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Syndiotactic polystyrene/thermoplastic polyurethane blends using poly(styrene-*b*-4-vinylpyridine) diblock copolymer as a compatibilizer

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Abstract

The effect of adding diblock copolymer poly(styrene-*b*-4-vinylpyridine) (P(S-*b*-4VPy), to immiscible blends of syndiotactic polystyrene (sPS)/thermoplastic polyurethane (TPU) on the morphology, thermal transition, crystalline structure, and rheological and mechanical properties of the blends has been investigated. The diblock copolymer was synthesized by sequential anionic copolymerization and was melt-blended with sPS and TPU. Scanning electron microscopy (SEM) showed that the added block copolymer reduced the domain size of the dispersed phase in the blends. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) revealed that the extent of compatibility between sPS and TPU affected the crystallization of the sPS in the blends. Tensile strength and elongation at break increased, while the dynamic modulus and complex viscosity decreased with the amount of P(S-*b*-4VPy) in the blend. The compatibilizing effect of the diblock copolymer is the result of its location at the interface between the sPS and the TPU phases and penetration of the blocks into the corresponding phases, i.e. the polystyrene block enters the noncrystalline regions of the sPS, and the poly(4-vinylpyridine) block interacts with TPU through intermolecular hydrogen bonding. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Blending of polymers has been the subject of intensive research in both academic and industrial laboratories [1,2]. In recent years, the new semicrystalline polymer syndiotactic polystyrene (sPS) has attracted much interest due to its unique physical characteristics. As the result of its completely ordered chain configuration, it is endowed with: (i) a high melting temperature (270°C); (ii) a rapid crystallization rate; and (iii) a controllable crystallinity. Therefore, sPS exhibits not only good chemical resistance but enhanced mechanical performance at elevated temperatures as well [3–10]. However, it has notable shortcomings in properties, such as its high brittleness and poor impact- and tear-resistance [11]. In order that sPS can be of commercial utilization, the practice of blending with an elastomer, just as in the toughening of polypropylene (PP) [12–14], seems to be the way out.

Many commercial rubbers could be used to improve the impact strength at low temperatures and environmental stress cracking resistance of sPS. Yet, so far, not many academic studies have been published. In order to broaden the practical application of sPS, our interest is to study the blending of sPS with other polymers, especially polar elastomers.

Thermoplastic polyurethane (TPU) is an important class of elastomers that has found many novel and specialized applications where high mechanical and chemical performances are prerequisites. They are known for their good mechanical strengths, wear and tear resistance, and low-temperature elasticity [15,16]. Therefore, TPU is an excellent candidate for polymer blending [17,18]. In this work, we made use of TPU to modify sPS. However, the two polymers are immiscible. A block copolymer is the first choice to serve as a compatibilizer [1]. There are no copolymers containing an sPS block prepared as yet, although block copolymers containing atactic polystyrene block are easily synthesized via anionic polymerization. Thus, the diblock copolymer, poly(styrene-*b*-4-vinylpyridine) (P(S-*b*-4VPy)), is a desirable candidate compatibilizer, in which the PS block prepared is compatible with sPS [19], and the P4VPy block is known to be miscible with polar polymers as polyacids [20,21], poly(hydroxy ether of bisphenol-A) [22] and poly(vinyl phenol) [23] due to specific interaction between them. P(S-*b*-4VPy) can be prepared in a straightforward manner via a two-step anionic

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living polymerization, whereby the copolymer architecture and composition can be easily controlled. Since information on the potential of controlling the extent of dispersion in sPS/TPU blends by P(S-*b*-4VPy) and the properties and structure of the blends are lacking, the compatibilizing effect of P(S-*b*-4VPy) for sPS/TPU blends and the mechanism of compatibilization by the diblock copolymer are now investigated by means of scanning electron microscopy (SEM), differential scanning calorimetry (DSC), tensile property measurements, dynamic rheological analysis, wide-angle X-ray diffraction (WAXD) and FTIR.

2. Experimental

2.1. Materials

sPS was synthesized in our laboratory with a cyclopentadienyltitanium trichloride ($CpTiCl_3$)/methyl aluminoxane (MAO) polymer-supported catalytic system at 50°C [24]. The resulting polymer was stirred in a 5 wt% methanol solution of HCl for 2 h to remove the residual metal catalyst, and then extracted with boiling methylethylketone (MEK) overnight to remove the atactic component. The unextractable fraction was characterized to have a very high steric purity ($>$ 99% in syndio units, calculated via ^{13}C NMR spectroscopy), and its number-average molecular weight ($\bar{M}_n$) and the polydispersity index ($\bar{M}_w/\bar{M}_n$) were 6.29×10^4 and 2.1, respectively, as determined by gel-permeation chromatography (GPC), against standard polystyrene.

