instruments, shrink tubing, and muscle sensors.

Sample Preparation

Both polymer resins were dried in an air oven at 50°C overnight before being melt-blended. Blends of different compositions of TPU/PVDF were prepared using a Haake Rheocord 90 torque rheometer fitted with an internal mixer. The internal mixer was fitted with sigma rotors and the resins were melt-blended at 170°C until a stabilized torque was established. Table I summarizes the blend compositions used in this study. The blends were then compression-molded between two acetate-sheet-lined stainless-steel plates into thin sheets at 170°C at a hydraulic pressure of 12.5 MPa.

Table I TPU/PVDF Blend Compositions (Percentage Weight)

	P1	P2	P3	P4	P5	P6	P7	P8	P9
TPU	100	90	75	60	50	40	25	10	0
PVDF	0	10	25	40	50	60	75	90	100

Density

Bulk densities of the blends were measured using an AccuPyc 1330 pycnometer (Micromeritics) to an accuracy of within a range of less than 0.05% error.

Mechanical Testing

The compression-molded sheet materials were cut into narrow-waisted dumbbell-shaped specimens with geometry die D in accordance with ASTM D412-92. An Instron 4206 Series universal tester was used to determine the ultimate tensile strength, breaking strain, energy at break, and the Young's modulus of the blends. The strain rate was set at 100 mm/min.

Microscopy

All test specimens (5 mm wide × 50 mm length) were freeze-fractured in liquid nitrogen and gold-sputtered for scanning electron microscopy (SEM) examination. The SEM used was the Cambridge-360 stereoscan SEM.

RESULTS AND DISCUSSION

Miscibility (Theoretical Considerations)

The miscibility of two polymers is known to be governed by at least two important factors: (i) the Gibbs free energy of mixing ΔG_{mix} and (ii) the degree of intermolecular chain interactions.

The Gibbs free energy of mixing ΔG_{mix} is defined as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

where ΔH_{mix} is the enthalpy heat of mixing; T , the absolute temperature, and ΔS_{mix} , the entropy of mixing. Polymer miscibility is favored when the Gibbs free energy of mixing has a negative value. Generally, for a polymer, ΔS_{mix} is very small and the heat of mixing, ΔH_{mix} , is related to the Hildebrand solubility parameter, δ , as shown below⁸:

$$\Delta H_{\text{mix}} = V\phi_1\phi_2(\delta - \delta_2)^2 \quad (2)$$

where V is the total volume of the mixture and ϕ_1 , ϕ_2 and δ_1 , δ_2 are the volume fractions and solubility parameters of polymers 1 and 2, respectively. It is often postulated that the blend miscibility is dependent on the difference in the solubility parameters of both polymers. When the difference between the two polymers' solubility parameters is small, $< 4 \text{ MPa}^{1/2}$, miscibility of the polymers is favored.⁸ The solubility parameter δ for any given polymer can be determined using the following equation^{9,10}:

$$\delta = \frac{\rho \sum E}{M} \quad (3)$$

where $\sum E$ and M are the sum of the molar attraction constants and molar mass of the polymer structural repeat unit, respectively, and ρ is the density of the polymer.

As a sample calculation based on PVDF having a density of 1.67 g/cm^3 , a molar mass of the structural repeating unit, $-\text{CH}_2\text{CF}_2-$, of 64 g/mol , and a small group molar attractive constant for $-\text{[CH}_2\text{]}-$ and $-\text{[CF}_2\text{]}-$ of 269 and 307 $(\text{MPa})^{1/2} \text{ cm}^3/\text{mol}$, respectively,¹¹ the solubility parameter for PVDF was calculated as

$$\delta = \frac{1.67(268.7 + 307.0)}{64} = 15.0 \text{ MPa}^{1/2}$$

Similarly, TPU was calculated to have solubility parameters of 21.4 and 26.5 $(\text{MPa})^{1/2}$ for its soft and hard segments, respectively.¹² The difference in the solubility parameters of the soft segment of TPU and PVDF was calculated as 6.4 $(\text{MPa})^{1/2}$, and in the case of the hard segment and PVDF, the difference was 11.5 $(\text{MPa})^{1/2}$. Because of the large differences in the solubility parameters between the various components in the blend system, the TPU/PVDF blend was expected to be immiscible.

