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Crystallization Behavior and Rheological Properties of Syndiotactic Polystyrene/Poly(2,6-dimethyl-1,4-phenylene oxide) Blends

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INTRODUCTION

Since the successful synthesis of syndiotactic polystyrene (sPS) using stereospecific polymerization, there has been a considerable interest in characterizing this new material[1,2]. It has been reported that the polymorphic behavior of sPS is very complex and studies on sPS have been focused on the analysis of crystal structure[3]. Four major crystalline phases have been proposed. Two crystalline forms, α- and β-phase, containing molecular chains with a planar zigzag conformation (T_4), and two crystalline forms, γ- and δ-phase, containing molecular chains with a helical conformation (T_2G_2) have been described. Enhanced mechanical properties are expected for sPS, especially at high temperature, due to its crystalline structure. Furthermore, a rapid crystallization rate relative to that of isotactic polystyrene, and possible high tensile modulus lead to a potentially commercial application of sPS as an engineering plastic. However, the production cost of sPS is still much higher than that of other commercial engineering plastics. It is well-known that polymer blends give an efficient way of developing materials with tailored properties. It has been reported that atactic polystyrene (aPS)/poly (vinyl methyl ether) (PVME) and aPS/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends are miscible at room tempetature. However, few data on sPS-based blends have been reported in the literature. Studies on sPS/PVME and sPS/PPO blends have been focused on the crystallization behavior and miscibility of blends[4]. In the polymer processing, it is very important to have a knowledge of the rheological properties (i.e., melt viscosity, shear modulus, etc) of polymers. However, studies on the rheological properties of sPS and sPS-based blends are lacking. In the present study we have investigated the crystallization behavior, especially for the melting behavior, and rheological properties of sPS/ PPO blends.

EXPERIMENTAL

The sPS (M_w = 4.0x10^5 g/mol, T_g = 100.2 °C, T_m = 271.0 °C) was obtained from Idemitsu Kosan Co., Ltd., Japan. The PPO (M_w = 4.5x10^4 g/mol, T_g = 219.1 °C) was supplied by the Nippon Polyester Co., Ltd., Japan. The molecular weights of all samples were determined by GPC. The sPS/PPO blends were melt-mixed and injection-molded in a Mini-Max molder (CS-183 MMV, Custom Scientific Instruments, Inc.) at 300 °C for 7 min. A Perkin-Elmer DSC 7 differential scanning calorimeter was used for the thermal analysis. All scans were run under nitrogen gas to minimize the oxidative degradation. The samples were first heated from room temperature to 300 °C, maintained at this temperature for 5 min to ensure the complete melting of sPS crystals, and quenched to room temperature. The samples were then reheated to 300 °C at a heating rate of 20 °C/min (figure 1), maintained for 5 min, and cooled to room temperature at a cooling rate of 20 °C/min (figure 3). In the isothermal crystallization experiments, the samples were heated up from room temperature to 300 °C, kept at this temperature for 5 min, and rapidly cooled to the desired crystallization temperature, T_c. For the rheological measurements, all samples were injection-molded into a disc of 2 mm thickness and 25 mm diameter in a Mini-Max molder. The rheological properties were measured by Rheometrics Mechanical Spectrometer (RMS-800) with a parallel plate fixture. The rheological measurement was carried out by sinusoidal oscillation with a maximum frequency of 100 rad/s and a minimum frequency of 0.1 rad/s. Before the rheological measurement, strain sweep tests at various frequencies were performed to make sure that the applied deformation did not exceed the limit of linear viscoelatic region.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms of sPS/PPO blends. It is observed that sPS/PPO blends exhibit single, composition-dependent T_g's, indicating the miscibility over entire compositions. The sPS/PPO (80/20) blend shows an exothermic crystallization peak with its maximum at 190.1 °C, followed by melting endotherm at 268 °C. As the amount of PPO exceeds 40 wt%, there is no melting endotherms in the DSC thermograms, indicating that the crystallization of sPS is hindered by the addition of PPO. Figure 2 shows the composition dependence of the glass transition temperature for sPS/PPO blends. These data can be analyzed by the Gordon-Taylor equation:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{1}$$

