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Mechanical and thermal properties of syndiotactic polystyrene blends with poly(*p*-phenylene sulfide)

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Abstract

Melt blends of syndiotactic polystyrene (sPS) and poly(*p*-phenylene sulfide) (PPS) have been prepared by using an internal mixer at 300 °C. The thermal, mechanical and morphological properties of binary blends of sPS with PPS have been investigated in this paper. The thermal and morphological properties show the immiscible binary blend evidences, which have a clear phase separation between the components at all compositions and a lack of adhesion at the interface. According to the X-ray diffraction patterns of blends, the crystalline structure of sPS in the blend is not altered from α form to β form. Indeed, the results for tensile test reveal that there is no synergism of the modulus of elasticity for sPS/PPS blend system.

Keywords: Syndiotactic polystyrene; Poly(*p*-phenylene sulfide); Melt blends; Miscibility; Mechanical properties; Thermal properties

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1. Introduction

In the plastic industry, polymer blends are preferred than the synthesis of new polymers due to its lower production cost and adaptability to fulfill the various and multiple material properties in use.

Generally, polystyrene is one of the most important commodity polymers in the industry. Its applications range from high modulus, transparent grade to rubber modified, tough resins and blends with outstanding impact resistance and mechanical properties. Recently, coordination polymerization techniques were introduced for preparation of polystyrene, which has an entirely new range of possibilities and the feasibility to prepare a highly stereoregular, syndiotactic polystyrene (sPS) was demonstrated [1]. sPS prepared by coordination polymerization is a new semicrystalline thermoplastic material with high melting temperature (270 °C) and excellent chemical resistance. Also, sPS has been reported to show polymorphism according to crystallization conditions like as isotactic-polypropylene, isotactic-poly(butene), isotactic-poly(1-butene), and syndiotactic-poly(1-butene) [2–7]. However, because sPS has some economic disadvantages such as low strength [8], higher processing temperature [9], and efficiency of polymerization catalyst, it has been restricted to a few applications. So, many researchers are still interested in blending with secondary polymer materials to reduce the product cost.

Some previous results have shown immiscibility of sPS with poly(vinyl methyl ether) [10–12] and poly(styrene-co-maleic anhydride) [13]. Whereas, other research results show a single glass transition temperature of sPS with poly(2,6-dimethyl-1,4-phenylene oxide) [14,15] and tetramethyl polycarbonate [16] at all compositions. Of course, the various properties of sPS blends with several polymers have investigated by many research groups. Bonnet and co-workers reported that the miscibility of

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sydiotactic polystyrene blends with atactic polystyrene in the melt and their thermo-mechanical properties [17].

In this paper, we characterized the thermal, morphological and physical properties of sPS blends with poly(*p*-phenylene sulfide) (PPS). PPS was chosen because it is presently finding increasing usage particularly as a high strength/high temperature molding resin. Indeed, PPS is generally known to be insoluble in any solvent below 200 °C. It has a high degree of crystallinity and good retention of physical properties at elevated temperatures, so it is widely used for applications including electrics and electronics [18–20]. Therefore, this study represents a preliminary step to the scientific and technological development of more complex systems containing further components such as another polymer, inorganic fillers, and nucleating agents and displaying improved thermo-mechanical properties.

2. Experimental

2.1. Materials

sPS sample was supplied from Idemitsu Kosan Co., Ltd. (Japan), and has a tacticity of 98% (by ^{1}H-NMR), a molecular weight of $M_w = 226,000$. PPS polymer used in this paper was Ryton E2480 manufactured by Phillips Petroleum Co. and shape of the PPS polymer was a white colored granular type. The Ryton E2480 PPS is a linear crystalline polymer and the density is 1.34 g/cm^3. In this experiment, all materials were used without further purification.

2.2. Blend preparation

Blends of sPS with PPS were prepared by melt mixing the two polymers in a Brabender internal mixer at 300 °C for 6 min and at a rotor speed of 80 rpm. Before the blends were processed, the sPS and PPS were carefully dried in a vacuum oven at 120 °C for 48 h. sPS/PPS blends with weight ratios 80/20, 60/40, 40/60 and 20/80 were prepared. The pure polymers were also processed under the same conditions.

2.3. Characterization and measurements

The thermal characterization studies were carried out using a Perkin–Elmer, DSC-7. The calibration of the instrument was carried out using high purity indium and zinc. To observe thermal properties of sPS/PPS blends and neat polymer, after a first scan up to 300 °C to provide the same thermal history for all samples, and than steadily cooling to 30 °C, the DSC curves were recorded at a heating rate of 20 °C/min.