TPU was obtained from the Tianjin Polyurethane Products Factory: hardness Shore A 80; intrinsic viscosity 1.02 dl g^{-1} (*N*,*N*-dimethylacetamide, 30°C), the hard segment being 4,4′-diphenylmethane diisocyanate (MDI), the soft segment poly(tetramethylene oxide) (PTMO), and the chain extender 1,4-butanediol.

P(S-*b*-4VPy), was synthesized via sequential anionic copolymerization [24,25]. All reagents had been strictly purified before use. Dry tetrahydrofuran (THF) (300 ml) and styrene (20 g) were added to a 800 ml capped bottle. The bottle was purged with argon and degassed for 30 min. *n*-Butyllithium (0.63 mmol) in hexane was then added. The fresh red-colored solution was agitated and maintained at 25°C. After the reaction had proceeded for 1 h, a 2 ml sample was withdrawn and terminated with a small amount of methanol for GPC determination of molecular weight. The reaction mixture was cooled to −78°C, after which 0.75 mmol of 1,1-diphenyl ethylene in THF was added. The red solution was shaken for 10 min and then 4-vinylpyridine (20 g) was added. The deep-red solution was agitated to maintain the temperature at −78°C for 2 h. The reaction was quenched with 5 ml methanol, and the solution was poured into a large amount of hexane. The precipitate was filtered, washed and then dried in vacuo. The product was extracted successively with boiling cyclohexane and methanol/water (90/10 v/v) mixture. The final copolymer was characterized by g.p.c and ^1H NMR. Its $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were 7.32×10^4 and 1.10, respectively, and the content of the PS block was 47 wt%.

P4VPy and aPS were prepared by anionic polymerization. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were 3.37×10^4 and 1.07 for P4VPy, and 3.41×10^4 and 1.05 for aPS, respectively.

2.2. Blend preparation

TPU/P4VPy binary blends and blends with different compositions of sPS/TPU/P(S-*b*-4VPy) were prepared by a solution/precipitation method. THF solutions of the polymers were mixed at room temperature until a homogeneous solution formed. This was added to a large amount of hexane and the precipitate was dried under vacuum at 50°C for two days. The preparation of sPS/aPS and sPS/P(S-*b*-4VPy) binary blends was similar to that for TPU/P4VPy blends; the solvent used for preparing the blends, however, was *o*-dichlorobenzene, and the blending temperature was 135°C and the drying temperature was 140°C.

All blend samples containing sPS for mechanical property measurements were prepared by pressing in a mould on a hot press at 290 ± 2°C for 7 min and 10 MPa, and then cooled to ambient temperature in air. Thickness of the samples was 1.5 mm for mechanical property and WAXD measurements and 2.5 mm for dynamic rheological analysis.

2.3. Testing and characterization

The fracture surface of sPS/TPU blends with and without addition of P(S-*b*-4VPy) for SEM observation was prepared by dipping the sample in liquid nitrogen and then fracturing. The fracture surface was etched with THF at room temperature to remove the TPU phase. The morphology of the surface of cryogenically fractured samples was observed with a JEOL JAX-840 scanning electron microscope after coating with gold.

Thermal analysis was made using a Perkin-Elmer DSC-2C under a nitrogen atmosphere. For samples containing sPS, the following procedure was used: samples were heated at 290°C for 5 min in order to eliminate the influence of thermal history and the effect of thermal treatment on the crystalline structure of sPS, then cooled down to −70°C and reheated to 290°C, all at a rate of 40°C min^{-1}. The normalized crystallinity of sPS, χ_c is given by the following equation:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^{\circ}}/w \times 100\% \qquad (1)$$

where, ΔH_f is the melting enthalpy of the blend, ΔH_f° the melting enthalpy of 100% crystalline sPS ($\Delta H_f^{\circ} = 53$ j g^{-1} [7]) and w is the weight fraction of sPS in the blend.

Mechanical properties of the blends were measured at 25°C on an Instron 1121 electronic testing machine, the drawing rate being 25 mm min^{-1}.

The linear viscoelastic properties of the melts were performed with a cone-and-plate type rheometer (CP8, Contraves Rheomat 120) at 290°C under a nitrogen atmosphere. The samples for measurements were cut into discs of 25 mm in diameter.

Wide angle X-ray diffraction [26] was carried out on a Philips PW-1700 X-ray diffraction spectrometer.