The other factor known to affect polymer miscibility is the specific molecular interactions between the polymers. It was reported that although PVDF has specific interactions with functional groups such as the carbonyl and ester, i.e., >C=O and $-\text{COO}-$, respectively, the presence of bulky functional groups such as the phenyl group could minimize favorable molecular interactions through steric hindrance.¹³ This meant that PVDF chains were unlikely to interact favorably with TPU because of the large phenyl groups present in the polyurethane chains.

Density

Figure 1 shows the effect that %PVDF had on the bulk density of the blend. Bulk density measurements were used to assess the degree of mixing achieved through melt blending. The broken line indicated the theoretical blend density obtained using the following modified equation derived from the Rule of Mixtures¹⁴:

$$D_b = D_1V_1 + D_2V_2 \quad (5)$$

where D_b is the blend density, D and V are the density and volume fraction of the polymer, respectively, and the subscripts denote polymer components 1 and 2. The theoretical and experimental density values of the blends showed good agreement at all compositions. This showed that the two polymers were well mixed during melt blending. The results should not be used for evaluating polymer miscibility as it would be shown later that TPU and PVDF were immiscible.

Mechanical Properties

Figure 2 shows the effect PVDF had on the ultimate tensile strength of the blends. It could be seen that the 50/50 TPU/PVDF blend had the lowest mechanical strength. However, with blends containing greater than 50% PVDF, the mechanical strength increased proportionally with PVDF content. This behavior could be explained by considering the concentration effect of PVDF on the blends. At low PVDF concentrations, i.e., $< 50\%$, PVDF formed the dispersed phase in a predominantly TPU continuous matrix, as shown in Figure 8. As the me-

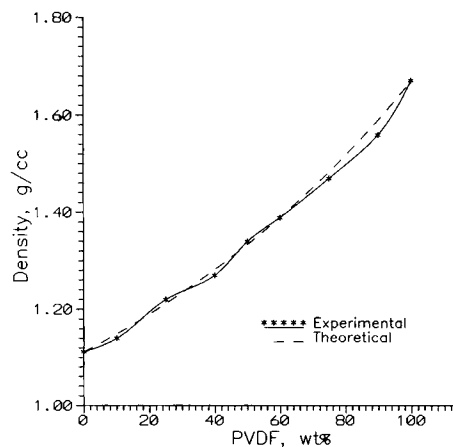


Figure 1 Blend density as a function of %PVDF content.

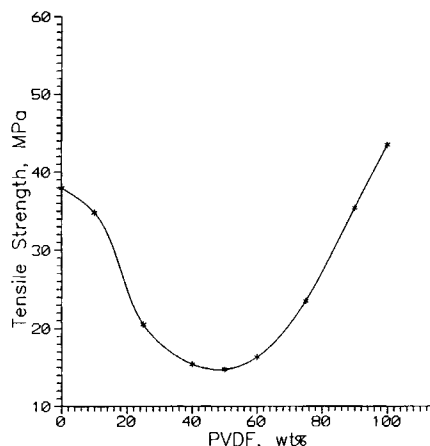


Figure 2 Stress at break as a function of blend composition.

chanical properties of TPU were known to be dependent on the degree of interchain hydrogen bonding,³ any disruption to this interaction would be detrimental to the material property. The addition of PVDF, because of its immiscibility with TPU, caused disruptions to the TPU interchain hydrogen bonding by acting as particulate barriers between TPU chains. Owing to little or no interactions between the two polymers, this disruption caused the lowering of the mechanical strength in the blends. Hence, as the %PVDF in the blend was increased, more disruption to the TPU interchain interactions resulted, causing further reduction in the mechanical strength. The result indicated that the critical %PVDF concentration in the blend was approximately 50%. At this critical concentration of PVDF, both the PVDF and TPU coexisted as the continuous matrix and the blend was found to have the lowest mechanical strength. Figure 9 shows that at this critical PVDF concentration distinct but continuous layers of TPU and PVDF coexisted. However, above the critical PVDF concentration, TPU could no longer coexist as the continuous phase with PVDF; as shown in Figure 10, TPU now formed the dispersed phase. Since PVDF had an inherently higher mechanical strength in comparison with TPU, the properties of the blend would be expected to be dominated by PVDF.

