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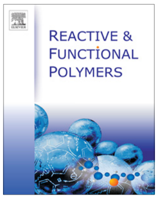

Effect of photofunctional organo anion-intercalated layered double hydroxide nanoparticles on poly(ethylene terephthalate) nonisothermal crystallization kinetics

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ABSTRACT

Very recently, we report a facile preparation and strong UV-shielding function of poly(ethylene terephthalate) (PET) nanocomposites using 4,4′-diaminostilbene-2,2′-disulfonic acid anion-intercalated layered double hydroxide (LDH_DDA). Herein, the effect of the photofunctional organo anion-intercalated LDH nanoparticles on nonisothermal crystallization kinetics of PET is reported by differential scanning calorimetry technique. First, the nonisothermal crystallization behaviour is discussed by several basic parameters including crystallization peak temperature, relative degree of crystallinity with temperature or time, and half-time of crystallization. Then, Avrami and Jeziorny method, as well as Mo model were applied for the PET/LDH_DDA nanocomposites. Finally, the crystallization activation energy was investigated by Kissinger method and Flynn conversion. The results reveal that the incorporation of LDH_DDA nanoparticles acted as nucleating agent and significantly accelerated the PET nonisothermal crystallization process, whereas had little effect on the three-dimensional growth pattern of spherulites.

1. Introduction

Compared with neat polymers and their conventional composites, polymer/inorganic nanocomposites often display greatly improved mechanical, thermal stability, gas-barrier and flame-retardant properties [1]. Recently, polymer nanocomposites using functional inorganic nanoparticles, such as carbon nanotubes (CNTs) [2–5], layered double hydroxides (LDHs) [6–8] and graphene [9,10], have attracted considerable interest. For example, in our laboratory, atactic polystyrene (aPS)/CNT [2] and syndiotactic polystyrene (sPS)/CNT [3] nanocomposites with enhanced electrical conductivity and thermal stability were successfully prepared, aided by a self-designed gemini surfactant [2] or N-methyl-2-pyrrolidinone [3]. Subsequently, the crystallization [3], orientation [4], and unexpected flower-like patterns [5] for the sPS/CNT nanocomposites were reported.

LDHs, also known as "anionic clay" and hydrotalcite-like compounds, are a class of host–guest layered inorganic materials with a layer thickness of 0.48 nm and interlayer anion exchangeability [11]. Due to their unique structure and excellent properties, LDHs have been extensively studied in the fields of catalyst [12], thermal stabilizer [6], enhanced oil recovery [7] and hydrogel [8] etc. Very recently, we report a facile preparation of poly(ethylene terephthalate) (PET)/LDH nanocomposites using organo UV-absorber, 4,4′-diaminostilbene-2,2′-disulfonic acid (DDA), intercalated LDH (LDH_DDA) [13]. Interestingly, the nanocomposite films were found to exhibit strong UV-shielding functions, which provide an opportunity to greatly broaden the applications of PET materials [13].

For semi-crystalline polymers, crystallization is a major issue in polymer physics, processing and materials' properties (especially mechanical properties). Among the studies of polymer crystallization, nonisothermal crystallization kinetics is extremely vital because most of the current industrial processing techniques for polymeric materials proceed under nonisothermal conditions [14,15]. In particular, due to PET low crystallization rate, melt injection moulding processing of PET is rather limited in industrial applications. Nucleation agents are often required to be added to increase the crystallization rate. Therefore, the study of nonisothermal crystallization kinetics for PET/inorganic nanocomposites is of great importance.

Herein, we focus on the nonisothermal crystallization kinetics of the recently-reported PET/LDH_DDA nanocomposites with strong UV-shielding functions [13] by differential scanning

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calorimetric (DSC) technique. First, the basic parameters for characterization of nonisothermal crystallization kinetics including crystallization peak temperature (T_p), the relative degree of crystallinity with temperature (X_T) or time (X_t), and the half-time of crystallization ($t_{1/2}$) were discussed. Then, various mathematical models including Avrami and Jeziorny model, as well as Mo model were employed to analyse the nonisothermal crystallization kinetic process. Finally, the activity energy (ΔE) was investigated using Kissinger method and isoconversional Flynn theories.

2. Experimental

2.1. Materials

All of the reagents, including magnesium nitrate, aluminum nitrate, sodium hydroxide and sodium nitrate are of analytical reagent pure (A.R.) grade. The UV absorber of DDA was bought from TCI Company with purity higher than 98%. Before use, the deionized water was distilled to get rid of dissolved carbon dioxide. The pure PET resin was kindly provided by Professor Peng Chen at Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences. The samples of PET-1, PET-3 and PET-5 refer to the PET/LDH_DDA nanocomposites with LDH_DDA contents of 1, 3 and 5 wt%, respectively.

2.2. Preparation of PET/LDH_DDA nanocomposites

The PET/LDH_DDA nanocomposites were prepared according to our previous work [13].

