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BINARY BLENDS OF POLYETHER-BASED POLYURETHANE BLOCK COPOLYMER AND POLY(VINYLIDENE FLUORIDE): PHYSICAL AND THERMAL PROPERTIES

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Key Words: Thermoplastic Polyetherurethane, Poly(Vinylidene Fluoride), Soft Segment, Blending, Melting Temperature, Phase Separation, Thermal Stability

ABSTRACT

Miscibility and phase behavior studies of thermoplastic polyether-based polyurethane (TPEU) and poly(vinylidene fluoride) (PVF_2) blends were investigated by means of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TGA), and mechanical behavior. TPEU based on 1,6-diisocyanohexane (HDI), 1,4-bu-tanediol (BD), and 1000 molecular weight poly(tetramethylene oxide) (PTMO) was synthesized. It was shown by FTIR that the addition of PVF_2 to TPEU disrupted the intermolecular interactions between soft and hard segments in TPEU, and the interactions between an urethane carbonyl and protons of PVF_2 was stronger than that between urethane carbonyl and urethane NH. It was found that PVF_2 was immiscible with soft segment (PTMO) and miscible with hard segment and the degree of phase purity of the soft domain increased with increasing PVF_2 content. The presence of a specific intermolecular interaction between the hard

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segment and PVF_2 was suggested by an observed systematic depression in the melting point of the PVF_2 component. It was also found that the thermal stability, tensile strength, and Young's modulus increased proportionally to PVF_2.

INTRODUCTION

The phase behavior of miscible copolymer blend has been extensively studied in recent years, although much work must still be done to understand the complex balance of interactions. Among other factors [1-3], the phase behavior of a copolymer blend depends on the inter- and intra-molecular interactions, the molecular weight of the components, and the differences in conformation and chain flexibility of the polymer chains. The unique and novel properties of linear thermoplastic polyurethane elastomers are usually formed from a polyether or polyester macroglycol soft segments and urethane hard segments having the glass transition temperatures below and above the use temperature of the sample, respectively. A wide range of physical properties and morphologies have been observed, depending on the composition and chemical structure of the hard and soft segments [4-12]. The driving force for phase separation in these systems is the incompatibility of the two segment types due to urethane segments and are more polar than the polyether soft segments. The urethane hard segment domains are held together by intra-urethane and inter-urethane hydrogen bonds, and function as physical crosslinks for the rubbery modulus. Combination of these properties and the presence of polar urethane groups in the polymer chains make PUs excellent candidates for blending [2, 13-21].

Poly(vinylidene fluoride) (PVF_2) ($(\text{-}CH_2\text{-}CF_2\text{-})_n$) is a semicrystalline polymer of large technological interest for its excellent resistance to solvent and thermooxidative degradation. It also has high mechanical strength, stiffness, and toughness [22]. PVF_2 is a flexible polymer of intermediate crystallinity whose β crystal phase exhibits piezo and pyroelectric properties. PVF_2 has been found to form miscible blends with poly(pivalolactone) [23], poly(3-hydroxy-butyrate) [24, 25], poly(vinylacetate) [26-28], poly(methylmethacrylate) [29-34], poly(acrylates) [34-37], and poly(vinyl methyl ketone) [38]. Miscibility in these amorphous/semicrystalline blends was suggested to arise from hydrogen bonding between the acidic hydrogens of the ($\text{-}CH_2\text{-}CF_2\text{-}$) segments and the doubly bonded ester oxygen of the carbonyl group [25]. Though it has been claimed that PVF_2 chains are unlikely to interact favorably with PU because of the large phenyl groups present in the polyurethane chains and the large differences in the solubility parameters in the blend system. To the best of our knowledge, no previous work has been reported on the PEU/PVF_2 blends, which are investigated here. Earlier work has been done on the blends of PVF_2/PEU based on 4,4'-diphenylmethane diisocyanate (MDI) by Yue and Chian [21]. However, their results only give the mechanical properties and morphology studies by SEM of the two systems.