Infrared spectra were obtained on a BIO RAD FTS-7 Fourier transform infrared. Sample films were cast on an NACl plate from a 1.0 wt% THF solution of TPU/P4VPy blend and dried under vacuum.

3. Results and discussion

3.1. Compatibility of sPS and P(S-*b*-4VPy)

Before the compatibilizing effect of P(S-*b*-4VPy) for sPS/TPU blends was studied, it was desirable to investigate the compatibility of the diblock copolymer P(S-*b*-4VPy) with sPS. It can be seen from the DSC data of the binary blends of different compositions (Table 1) that all the thermal properties of sPS do not change much, indicating that the added P(S-*b*-4VPy) has no effect on crystallization and the crystalline structure of sPS, as also proved by the constant WAXD pattern (not shown).

3.2. Compatibilizing effects of P(S-*b*-4VPy)

3.2.1. Morphology

SEM observation was made on the etched, cryogenically fractured surface of the sPS/TPU 70/30 (wt/wt) blends with various levels of P(S-*b*-4VPy) (Fig. 1) to examine the morphology of the compatibilized blends, especially the compatibilizing effect of the block copolymer on the blends. The noncompatibilized sPS/TPU blend shows the typical characteristics of an immiscible blend [Fig. 1(a)]. The spherical domains of the dispersed TPU phase are large and the interface between the sPS matrix and the TPU is smooth and clear, indicating a poor interfacial adhesion between the two phases. When 2.9 wt% of the block copolymer is added, the domains of the dispersed phase interconnect, and the interface between the sPS and the TPU phases becomes rough [Fig. 1(b)], depicting an enhanced interfacial adhesion. When the amount of the block copolymer is up to 7.4 wt%, the domain size of the dispersed phase becomes even smaller [Fig. 1(c)], implying that interfacial adhesion between the two phases improves further. When the amount of P(S-*b*-4VPy) is up to 9.1 wt%, the interface between the blend phases becomes undistinguishable [Fig. 1(d)]. The SEM results indicate that the P(S-*b*-4VPy) block copolymer acts as an effective compatibilizer; it reduces the interfacial tension between the two incompatible polymers, sPS and TPU, and enhances the interfacial adhesion between the two phases.

Table 1
Thermal properties of sPS in sPS/P(S-*b*-4VPy) blends

sPS/P(S-*b*-4VPy) (wt/wt)	100/0	90/10	70/30
$T_{g,sPS}$ (°C)	99.4	100.2	102.1
$T_{m,sPS}$ (°C)	258.4	258.3	258.5
$\chi_{c,sPS}$ (%)	40.4	39.9	40.0
$T_{c,sPS}$ (°C)	223.8	223.9	224.2

3.2.2. Thermal analysis

DSC is an useful tool for studying compatibilization of blends, especially blends containing crystalline polymers, used not only to estimate the compatibilizing effect but also to investigate the location of the compatibilizer in a blend. The thermal properties of the sPS/TPU blends with and without P(S-*b*-4VPy) measured by DSC are summarized in Table 2.

The glass transition temperatures (T_gs) of pure sPS and pure TPU are 99.4°C and −55.3°C, respectively. Two distinct T_gs at 99.1°C and −54.7°C for a pure sPS/TPU blend indicate the immiscibility of the two components. The block copolymer has two glass transitions, at 106.1°C and 141.7°C, implying that it has a two-phase structure, the lower T_g corresponding to the PS block and the upper T_g to the P4VPy block. When P(S-*b*-4VPy) is added to an SPS/TPU (70/30) blend, the two T_gs corresponding to the blend components move toward each other with increasing P(S-*b*-4VPy), indicating that the compatibility of sPS and TPU is enhanced through interpenetration of sPS and TPU at the interface. Since all polymer components except TPU have higher T_gs than sPS, the decrease in T_g of sPS in the blends results from the penetration of the TPU into the sPS domains promoted by the block copolymer. The depth of such penetration is controlled by interfacial tension of the blend components [27–29]. Thus, the addition of P(S-*b*-4VPy) causes a decrease in interfacial tension of sPS/TPU, an increase in thickness of the interface and a deeper penetration of TPU into sPS.

The decrease in normalized crystallinity of sPS in the blends, χ_c, is probably due to the penetration of TPU into sPS domains enhanced by the block copolymer. The fact that χ_c, which is 40.4% for the pure sPS, is still 40.2% in the binary sPS/TPU blend with 30 wt% TPU, shows that the decrease in χ_c is not a simple impediment by TPU.

