



Crystallization and melting behavior of poly(butylene succinate)/silicon nitride composites: The influence of filler's phase structure



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ABSTRACT

Poly(butylene succinate) (PBS) composites containing 10 wt% amorphous-Si₃N₄, α-Si₃N₄ and β-Si₃N₄ were prepared by melting mixing. The effect of Si₃N₄ phase structure on the crystallization and melting behavior of PBS was investigated by Differential Scanning Calorimetry (DSC) and Wide-Angle X-ray Diffraction (WAXD). The non-isothermal crystallization kinetics of PBS and PBS/Si₃N₄ composites was studied by Jeziorny methods. The crystallization activation energy and nucleation activity of PBS and PBS/Si₃N₄ composites were calculated according to Friedman and Dobreva methods, respectively. The results show that Si₃N₄ particles have obvious heterogeneous nucleation for PBS crystallization, increasing the crystallization temperature and reducing the crystallization activation energy. Among those Si₃N₄ particles studied, α-Si₃N₄ particles have the strongest heterogeneous nucleation for PBS crystallization, which indicate that the phase structure of Si₃N₄ particle have great influence on the crystallization behavior of PBS.

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1. Introduction

As a kind of biodegradable aliphatic polyesters, poly(butylene succinate) (PBS) has attracted tremendous interest due to its good biodegradability, superior processibility, relatively low cost, superior thermal and mechanical properties [1–4]. PBS has been widely used in many fields, such as agricultural films, biomedical materials, packing, fibers and injection-molded products [5–7].

There are two kinds of crystal modifications (α and β forms) in PBS [8]. PBS shows multiple melting behavior during melting process, and the mechanism of the multiple melting behavior has been widely studied, and it is considered to the process of melting of various original crystals, re-crystallization, and melting of re-crystallized crystals [9–13]. As a semicrystalline polymer, the mechanical properties and biodegradability of PBS are greatly affected by crystalline morphology, which is relative to the crystallization behavior. Bikiaris et al. [14] found that PBS exhibits low biodegradation rate compared to other familiar polyesters like

poly(propylene succinate) because of its higher crystallinity. Sinha Ray et al. [5] observed that addition of layered silicate can change the crystallinity of aliphatic polyesters, and thus its hydrolysis rate. Jin et al. [15] reported that graphene oxide (GO) has an accelerating effect on PBS hydrolytic degradation due to the well dispersion of GO in the PBS matrix, which decreased the size of spherulite effectively and made the spherulitic boundaries become loose. Thus, many researchers [16–20] have focused on searching the efficient nucleating agents for PBS crystallization, in order to change the crystallization properties of PBS and then improve its performance.

For semicrystalline polymer composites, many filler particles can act as nucleating agents to increase the crystallization rate and crystallization temperature as well as decrease the crystal size of PBS. For a given polymer matrix and filler, the heterogeneous nucleation of filler depends on the intrinsic surface chemical [21] and physical characteristics (i.e., crystal lattice structure [22], surface roughness [23], surface treatment [24], geometry and size [25]) of the filler. For PBS, Papageorgiou et al. [26] investigated the effect of nanofiller's size and shape on the crystallization of PBS and found that spherical nanofillers have higher nucleation effect than these with nanosheets or nanotubes. Tan et al. [27] investigated the effect of surface modification of single-walled carbon nanotube by acyl aminopropyltriethoxysilane (SWCNT-APTES) on the crystallization behavior of PBS. The results showed that the addition of SWCNT-APTES enhanced the crystallization of the PBS

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in the nanocomposites for both approaches of hydrolysis and physical blend due to the heterogeneous nucleation effect. Especially, a more significant increase of crystallization rate for physical blend was present as comparison to PBS/SWCNT-APTES after hydrolysis due to the higher diffusion constant, which is attributed to the change of surface properties of nanotubes. However, to our knowledge, the effect of phase structure of fillers on the crystallization behavior of PBS has not been reported.

Si_3N_4 is an important ceramic material due to its unique mechanical, thermal, and electronic properties. And it has been used in many applications, especially in automobile, aerospace and micro-/nano-electronics industries [28]. Recently, the mechanical properties [29], thermal conductivity [30], wear resistance [31] and crystallization behavior [32] of Si_3N_4 filled polymer composites has been investigated.

In order to investigate the effect of phase structure of fillers on the crystallization and melting behavior of PBS, Si_3N_4 with different phase structure (amorphous and crystalline $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$) was used as fillers to prepare PBS composites by melting mixing in the present manuscript. The effect of phase structure of Si_3N_4 on the crystallization and melting behavior of PBS was investigated by DSC and WAXD. The non-isothermal crystallization kinetics of PBS/ Si_3N_4 composites were compared using Jeziorny model. The nucleation activity of Si_3N_4 and the effective activation energy were also determined by Friedman and Dobreva methods, respectively.