The present paper focuses on the miscibility behavior and interactions between PVF_2 and segments of PEU. For this study, one series of thermoplastic polyether based polyurethane (TPEU) is prepared from 2:1:1 molar ratio of 1,6-diisocyanohexane (HDI), poly(tetramethylene oxide) (PTMO; Mn = 1000) and 1,4-butanediol (BD). Fourier transform infrared spectroscopy is employed to study hydrogen-bonding interactions between soft and hard segments of PEU as well as PVF_2 blends. Thermal transition temperatures and the melting point depression and the thermal stability of two blend systems as well as stress-strain testing are investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) .

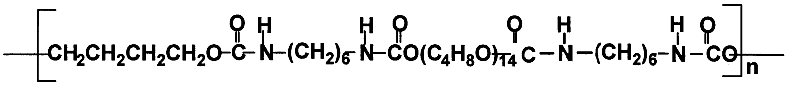
EXPERIMENTAL

Materials

Poly(tetramethylene oxide) of molecular weight 1000 (PTMO, Aldrich) was dried under vacuum for 24 hours at 60°C prior to use. 1,6-Diisocyanohexane (HDI, Aldrich), 1,4-butanediol (BD, Aldrich), and dibutytindilaurate (T-12, Aldrich) were used as received. Poly(vinylidene fluoride) (PVF_2) was purchased from Aldrich in pellet form. PVF_2 was purified by a twofold filtration and precipitation from a 5 wt% polymer in DMF solution at 80°C into an ice-water mixture. A dry nitrogen flow was used during purification process to minimize polymer and solvent degradation.

Synthesis of Polyurethane

The segmented thermoplastic polyetherurethane (TPEU) was prepared by a two-stage process in a manner previously described [19, 39] and the structure of TPEU is shown in Scheme 1. The isocyanate-terminated PEU was prepared by reacting HDI and PTMO at a molar ratio of 2:1 under a dry nitrogen atmosphere at 80°C. The reaction was allowed to proceed until the isocyanate



$$-\!\left[CH_2CH_2CH_2CH_2O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}O(C_4H_8O)_{14}\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}O\right]_n-$$

Scheme 1. Structure of repeating unit of TPEU.

content (NCO%) reached the theoretical value of 6.34% as determined by di-n-butylamine titration method. Then, the chain extender 1,4-BD and 0.15% T-12 were added, and chain extension was allowed to proceed at 75-80° in DMF solution.

Blend Preparation

All blends were prepared in a nitrogen atmosphere. PVF_2 and TPEU were dissolved separately in DMF to form 5 w/v% solutions. Predetermined amounts of the solutions were mixed at 80°C and stirred for 30 minutes under a dry nitrogen atmosphere. The homogeneous solutions were cast in glass dishes at 80°C in an oven, and the resulting films were further dried in a vacuum oven at 80°C for 3 days to completely remove any residual solvent. Blends with weight ratios of 80//20, 60/40, 40/60, and 20/80 TPEU/ PVF_2 were prepared.

Measurements

Thin films of the blends prepared for Fourier transform infrared spectroscopy (FTIR) measurements were cast from 1% (w/v) DMF solutions onto KBr windows at 80°C . The drying conditions were identical to the method used in bend preparation section. The FTIR spectra were recorded on a Mattson 500 FTIR spectrophotometer model GL-5020. The glass transition temperature of the soft segment (T_{gs}) in TPEU and melting points of samples were studied by using a TA 2000 instrument equipped with 910 differential scanning calorimetry (DSC). The glass transition temperature measurements by DSC were performed on 10 ± 2 mg samples under a dry nitrogen. The samples were first heated from ambient temperature to 200°C and maintained for 2 minutes before rapid quenching to liquid nitrogen temperature. The thermal behavior of the quenched samples were probed by heating from -100°C to the molten state at a heating rate of 10°C/min. The T_gs were taken as the midpoint of the transition. For observing the melting temperature the samples were heated to 200°C and kept at this temperature for 5 minutes in the DSC pan and cooling at 10°C/min to room temperature, and finally heated at a rate of 10°C/min. The melting temperatures for the various samples were taken as the maximum in the endothermic peak. The thermal stability of the samples were studied by thermogravimetric analysis (TGA) (951-TG module). Measurements were carried out at a heating rate of 20°C/min under a dry nitrogen purging at a flow rate of 50 cm^3/ min. Uniaxial stress-strain data were obtained with an Instron model 1026 testing instrument at a strain rate of 5 cm/min. Measurements were performed at 25°C with a film thickness of about 300 μm and stamped out with an ASTM D412 die.

