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Non-isothermal crystallization kinetics of reactive microgel/nylon 6 blends☆

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ABSTRACT

The non-isothermal crystallization kinetics of reactive microgel/nylon 6 blends was investigated by differential scanning calorimetry (DSC). The Mo equation was employed to analyze the non-isothermal crystallization data. The crystallization activation energies were also evaluated by the Kissinger method. The results show that the crystallization onset temperature (T_{onset}) and crystallization peak temperature (T_p) decrease with the increase of the content of reactive microgel, while ΔT ($T_{onset}-T_p$), the crystallization half-time ($t_{1/2}$) and the crystallization enthalpy (ΔH_c) increase. The required cooling rates of blends are higher than that of neat nylon 6 in order to achieve the same relative crystallinity in a unit of time. The crystallization activation energies of the reactive microgel/nylon 6 blends are greater than those of the neat nylon 6. When the content of reactive microgel is 30%, the relative crystallinity (X_t) reaches the maximum.
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1. Introduction

Nylon 6 is an important class of crystalline engineering thermoplastics which has been applied widely [1–3]. However, the low notched impact strength of nylon 6 limits its application, and thus it is important to modify nylon 6 [4]. The most common method is blending the elastomer or plastic with nylon 6 [5–7]. The addition of the elastomer or plastic into nylon 6 is an effective method to improve the impact strength, but the effect is not very obvious due to poor compatibility.

Reactive microgel is an intramolecular crosslinked macromolecule in the size of 1 nm–1000 nm with different reactive groups such as carboxyl, hydroxyl, sulfonyl and amino groups on the surface or inside [8]. This microgel can be crosslinked with other monomers or macromolecule under appropriate conditions to get the heterogeneous network polymer [9]. Thus, blending reactive microgel with nylon 6 can improve the compatibility of the blends. It has an important theoretical significance and application prospects in improving the rheological and mechanical properties. As a combination of organic nano-particles and thermoplastic elastomer, reactive microgel is expected to provide a new idea for modifying nylon 6.

In this paper, the non-isothermal crystallization behavior of nylon 6 with varying content of reactive microgel was investigated by using differential scanning calorimetry (DSC). It is well known that properties of

the crystalline polymer such as mechanical and thermal properties are strongly related to the crystallization behavior and crystal morphology of the materials. Therefore, to search for the best processing conditions in an industrial process and resulting products with better performance, it is necessary to study the crystallization behavior of crystalline polymer [10,11]. Currently, there are many papers reporting methods for studying the non-isothermal crystallization kinetics of polymer, such as the Jeziorny theory [12], the Ozawa theory [13] and the Mo theory [14]. Huang Zhaoge *et al.* [15] investigated the non-isothermal crystallization kinetics of nylon 6 by these three methods, and found that the Mo equation was more suitable to analyze the non-isothermal crystallization data comparing with the Jeziorny and the Ozawa theories. Thus, the Mo theory was used to study the non-isothermal crystallization kinetics of neat nylon 6 and reactive microgel/nylon 6 blends. The non-isothermal crystallization activation energies based on Kissinger's equation were also calculated.

2. Experimental

2.1. Materials

Nylon 6 was obtained from Hunan Yueyang Baling Petroleum & Chemical Co., Ltd. The reactive microgel was self-prepared according to the method of Jana Machotová and Jaromír Šňupárek [16]. The reactive microgel was synthesized with the monomers of 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and allyl methacrylate (AMA) using ammonium persulfate as initiator by emulsion polymerization. The glass transition temperatures (T_g) of the reactive

microgel was 122 °C and the particle size in water phase of the reactive microgel was 110 nm.

2.2. Sample preparation

Nylon 6 was blended with reactive microgel (drying at 80 °C under vacuum for two hours) in an internal mixer (type SU-70C, Changzhou Suyan Science and Technology Co., Ltd. China). The mass ratios of reactive microgel to nylon 6 in the blends were 20%, 30%, 40% and 50%. The temperature of the barrel was set at 250 °C and the rotational speed was 230 r·min^{-1}.

