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Non-isothermal crystallization kinetics of poly(trimethylene terephthalate)/poly(ethylene 2,6-naphthalate) blends

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Abstract

The glass-transition temperature and non-isothermal crystallization of poly(trimethylene terephthalate)/poly(ethylene 2,6-naphthalate) (PTT/PEN) blends were investigated by using differential scanning calorimeter (DSC). The results suggested that the binary blends showed different crystallization and melting behaviors due to their different component of PTT and PEN. All of the samples exhibited a single glass-transition temperature, indicating that the component PTT and PEN were miscible in amorphous phase. The value of T_g predicted well by Gordon–Taylor equation decreased gradually with increasing of PTT content. The commonly used Avrami equation modified by Jeziorny, Ozawa theory and the method developed by Mo were used, respectively, to fit the primary stage of non-isothermal crystallization. The kinetic parameters suggested that the PTT content improved the crystallization of PEN in the binary blend. The crystallization growth dimension, crystallization rate and the degree of crystallinity of the blends were increased with the increasing content of PTT. The effective activation energy calculated by the advanced iso-conversional method developed by Vyazovkin also concluded that the value of E_a depended not only on the system but also on temperature, that is, the binary blend with more PTT component had higher crystallization ability and the crystallization ability is increased with increasing temperature. The kinetic parameters U^* and K_g were also determined, respectively, by the Hoffman–Lauritzen theory.

Keywords: Poly(trimethylene terephthalate); Poly(ethylene 2,6-naphthalate); Non-isothermal crystallization kinetics; Binary blends; Effective activation energy

1. Introduction

Poly(trimethylene terephthalate) (PTT) was first patented by Whinfield and Dickson [1] in 1946 and commercial produced by Shell Chemicals until the 1990s. Many properties of PTT are between those of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), such as crystallization rate and glass transition temperature. Moreover, it combines the two key advantages of PET and PBT into one polymer, and it has an important application in the textile industry [2] and as a promising engineering thermoplastic [3]. Poly(ethylene 2,6-naphthalate) (PEN), featuring a molecular structure of a naphthalene ring instead of the benzene ring in PET, is used as a high-performance polymer and that has superior strength, heat stability, and barrier properties due to its increased chain stiffness [4]. Thus, PEN has found for a variety of applications, such as tire cords of automobiles [5] and base films of videotapes [6–8], etc.

Polymer blending is an attractive alternative for producing new polymeric materials with desirable properties without having to synthesize a totally new material. Other advantages for polymer blending are versatility, simplicity, and inexpensiveness. Due to the similarity in the chemical structure of these linear aromatic polyesters, numerous research works related to various aspects of polyesters' blends are available in the reported literatures. Blends of polyesters were investigated wildly, such as PEN and poly(butylene 2,6-naphthalate) (PBN) [9]; PET and PBT [10]; PET and PEN [11]; PTT and PET [12]; PTT and PBT [13]; and PTT and PEN [14], etc. To meet the growing demands of the plastics industry, the combination of the economics of PTT and the superior properties of PEN may become very important.

Recently, Supaphol [14] studied the miscibility, melting and crystallization behavior of PTT/PEN blends. PTT and PEN were miscible in the amorphous state in all of the blends compositions studied, as evidenced by a single, composition-dependent glass transition temperature (T_g) observed for each

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blend composition. The variation in the T_g value with the blend composition was well predicted by the Gordon–Taylor equation, with the fitting parameter being 0.57. The cold-crystallization peak temperature decreased with increasing PTT content, while the melt-crystallization peak temperature decreased with increasing amount of the minor component. The subsequent melting behavior after both cold- and melt-crystallization exhibited melting point depression, in which the observed melting temperatures decreased with increasing amount of the minor component. During melt-crystallization, both components in the blends crystallized concurrently just to form their own crystals. The blend with 60% (w/w) of PTT exhibited the lowest total apparent degree of crystallinity.

Studies related to the kinetics of polymer crystallization are of great importance in polymer processing, due to the fact that the resulting physical properties are strongly dependent on the morphology formed and the extent of crystallization occurring during processing. In the present study, blends of PTT and PEN were prepared and characterized for their non-isothermal crystallization kinetics and melting behavior by using DSC measurements. The objectives for this work are: (1) to investigate the effect of blend composition on melt-crystallization and melting behavior, (2) to investigate the effect of blend composition on non-isothermal crystallization kinetics, and (3) to assess the effect of the cooling rate on the crystallization behavior of the binary blend.