RESULTS AND DISCUSSION

Figure 1 shows the IR survey spectra, recorded at room temperature, for both TPEU and PVF_2 and two blend samples containing 60% and 40% PVF_2 cast from DMF solutions. In TPEU and blend samples, the hydrogen-bonded NH groups of the urethane linkage groups is observed as a sharp peak at 3322 cm^{-1}, but the peak at 3460 cm^{-1} due to free NH is not present, indicating that the NH groups appear to be completely hydrogen-bonded. For the TPEU, the C=O bands from the urethane group have a peak at 1721 cm^{-1} and a shoulder at 1695 cm^{-1} corresponding to nonbonded and bonded (interurethane) C=O , respectively. Since the NH groups is mostly hydrogen bonded while the carbonyl group is not, it appears that the NH groups are bonded to soft segment ether groups of PTMO [40]. The hydrogen bonding between urethane carbonyl and ether groups of PTMO is suggestive a one phase morphology with hard segments dispersed in a soft segment matrix. For blend samples, the absorption of the urethane carbonyl band is split into two peaks. The one centered at 1732 cm^{-1} is more intense than the one at 1686 cm^{-1}. The new peak can be reasonably considered as the contribution of the urethane carbonyl groups which are bonded with the protons of PVF_2 through hydrogen bonding. The frequency of this peak is just slightly lower than the interurethane peak (1695 cm^{-1}) suggesting the interaction between an urethane carbonyl and protons of PVF_2 is stronger than that between urethane carbonyl and urethane NH. As shown in Figure 1, an increase in PVF_2 content in the blends lead to an increase in the relative intensity of hydrogen bonded carbonyl band at 1686 cm^{-1} as compared with the free carbonyl peak, indication that more urethane carbonyl groups involved in hydrogen bonding with the protons of PVF_2 when the PVF_2 concentration in the blends is increased. This behavior is typical of a phase- separated between hard and soft segments.

