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ScienceDirect
Polymer 48 (2007) 3858–3867
polymer
www.elsevier.com/locate/polymer

Isothermal crystallization, melting behavior and crystalline morphology of syndiotactic polystyrene blends with highly-impact polystyrene

Weihua Zhou, Ming Lu, Kancheng Mai*

Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Key Laboratory of Polymeric Composites and Functional Materials, The Ministry of Education, Guangzhou 510275, People's Republic of China

Received 18 October 2006; received in revised form 2 February 2007; accepted 29 March 2007
Available online 13 April 2007

Abstract

Syndiotactic polystyrene (sPS) blends with highly-impact polystyrene (HIPS) were prepared with a twin-screw extruder. Isothermal crystallization, melting behavior and crystalline morphology of sPS in sPS/HIPS blends were investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarized optical microscopy (POM). Experimental results indicated that the isothermal crystallization behavior of sPS in its blends not only depended on the melting temperature and crystallization temperature, but also on the HIPS content. Addition of HIPS restricted the crystallization of sPS melted at 320 °C. For sPS melted at 280 °C, addition of low HIPS content (10 wt% and 30 wt%) facilitated the crystallization of sPS and the formation of more content of α-crystal. However, addition of high HIPS content (50 wt% and 70 wt%) restricted the crystallization of sPS and facilitated the formation of β-crystal. More content of β-crystal was formed with increase of the melting and crystallization temperature. However, α-crystal could be obtained at low crystallization temperature for the specimens melted at high temperature. Addition of high HIPS content resulted in the formation of sPS spherulites with less perfection.

Keywords: Syndiotactic polystyrene; Highly-impact polystyrene; Isothermal crystallization

1. Introduction

Syndiotactic polystyrene (sPS) is known for its complex polymorphism, including α, β, γ and δ, four different crystal forms. In addition, α- and β-crystal forms are always generated through bulk crystallization process while γ- and δ-crystal forms could be obtained by the treatment of solvents [1–8].

Many studies have been devoted to understand the crystallization effects on polymorphic behavior of sPS. Complex crystallization and polymorphic behavior have been found. The formation of α-crystal was believed to be either the result of the kinetically controlled process or the memory effect of α nuclei. The formation of the thermally stable β-crystal was dependent on the thermal histories and crystallization conditions. The parameters affecting the formation of α- and β-crystal forms of sPS included the maximum temperature at the melt, the permanent time at the melt, the crystallization temperature, the crystallization time, the starting material, the cooling rate and so on [2,9–13]. The maximum temperature at melt was found to be the most intrinsic factor in affecting the polymorphism of sPS [14,15]. In addition, He et al. [16] found that there existed the process of transformation of α-crystal to β-crystal as sPS was in supercritical carbon dioxide.

sPS based blends such as sPS/aPS (atactic polystyrene) [17–25] and sPS/PPO poly(phenylene oxide) [26–31] were also extensively studied. The corresponding results showed that these blends were miscible and the addition of second component facilitated the formation of more content of β-crystal and affected the melting behavior of sPS. Chiu and Peng [19] found that the incorporation of aPS decreased the non-isothermal crystallization peak temperature and reduced the crystallization rate of sPS. Similar phenomenon was also

* Corresponding author. Tel./fax: +86 20 84115109.
E-mail address: cesmkc@mail.sysu.edu.cn (K. Mai).

0032-3861/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2007.03.078

observed in other blending systems of sPS/PPE (polyphenylene ether) [32], sPS/TMPC (tetramethyl polycarbonate) [33] and so on. For the other partly miscible and immiscible blends of sPS/SEBS (atactic polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-atactic polystyrene) [34], sPS/HDPE (highly-density polyethylene) [35,36], sPS/iPP (isotactic polypropylene) [37], sPS/PA6 (polyamide 6) [38,39], sPS/PA66 (polyamide 66) [40], sPS/EPR (ethylene–propylene rubber) [41,42] and so on, researchers focused on the improvement of compatibility of the blends, and on the morphology, thermal properties, mechanical properties of the blends.

sPS is known for its high melting point, resistance to chemicals and good mechanical properties, however, the low impact strength of sPS restricts the application in more fields. Highly-impact polystyrene (HIPS) is composed of rubber phase of 1,4-polybutadiene and atactic polystyrene. It is known for its good toughness and the relatively high impact strength. Addition of HIPS is expected to be a reasonable way to improve the impact strength of sPS. Generally, the mechanical properties of crystallized polymers and its blends not only depend on the crystallization behavior and morphology, but also on the blend ratio and interfacial interaction between the components. Therefore, sPS blends with different contents of HIPS were prepared by a twin-screw extruder. The isothermal crystallization and melting behaviors of sPS and its blends were investigated by differential scanning calorimetry (DSC), and the corresponding polymorphism was analyzed by the wide-angle X-ray diffraction (WAXD). Polarized optical microscopy (POM) was also used to observe the crystalline morphology of sPS and its blends.

