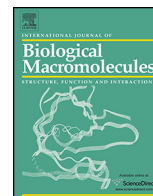




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Effect of annealing on the thermal properties of poly (lactic acid)/starch blends

Shanshan Lv, Jiyu Gu, Jun Cao, Haiyan Tan, Yanhua Zhang*

College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, PR China

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ABSTRACT

A comparative study of the thermal behavior of PLA/starch blends annealed at different temperatures has been conducted. Annealing was found to be beneficial to weaken and even eliminate the enthalpy relaxation near T_g . The degree of crystallinity was evaluated by means of DSC, and the results showed that the crystallinity of the samples increased as the annealing temperatures were increased. It was observed that, during the annealing process, the disorder α (α') crystal modification tended to transform into the order α crystal modification. All of the PLA/starch blends showed a double melting behavior. With the increase of annealing temperatures, the lower T_{m1} increased, while the T_{m2} showed no evident change. The XRD patterns also showed that annealing was beneficial to the samples to form higher crystallinity. The TGA results indicated that the annealed samples did not show any higher thermal stability than the virgin samples. The activation energy calculated by the Flynn–Wall–Ozawa method at lower conversion degrees confirmed that the annealing slightly slowed the degradation. The activation energy did not show any dependence on the conversion degree, which indicated that there existed a complex degradation process of the PLA/starch blends. The average activation energy did not show obvious differences, indicating that the annealing treatment had little influence on the degradation activation energy.

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1. Introduction

Poly (lactic acid) (PLA) is a linear aliphatic thermoplastic polyester. It has numerous interesting properties, including renewability, biodegradability and low environmental impact [1]. As a biodegradable material, it has a wide range of applications in packaging, biomedical and agriculture fields [2]. Considering the aforementioned advantages of PLA, it is quite a good alternative to replace the traditional chemical petrol-based materials, such as polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC) and polystyrene (PS).

PLA is known to form three kinds of crystal modifications (α , β , and γ forms) [3]. The glass transition temperature (T_g) of PLA locates around 60 °C (higher than room temperature). Therefore, during the rapid cooling process of PLA from the melting state to room temperature or even lower, the molecular mobility slows down, the segments are frozen, and the material becomes a thermodynamically unstable glass. Then, from this non-equilibrium glassy state, the material system will tend to reach an equilibrium state through slow rearrangements, which are referred to

as the relaxation of the polymer chains or physical aging. As a consequence, an endothermic enthalpy relaxation peak near the T_g which appears during the heating process is characterized by DSC. When the PLA is quenched from melting to a low temperature (below T_g), the PLA is almost amorphous. In order to increase its crystallinity, annealing is utilized to enhance the segmental mobility and the molecular chains' rearrangement into a crystal lattice. Recently, a new crystal modification referred to as α' form (disorder α) has been proposed for the PLA samples crystallized below 120 °C, which is different from the order α form crystallized at higher temperatures (>120 °C) [4–6]. Therefore, different crystal modifications can be achieved through annealing at various temperatures (above and below 120 °C). Meanwhile, during the heating process at an appropriate rate, the unstable and disordered crystal phase tends to transform into a stable and ordered crystal form, and the different crystal forms appearing during this process will cause a multiple melting phenomenon for the PLA.

Although PLA has good mechanical performances, thermal stability and processability, the material melting is responsible for a certain degree of depolymerization during the material processing [7]. Indeed, due to its thermally unstable nature [8], small molecules formed and volatilized, such as extrusion, injection and compression molding during the processing, which thereby led to a lower thermal stability. According to Taubner [9], during

* Corresponding author. Tel.: +86 451 82191330; fax: +86 451 82191330.
E-mail address: zyhnefu@163.com (Y. Zhang).

thermal processing or under hydrolytic conditions, PLA degrades and has a rapid reduction of molecular weight that affects the final properties of the material, such as its mechanical strength. Recently, it was reported that the molecular weight reduction of polyesters is primarily caused by the hydrolysis of the ester linkage, which randomly takes place in the polymer [10]. It is well known that the thermal degradation mechanisms of PLA are complex. The mechanisms include hydrolysis, intermolecular transesterification, intramolecular transesterification (depolymerization) and oxidative degradation [8,11–14].

It is considered that the sensitivity to temperature and decomposition of compounding processes are limitations in the use of polymers in engineering fields [15]. Such factors reduce the mechanical properties and thermal stability. Therefore, knowledge of the thermal behavior of mixtures is of great importance from the point of view of processing. In this sense, many research studies have been devoted to the analysis of the thermal properties [10,16–20]. Of course, the thermal degradation also occurs in the PLA/starch blends. In particular, during the preparation process of PLA/starch blends extruded by twin-screw extruder, except for the aforementioned thermal degradation mechanism, the polymer chains undergo a strong shear force which leads to the molecular chains fragmenting into shorter chains that emerge with lower thermal stability.