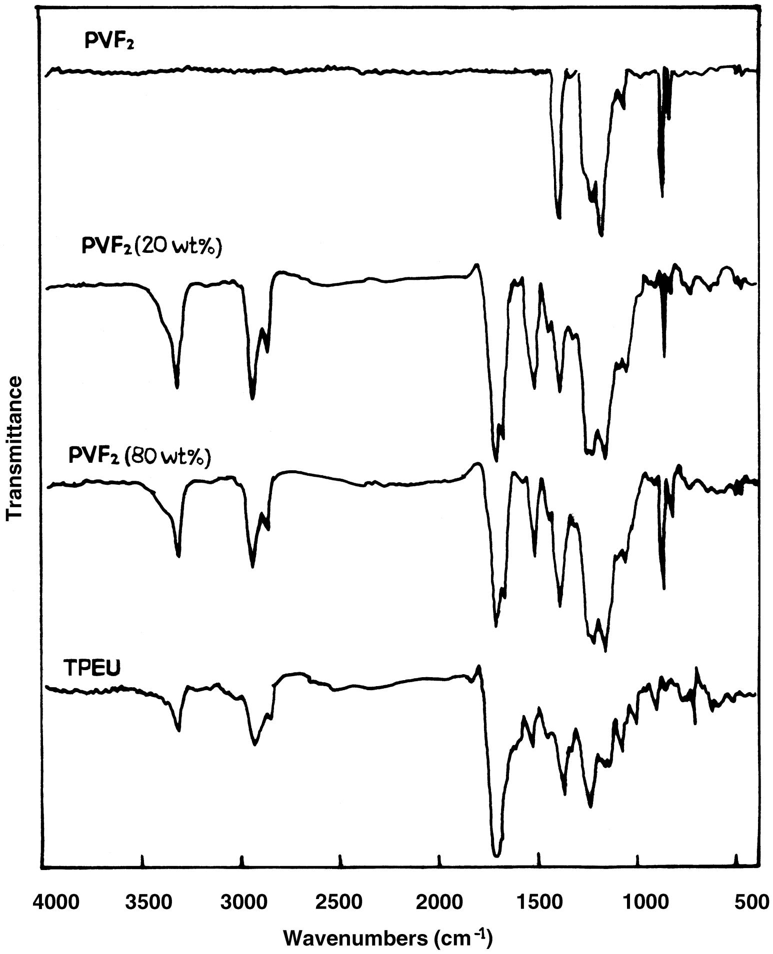


Figure 1. Typical FTIR spectra of PVF_2 , TPEU, and TPEU/PVF_2 blend samples.

Thermal Properties

Figure 2 shows DSC curves of blend samples which are analyzed in three scans for each sample, i.e., a first heating, second heating, and third heating scans. The first heating scan is shown as a solid line and was done after the samples annealed at 50°C for two weeks. The second heating scan is shown as dashed line and was done after quenched from 200°C to -120°C following the first heating. The third heating scan was done after the sample was kept at 200°C in the second heating process for 5 minutes in the DSC pan and cooling at 10°C/min to room temperature. The DSC curves (Figure 2) of all blend samples

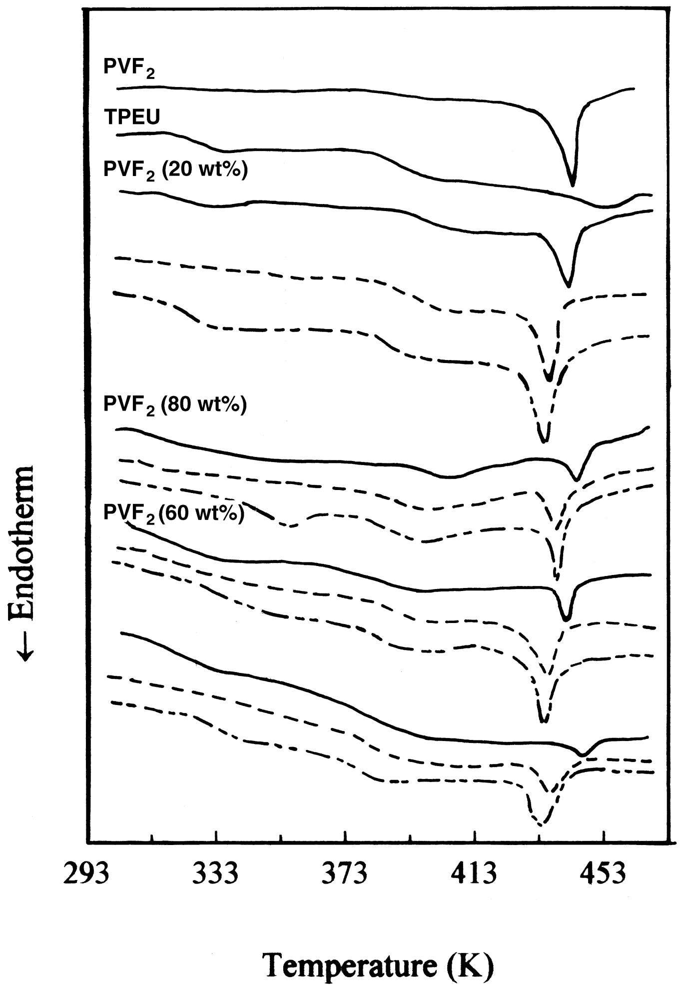


Figure 2. DSC high- temperature thermograms for a series of TPEU/PVF$_2$ blend samples: (—) first heating; (– –) second heating; (– --) third heating.