A commonly used equation to predict the property of polymer blends is shown in the following equation¹⁵:

$$P_{12} = P_1C_1 + P_2C_2 + IP_1P_2 \quad (6)$$

where P_{12} is a blend property, C is the concentration of the polymer, and the subscripts 1 and 2 represent

polymers 1 and 2, respectively. I is an interaction coefficient that describes the level of synergism, or thermodynamic compatibility, of the components in the blend. Applying eq. (6) to our blend system, the coefficient of interaction I for the TPU/PVDF blend was found to be negative, indicating the incompatibility of TPU/PVDF blends. This affirmed the theoretical considerations discussed earlier.

Figure 3 shows that the breaking strain of the blend decreased rapidly with increased PVDF up to approximately 40% PVDF content, beyond which a stabilized strain of 20% was obtained. This could be caused by the low breaking strain of PVDF chains, i.e., 24%, which could be broken at a much lower strain than could the TPU chains. These dissimilar breaking strains of PVDF and TPU in the blends could result in uneven stress distribution during experimental loading, resulting in the lowering of the breaking strain values. As PVDF had a lower breaking strain value than that of TPU, the breaking strain of the blend decreased with increased PVDF contents, reaching a stabilized breaking strain of 20% at approximately 40% PVDF. Another possible reason for the lower breaking strain with increased levels of PVDF in the blends could be due to the disruptive influence of PVDF on TPU interchain interaction, as previously discussed.

Figure 4 showed that the blend's Young's modulus increased with PVDF content. Although PVDF was found to have lowered the overall mechanical strength of the blend, this was not observed in the Young's modulus results. This was expected since the modulus of PVDF was considerably higher than that of TPU; the blend modulus was inevitably dominated by PVDF. Above 25% PVDF, the

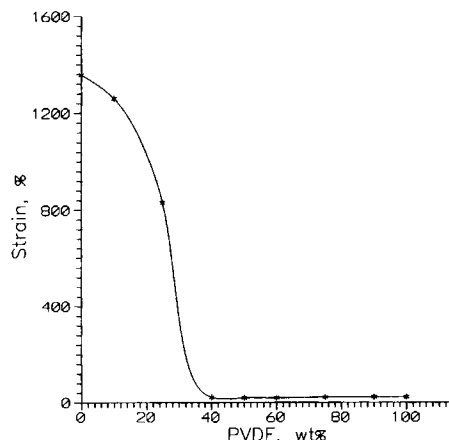


Figure 3 Breaking strain as a function of blend composition.

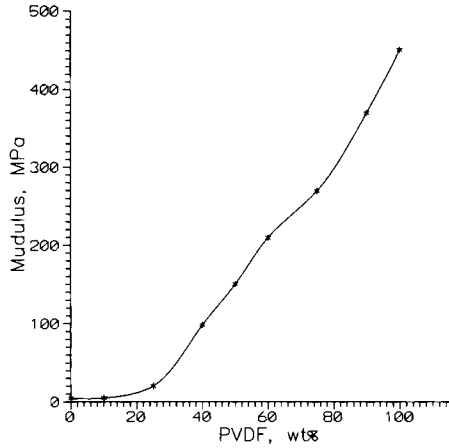


Figure 4 Young's modulus as a function of blend composition.

Young's modulus of the blend increased almost linearly with PVDF concentration.

