Polymer 54 (2013) 3417–3425

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Crystallization behavior of poly(lactic acid)/microfibrillated cellulose composite

Yanan Song [a], Kohji Tashiro [b], Duigong Xu [a], Jun Liu [a], Yuezhen Bin [a,*]

[a] Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116023, China
[b] Department of Future Industry-Oriented Basic Science and Materials, Graduate School of Engineering, Toyota Technological Institute, Hisakata, Tempaku, Nagoya 468-8577, Japan

ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form
18 March 2013
Accepted 22 April 2013
Available online 1 May 2013

Keywords:
MFC
PLA
Crystallization

ABSTRACT

The effects of fillers on the crystal formation and crystalline structure of poly(lactic acid) (PLA) are unclear. In this study microfibrillated cellulose (MFC) was used as filler to compound with PLA and the crystallization behavior of PLA/MFC composites was investigated. The crystallization process of PLA/MFC composites was observed by wide angle X-ray diffraction (WAXD) and differential scanning calorimeter (DSC) synchronously to investigate the effect of MFC on the formation of crystal and evolvement of crystalline structure of PLA. Results showed that MFC enhanced the crystallization rate drastically, but had no much influence on the crystal form of PLA when isothermally crystallized at different temperature. However, different crystal forms of PLA were obtained respectively from the pure PLA and PLA/MFC composites during the same cooling process. Detailed analysis indicated that the primary cause for the phenomenon was the enhancement of the crystallization temperature of PLA due to the addition of MFC.

1. Introduction

PLA has been highlighted recently because of its excellent mechanical properties and availability from renewable plant resources [1]. Although it has been widely used in industrial packaging as well as in the production of biocompatible/bioabsorbable medical devices, it has many drawbacks, such as brittleness, slow crystallization and poor heat resistance [2]. The objective of this work is to improve the strength and crystallization rate of PLA by compounding with one kind of fibrillar filler, and study the effect of filler on the crystallization behavior of PLA, especially the evolvement of crystalline structure during thermal cycles.

In recent years, various inorganic fillers and polymers, e.g., the talcum powder, clay, cellulose fibers, poly(styrene-b-methyl methacrylate-b-glycidyl methacrylate), PLLA/PDLA stereocomplex and so on were used to improve the mechanical and crystallization properties of PLA [3–10]. Comparing with the above-mentioned fillers, plenty works focused on the application of micro- or nano-scale cellulose materials, such as the microfibrillated cellulose (MFC), microcrystalline cellulose (MCC) and cellulose nanocrystals (CNC) because of their potential both on reinforcing and crystallization accelerating for PLA [11,12]. MFC, also named cellulose nanofiber, is a new kind of expanded high-volume cellulose fiber with 10–40 nm in diameter and lengths varying from one to several micrometers [13]. It has merits of biodegradability, high strength and modulus, low thermal expansion, and higher aspect ratio than CNC and MCC. As potential reinforcement of polymer it has attracted much attention [14–16]. Studies indicated that MFC could not only improve the rigidity of PLA at high temperatures, but also deliver faster crystallization time [17–19].

The physical and thermal properties are closely related to the crystalline structure of polymer [20]. Materials with preferable properties were obtained via adjusting the crystalline structure or morphology by stretching, thermal treatment and introducing additions [21–23]. Effects of additions on the crystalline structure are fundamental importance for the properties of PLA based composites. As known, PLA is a polymer with multiple crystal forms. Three different crystalline conformations (α, β, γ) of PLA have been identified upon changing the preparation conditions. The most common α form can be developed from the cold or melt crystallization above 120 °C [24]. The β crystal was produced by stretching the α form at high drawing ratio and high temperature [25]. The γ form was obtained by epitaxial growth on the hexamethylbenzene substrate [26]. Recently, a new disorder crystal form, named α′ form was proposed for the PLA sample crystallized below 120 °C [27]. The complex crystallization and melting behavior, the difference between α and α′ form crystal, and the transition process from α′ to α form crystal of PLA have been widely studied in the last several years [27–34]. PLA showed a clear deviation from the usual bell-

* Corresponding author. Tel.: +86 411 84986093.
E-mail addresses: binyz@dlut.edu.cn, binyuezhen2007@yahoo.com.cn (Y. Bin).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.04.054

shaped curve of polymer crystal growth, and a fastest crystallization rate in the region of 100–120 °C [27]. Thus PLA is usually molded at 100–120 °C in the industrial melt processing. However, a mixture of α′ and α will form in this temperature region indicating that the PLA α′ form crystal exists widely in many PLA-based products [28,31]. Effect of additions on the crystal formation of PLA need be studied in detail.

However, there were few literatures reported the effect of additions on the crystal form of PLA until now. The nucleating efficiency of MFC has not been studied in detail as well. In this study, MFC was used as nucleation agent to compound with PLA by solvent evaporating method. The morphology and isothermal crystallization behaviors of composites were investigated by polarized optical microscope (POM) and DSC. The WAXD-DSC simultaneous measurement was used in this study to detect the phase transition and crystallization of PLA and PLA/MFC composite in time during the heating and cooling process. Results showed that the crystallization rate of PLA was improved drastically by addition of MFC. MFC had no much influence on the crystal form of PLA under isothermally crystallization but affected it during the cooling process. Analysis indicated that the enhancing of the crystallization temperature of PLA was the primary cause.

