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Effect of nanoscale fully vulcanized acrylic rubber powders on crystallization of poly(butylene terephthalate): Isothermal crystallization

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Abstract

Poly(butylene terephthalate) (PBT) was blended with nanoscale fully vulcanized acrylic rubber (FVAR) powders in a twin extruder, and the FVAR powders were dispersed well in PBT from scanning electron microscopy (SEM) and transmission electron microscope (TEM) investigation. The isothermal crystallization kinetics of PBT/FVAR blends were investigated by differential scanning calorimeter (DSC) and simulated by Avrami model. Equilibrium melting temperature was estimated by the nonlinear Hoffman–Weeks relation. The active energy (ΔE) and nucleation parameters (K_g) increased with the addition of FVAR, suggesting that FVAR particles hindered the crystallization; however more content FVAR had a lower ΔE and K_g because FVAR powders acted as heterogeneous nuclei in the nucleation of crystallization and facilitated the crystallization of PBT. The crystallization ability followed the order: PBT > PBT/FVAR6 > PBT/FVAR3 > PBT/FVAR1 when undercooling was considered.

Keywords: Elastomeric nano-particles; Dispersion; Isothermal crystallization; Poly(butylene terephthalate)

1. Introduction

Poly(butylenes terephthalate) (PBT) is an importance thermoplastic material for a large number of applications because of its good combination of properties, such as rigidity, solvent resistance. Its low impact strength can be overcome by blending with elastomers, such as poly(ethylene octene) (PEO) [1–3], poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) [4–7], ethylene–propylene–diene (EPDM) [8], ethylene–propylene rubber [9,10] and poly(ethylene-*co*-glycidyl methacrylate) [11]. The toughness and crystallization of PBT depends on the compatibility and interactions between components induced by chemical reactions.

A new kind of highly cross-linked nano-particle rubbers, ultra-fine full-vulcanized rubber powders (UFRP) with particle size between 30 nm and 2000 nm has been applied in toughening the polymers [12–14]. When the particle size is below 100 nm, the UFRP can be also recognized as elastomeric nano-particle. According to the toughening

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theory [15,16], the brittle-tough transition occurs at a very low rubber volume fraction if the particle size of rubber is small enough.

While the UFPR could be as a good toughening modifier, those fine particles also affect the crystallization process. To control crystallization is of great importance in polymer processing. Most of the properties of the polymer are affected by crystalline and crystallization rate. In this article, crystallization of PBT was studied via blending with nanoscale fully vulcanized acrylic rubber (FVAR). The dispersion was observed by scanning electron microscopy and transmission electron microscope (TEM), and isothermal crystallization was measured by differential scanning calorimetry (DSC) and described by Avrami model.

2. Experimental

2.1. Materials

Commercial grade PBT was supplied by ChangChun Group (trade name: 2000-201D). Nanoscale fully vulcanized acrylic rubber (FVAR) powder (trade name: VP-301) with particle size of 50–100 nm was offered by Beijing Research Institute of Chemical Industry, SINOPEC, China. All materials were used as received without purification.

2.2. Sample preparation

All materials were dried at 373 K in a vacuum oven for 6 h before compounding. PBT was compounded with FVAR powder in a twin-screw extruder (Continent Machinery Company, Model CM-MTE) at 623 K and 100 rpm to prepare PBT/FVAR blends. FVAR contents were 1 wt% (PBT/FVAR1), 3 wt% (PBT/FVAR3) and 6 wt% (PBT/FVAR6). Neat PBT for comparison also went through similar thermal history.

2.3. Morphology

In order to characterize the morphology of the blends, the samples were fractured in liquid nitrogen and examined with scanning electron microscope (TOPCON ABT-150S). Transmission electron microscope (TEM), cryo-transmission electron microscope, was also used to observe the dispersibility of FVAR particles in blends using an acceleration voltage of 120 kV.

2.4. Isothermal crystallization

The crystallization behaviors of the PBT/FVAR blends were investigated with a differential scanning calorimeter, Perkin–Elmer Pyris-1 DSC. The differential scanning calorimeter was calibrated using indium with samples weights of 8–10 mg. All operations were carried out in a nitrogen atmosphere. Before data gathering, the samples were heated to 583 K and held in the molten state for 5 min to eliminate the influence of thermal history. The sample melts were then subsequently quenched at a rate of 100 K/min to reach the specific temperatures. When the isothermal crystallization had completed, the samples were heated to 583 K at a rate of 10 K/min to measure the melting temperatures.

3. Results and discussion

3.1. Morphology of the PBT blends

Fig. 1 shows the SEM micrographs of the fractured surface roughly normal to the extrusion direction. From SEM micrographs, FVAR particles were hardly distinguishable from the PBT matrix in PBT/FVAR blends; only PBT/FVAR6 (Fig. 1c) shows a few aggregates. In order to confirm the nanoscale dispersion of FVAR particles, the morphology of PBT/FVAR blends were also observed by TEM. In Fig. 2a and b (PBT/FVAR1 and PBT/FVAR3) shows the FVAR particles are well dispersed in PBT. Only Fig. 1c (PBT/FVAR6) exhibits a few aggregates. The results show that a highly cross-linked structure within each nano-particle can effectively prevent the aggregates together in the blends.

3.2. Isothermal crystallization kinetics

Fig. 3 shows a representative isothermal crystallization DSC curves for the PBT/FVAR3 blend. A sample with higher crystallization temperature requires a longer time to complete crystallization. Crystallinity (X_t) was calculated as the ratio of the exothermic peak areas at time t and infinite time [17–19]

$$X_t = \frac{\int_0^t \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^\infty \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right)\mathrm{d}t} \tag{1}$$

where $\mathrm{d}H_c$ is the enthalpy of crystallization released during an infinitesimal time interval $\mathrm{d}t$. Fig. 4 shows a typical relative crystallinity of PBT/FVAR3