The modulus of the TPU/PVDF blend, E_{12} , could in theory be predicted using the following equation¹⁶:

$$E_{12} = W_1E_1 + W_2E_2 + \beta_{12}W_1W_2 \quad (7)$$

where the empirical parameter (β_{12}) could be defined as

$$\beta_{12} = 4E_{12} - 2(E_1 + E_2) \quad (8)$$

E_1 and E_2 are the moduli of the original polymers, respectively, W_1 and W_2 , the weight fractions; and E_{12} , the modulus of the 50/50 blend. The interaction term β_{12} could be used as a relative measure of the blend compatibility. Applying eq. (8) to the 50/50 PVDF/TPU blend, β_{12} was found to be -318 . This

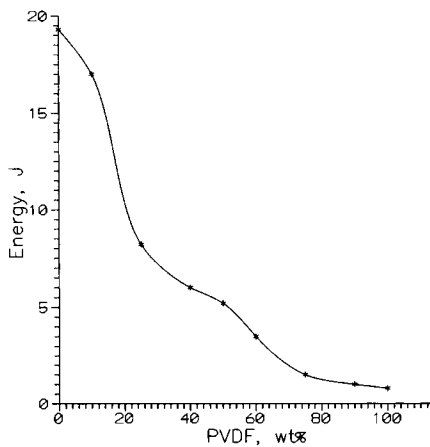


Figure 5 Energy at break as a function of blend composition.

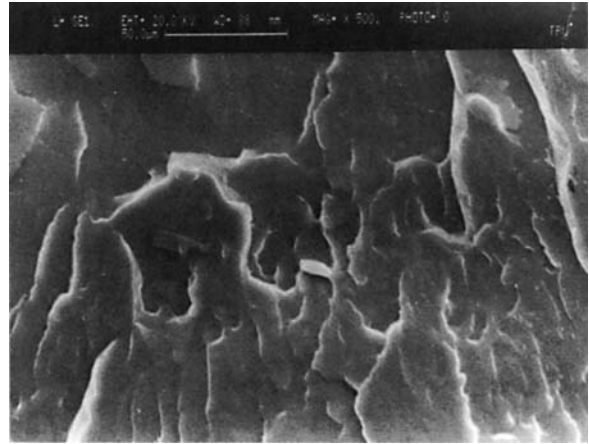


Figure 6 SEM of a freeze-fractured TPU surface.

negative value indicated the incompatible nature of the blends.

Figure 5 shows that the breaking energy of the blend decreased with increased PVDF in the blend. This behavior could be explained in terms of the effect of PVDF had on the interchain interactions between TPU polymeric chains. It is believed that the important hydrogen bonding occurring between TPU chains is disrupted by the bulky and immiscible PVDF polymers. This reduction in hydrogen bonding was reflected by the lower energy at break in the blends with increased PVDF concentration.

Morphology

The properties of TPU are known to be very dependent on the morphology of the polymer.³ Figures 6–10 show scanning electron micrographs of the fractured surfaces of pure TPU and PVDF and 75/

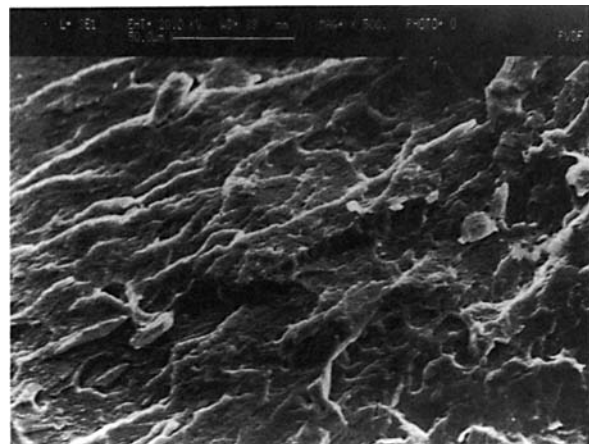


Figure 7 SEM of a freeze-fractured PVDF surface.

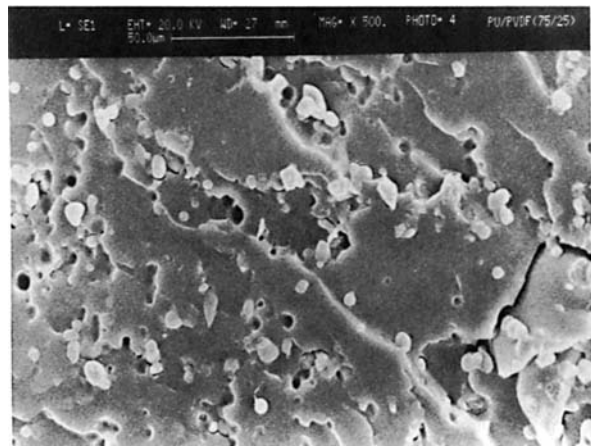


Figure 8 SEM of (75/25) TPU/PVDF blend fractured surface.

