



Thermal characterization, melting behaviors, dynamic mechanical properties, and morphology in the polymorphism of syndiotactic polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide)

Jian-Shian Lin^{a,*}, Ming-Hua Chung^b, Chen-Ming Chen^b, Mark O. Liu^b

^a Mechanical and System Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan 30011, ROC

^b Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan 30011, ROC

ARTICLE INFO

Article history:

Received 3 September 2008

Received in revised form 15 June 2009

Available online 24 July 2009

PACS:

61.41.+e

62.20.-x

65.60.+a

Keywords:

Glass melting

Mechanical, stress relaxation

Polymers and organics

Calorimetry

Thermodynamics

ABSTRACT

The thermal characterization, melting behaviors, dynamic mechanical properties, and morphology of syndiotactic polystyrene and its blends with poly(2,6-dimethyl-1,4-diphenylene oxide) were examined by differential scanning calorimetry, dynamical mechanical analyzer, and scanning electron microscope. With differential scanning calorimetry and scanning electron microscope results, two melting endothermic peaks and blending morphology were observed. We suggest that the lower melting endothermic peak is due to the melt of syndiotactic polystyrene, however, the higher melting endothermic peak comes from the melt of recrystallized syndiotactic polystyrene crystals during the differential scanning calorimetry scan. With dynamical mechanical analyzer results, we find that addition of poly(2,6-dimethyl-1,4-diphenylene oxide) into syndiotactic polystyrene can increase the soft temperature and toughness. Moreover, the experimental results also reveal that crystallization of syndiotactic polystyrene in the syndiotactic polystyrene/poly(2,6-dimethyl-1,4-diphenylene oxide) blend is impeded in the presence of poly(2,6-dimethyl-1,4-diphenylene oxide) and the melting behaviors of syndiotactic polystyrene/poly(2,6-dimethyl-1,4-diphenylene oxide) blends are homogeneous.

© 2009 Published by Elsevier B.V.

1. Introduction

The multiple melting behaviors of semicrystalline polymers crystallized from the melt have been investigated extensively [1–3]. These semicrystalline polymers such as poly(ethylene terephthalate) and polyamides [2] are known to exhibit two or more melting endotherms. A literature search for all related studies on multiple melting indicates that two main mechanisms, (I) dual morphology and (II) melting–recrystallization–remelting, are often proposed for the interpretation of multiple melting peaks in polymers. The mechanism of dual morphology [4] is based on the evidence of two or more different crystalline structures (unit cells, lamellae, spherulites, etc.) existing in the crystallized polymers. The different crystal entities in polymers are not a result of the thermal process of DSC scanning, but already formed during crystallization before DSC characterization. Oppositely, the melting/recrystallization mechanism proposes a different view. The recrystallization–remelting mechanism suggests that the crystallization produces initially crystals of a lower degree of perfection or thinner

lamellae. During the DSC scan (or thermal/annealing processes), these thinner lamellae can then melt and re-crystallize to yield crystals of better perfection or greater thickness upon a heating scan from low to high temperature. The melting of thinner lamellae/crystals, recrystallization to thicker ones, and remelting of the thickened lamellae together yield the phenomenon of multiple melting peaks of polymers during the DSC scan. As these two mechanisms are somewhat mutually exclusive, this issue has been controversial and debates go on. Recent studies [5] led to the conclusion that a combination of these two mechanisms might be appropriate for providing a plausible explanation.

Since syndiotactic polystyrene (sPS) with a very high degree of stereospecificity (>96%) has been synthesized successfully by stereospecific polymerization [6], there has been considerable interest in characteristics of this new material [7–10]. Excellent mechanical properties are expected for sPS, especially at high temperature, due to its crystalline structure. Furthermore, a large crystallization rate of sPS relative to that of isotactic polystyrene and its high tensile modulus lead to a potential engineering plastic. It has been reported that the polymorphic behavior of sPS is very complex. Hence, many studies on sPS have focused on the analysis of the crystal structure. Four major crystalline forms, α , β , γ , and δ , have

* Corresponding author. Tel./fax: +886 3 5716735.

E-mail address: JohnnyLin@itri.org.tw (J.-S. Lin).

been proposed. The α and β forms produced by molecular chains with a planar zigzag conformation (T_4) are primary crystalline polymorphs and can be formed by thermal treatment. The α and β forms are of particular interest, since the extended chain conformation imparts an inherently stiff chain backbone to the sPS, resulting in improved mechanical properties. The α form has been reported to exist in a hexagonal [9] or rhombohedral [11] structure, whereas the β form possesses an orthorhombic structure [12]. The γ and δ forms produced by molecular chains with a helical conformation (T_2G_2) can only be formed from solvent swelling of glassy sPS, and both forms have been known to exhibit the same monoclinic crystalline structure [13,14]. γ forms are completely dried crystalline structures, nevertheless, δ forms are always generated in the presence of a solvent and seems to include some solvent molecules.

A few studies on sPS-based blend such as sPS/poly(vinyl methyl ether) (PVME) have been reported in the literature [15] and focused on the crystallization behaviors and miscibility of the blends. However, systematic researches for the melting behaviors of sPS and its blends with PPO, which is essential to understand the properties of semicrystalline polymers, are less reported. In this paper, we have investigated the nature of multiple melting behaviors of sPS and its blends with PPO. The multiple melting behaviors are highly correlated with the polymorphism of the sPS crystal.