Table 2
Effects of P(S-*b*-4VPy) on thermal properties of 70/30 sPS/TPU blends

Amount of P(S-*b*-4VPy) (wt%)	0	2.9	4.8	7.4	9.1
$T_{g,sPS}$ (°C)	99.1	95.7	93.1	92.2	92.3
$T_{g,TPU}$ (°C)	−54.7	−50.1	−48.2	−46.5	−45.2
$T_{m,sPS}$ (°C)	258.2	258.1	257.9	258.0	257.8
$\chi_{c,sPS}$ (%)[a]	40.2	39.5	39.0	38.7	38.4
$T_{c,sPS}$ (°C)	223.9	220.2	217.5	216.0	216.1
$W_{1/2}$ (°C)[b]	29.7	33.4	35.7	38.2	38.8

[a] χ_c: normalized crystallinity of sPS.

[b] $W_{1/2}$: width of crystallization peak.

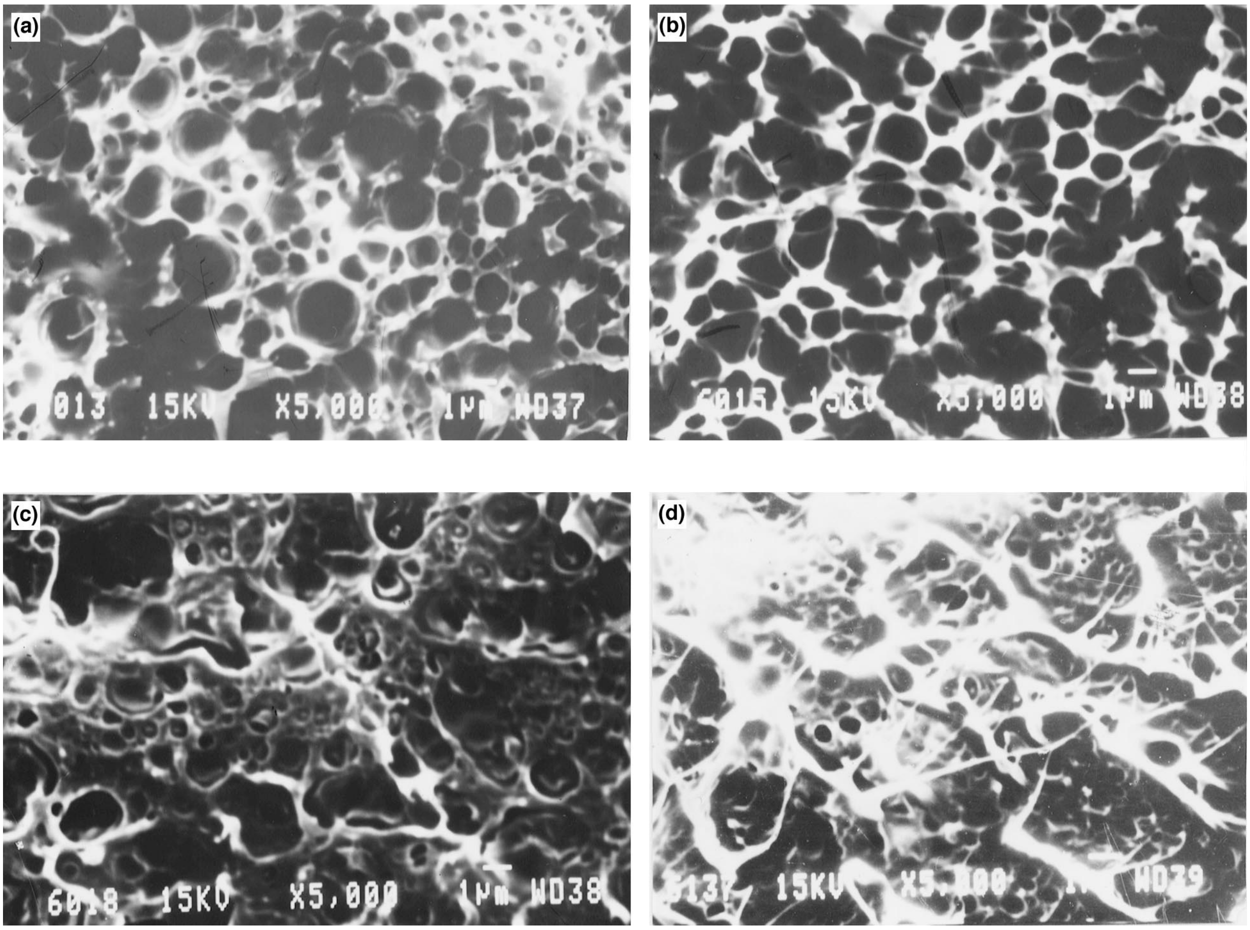

Fig. 1. SEM micrographs of fractured surfaces for the sPS/TPU 70/30 blends with: (a) 0; (b) 2.9 wt%; (c) 7.4 wt%; and (d) 9.1 wt% P(S-*b*-4VPy).