The aim of this work is to test the thermal changes of PLA/starch blends that suffer during annealing by thermal analysis techniques. The thermal behavior was discussed on the basis of differential scanning calorimetric (DSC), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA) results. That is, the effects of annealing on crystal and melting behavior of PLA/starch blends were investigated by using DSC and XRD, and the thermal stability properties were characterized by using TGA.

2. Experiments

2.1. Materials and sample preparation

PLA, granular, was purchased from Ningbo Huanqiu Plastic Products Co., Ltd. (Ningbo, Zhejiang, China). Corn starch, industrial grade, was obtained from Dacheng Corn Development Co., Ltd. (Changchun, Jilin, China). All the raw materials were dried at 50 °C for 24 h under the vacuum oven in order to eliminate the moisture before use.

The PLA/starch blends were made by extrusion molding in which the raw materials were first processed using a co-rotating twin-screw extruder, and then fed into a single-screw extruder in order to obtain the rectangular samples. Then the samples were placed for one week at room temperature in 60% RH (relative humidity). The samples used for testing were annealed on the hot-stage at various desired temperatures (defined as T_A in this paper), which were 50 °C, 60 °C, 80 °C, 100 °C and 120 °C, respectively. For the sake of convenience, the samples annealed at various temperatures were respectively referred to as AN50, AN60, AN80, AN100 and AN120.

2.2. Differential scanning calorimetric analysis (DSC)

A differential scanning calorimeter of NETZSCH DSC 204 was used for the calorimetric measurements. The samples (3–5 mg) were sealed in the aluminum pans, DSC scans were performed at a temperature range between 25 °C and 200 °C, and run at a heating rate of 10 °C/min with a nitrogen gas purge set at 50 mL/min. The results were analyzed using the NETZSCH Instruments Proteus Analysis software. The glass transition temperature (T_g) was taken at the midpoint of the temperature range over which the

glass transition takes place between the onset and end of the inflectional tangent. The melting (T_m) and cold crystallization (T_c) temperatures were also recorded following standard procedures.

For the samples crystallized during the DSC measurements, the degree of crystallinity (X_c) was calculated as follows:

$$X_c = \frac{1}{w_f} \left[\frac{\Delta H_m - \Delta H_c}{\Delta H_{m0}} \right] \quad (1)$$

In this equation, ΔH_m is the enthalpy for melting, ΔH_c is the enthalpy for cold crystallization, ΔH_{m0} is the melting enthalpy of the 100% crystalline PLA, taken as 93 J/g [21,22] and w_f is the weight fraction of PLA in the composites (in this paper, it is taken as 70%).

2.3. X-ray diffraction (XRD)

The X-ray diffraction data were determined from the annealed sample surfaces, using a X-ray diffraction equipment (Rigaku D/max220, Japan). The generator was set up at 40 kV and 30 mA, using Cu- K_α radiation ($\lambda = 0.1542$ nm) as the X-ray source, together with a Ni-filter to extract the K_α radiation. The data were collected over a range of scattering angles (2θ) of 5°–40°. All the measurements were carried out at room temperature under atmospheric pressure.

2.4. Thermo gravimetric analysis (TGA)

TGA data were obtained on the NETZSCH thermo gravimetric analyzer, model TG 209 F1. Samples of approximately 10 mg were heated from room temperature to 600 °C at various heating rates (5, 10, 15, 20 °C/min), under a dry nitrogen gas flow rate of 40 mL/min.

3. Results and discussion

3.1. DSC analysis of PLA/starch blends

After extruding from melting stage, the PLA/starch blends were quickly quenched to room temperature, so that the polymer chains were frozen and the segmental mobility was drastically reduced. Even when stored below the T_g , as a non-equilibrium state, the glassy polymers undergo a state closer to the equilibrium state due to the interactions of the polymer chains, which is usually accompanied by changes in physical properties [23]. Annealing can also promote the rearrangement of the molecular chains to a thermodynamically stable state. In this section, the annealing treatment was used to analyze the molecular rearrangement, crystallization and melting phenomena of PLA/starch blends. DSC heating curves for PLA/starch samples annealed at various temperatures (close and above T_g) for 4 h are shown in Fig. 1.

Unlike in the usual DSC heating thermogram, sharp endothermic peaks were observed close to T_g , rather than a step-like change. This behavior is attributed to physical aging [24,25] or stress relaxation [26]. With the aging of the materials below T_g , the segmental rearrangement causes volume relaxation and therefore a reduction of the free volume. During this process, the relaxation of the polymer chains leads to the densification of the amorphous phase, which reflects on the DSC heating curves as an endothermic enthalpy relaxation peak near the T_g . With the increase of T_A , the enthalpy of relaxation is reduced, and even disappears when the T_A reaches 80 °C. This can be explained as follows: when the samples were annealed at a certain temperature, the segmental mobility may cause a reduction of the free volume, therefore less energy was needed for the segmental recovery, which resulted in a smaller enthalpy. When the T_A is high enough, the movement of the molecular chains will become easier than the previously constrained motion beforehand; the chains diffuse at the growth front

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