2.2.1. Synthesis of LDH_NO$_3$ particles

LDH_NO$_3$ was synthesized by a typical coprecipitation method. Briefly, an aqueous solution of Mg(NO$_3$)$_2$ (**0.50** mol L^{-1}) and Al(NO$_3$)$_3$ (0.25 mol L^{-1}) and a solution of NaOH (1 mol L^{-1}) were added drop-wisely into the NaNO$_3$ solution (0.1 mol L^{-1}). During the adding process, the pH value was kept at pH = 10.0 under stirring in nitrogen atmosphere. Then, the mixture was aged at 80 °C for 8 h. Finally, the resultant was filtrated, washed with deionized water, and dried in a vacuum oven at 50 °C for 24 h.

2.2.2. Synthesis of LDH_DDA

The LDH_DDA was obtained by anion-exchange reaction between DDA^{2-} and LDH_NO$_3$. About 0.10 g of the LDH_NO$_3$ was added into 100 mL of DDA solution (0.1 mol L^{-1}). The exchange was completed in aqueous solution at 80 °C for 24 h.

2.2.3. Synthesis of PET/LDH nanocomposites

The PET nanocomposites were prepared by a solution mixing procedure. Typically, PET was first dissolved in m-cresol at 140 °C, and LDH_DDA was ultra-sonically dispersed in cyclohexanone by ultrasonic treatment. Later, the obtained LDH_DDA suspension was added into the PET solution. After stirring for 30 min, the mixture was poured into ethanol to precipitate. Finally, the resultant product was filtrated, washed and dried.

2.3. Nonisothermal crystallization measurements

The measurements were carried out under nitrogen purge to prevent thermal degradation with a TA instruments Q2000 differential scanning calorimeter. The sample weight varied 4–5 mg. The measurements started by heating the sample from ambient temperature to 280 °C at a heating rate of 50 °C/min, and held for 8 min to remove the thermal history and eliminate small residual nuclei that might act as seed crystals. Then, the melt was cooled down to crystallize at cooling rates (α) of 2, 5, 10 and 20 °C/min, respectively.

3. Result and discussion

3.1. Basic parameters for nonisothermal crystallization processes

Fig. 1 shows the DSC exothermic curves of the nonisothermal crystallization processes for pure PET (A) and PET/LDH_DDA nanocomposite (B). Importantly, these thermograms can provide diverse information on the nonisothermal crystallization behaviour, including main parameters of the exothermic T_p, the X_T, and the $t_{1/2}$.

3.1.1. The T_p

The T_p was obtained directly from Fig. 1, and the corresponding values are shown in Fig. 2. Obviously, the exothermic peaks become wider, and the T_p shifts to low temperature with the increase of cooling rate (α). This reveals that when the cooling process was fast, nonisothermal crystallization happened at low temperature range due to the shorter crystallization time applied. In contrast, at a slow α, there was sufficient time to activate nuclei; thus, the crystallization could occur at a relatively high temperature [16].

On the other hand, it is obvious that for the PET/LDH_DDA nanocomposites (PET-1, PET-3 and PET-5), the T_p at a given cooling rate are higher than that for the pure PET. Moreover, the T_p increased with the LDH_DDA content. This phenomenon can be explained by the nucleation effect induced by the LDH_DDA nanoparticles on the PET macromolecular segments, which led to the crystallization of PET to occur at a relatively high crystallization temperature (T).

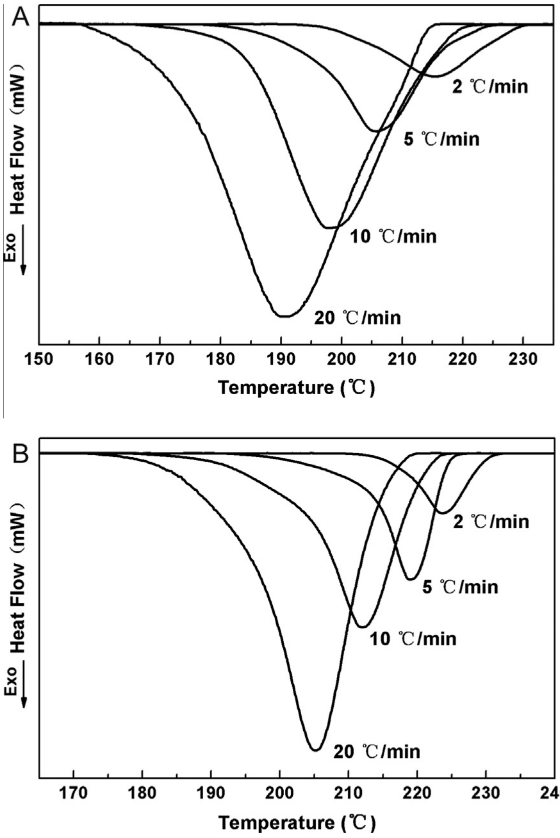

Fig. 1. DSC thermograms of nonisothermal crystallization processes at different cooling rates for (A) pure PET and (B) PET-5.