2. Experimental

2.1. Materials

The PTT homopolymer was supplied in pellet form by Shell Chemicals (USA) with an intrinsic viscosity of 0.92 dL/g measured in a phenol/tetrachloroethane solution (60/40, w/w) at 25 °C. The PEN homopolymer was supplied in pellet form by Honeywell (USA) with an intrinsic viscosity of 0.89 dL/g measured in phenol/tetrachloroethane solution (50/50, w/w) at 30 °C.

2.2. Blends preparation

The materials were dried in a vacuum oven at 140 °C for 12 h before preparing blends. The dried pellet of PTT and PEN were mixed together with different weight ratio of PTT/PEN as following: B1, 0/100; B2, 20/80; B3, 40/60; B4, 60/40; B5, 80/20; B6, 100/0, and then melt-blended in a ZSK-25WLE WP self-wiping, co-rotating twin-screw extruder, operating at a screw speed of 60 rpm and at a die temperature of 300 °C. The resultant blend ribbons were cooled in cold water, cut up, re-dried before being used in DSC.

2.3. Differential scanning calorimetry (DSC)

The glass-transition temperature, cold crystallization, and subsequent melting behavior of six samples were studied by the Perkin-Elmer Diamond DSC instrument that calibrated with indium prior to performing the measurement, and the weights of all samples were approximately 6 mg. The samples were heated to 300 °C at 150 °C/min under a nitrogen atmosphere, held for 5 min to reset previous thermal histories, after which all of the samples were immediately quenched under a cooling rate of 200 °C/min to obtain the completely amorphous state of six samples, and then heated them with a heating rate of 10 °C/min.

The melt-crystallization and subsequent melting behaviors of various binary blends were performed as following: the samples were heated to 300 °C at 150 °C/min under a nitrogen atmosphere, held for 5 min and then cooled to 50 °C at a constant cooling rate of 10 °C/min, and then heated them to 300 °C at a heating rate of 10 °C/min, the cooling process and the second heating process were recorded, respectively.

The non-isothermal crystallization behaviors of two blends (B2 and B3) were performed as following: the sample was heated to 300 °C in nitrogen, held for 5 min and then cooled to 50 °C at constant cooling rates of 5, 10, 15, and 20 °C/min, respectively. It is worth noting that each sample was used only once and its weight is around 6 ± 0.5 mg. The exothermic curves of heat flow as a function of temperature were recorded and investigated.

3. Results and discussion

3.1. Miscibility of the blends

Generally, a single T_g and/or its shift in the blends represent miscibility or partial miscibility [15–17]. In our experiment, all the blends are thought to be miscible in the amorphous phase. This is in good agreement with the report of Krutphun and Supaphol [14]. Fig. 1 displays the DSC curves of glass transition, cold-crystallization and subsequent melting for quenched six samples recorded with a heating rate of 10 °C/min. The dependence of T_g on the blend composition can be predicted by the Gordon–Taylor [18] and Fox [19] equations. In this paper, Gordon–Taylor equation is employed to describe the relationship between T_g and blend composition, and the result is shown

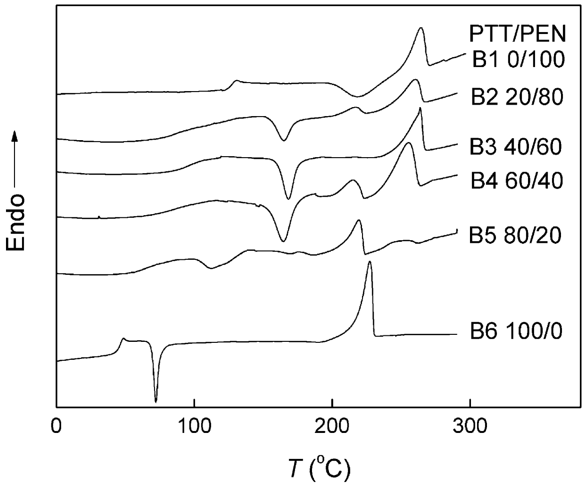

Fig. 1. The glass-transition temperature, cold-crystallization, and subsequent melting thermograms of six quenched samples under a heating rate of 10 °C/min.