Construction and Building Materials 144 (2017) 525–531

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effect of glycerol introduced into PLA based composites on the UV weathering behavior

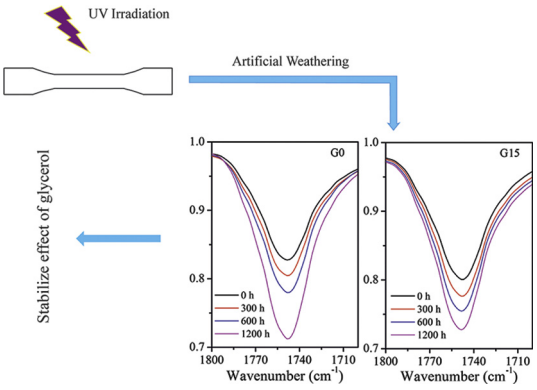
Shanshan Lv, Xiaojing Liu, Jiyou Gu *, Yang Jiang, Haiyan Tan, Yanhua Zhang *

Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, PR China

HIGHLIGHTS

- The crystal structure of starch/wood flour/PLA composite was damaged after UV weathering.
- Carboxylic acid was formed on the surface of composite when underwent UV weathering.
- Glycerol had a stabilize effect on the UV durability of the composite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 October 2016
Received in revised form 18 February 2017
Accepted 27 March 2017
Available online 5 April 2017

Keywords:
Poly (lactic acid)
UV weathering
Degradation behavior

ABSTRACT

Effect of accelerated weathering time and glycerol on the photodegradation behavior of starch/wood flour/PLA composites was studied. The decreased intensity of diffraction peaks characterized by XRD indicated that the crystal structure was damaged. The chemical structure changes characterized by FTIR showed the formation of carboxylic acid. The decreased extent of the C=O absorbance intensity of the composite with 15% glycerol proved that glycerol had a stabilize effect on the UV durability of the composites. After weathering, the maximum decomposition temperature decreased prominently due to the chain cleavage. With the prolonged weathering time, the tensile and flexural strengths decreased gradually.

1. Introduction

The massive increase in the accumulation of non-biodegradable synthetic plastics has caused serious environmental pollution [1]. Therefore, most researchers have focused their attention on the study of renewable and biodegradable polymer plastic. Among the biodegradable polymers, Poly (lactic acid) (PLA) is one of the most promising plastics to replace the non-biodegradable plastics due to its biodegradable and renewable properties [2].

PLA is an aliphatic biodegradable polyester, which is derived from renewable resources such as cornstarch [3], and it can be completely degraded by microorganisms under suitable conditions [4]. However, the cost of PLA is still too expensive to be used widely in daily life [5]. To overcome this drawback, blending PLA with other polymers or fillers is an effective approach. Another drawback of PLA is its slow degradation rate. In order to accelerate

* Corresponding authors.
E-mail addresses: dldgujy@163.com (J. Gu), zhangyanhua@nefu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.conbuildmat.2017.03.209
0950-0618/

the degradation of PLA, some natural polymers, such as starch and wood flour, can be blended with PLA, due to their complete and fast degradation rate in natural environment.

Polymer degradation is important not only in terms of the durability within its usability period, but also in terms of the post-consumption period when it dominates the possibility of recycling or utilization of the material [6]. As we all know, the polymers may degrade when exposed to UV-light with the presence of air, which will affect its service life [7]. Indeed, the material will suffer photodegradation during its service life for outdoor applications [8]. UV irradiation may induce obvious physical-chemical changes in polymers involving a reduction of molecular weight and a decrease in mechanical performance [9].

PLA is a potential candidate to be used widely in future life. Hence, the research of its weathering performance is important. PLA is sensitivity to UV irradiation, moisture and temperature (the influence factors of natural weathering) [10]. In recent years, some studies have been performed on the UV weathering performance of PLA [3,6,11,12] and PLA based composites [5,10,13–16]. Two photodegradation mechanisms have been reported. One of the mechanisms is Norrish II-type cleavage which can lead to a breakage of the backbone C—O bond [17–19]. As a result, the new groups of C=C and carboxylic acid are formed, resulting in a decrease in molecular weight [18]. The other mechanism indicates that the reaction is random scission of main chains, its degradation products are carboxylic acid and diketone groups [20].

As far, the research on UV ageing degradation of PLA and its composites is widely, and the influence factors of the UV ageing are various. The aim of this study is to analyze the influence of glycerol on the weathering behavior of starch/wood flour/PLA composites by comparing their mechanical properties, thermal behavior, crystal properties and surface performance. Based on the degradation behavior, the degradation regular can be evaluated, which may provide a theoretic guide for the estimation of the service life of PLA based materials.