The dynamic mechanical measurements were performed by a Rhometrics, DMTA-IV at constant frequency of 10 rad/s. The temperature was varied from 0 °C until sample failure at heating rate of 3 °C/min. To study the morphology of the blends, fractured surfaces were coated with gold palladium for the microscopy and observed with a Jeol, JMS-6400 scanning electron microscope. The dumbbell type specimens were prepared by using a mini-injection machine (CSI; Mini-Max Molder, CS-183MMX). The dimensions of the dumbbell type specimens were 9 mm in length and 1.6 mm in diameter. The barrel and the mold temperature during the injection molding were 300 and 40 °C, respectively. The tensile test was carried out using Instron, UTM (Model 4202). A crosshead speed of 0.5 mm/min was used in all measurements. The X-ray diffraction patterns of the samples were determined by a wide angle X-ray diffractometer (MAC Science Co., Ltd.; M18XHF^{22}-SRA) using CuKα radiation under 100 kV, 50 mA.

3. Results and discussion

In Table 1, the thermal characteristics of sPS/PPS blends and neat polymers are shown. With increasing the PPS concentration, the cold crystallization temperature of blends decreased, but the melting temperatures did not shift. In case of miscible blend system, a melting temperature depression phenomenon is occurred, whereas sPS/PPS blends were not detected. These results imply that there are no physical interactions, which are hydrogen bonding, Van der Waals forces, and electrostatic forces between sPS and PPS. In other words, sPS

Table 1
Thermal characteristics of sPS/PPS blends and neat polymers

PPS content (wt.%)	T_g (°C)		T_c (°C)	T_m (°C)	
	By DSC	By DMTA		sPS	PPS
0	101	113	238	267	–
20	102	112	238	266	282
40	101	111	234	266	281
60	102	111	234	266	282
80	102	112	230	265	281
100	104	116	229	–	280

is immiscible with PPS. The glass transition temperatures of blends and neat polymers that induced by DMTA and DSC are also shown in Table 1. For sPS/PPS blends, the difference between the two T_gs was too small to define the resolution of two T_gs by DMTA and DSC.

The X-ray diffraction patterns of sPS/PPS blends prepared by compression molding are shown in Fig. 1. When sPS is melt crystallized, it presents a complex polymorphic pattern, both crystalline forms containing planar-zigzag conformation (α and β) in the pure or mixed state, depending on the processing method. The crystalline α form, which can be obtained by compression molding [21,22], is characterized by trigonal chain packing, whereas the crystalline β form, which can be obtained by solvent casting at high temperature is characterized by orthorhombic chain packing [23]. As shown in Fig. 1, the crystalline structure of sPS is not altered for sPS/PPS blend system. Under these conditions, the formation of the α forms of sPS/PPS blends, as in pure sPS, are clearly indicated. Moreover, in the sPS/PPS (20:80, wt.%) blend, the crystalline α form is still detected. These results indicate that the growth of the sPS crystalline is not hindered by second component (PPS) in these blends. In fact, typical reflection peaks of the crystalline α form are $2\theta = 6.7°$, $2\theta = 11.7°$, $2\theta =$

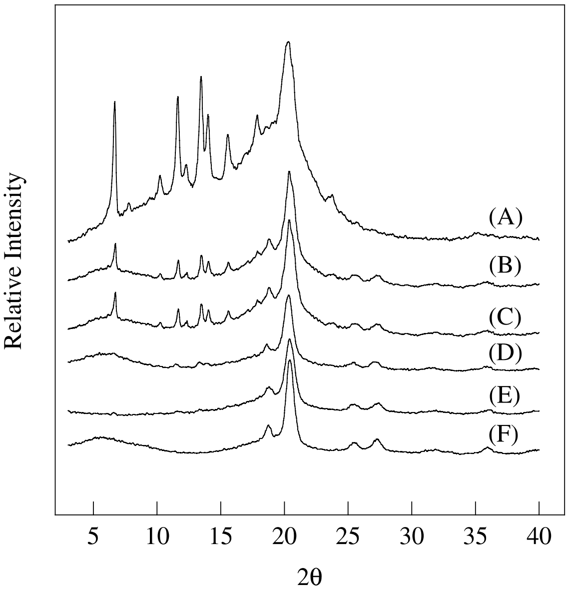

Fig. 1. X-ray diffraction patterns of sPS/PPS blends: (A) pure sPS, (B) 80:20 (sPS:PPS), (C) 60:40, (D) 40:60, (E) 20:80 and (F) pure PPS