T_m of sPS does not change after its blending with TPU; apparently the contents of the interface area between the sPS and the TPU phases in an sPS/TPU blend is too small to affect the crystal lamellar thickness in the melts of the blend. With the addition of P(S-*b*-4VPy), enhancement in the compatibility causes a lower crystallization temperature (T_c) of sPS in the blend and a broader crystallization peak.

3.2.3. Mechanical properties

The non-compatibilized sPS/TPU (70/30) blend has a macrophase-separated structure. It is too brittle to be cut into desired specimens for tensile measurements, and thus corresponding tensile properties were not obtained. When the block copolymer P(S-*b*-4VPy) was added, the properties of the blend were enhanced and its tensile properties are shown in Fig. 2. It can be seen that both tensile strength and elongation at break are much improved, but the tensile modulus decreases with the block copolymer. At higher than 7.4 wt% of the compatibilizer, the tensile properties do not show much change, probably due to saturation of the block copolymer at the interface.

It seems unusual that the tensile modulus decreases with increasing P(S-*b*-4vpy), a phenomenon also appearing in other compatibilized blends [30,31]. There are many models explaining such changes in modulus of multiphase materials [32–34]. In light of the interconnected interface model of Hashin [34], it is suggested that the block copolymer is distributed at the interface between the matrix and the dispersed phase, and the blocks selectively penetrate into the two phases to provide good adhesion without forming a separated phase at a low concentration of the compatibilizer. Since TPU has a much lower modulus than sPS, hence a better interconnection between the TPU phase and the sPS matrix, addition of P(S-*b*-4VPy) provides stress and strain transfer, mainly to the dispersed phase through the interface. Thus, the properties of the TPU phase play a more significant role in the properties of the blends.

3.2.4. Rheological properties

The variation of dynamic rheological properties, the complex viscosity (η^*) and the storage modulus (G') of the sPS/TPU blends, with shear frequency (ω), with and without addition of P(S-*b*-4VPy), was studied using a rheometer (Fig. 3). It was observed that addition of P(S-*b*-4VPy) gave rise to a decrease in η^* and G'. In terms of emulsion model linking the macroscopic behavior of a heterogeneous system and the microscopic interaction between the system components [35–37], it is qualitatively indicated that