where T_g is the glass transition temperature of the blend, w_i is the weight fraction of component i, T_{gi} is its glass transition temperature, and k is an adjusting parameter related to the degree of curvature of T_g -composition diagram. The full curve represents a fit to the Gordon-Taylor equation. For plotting equation (1), T_g values of 373.2 and 492 K were used for sPS and PPO, respectively. The parameter k can be taken as a semiquantitative measure of the strength of interaction between the functional groups of the components of the blends. From the best fit of equation (1), the value of k is determined to be 0.578. Figure 3 shows the nonisothermal crystallization behavior of sPS/PPO blends. The crystallization of sPS in sPS/PPO (80/20) blend occurs at lower temperatures and the shape of peaks becomes broader. The crystallization process is retarded due to a dilution effect of PPO. As the amount of PPO exceeds 40 wt%, the nonisothermal crystallization of sPS is hindered by PPO. Figure 4 shows the temperature dependence of complex viscosity for sPS/PPO (60/40) blend. It is shown that , as is typical for most polymers, the complex viscosity becomes progressively lower as the temperature increases. Figure 5 shows the composition dependence of complex viscosity for sPS/PPO blends. It is observed that the complex viscosity of sPS/PPO (60/40) blend is higher than that of sPS homopolymer.

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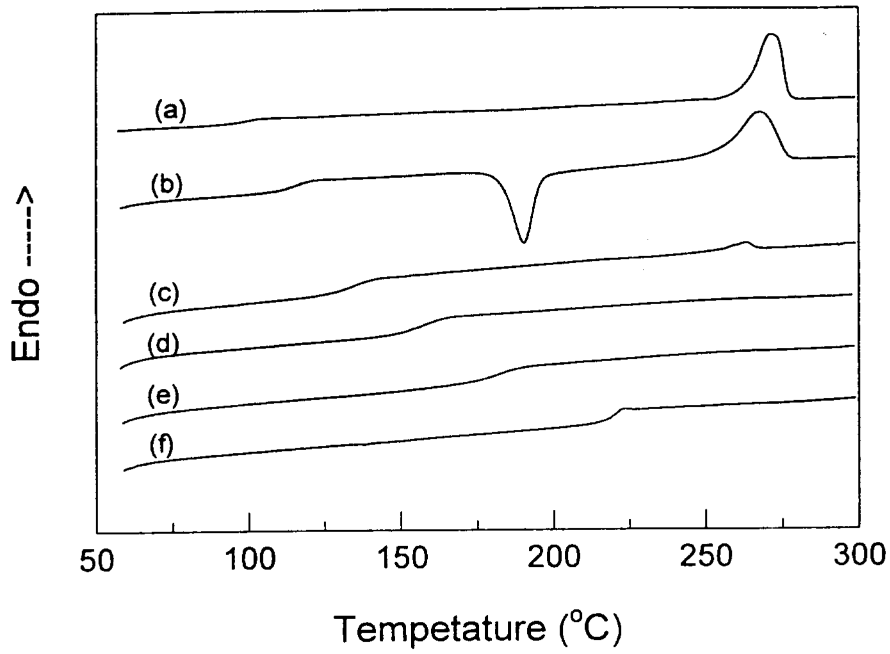

Figure 1. DSC thermograms of sPS/PPO blends: (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80; (f) 0/100

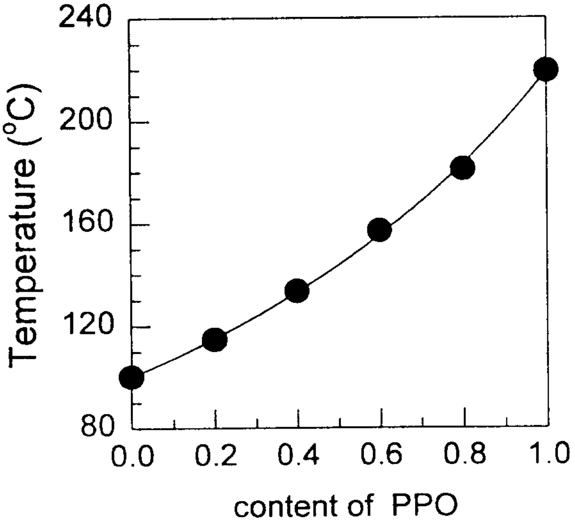

Figure 2. Composition dependence of the glass transition temperature for sPS/PPO blends.