studied in this investigation show three endothermic transitions. The first endotherm appears below 100°C and shifts to higher temperature by annealing and disappears in the quenched samples. It has been suggested that this endotherm reflects the dissociation of short range order in the hard segment microdomain of TPEU [44, 45]. The second endotherm reflects a microphase separation transition (MST) which involves the disruption of microdomain structure to form a homogeneous mixed phase [7]. The MST temperature appears in the range 106-125°C and depends upon blend composition and is sensitive to small changes in the annealing temperature. The third endotherm reflects melting temperature of PVF_2 with a peak maximum at 170°C for pure PVF_2. As TPEU is blended with PVF_2, the endothermic melting peak of PVF_2 tends to a slight shift to lower temperature when its proportion in the blend decreases. The PVF_2 melting point decreases from 170°C for pure PVF_2 to 160°C for a blend containing 80 wt% TPEU. The MST endotherm temperature (T_{MST}) of TPEU obtained from third scan displays similar behavior and decreases from 125 to 106°C for a blending containing 80 wt% PVF_2. On blending a crystalline polymer with other polymers, a decrease in melting temperature is indicative of miscibility of the polymers in the amorphous state and is governed by the equation [33]:

$$1/T_m - 1/T_m^o = - R/\Delta H_f \left(\upsilon_{2\mu} / \upsilon_{1\mu}\right) \varphi \upsilon_{2\mu}^2 \chi_{12}$$

Where T_m and T_m^o are equilibrium melting temperatures of the blend and pure polymer; $\upsilon_{2\mu}$ and $\upsilon_{1\mu}$ are the molar volumes of the repeat units of crystalline and amorphous polymer, respectively; ΔH_f is the enthalpy of fusion of the perfect crystal; φ_1 is the volume fraction of the amorphous polymer; and χ_{12} is the polymer-polymer interaction parameter and is dependent on heat of mixing and is independent of combinatorial entropy of mixing [33, 41]. Thus melting-point depression is dependent only on the amount of interaction provided the samples are crystallized and melted in a similar fashion [42, 43]. Since the correct determination of interaction parameter requires equilibrium melting-point determination very accurately, the non-equilibrium melting point depression with composition can be used to obtain a qualitative idea of interaction between polymer segments rather than any quantitative measurement. Figure 3 shows plots of PVF_2 melting temperature (T_m) and T_{MST} against the weight percent of PVF_2 in the blend samples. It is noted that the T_m values in blend samples decrease with increase of the overall content of the amorphous component as usually observed for amorphous/ semicrystalline miscible blends. Since this phenomena alone is not absolute proof of miscibility, more direct proof can be obtained by observing the behavior of the T_g with the blend composition.

Figure 4 shows DSC curves for a series of TPEU/PVF_2 samples and these curves refer to the result of the second heating scans of the quenched samples from 200°C to liquid nitrogen temperature. Thermal transition data are summarized in Table 1. From the midpoint of the DSC base-line, the glass transition temperatures of the PVF_2 (T_{gPVF2}) and PTMO-based TPEU (T_{gs}) are found to be -40 and -26°C, respectively. The soft segment (PTMO) has a sharp glass transi-