2.3. DSC measurements

The non-isothermal crystallization kinetics was investigated by using a differential scanning calorimeter (type TG-DTA6300, Perkin Elmer Instrument Co., Ltd.). All analyses were performed under a nitrogen atmosphere and the temperature scale of the DSC was calibrated with high purity (99.999%) indium metal. Sample with mass of 6–8 mg was heated at a rate of 20 °C·min^{-1} from 25 °C to 250 °C and held there for 5 min to eliminate any previous thermal history, and then was cooled to the predetermined temperature (50 °C) at a constant cooling rates of 10, 15, 20 and 25 °C·min^{-1}, respectively. The non-isothermal crystallization curves were recorded as a function of time.
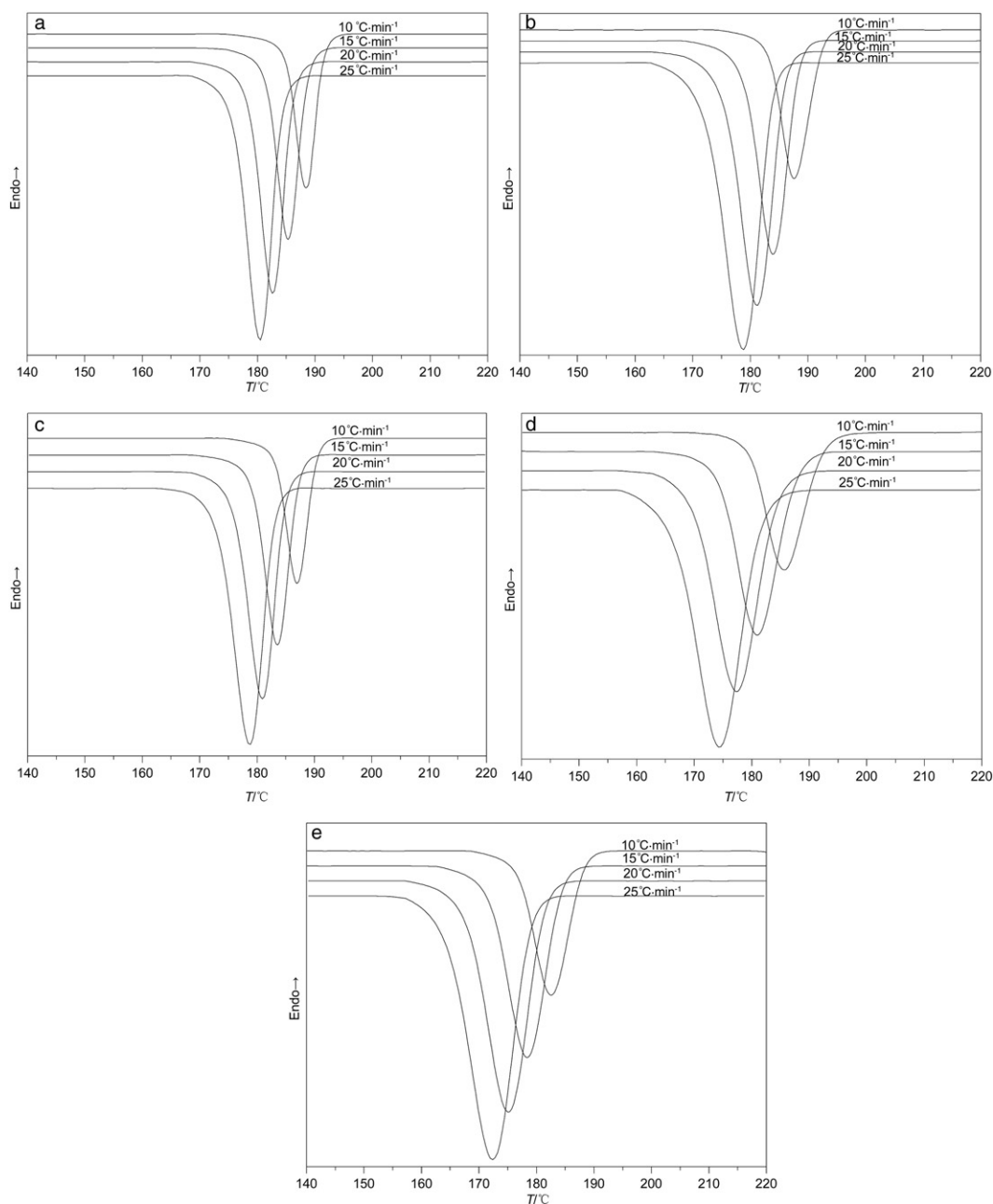
Fig. 1. DSC thermograms of non-isothermal crystallization process for nylon 6(a), reactive microgel/nylon 6 (20/80) (b), reactive microgel/nylon 6 (30/70) (c), reactive microgel/nylon 6 (40/60) (d) and reactive microgel/nylon 6 (50/50) (e) blends at different cooling rate of 10, 15, 20 and 25 °C·min^{-1}.