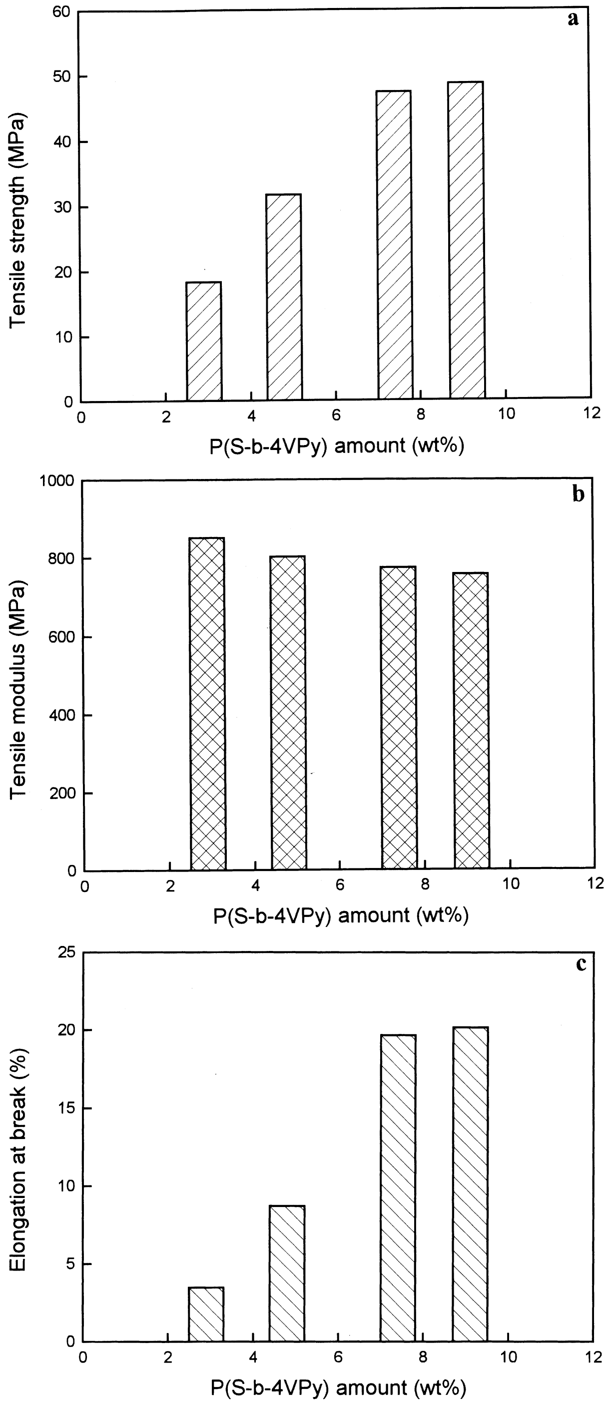

Fig. 2. Variation of tensile properties of 70/30 sPS/TPU blends on addition of P(S-*b*-4VPy): (a) tensile strength; (b) tensile modulus; and (c) elongation at break.

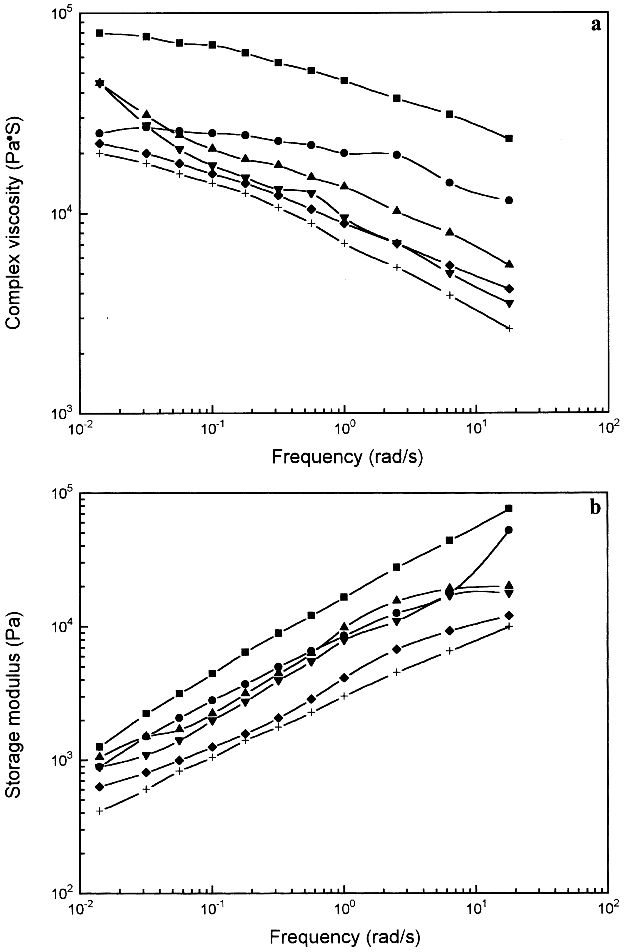

Fig. 3. (a) Complex viscosity; and (b) storage modulus of pure sPS (+) and the sPS/TPU 70/30 blends with: (a) 0 (-■); 2.9 wt% (-●); 4.8 wt% (-▲); 7.4 wt% (-▼); and 9.1 wt% (-◆) P(S-*b*-4VPy).

addition of P(S-*b*-4VPy) lowers the interfacial tension between the sPS and the TPU phases in the melt of the sPS/TPU blends. This is undoubtedly the result of the compatibilizing effect of P(S-*b*-4VPy).

For compatibilized blends of 70/30 sPS/TPU containing 2.9 wt% or 4.8 wt% P(S-*b*-4VPy), a yielding behavior at the lower shear frequency is observed. In a two-phase polymer blend, a three-dimensional network is formed through interacting droplets of the dispersed phase. Yielding is observed when the association structure has a long relaxation time [38–41]. It is more likely that the deformed particles will have a long relaxation time as the interfacial tension between the dispersed phase and the matrix becomes smaller. Therefore, the yield behavior for the two compatibilized blends with P(S-*b*-4VPy) may cause a lower interfacial tension induced by the block copolymer. On the other hand, with the blends containing 7.4 wt% and 9.1 wt% P(S-*b*-4VPy), because of the more stable structure and smaller particle sizes, the yielding behavior at low shear frequency is not observed. This means that a larger amount of the block copolymer is beneficial in assimilating stresses and strains without disruption of the established structure, i.e. the domains of the dispersed phase do not become coalescent even in a shear field.