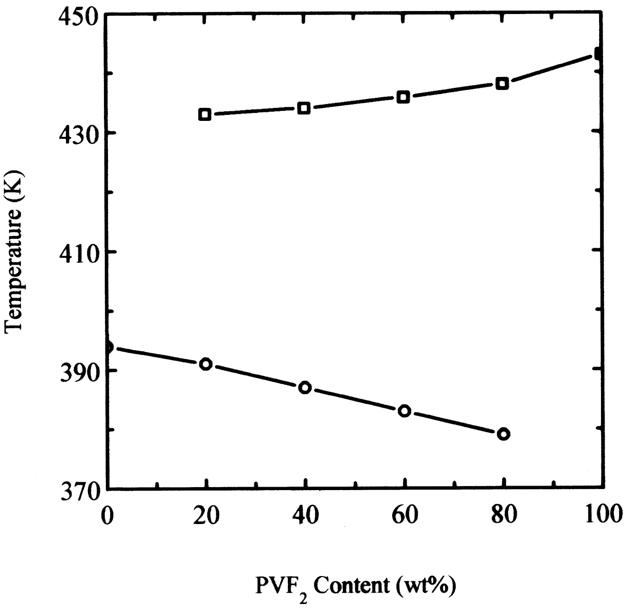


Figure 3. Composition dependence of thermal transitions, determined by DSC (from third heating) for TPEU/PVF$_2$ blends. (O) melting point (T_m) of PVF$_2$; (□) microphase-separation transition temperature (T_{mst}) of TPEU in blend samples.

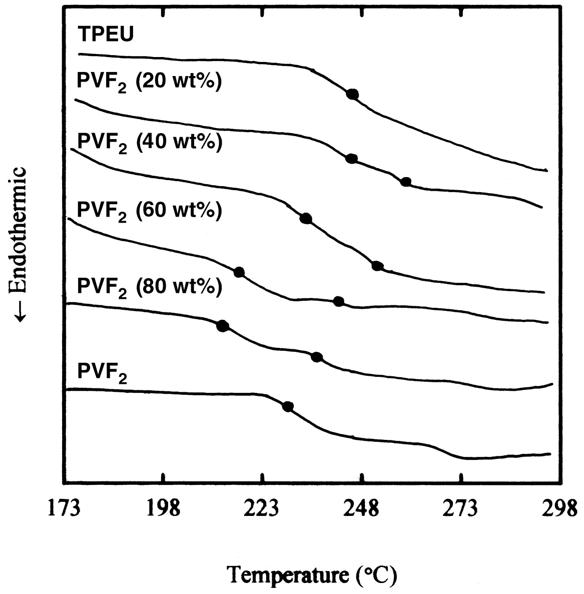


Figure 4. DSC low-temperature thermograms for TPEU/PVF2 blend samples.

TABLE 1. TGA and DTGA Results for $TPEU/PVF_2$ Blends

Composition	TGA[a]			DTGA[b]		
$TPEU/PVF_2$	T_5 (°C)	T_{10} (°C)	T_{20} (°C)	T_{1max} (°C)	T_{2max} (°C)	T_{3max} (°C)
100/0	325	342	358	-	-	410
80/20	340	362	390	330	385	445
60/40	350	370	400	342	397	460
40/60	355	375	405	355	423	472
20/80	365	390	427	390	445	485
0/100	470	482	492	-	-	505

[a] (T_5) 5% weight loss;(T_{10})10% weight loss; (T_{20}) 20 % weight loss

[b] (T_{1max}) maximum decomposition temperature of the first step (T_{1max}), second step (T_{2max}), and third step (T_{3max}).

tion zone unaffected by quenching, characteristic of a one-phase material. This conclusion is also confirmed by FTIR results described previously suggesting that the material is not phase separated. All the blends have two T_gs which varied with overall blend composition as indicated in Figure 4. However, it is noted that the soft segment T_{gs} in blend samples decreases while the T_{gPVF2} of PVF_2 increases with increasing PVF_2 content as illustrated in Figure 5. This phenome-

