Non-isothermal crystallization behavior of PLA/LLDPE/nanoclay hybrid: Synergistic role of LLDPE and clay

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ABSTRACT

The non-isothermal crystallization behavior of polylactic acid (PLA) in presence of linear low-density polyethylene (LLDPE) and two different commercial-grade nanoclays, Cloisite 30B and Cloisite® 15A at different conditions were investigated using DSC and WAXS. The results showed that crystallization of neat PLA was very difficult from the melt in the non-isothermal quenching process and presence of nanoclays only improved the crystallization of PLA during heating. LLDPE as an efficient plasticizer enhanced the mobility of PLA chain segments, which led to the increased crystallization rate during heating. In PLA/LLDPE/clay hybrid, PLA component could crystallize only during heating and a fractionated crystallization of LLDPE was occurred during cooling. Cloisite® 15A as a good nucleating agent and LLDPE as an efficient plasticizer promoted the crystallization of PLA in a certain degree indicating the synergistic effects of LLDPE and nanoclays on PLA crystallization particularly at low nanoclays content.

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1. Introduction

Poly (lactic acid) (PLA) is a commercially available biodegradable aliphatic polyester, produced from renewable resources. It has received much attention in the research of the alternative biodegradable polymers. The most common synthetic route to PLA is the ring-opening polymerization of lactide, the cyclic dimer of lactic acid. Commercial PLA grades are copolymers of poly (L-lactic acid), noted PLLA, and poly (D, L-lactic acid), noted PDLLA, which are produced from L-lactides and D, L-lactides, respectively. The ratio of L- to D, L-enantiomer is known to affect the properties of the polymer obtained, such as melting temperature and degree of crystallinity [1–3]. Schmidt et al. [4] found that the addition of poly (D-lactide) (PDLA) into poly (L-lactide) (PLLA) led to the reduction in the overall extent of PLLA crystallization. Baratian et al. [5] also found that with increasing the content of D-lactide, crystallinity and spherulite growth rate decreased substantially. The thermal behavior of polylactic acid (PLA) has attracted much attention since differential scanning calorimetry (DSC) studies detected multiphase transitions [6–19] such as glass transition, cold crystallization and melting. Of these thermal properties, crystallization is

the most important from both a scientific and commercial point of view, because many mechanical properties and biodegradability of PLA significantly depend on its crystallinity. The cold crystallization of PLLA was studied by Mano et al. [7] by means of simultaneous small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS); they found that the crystallization rate of PLLA decreased with increasing molecular weight. Miyata and Masuko [8] studied the effect of molecular weight on the crystallization characteristics of PLLA too. Composition also had an effect on the crystallization rate [11,12]. Although PLA possesses many desirable properties, its crystallization rate is extremely slow in comparison with commercial thermoplastics. Achieving high degree of crystallinity in PLA is difficult. In this case, the amorphous content of PLA plays a very important role on the final properties of the articles. Similar to other semi-crystalline polymers, the crystallization behavior of PLA depends on both the nucleation activation energy and the mobility of chain segments. The most viable method to increase the overall crystallization rate is the blending of nucleating agent and plasticizers. The presence of additives in a pristine polymer resin can influence the crystalline morphology and kinetics by providing nucleating sites for initiating the crystallization or increasing the polymer chain mobility and therefore enhancing the crystallization rate. Several types of common physical nucleating agents for PLA, including talc and nanoclays have been examined in the literature [20–22]. Yu et al. [20] found that compressed CO_2 increased

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the mobility of PLA chains in solid state, resulting in an increased rate of cold crystallization. The kinetics of overall crystallization is controlled by nucleation-controlled and crystal-growth regions separately. Increasing temperature will accelerate crystallization in the crystal-growth region, but it will decrease crystallization in the nucleation-controlled region. A plasticizer can increase the crystallization rate through accelerating the spherulite growth rate, while a nucleation agent can enhance the crystallization rate through increasing the nuclei density. The isothermal cold crystallization kinetics of PLA/nucleating agents ($CaCO_3$, TiO_2, and $BaSO_4$, content from 0.5 to 2.0 wt%) was investigated by Liao et al. [21]. Their findings showed that by blending nucleating agents PLA had a maximum crystallinity of 14.9%. Although much work has been done to investigate the effect of nucleating agent or the plasticizer on the crystallization of PLA, less work has been done to investigate the combined effects of plasticizer and nucleating agent on PLA crystallization [23,24]. Li et al. [23] found that once polyethylene glycol (PEG) and functional multi wall carbon nanotubes (FMWCNTs) are present in the materials simultaneously, the crystallization rate of PLLA was greatly enhanced and higher crystallinity was obtained, indicating the synergistic effects of polyethylene glycol (PEG) and FMWCNTs on PLLA crystallization. In fact, we can design a PLA composite with plasticizer and nucleating agent simultaneously. Plasticizer improves the mobility of chain segments meanwhile nucleating agent decreases the nucleation activation energy of PLA. Thus, in this work, linear low density polyethylene (LLDPE) is introduced into PLA with the aim to improve the mobility of PLA chain segments. Meanwhile, nanoclays are chosen as the nucleating agent due to their great heterogeneous nucleation and reinforcing effect for polymers. The synergistic effects of two different kinds of nanoclays, and LLDPE on the non isothermal crystallization behavior of PLA at different crystallization conditions are explored.