3.2.5. WAXD analysis

The sPS shows a complex polymorphism, and different crystalline forms can be obtained, depending on thermal

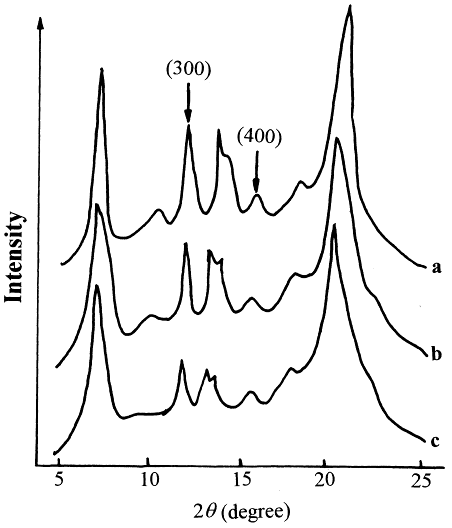

Fig. 4. WAXD patterns of: (a) sPS; (b) 70/30 (wt/wt) sPS/TPU blend; and (c) sPS/TPU/P(S-*b*-4VPy) 70/30/5 (wt/wt/wt) blend.

and/or solvent treatments. Two forms, α and β, characterized by a zigzag conformation, can be obtained by thermal crystallization [42–44], and the other two forms, γ and δ, characterized by a helix conformation, can be obtained in solvent-induced crystallization [45–49]. Fig. 4 shows the WAXD patterns of samples of pure sPS and sPS/TPU (70/30) blends, non-compatibilized and compatibilized, prepared under the same conditions. The compression-molded pure sPS sample shows the α-form crystallinity and its unit cell has hexagonal axes, $a = -2.626$ nm and $c = 0.504$ nm [43]. The sPS/TPU blend has a similar WAXD pattern. Addition of P(S-*b*-4VPy) leads to a decrease in I_{300}/I_{400}, a parameter sensitive to the crystalline structure of sPS [43]. This implies that the influence of compatibility between TPU and sPS on the crystallization of sPS is different on the (300) and the (400) planes. The fraction of TPU that penetrates into the sPS domains impedes the growth of crystallization on the (300) plane of sPS but promotes the growth of crystallization on the (400) plane. This can be proved from the change of crystallite size. D_{300} of sPS in the compatibilized sPS/TPU blend is smaller than that of pure sPS and of the pure sPS/TPU blend; for D_{400} the opposite is true (Table 3).

3.3. Mechanism of compatibilization

For P(S-*b*-4VPy) as an A-*b*-B type compatibilizer for a C/D blend, the PS and P4VPy blocks should be miscible with the corresponding polymers, sPS and TPU [50]. So far, compatibility between TPU and P4VPy has not been reported. To simplify the investigation of the compatibilization mechanism, we discuss below, separately, the compatibility of the sPS and PS homopolymers, and of the TPU and P4VPy homopolymers.

Table 3
WAXD data of sPS and its blends

	sPS	sPS/TPU[a]	sPS/TPU/ P(S-*b*-4VPy)[b]
I_{300}/I_{400}	1.58	1.55	1.31
a (mn)	2.626	2.633	2.630
c (nm)	0.504	0.508	0.512
D_{300} (nm)	18.33	17.86	15.12
D_{400} (nm)	12.23	12.32	14.05

[a] The composition is 70/30 (wt/wt).

[b] The composition is 70/30/5 (wt/wt/wt), i.e. the amount of P(S-*b*-4VPy) in the blend is 4.8 wt%.

3.3.1. Compatibility of PS with noncrystalline regions of sPS

We have shown earlier [19] that aPS was compatible with the noncrystalline regions of sPS. The unchanging unit cell parameters of sPS after mixing with aPS indicated the barring of aPS from entering the unit cells of sPS crystallites.

3.3.2. Partial compatibility of TPU and P4VPy through specific interaction

TPU consists of alternating soft- and hard-segments, and is thus a microscopically multicomponent system. The hard segments are distributed in three locations [51,52]: some in forming hydrogen bonds among themselves; some distributed in the soft segment regions; and some in the disordered interface. The added P4VPy affects the locations and states of the hard segments.

The DSC data of the TPU/P4VPy blends of different blend compositions are summarized in Table 4. The two separated T_gs indicate a two-phase structure: the TPU- and the P4VPy-rich phases. The moving of the two T_gs toward each other with respect to those of the pure components signifies the partial miscibility of TPU with P4VPy.

FTIR was used to investigate the driving force of partial miscibility between TPU and P4VPy. The representative room temperature infrared spectra in the C=O stretching region (1640–1780 cm^{-1}) and the N–H stretching region (3100–3500 cm^{-1}) of TPU and the TPU/P4VPy 50/50 (wt/wt) blend are shown in Fig. 5. It is known that the N–H and C=O groups in a polyurethane can interact and form intermolecular hydrogen bonding [52,53].