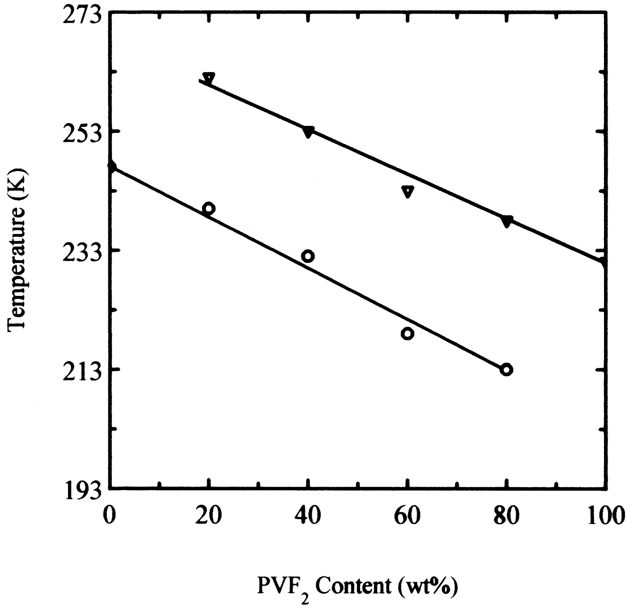


Figure 5. Glass transition temperature (T_g) versus composition of $TPEU/PVF_2$ blends: (O) T_g of PTMO in TPEU; (▽) T_g of PVF_2.

non indicates that the hard segment must have some higher Tg and miscibility with this segment follow a composition dependency increasing Tg of PVF_2 in the blend. The appearance of two Tgs indicates that the PVF_2 is immiscible with PTMO and the degree of phase purity of the soft domain increases with increasing PVF_2 content. The variation in the soft segment glass transition temperature reflects changes in the extent of microphase separation. This is due to the hydrogen bonding interaction between the hard segments of TPEU and the protons of PVF_2 [25] which leads to a decrease in the hard segment solubilization in the soft segment matrix. The increasing of PVF_2 content in the blend composition clearly indicates that the hard segment domain cohesion reduces, as indicated by the hard segment microphase separation transition temperature (T_{MST}) moving to lower temperature. This ordering and phase separation closely parallel the change from mostly free to mostly bonded urethane carbonyl groups as seen in the IR spectra.

In terms of the optical properties, the pure TPEU, as well as the blend samples containing up to 40% PVF_2, are clear. Some cloudiness is observed for the 40% sample, and the cloudiness increases progressively with increasing PVF_2 content.

The typical TGA patterns for the TPEU, PVF2 and one blend sample are presented in Figure 6. The PVF_2 and TPEU show the highest and lowest onset degradation temperature of 440 and 290°C, respectively. The TGA curves of TPEU and PVF_2 display one distinct region of weight loss which are reflected in one peak in the derivative thermogravimetric analysis (DTGA) curves. The blends of TPEU/PVF_2 show the midrange thermal stability between the two pure components and TPEU stability is enhanced a little than the expected values based on the weight fractions of the two component. The TGA curves of blend samples display three distinct regions of weight loss which are reflected in three peaks in the DTGA curves. Qualitative characterization of the degradation process is illustrated by the maximum temperatures of the first step, T_{1max} second step T_{2max} and third step T_{3max}. Table 1 presents the characteristic degradation temperatures of all samples at a heating rate 20°C/min. From Table 1, it is evident that the temperature of 5, 10, and 20% weight loss increases with increasing the PVF_2 content.

Mechanical Properties

The tensile strength and elongation at break is plotted as a function of composition in Figure 7. Generally, the effects of increasing PVF_2 in blend is to

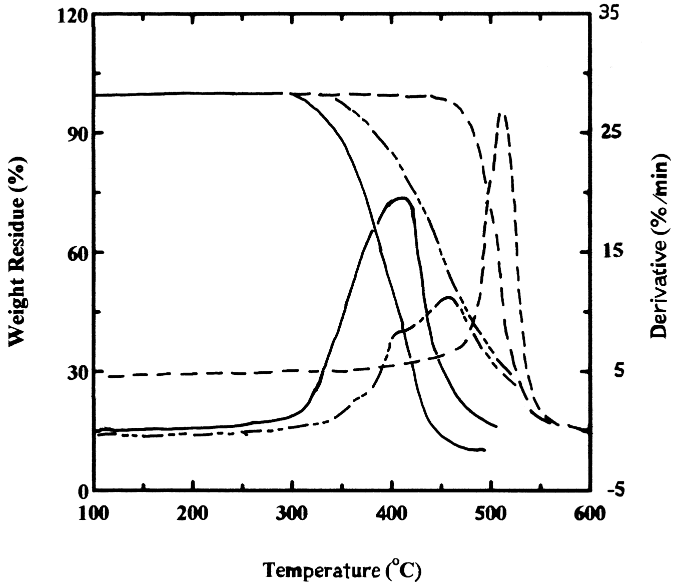


Figure 6. Typical TGA and DTGA curves for TPEU/PVF$_2$ blends. (—) TPEU; (– –) PVF$_2$; (– --) PVF$_2$ (60 wt%).