2. Experimental details

2.1. Instruments

A differential scanning calorimeter (Perkin–Elmer DSC 316) was used for the thermal characterization within the precision of $\pm 5^\circ\text{C}$. All scans were run under a nitrogen gas purge to minimize thermo-oxidative degradation. To determine the miscibility of sPS/PPO blends from the glass transition temperature, the samples were first heated from room temperature to 300°C , maintained at 300°C for 3 min to ensure complete melting of sPS crystals, and then quenched to room temperature. The samples were immediately reheated up to 300°C at a heating rate of $10^\circ\text{C min}^{-1}$. To examine the melting kinetics behaviors of the sPS/PPO blends, all specimens were isothermally crystallized in the DMA (Dynamical Mechanical Analyzer, Perkin–Elmer) and heated from room temperature to 200°C (heating rate = 5°C/min). The errors in the measurement of DMA were $\pm 5^\circ\text{C}$. The morphology, the phase structure, and the isothermal spherulite growth rate were studied with scanning electron microscope (SEM, Hitachi 4100).

2.2. Materials

Semicrystalline syndiotactic polystyrene (sPS) was obtained as a courtesy sample from Industrial Technology Research Institute (ITRI) with $M_w = 2,100,000$ and polydispersity index (PDI; M_w/M_n) = 3.73. Amorphous poly(2,6-dimethyl-p-phenylene oxide) (PPO) ($M_w = 60,000$, $T_g = 230^\circ\text{C}$), purchased from Nippon Polyester Co. Ltd. of Japan., was used in this study to investigate the melting behaviors of sPS/PPO blends in the miscible melt. The composition of sPS/PPO blends were tabulated in Table 1.

Table 1

The composition of sPS/PPO blends.

	Ca-1	Ca-2	Ca-3	Ca-4	Ca-5
sPS (wt.%) $\pm 1\%$	90	75	50	25	10
PPO (wt.%) $\pm 1\%$	10	25	50	75	90

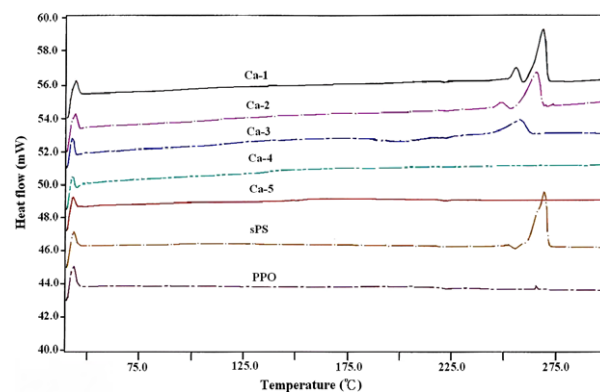


Fig. 1. The DSC results of sPS/PPO blends.

3. Results

3.1. Miscibility

To investigate the miscibility of sPS/PPO blends, the glass transition temperature was measured by the DSC scanned at heating rate of $10^\circ\text{C min}^{-1}$ (Fig. 1). The glass transition temperatures of sPS/PPO blends depended highly on the composition, indicating the miscibility of blends occurs.

By Eqs. (1) and (2) (Flory–Huggins equation), we can determine the interaction energy density (B) and interaction parameter $\chi_{1/2}$:

$$1 - T_m/T_m^0 = -BV_2\phi_1^2/\Delta H_2, \quad (1)$$

$$\chi_{1/2} = BV_1/RT, \quad (2)$$

where subscripts 1 and 2 represent the amorphous (PPO) and crystalline (sPS) components, respectively; T_m^0 , ϕ_1 , V_i are the melting point of pure crystalline component, the volume fraction of component 1, and the molar volume of the repeating unit of component i , respectively. Fig. 2 illustrates the dependence of $1 - T_m/T_m^0$ on ϕ_1 . With Fig. 2, we can obtain slope ($-BV_2/\Delta H_2$) and then determine B (-4.6 J/cm^3) and $\chi_{1/2}$ (-0.1) since $\Delta H_{2(\text{sPS})}$, $V_{2(\text{sPS})}$, and $V_{1(\text{sPS})}$ are $2.58 \times 10^3 \text{ J/mol}$, $94.1 \text{ cm}^3/\text{mol}$, and $103.7 \text{ cm}^3/\text{mol}$, respectively. Since B and $\chi_{1/2}$ are negative, we demonstrate that sPS and PPO can attract and melt each other [15].

The dependence of storage moduli for sPS, PPO, and sPS/PPO blends on the temperature are shown in Fig. 3. At low temperature, no vibration, rotation and translation occur because molecules have no enough energy; therefore, the storage modulus curve is

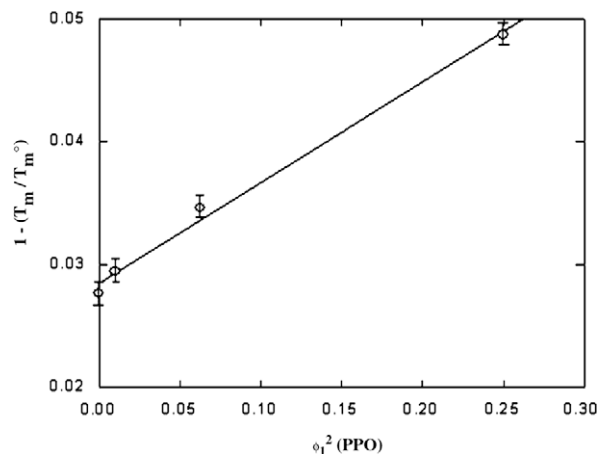


Fig. 2. The dependence of $1 - T_m/T_m^0$ on ϕ_1^2 .

Download English Version:

<https://daneshyari.com/en/article/1483637>

Download Persian Version:

<https://daneshyari.com/article/1483637>

[Daneshyari.com](https://daneshyari.com)