2. Experimental section

2.1. Materials

PLA pellets (4032D) comprised 98% L-lactide were purchased from Natureworks (America). Its weight-average molecular weight (*M*w) is 207 kg mol^{-1} and the polydispersity is 1.73. MFC, trade name KY-100G, was provided by DAICEL chemical industries, Ltd., Japan. It consists of 10 wt% fiber slurry and 90 wt% water. Acetone and dichloromethane were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) without further purification.

2.2. Preparation of PLA/MFC composites

MFC is difficult to be directly dispersed in the hydrophobic polymer because of the strong hydrogen-bonding interaction between the cellulose fibers and water which containing in the slurry. Therefore, a solvent exchange method was firstly used to remove the water. Strong stirring and ultrasonic treating were used to destroy the hydrogen-bonding interaction between fibers to promote their dispersion. The flowchart of process was shown in Fig. 1. Firstly the MFC slurry was dispersed in acetone, stirred and ultrasonic treated for 2 h to extract the water in the slurry. And then the suspension was filtrated using a Buchner funnel. The above process was repeated for 4 times to remove the water completely. After that, the MFC slurry was dispersed in dichloromethane, stirred and ultrasonic treated for 2 h. PLA pellets were added into the suspension and stirred until fully dissolved. The ratio of MFC aqueous suspension (wt)/acetone (v) was 1/40, and the ratio of PLA (wt)/dichloromethane (v) was 1/10. Later the mixture was poured into a Teflon box and dried more than 48 h in a fume hood at ambient temperature. At last the obtained compound sheet was hot-pressed at 180 °C under a pressure of 5 MPa for 3 min. The composite films with 1 mm thickness were cut into different shapes for measurement. The PLA/MFC composite films containing 1 wt%, 3 wt%, 5 wt%, 10 wt% and 20 wt% were named C-1, C-3, C-5, C-10 and C-20 respectively.

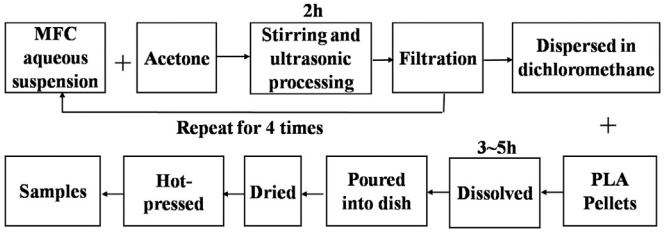

Fig. 1. Flowchart of the PLA/MFC composites' preparation.

2.3. Optical observation

MFC dispersed in water and the composite films with a thickness about 100 μm were analyzed by a Nikon OPTIPHOT2-POL polarized optical microscope.

The spherulitic morphology of the PLA and PLA/MFC composite was investigated using an Olympus (Tokyo, Japan) polarized optical microscope (BX50). The photos were taken after the sample isothermally crystallized at 120 °C for 60 min.

2.4. DSC measurement

The melting and isothermal crystallization behaviors of PLA and PLA/MFC composites were measured by using a differential scanning calorimeter (TA DSC Q1000) under a nitrogen gas atmosphere.

For the melting behaviors, a sample was firstly heated from −20 °C to 220 °C at a rate of 10 °C/min and held for 2 min at 220 °C to erase the thermal history. Then cooled the sample at the same speed to −20 °C and held for another 2 min. Finally, the sample was scanned again to 220 °C.

The degree of crystallinity (χ) was calculated using the equation presented below.

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{f \cdot \Delta H_m^0} \times 100\% \quad (1)$$

where f is the weight fraction of PLA in the composite; ΔH_m is the enthalpy of melting; ΔH_{cc} is the crystallization enthalpy during the DSC heating scan, and ΔH_m^0 is the enthalpy of melting of 100% pure PLA taken as 93.7J/g [35].

For the isothermal crystallization, a sample was firstly heated to 220 °C at a rate of 10 °C/min and kept for 2 min to eliminate its thermal history. Then, it was rapidly cooled to the desired isothermal crystallization temperature, and crystallized for 60 min. The heat evolved during cold crystallization was recorded as a function of time. The starting time for the crystallization was taken as the time at which the sample temperature reached the programmed crystallization temperature value. The weight fraction of the material crystallized after time t (X_t) was evaluated from the ratio of the crystallization area at time t to the total area. When the isothermal crystallization was finished completely, the samples were heated to 220 °C at a rate of 10 °C/min to estimate melting behavior.

2.5. WAXD-DSC simultaneous measurements

The X-ray diffraction-DSC system used in this study consisted of a goniometer of Rigaku RINT/TTR-III and a DSC unit based on Rigaku/Thermo Plus DSC-II. The X-ray beam used was Cu Kα radiation. The X-ray diffraction patterns were measured in the 2θ range of 5–35° at a scanning rate of 20°/min, and the DSC heating rate was 2 °C/min during the heating and cooling process.

3. Results and discussion

3.1. Dispersion of MFC

Optical micrographs of MFC and PLA/MFC composites as shown in Fig. 2 were taken to observe the dispersion of MFC. MFC