2. Experimental

2.1. Materials

The PLA (306DX), purchased from Ningbo Huanqiu Plastic Products Co., Ltd. (Ningbo, Zhejiang, China), is a semi-crystalline extrusion material. The weight average molecular weight of PLA was about 1.0×10^5–1.2×10^5, the melting index was 16–19 g 10 min^{-1}, and the density of PLA was 1.2 ± 0.05 g cm^{-3}. Corn starch, industrial grade, was obtained from Dacheng Corn Development Co., Ltd. (Changchun, Jilin, China). Wood flour (WF) with particle sizes between 80 and 100 meshes was supplied by Linyi Fengming wood flour factory (Shandong, China).

2.2. Processing procedure

All of the raw materials were dried at 50 °C for 8 h prior to use in the vacuum oven in order to eliminate the moisture. The wood flour and starch with the ratio of 3/7 (w/w) were well mixed for 15 min using a high-speed mixer. Then, 15% glycerol and PLA were added to the mixture and the combination was evenly blended. The final mixture was fed into a co-rotating twin-screw (L/D ratio of 40, Nanjing Giant SHJ-20) set at 100 rpm to obtain the granules. The temperatures at each zone were set at 135–150-170–170-135 °C (from the feeder zone to the die). Afterwards, the standard specimens according to ASTM D638-10 were processed by means of injection molding (JPH180C, Guangdong ONLY Machinery Co., Ltd.). The temperature profile of injection molding was the following: 180–180-170–170 °C. The injection pressure was kept at 65 MPa and mold temperature was kept at 30 °C. In this paper, the composites with and without 15% glycerol were defined as G0 and G15.

2.3. Accelerated weathering

In order to investigate the weathering behavior of starch/wood flour/PLA composites, a UV ageing chamber (2 N-P, Maijie, Shanghai) was used. The weathering conditions were in accordance with cycle 1 of the ASTM G154-06. Fluorescent lamps (UVA-340) with 0.89 W/m^2/nm irradiance (at 340 nm) were used with cycles of 8 h UV exposure irradiation followed by a condensation period of 4 h. The accelerated weathering was performed for three periods: 300 h, 600 h, and 1200 h. After each period, the samples were taken out from the chamber to analyze the performance.

2.4. Performance analysis of residual samples

2.4.1. X-ray diffraction (XRD)

The X-ray diffraction data were analyzed by using a X-ray diffraction equipment (Rigaku D/max220, Japan). The generator was set up at 32 kV and 30 mA, using Cu-Kα radiation ($\lambda = 0.1542$ nm) as the X-ray source, together with a Ni-filter to extract the Kα radiation. Diffraction patterns were collected over a range of scattering angles (2θ) of 5°–40°. All the measurements were carried out at room temperature under atmospheric pressure.

2.4.2. Fourier transform infrared (FTIR)

A surface analysis by attenuated total reflectance (ATR) infrared spectroscopy was carried out using a Bruker Tensor II instrument. Scans were run at a resolution of 4 cm^{-1}. For each sample, 32 scans were recorded in the range of 400 cm^{-1}–4000 cm^{-1}.

2.4.3. Differential scanning calorimetry (DSC)

Thermal analysis was performed using a TA instruments Q20 under nitrogen atmosphere. The samples (5–6 mg) were heated from room temperature to 200 °C at 10 °C/min with 50 mL/min nitrogen flow.

2.4.4. Thermo gravimetric analysis (TGA)

The thermal stability of weathered starch/wood flour/PLA composites was studied using a TG 209 F1 (NETZSCH, Germany). Samples of approximately 5–10 mg were heated from room temperature to 600 °C with 10 °C/min of heating rate and 50 mL/min of nitrogen gas flow.

2.4.5. Mechanical properties

The mechanical strengths of composites before and after weathering were performed at room temperature using a CMT-5504 Universal Testing Machine (Shenzhen SANS Test Machine Co., Ltd. China). The tensile strength was tested according to the ASTM D638-10 method at a crosshead speed of 10 mm/min. The flexural strength was measured according to the ASTM D790-10 at a crosshead speed of 5 mm/min. A minimum of five specimens were tested to obtain an average value.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of the composites before and after accelerated weathering. Before weathering, both the composites showed a diffraction peak at $2\theta = 16.7°$ which corresponded to (110)/(200) plane of α phase for PLA [21]. Unlike other literature, after weathering, the intensity at 16.7° decreased while