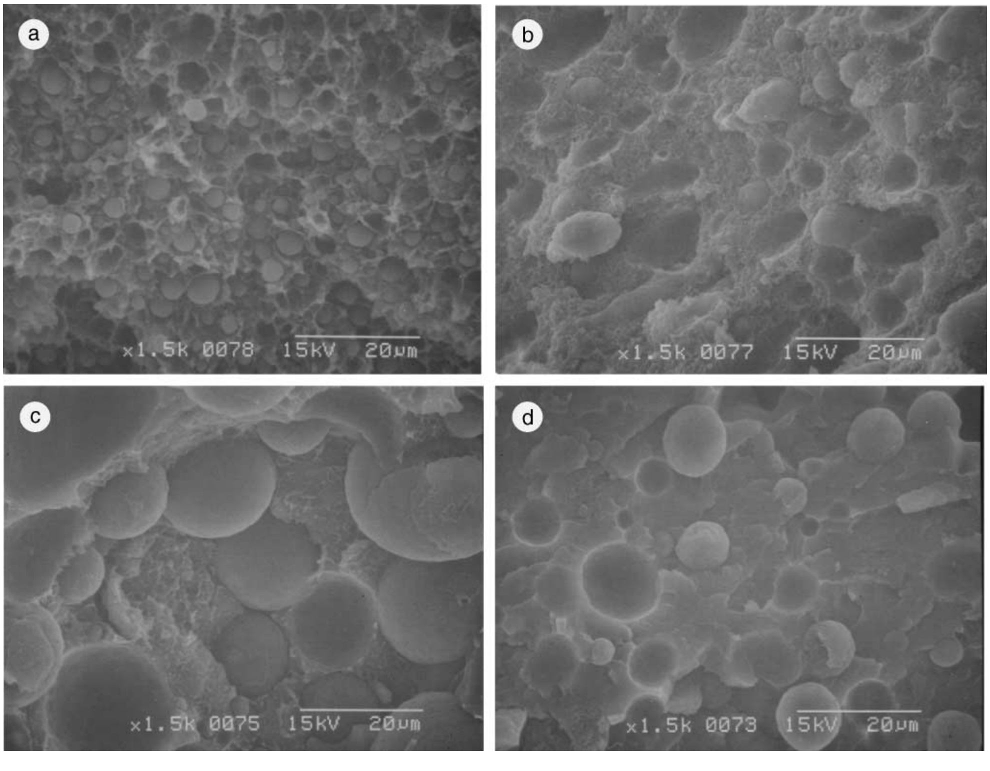

Fig. 2. SEM photographs of sPS/PPS blend cryo-fractured surfaces: (A) 80:20 (sPS:PPS), (B) 60:40, (C) 40:60 and (D) 20:80.

14.0°, $2\theta = 15.6°$, $2\theta = 18.0°$ and those of the crystalline β form are $2\theta = 6.1°$, $2\theta = 12.3°$, $2\theta = 18.6°$, $2\theta = 21.2°$. It is apparent that blending with PPO strongly interferes with the crystallization of sPS, reducing the degree of crystallinity for high PPO content and altering the polymorphic structure. In particular, the effect of blending with PPO is roughly a shift toward lower temperature of the sigmoidal curves typical of plots of the crystalline α form content versus T for sPS [14]. The polymorphic structure of sPS is not altered for immiscible blends or for blends with atactic polystyrene, which are probably miscible [13].

A morphology study was carried out using a scanning electron microscopy (SEM). The fractures of the blends shown in Fig. 2 represent the immiscibility of the sPS/PPS blends. In all blend samples, well-segregated spherical particles of the minor component with vary sizes of ca. 3–20 μm are observed. The boundaries of the particles are well defined and separated from the matrix; furthermore, many spherical voids are observed originating from the detachment of the particles during the cryo-fracture process. The observed macrophase separation points to immiscibility which is likely to stem the high interfacial tension occurring between components during the melt mixing process. Furthermore, the detachment of the dispersed particles indicates bad adhesion at the interface between the domain and the matrix. We observed that the domain size under PPS matrix is bigger than that under sPS matrix. This phenomenon is caused by melt viscosity difference between two homopolymers.