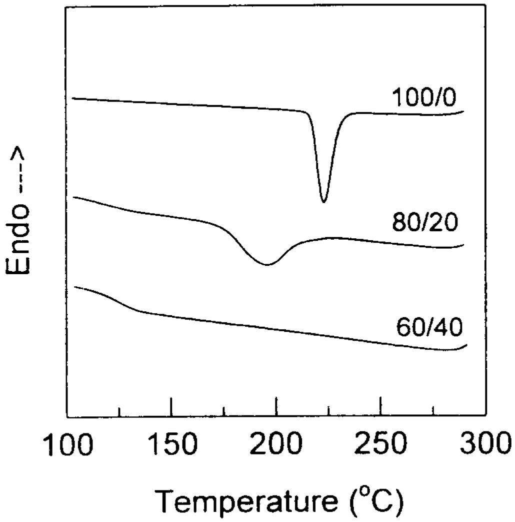

Figure 3. DSC thermograms for sPS/PPO blends at a cooling rate of 20 °C/min

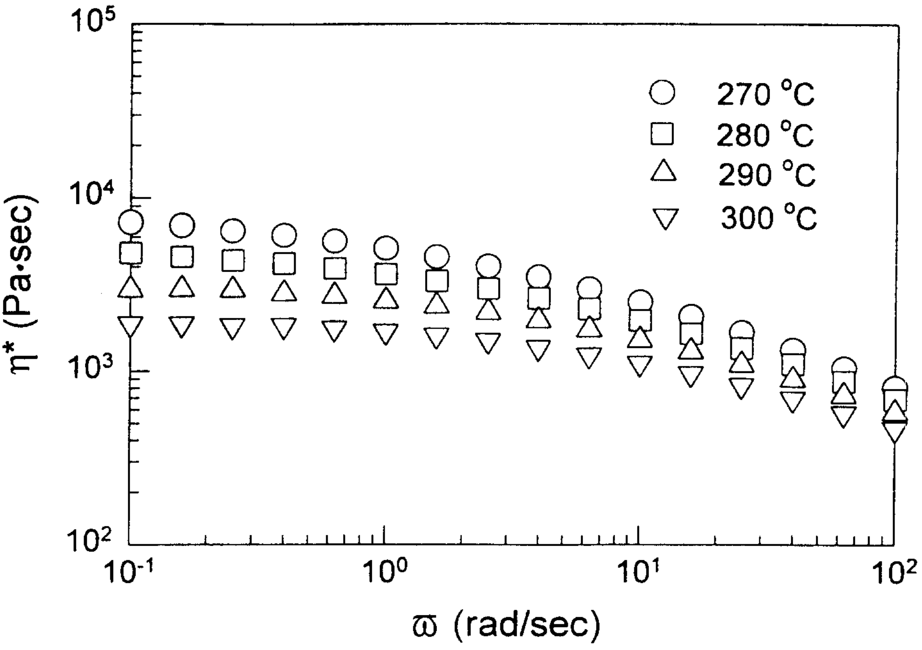

Figure 4. Complex viscosity *versus* frequency for sPS/PPO (60/40) blend at various temperatures

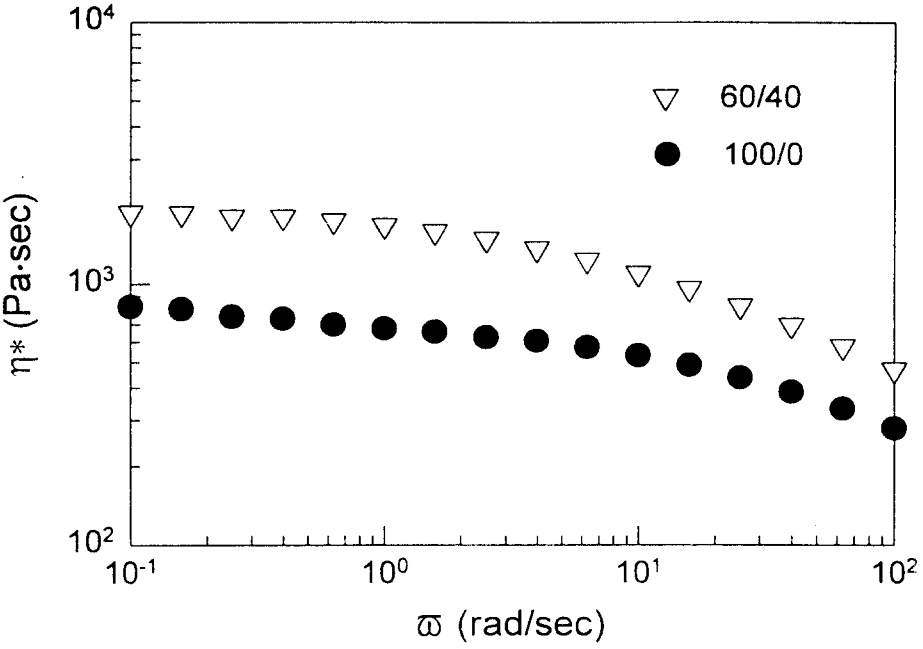

Figure 5. Complex viscosity *versus* frequency for sPS/PPO blends at 300 °C