The assignments of the infrared spectrum of pure TPU in the region of 3100–3500 cm^{-1} have been reported by many authors [54–56]. The band at 3120 cm^{-1} was considered to be an overtone of the band representing the NH bending mode mixed with the C–N stretching mode at 1530 cm^{-1}. The other four bands at 3440, 3324, 3266 and 3187 cm^{-1} are

Table 4
T_g of TPU/P4VPy blends with different compositions

TPU/P4VPy (wt/wt)	100/0	70/30	50/50	0/100
T_g (°C)	−55.3	−34.7	−15.2	
		109.2	127.7	142.6

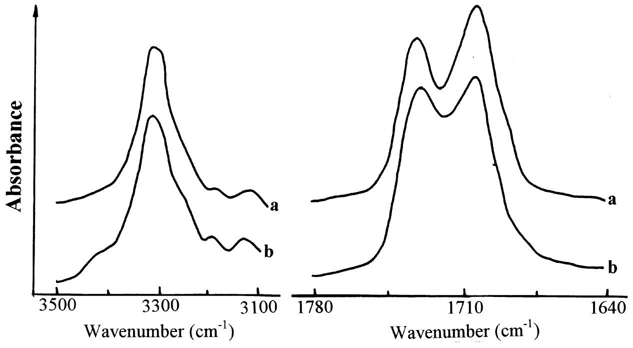

Fig. 5. The NH (left) and carbonyl (right) stretching vibration absorption for: (a) TPU; and (b) 50/50 (wt/wt) TPU/P4VPy blend.

all related to the NH stretching vibration, the first one being assigned to the 'free' N–H, and the latter three to hydrogen-bonded N–H and the *trans* and *cis* NH groups in the amide groups [54]. It is clear that most of the NH groups are hydrogen-bonded. There are two attractive bands: one is the band centered at $\sim 3324\,cm^{-1}$, which is assigned to urethane N–H groups that are hydrogen bonded to urethane C=0 groups; the other one is at $\sim 3440\,cm^{-1}$, which is assigned to the 'free' (nonhydrogen-bonded) N–H stretching band. When TPU is mixed with P4VPy, the 'free' N–H band increases in intensity with a bathochromic shift of the hydrogen bonded N–H. This shift is the result of the two hydrogen bonds: –N–H···O=C (self-association of TPU) and N–H···N (association of TPU to P4VPy [56].

The pure TPU is characterized by a major band centered at $\sim 1705\ cm^{-1}$, ascribed to hydrogen-bonded urethane C=0 groups and a well separated peak at $\sim 1732\ cm^{-1}$ attributed to 'free' C=0 groups (Fig. 5). Addition of P4VPy induces an increase in the relative proportion of the 'free' to the hydrogen-bonded carbonyls, with a bathochromic shift of the former, indicative of liberation of additional 'free' C=0 groups upon N–H groups, interacting with the pyridine rings. The strength of the two types of H-bonding:

$$\mathrm{N{-}H\cdots N > N{-}H\cdots O{=}C}$$

This explains the partial compatibility of TPU with P4VPy.

As the PS blocks and the P4VPy blocks in P(S-*b*-4VPy) penetrate into their corresponding blend components at the interface to form a 'wet-brush' structure [50,57], the interfacial adhesion is improved, the interfacial tension is reduced and the thickness of the interface [58] is increased.

4. Conclusions

P(S-*b*-4VPy) diblock copolymer, synthesized via sequential anionic copolymerization, was used as a compatibilizer for immiscible sPS/TPU blends. When a small amount of the block copolymer is added, more regular and finer dispersion is observed. DSC reveals that the addition of P(S-*b*-4VPy) improves the compatibility of sPS and TPU, and promotes the penetration of TPU into sPS, whereby crystallization of sPS is impeded. An increase in tensile strength and elongation at break and a decrease in tensile modulus on addition of P(S-*b*-4vpy) are due to enhanced interfacial adhesion. Dynamic rheological measurements support the view that the addition of P(S-*b*-4VPy) leads to a decrease in interfacial tension between sPS and TPU. WAXD experiments show that the P(S-*b*-4VPy) added does not change the sPS unit cells, but affects the crystalline structure of sPS in the blends.

The compatibilization mechanism of P(S-*b*-4VPy) in compatibilized sPS/TPU blends has been investigated by various techniques. Besides miscibility of the PS blocks in P(S-*b*-4VPy) with noncrystalline regions of sPS, the P4VPy blocks of P(S-*b*-4VPy) is partially miscible with TPU through intermolecular hydrogen-bonding, as shown by DSC and FTIR.

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