2. Experimental

2.1. Materials and blends preparation

The sPS is Questra F2250 from Dow Chemical Co., M_w and M_n were characterized by GPC and were 2.3×10^5 g/mol and 9×10^4 g/mol, respectively. The HIPS is MS 500, the product of the Idemitsu Co. The sPS and HIPS were first dried in a vacuum oven at 80 °C for 24 h before blending. All the blends were prepared by melt extrusion at 280 °C with an SJSH-Z-30 twin-screw extruder (Factory of Rubber and Plastic of Nanjing, China). The rate of the main machine was 100 rpm. The weight composition of sPS/HIPS blends was 10/0, 9/1, 7/3, 5/5 and 3/7.

2.2. Differential scanning calorimetry (DSC)

The characterization of crystallization and melting behaviors was carried out with the DSC-7 Perkin–Elmer instrument under a nitrogen atmosphere. The corresponding parameters of crystallization and melting enthalpies (ΔH_c and ΔH_m), crystallization peak time (t_p) and melting peak temperature (T_m) were involved. The heat flow and temperatures of DSC were calibrated with standard materials, indium and zinc. The weights of the specimens ranged from 4 mg to 5 mg. All the specimens were heated rapidly at a rate of 200 °C/min to various maximum melting temperatures (T_{max}) and melted for 10 min to erase the thermal history and then the specimens were rapidly cooled at 200 °C/min to different designed crystallization temperatures (T_c) for 30 min. The crystallized specimens were subsequently cooled to room temperature at 200 °C/min and then heated at rate of 10 °C/min to investigate the corresponding melting behaviors.

2.3. Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray diffraction patterns of the specimens were recorded at room temperature using a Rigaku D/Max 2200 unit equipped with Ni-filtered Cu Kα radiation in the reflection mode with a wavelength of 0.154 nm. The scanning 2θ angle ranged between 3° and 40° with a step scanning rate of 2°/min. For direct comparison, the specimens were thermally treated as those for DSC experiments.

2.4. Polarized optical microscope (POM)

The specimens pressed between two glass slides were first heated to 280 °C or 320 °C for 10 min and then were rapidly quenched to designated crystallization temperatures (240 °C) on the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer) for 30 min. Then, the specimens were rapidly cooled to room temperature to observe the morphology.

3. Results and discussion

3.1. The crystallization behavior of sPS and sPS/HIPS blends

DSC curves of sPS and sPS/HIPS 7/3 blend crystallized isothermally at various temperatures after melting at 320 °C and 280 °C are shown in Fig. 1, respectively. As anticipated by the nucleation-controlled crystal growth theory, the time needed to complete crystallization was longer for the specimens crystallized at higher crystallization temperature (T_c). While at the same T_c, the time needed to complete the crystallization for sPS and sPS/HIPS 7/3 blend after melting at 320 °C was longer than that at 280 °C. That is to say, sPS and its blend exhibited faster crystallization rate at lower T_{max}. Furthermore, at the same T_c, the t_p for sPS was shorter than that for sPS/HIPS 7/3 blend melted at 320 °C, and the t_p for sPS was longer than that for sPS/HIPS 7/3 blend melted at 280 °C. It is indicated that the crystallization rate of sPS was affected with the addition of HIPS.

Table 1 lists the t_p and ΔH_c for sPS and its blends. The relationship of reciprocal crystallization peak (i.e. t_p^{-1}) versus T_c for sPS and its blends is shown in Fig. 2. Generally, the t_p^{-1} is proportional to the crystallization rate. It is observed from Table 1 and Fig. 2 that the crystallization rate of sPS and its blends decreased with increase of crystallization temperatures. For the specimens melted at 320 °C, the crystallization rate of sPS decreased with increase of HIPS content,