25, 50/50, and 25/75 TPU/PVDF blends, respectively.

Figure 6 shows an uneven but relatively smooth fractured surface of a pure TPU. This is in contrast to the highly uneven and rough surface of freeze-fractured PVDF as shown in Figure 7. Both these figures were used for comparison with the blended polymers. In Figure 8 (the 75/25 TPU/PVDF blend), the PVDF was evident as the dispersed phase in the TPU matrix. The immiscibility of these two polymers could be seen by the presence of smooth boundaries around the PVDF particulates. At 50/50 TPU/PVDF, shown in Figure 9, there appeared to be two materials of different structures coexisting as the continuous phase. The TPU appeared as the smooth layer while the PVDF formed filamentous structures. Again, the immiscibility of the two polymers was shown by the presence of distinguishable

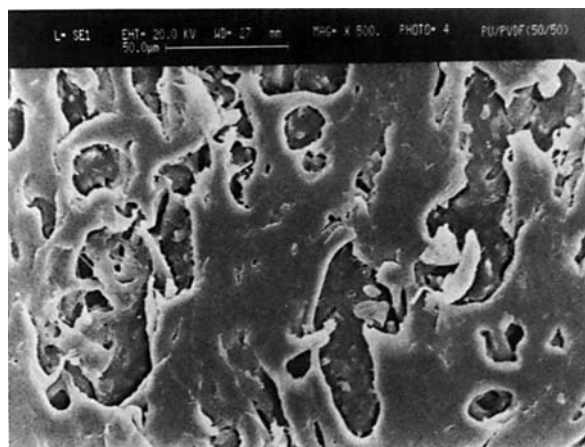


Figure 9 SEM micrograph of (50/50) TPU/PVDF blend fractured surface.

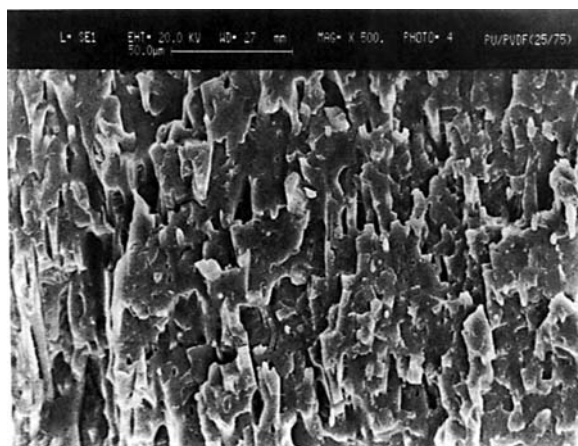


Figure 10 SEM micrograph of (25/75) TPU/PVDF blend fractured surface.

boundaries at the polymer interfaces. In Figure 10 (the 25/75 TPU/PVDF blend), PVDF appeared as the continuous phase while TPU appeared as the dispersed phase. The layered and ridgelike structures observed was typical of a semicrystalline polymer caused by the lamellae formation during crystallization from the melt. The structures found in the blend were similar to those of pure PVDF.

CONCLUSIONS

It could be concluded that both TPU and PVDF polymers were incompatible at all compositions. In spite of the good mixing process as shown by density measurements, poor miscibility of the polymers in the blends were obtained. The blends showed layered-type structures, due their immiscibility, which resulted in the low mechanical properties in the blends. PVDF was found to have disrupted the important interchain hydrogen bonding in TPU, resulting in lower mechanical properties. The critical PVDF concentration was found to be approximately 50% PVDF, whereby both polymers could coexist in a continuous phase but had the largest impact in decreasing the mechanical strength of the blend. The solubility parameter and structural considerations of the blend provided a reasonable estimation of the blend miscibility and correlated well with the mechanical and morphological studies undertaken.

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