2. Experimental

2.1. Materials and nanocomposite preparation

Polylactide (4042D) used in this study was a commercial product of NatureWorks (USA). Its L/D is about 96/4. The linear low density polyethylene (LLDPE) used was also a commercial grade (LL 4004EL) supplied by ExxonMobile Chemicals (USA), having a melt flow index of 3.6 g/10 min (190 °C, 2.16 kg). The Elvaloy® PTW (EBAGMA) which is a terpolymer of ethylene, butylacrylate (BA) and glycidylmethacrylate (GMA) with MFI of 12 g/10 min (190 °C, 2.16 kg) supplied by DuPont (USA) used as a reactive compatibilizer. Two different commercial nanoclays (Southern Clay Products, Inc.), Cloisite®30B (30B), MMT-Na+ modified with bis-(2-hydroxyethyl) methyl tallowalkyl ammonium cations and Cloisite 15A (15A), MMT-Na+ modified with dimethyl, dehydrogenated tallow, quaternary ammonium cations were used. Before mixing, all the polymers and the nanoclays were dried in a vacuum oven at 50 °C for 24 h.

A co-rotating twin-extruder (ZSK 30) equipped with gravimetric feeders and a strand pelletizer, were employed to compound the hybrids. A screw speed of 150 rpm and a feed rate of 10 kg/h were used for all runs. The extrusion temperature profile was set from 160 °C to 190 °C from hopper to die. The blend and nanocomposite pellets were then dried in a vacuum oven at 50 °C for 24 h prior to characterization and testing. In all hybrid samples the PLA/LLDPE and LLDPE/PLA ratios were 75/25 (w/w). The compatibilized blend and nanocomposites had about 5 wt% compatibilizer. The nanoclay loading in each nanocomposite samples was about 3, 4.5 and 6 wt% of the total mixture. The nanoclay and its type are indicated by the number and letter in the sample name (e.g., PLA/3%30B contains 3 wt% Cloisite 30B).

2.2. Characterization

Wide angle x-ray scattering (WAXS) analyses were performed on specimens with XRD 3003 (Seifert-FPM Freiberg/Sa) using Cu Kα X-ray source. The continuous scanning angle range used in this study was from 10° to 40° at 40 kV and 30 mA. The scanning rate was 1°/min with a step size of 0.05°.

The dispersion of nanoclay platelets in blend was studied by means of transmission electron microscopy (TEM). The samples were cryo-ultramicrotomed from extruded bars in thin section (approximately 60 nm thick) at −120 °C with a diamond knife. The sections were observed by means of a Carl Zeiss LIBRA® 200 CS-STEM, using an accelerated voltage of 200 kV.

Scanning electron microscopy (SEM) was used to characterize the morphology of the blends and nanocomposites. An extruded polymer strand was immersed in liquid nitrogen for some time and a brittle fracture was performed. All specimens after proper drying were sputter coated with 3 nm Pt prior to examination and observed under a NEON 40 EsB (Carl Zeiss, Oberkochen, Germany).

A TA-Instrument Q1000 DSC was used to study the thermal properties of the specimens. A sample of about 5 mg was scanned in a cycle of heating–cooling–heating from −80 to 180 °C at 10 K/min and 2 K/min in standard mode. The samples were held at 180 °C for 0.5 min to erase the thermal history. The glass transition temperature (T_g), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), melting temperature (T_m), crystallization enthalpy (ΔH_c), cold crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m) were determined from cooling and second heating scans. The degree of crystallinity (X_c) of samples was evaluated using the following equation:

$$X_c = \frac{\Delta H}{\Delta H_m^0 \cdot (1 - (\%\text{wt filler}/100))} \cdot 100 \tag{1}$$

where $\Delta H = \Delta H_c$ (for cooling curves, as ΔH_c is the crystallization enthalpy of the sample) or $\Delta H = \Delta H_m - \Delta H_{cc}$ (for second heating curves, as ΔH_m is the melting enthalpy of the sample, ΔH_{cc} is the cold crystallization enthalpy of the sample), $\Delta H°_m$ is the melting enthalpy of the 100% crystalline polymer matrix (93.0 J/g for PLA and 277 J/g for LLDPE [25]) and %wt filler is the total weight percentage of nanoclay and blend component [22].

3. Results and discussion

3.1. Morphology

The crystalline structures of neat nanoclays, blend components, nanocomposites and blend nanocomposites of PLA were characterized by WAXS and the results are shown in Fig. 1. The X-ray diffraction of LLDPE exhibits two strong diffraction peaks of (1 1 0)/(2 0 0) planes at $2\theta = 21.5°$ and 24° indicating the presence of crystallites. These are typical peaks related to the crystallographic planes of the orthorhombic form of polyethylene. The nature of Elvaloy diffractogram indicates that it is amorphous, with halo and two shoulders corresponding to the (1 1 0) and (2 0 0) planes, suggesting that short ethylene sequences in the terpolymer crystallize in the orthorhombic form, which is in accordance with that reported in the literature [26]. In PLA, no significant peak is observed, indicating an amorphous structure for this polymer. The WAXS pattern of 30B is characterized by the presence of four diffraction peaks at $2\theta = 19°$, 19.8°, 34.8° and 38.5°. Similar to the 30B, the WAXS pattern of the 15A shows two diffractions at $2\theta = 19.8°$ (0 2 0) and at 34.8°. As it can be seen from Fig. 1, the amorphous structure of the PLA matrix is not affected by the presence of nanoclays since no additional diffraction peaks related to PLA crystallization are seen for clay-filled PLA. For both systems only the (0 2 0) diffraction of nanoclays at 19.8° can be detected, indicating