The mechanical properties of the sPS/PPS blends are shown in Figs. 3 and 5. As shown in Fig. 3 where the tensile modulus of blends are shown, the overall trend is less than the arithmetic average of the modulus of the two pure components. Indeed, modulus of all blends were intermediate between sPS, with a modulus of 15.8 MPa, and PPS, with a value of 24.7 MPa. With respect to the synergism of the modulus of elasticity, it is known that the specific interactions that may give rise to miscibility usually produce a negative excess volume, which can be occurred by mixing [7]. These volume contractions would give a rise to increased moduli of elasticity [24] because of the decreasing in the free volume avail-

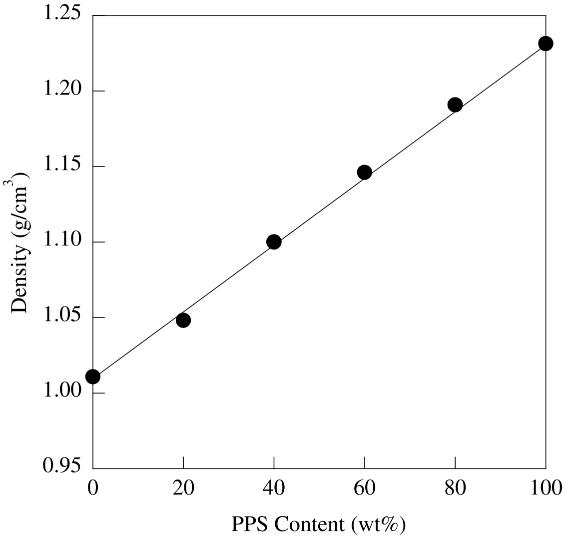

Fig. 4. Density of sPS/PPS blends.

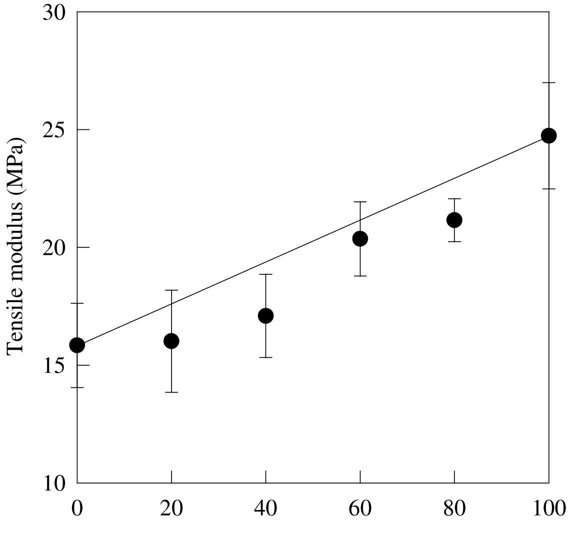

Fig. 3. Tensile modulus of sPS/PPS blends.

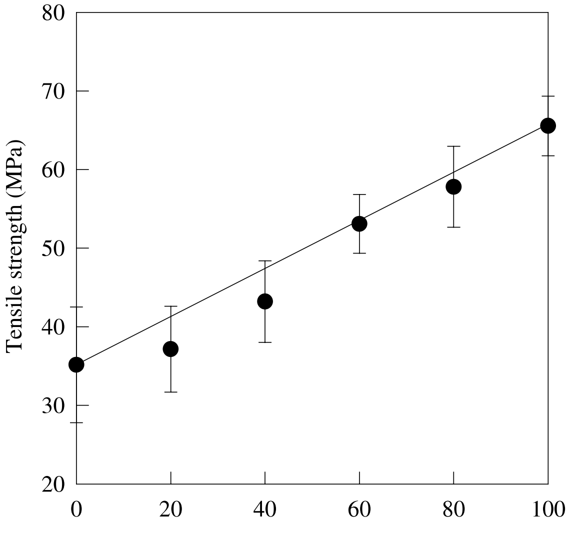

Fig. 5. Tensile strength of sPS/PPS blends.

able, although this is small [25]. Thus, density increasing should be associated with miscibility and synergism in the modulus of elasticity. As shown the plot (Fig. 4) is really linear, and no difference can be distinguished between the miscible part corresponding to the blends very rich in PPS and the rest of the blend compositions. This indicates that the synergism in the modulus of elasticity cannot be obtained from volume changes in this blend system.

Fig. 5 shows tensile strength as a function of PPS composition for sPS/PPS blends. As can be seen, the values are lower with respect to the arithmetic mean than those of the modulus of elasticity. But most of the features commented on above also appear in this property which despite being measured at a slightly greater deformation usually follows the tendency of the modulus of elasticity.

4. Conclusions

Melt-blended samples of sPS/PPS were investigated using thermal and mechanical analysis, SEM and X-ray diffractometer. Melt blends of sPS and PPS are immiscible because there are the binary blend evidence for a clear phase separation between the components at all compositions and a lack of adhesion at the interface. Indeed, we can not detect the changing of the polymorphic structure of sPS on the X-ray diffraction patterns of blends. However, although tensile properties of sPS/PPS blends do not reveal synergism of the modulus of elasticity, the mechanical properties of sPS/PPS blend show a simple ‘rule of mixtures’ which gives a straight-line relationship with compositions.

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