2. Experimental

2.1. Materials

PBS (Bionolle 1020, MFI=25.0 g/10 min at 190 °C and 2.16 kg, $M_w = 1.4 \times 10^5 \text{ g mol}^{-1}$, the density is 1.26 g/cm³) was provided by Showa Highpolymer Co., Ltd. $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$ and amorphous- Si_3N_4 were provided by Qinhuangdao Eno High-Tech Material Development Co., Ltd. The average particle sizes were about 0.5 μm , 1.0 μm and 20 nm for $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$ and amorphous- Si_3N_4 , respectively.

2.2. Sample preparation

PBS composites containing 10 wt % of Si_3N_4 particles were prepared by melt mixing on a ZG-120 open mill (Dongguan Zhengggong Mechanical and Electrical Equipment Technology Co., Ltd.) under 30 rpm for 5 min at 130 °C. Prior to melt-mixing, the fillers were dried in a vacuum oven at 130 °C for 24 h. The sample codes that will be used throughout the paper will be the following: PBS, PBS/ $\alpha\text{-Si}_3\text{N}_4$, PBS/ $\beta\text{-Si}_3\text{N}_4$ and PBS/amorphous- Si_3N_4 .

2.3. Differential Scanning Calorimetry (DSC)

The nonisothermal crystallization behavior and melting characteristics of PBS and its composites were carried on with a TA DSC Q20 differential scanning calorimeter (TA, USA) under a nitrogen atmosphere. About 5 mg of sample was heated from ambient temperature to 140 °C at a heating rate of 30 °C/min and held at this temperature for 5 min to eliminate the thermal and mechanical history. Then, the sample was cooled to room temperature at cooling rates of 5, 10, 15, 20 and 25 °C/min, respectively, and re-heated to 140 °C at a heating rate of 10 °C/min.

For isothermal crystallization behavior and melting characteristics of PBS and PBS/ $\alpha\text{-Si}_3\text{N}_4$, a sample was heated to 140 °C and held for 5 min to eliminate the thermal and mechanical history. Then, the sample was cooled to the desired crystallization temperature at a rate of 100 °C/min and held for a certain period of time

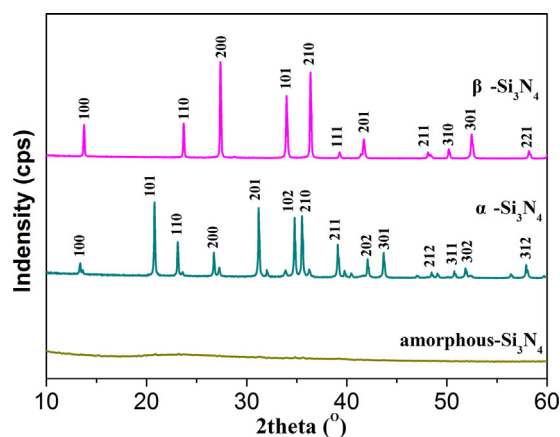


Fig. 1. X-ray diffractograms of Si_3N_4 particles.

until the crystallization was completed, and re-heated to 140 °C at a heating rate of 10 °C/min.

2.4. Wide-Angle X-ray Diffraction (WAXD)

Wide-Angle X-ray Diffraction experiments were conducted with a Rigaku D/max-2200 VPC X-ray diffractometer (Rigaku, Japan) with the Cu K α radiation at a voltage of 40 kV and a current of 30 mA. The scan speed was 4/min in a range of $2\theta = 5\text{--}70^\circ$ for fillers, PBS and its composites. The samples were pretreated by DSC, heating from 40 to 140 °C, holding for 5 min, and then cooling to 40 °C at a cooling rate of 5 °C/min and 20 °C/min, which were coded as “sample-5” or “sample-20”, respectively. For example, PBS-5 represented PBS cooled to 40 °C at a cooling rate of 5 °C/min.

2.5. Scanning Electron Microscopy (SEM)

The morphologies of fillers sputtered with gold under vacuum were observed on a ZEISS Ultra 55 scanning electron microscope (Zeiss, Germany) at an operating voltage of 5 kV.

3. Results and discussion

3.1. Characterization of silicon nitrides

The phase structure and morphologies of Si_3N_4 particles were characterized by WAXD and SEM, as shown in Figs. 1 and 2. Amorphous- Si_3N_4 does not show any diffraction peak, and the peaks of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ can be indexed as the hexagonal cell [33–35]. SEM micrographs show that the size of amorphous- Si_3N_4 particles is homogeneous. On the other hand, $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ particles exhibit irregular granules and have a broad size distribution from dozens of nanometers to several microns. The Si_3N_4 particles with different phase morphologies may lead to different effect on the crystallization of PBS.

3.2. Crystallization and melting behavior of PBS and PBS/ Si_3N_4 composites

The non-isothermal crystallization and melting behavior of PBS and PBS/ Si_3N_4 composites crystallized at different cooling rates were studied by DSC. Fig. 3 shows the crystallization curves of PBS and PBS/ $\alpha\text{-Si}_3\text{N}_4$ composite crystallized at different cooling rates. The crystallization peaks become broader and shift to lower temperatures with increasing cooling rate. Similar results are obtained for PBS/ $\beta\text{-Si}_3\text{N}_4$ and PBS/amorphous- Si_3N_4 composites (data not shown).

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