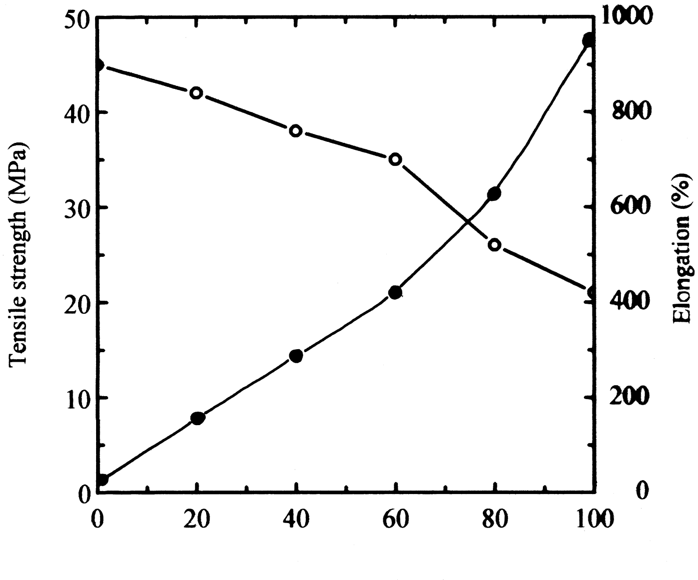


Figure 7. Tensile strength and elongation at break versus composition of TPEU/PVF$_2$ blends.

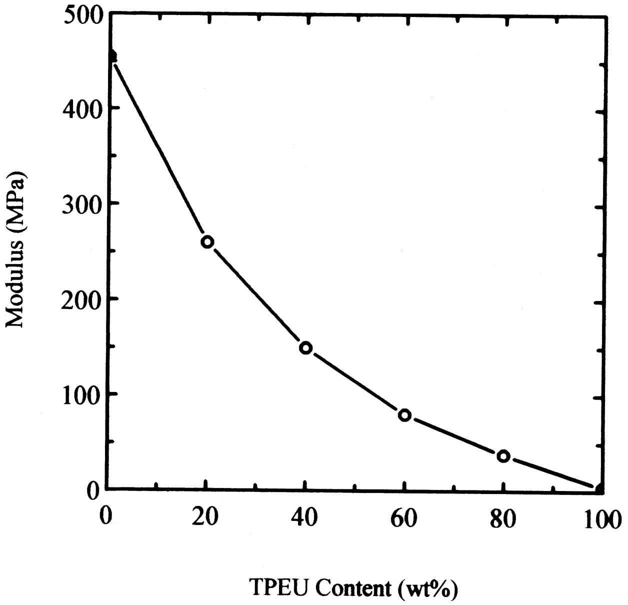


Figure 8. Young's modulus versus composition of TPEU/PVF_2 blends.

increase tensile strength while decreasing elongation at break. Such a remarkable improvement in tensile strength of TPEU is a direct result of the favorable interfacial adhesion occurring by virtue of the specific interactions among segments of TPEU and PVF_2. The elongation at break decreases almost linearly with increasing PVF_2 content. The possible reason for the elongation-composition behavior in the blends may be due to the mutual hydrogen bonding between PVF_2 and hard segments of TPEU.

Young's modulus versus composition is illustrated in Figure 8. The results show that the Young's modulus increases with PVF_2 content. The increase in Young's modulus would be expected since the modulus of PVF_2 is considerably higher than that TPEU; the blend modulus is inevitably dominated by PVF_2.

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