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Characterization of surface chemistry and crystallization behavior of polypropylene composites reinforced with wood flour, cellulose, and lignin during accelerated weathering

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ABSTRACT

In this study, six groups of polypropylene composites reinforced with wood flour (WF), cellulose, and lignin at different loading levels were exposed in a QUV accelerated weathering tester for a total duration of 960 h. The changes in surface morphology, chemistry, and thermal properties of weathered samples were characterized by atomic force microscope (AFM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and differential scanning calorimetric (DSC), respectively. The flexural properties of all samples were tested after different durations of weathering. The results showed that: (1) the surface roughness of all samples increased after weathering; (2) composites containing lignin showed less loss of flexural strength and modulus and less roughness on weathered surface compared with lignin-free composites, indicating the functions of stabilization and antioxidation of lignin; (3) the crystallinity of PP increased in all weathered samples due to chain scissions and recrystallization; (4) ATR-FTIR and XPS analyses demonstrated in detail that significant changes occurred in surface chemistry, accompanied by the photodegradation and photo-oxidation of lignin and cellulose with prolonged weathering time.

1. Introduction

In recent years, with the increasing concerns about decreasing forest area and diminishing petroleum-based resources, the use of lignocellulosic fibers as reinforcement in thermoplastic resin matrix are becoming more and more prevalent [1,2]. Compared to inorganic fillers, lignocellulosic fibers take advantages of biodegradability, wide availability, low density, competitive specific mechanical properties, and relatively low cost [3]. The lignocellulosic fibers that have been used in polyolefins include wood fiber (WF), cellulose fiber, flax, jute, rice husk, saw dust, wheat straw, coconut fiber, kenaf, cotton, basalt, bamboo fiber, banana fiber, palm fiber, and so on [4,5].

In terms of structure, lignocellulosic fibers mainly consist of three primary polymers, namely lignin, cellulose, and hemicellulose [6]. Lignin is an amorphous, highly complex polymer that made up of phenyl propane units [1]. Cellulose is a homopolymer consisting of repeating units of β-D-glucose. Hemicelluloses comprise a group of polysaccharides and lack the crystalline structures compared to cellulose.

Although lignocellulose-based composites are promoted as low-maintenance and high-durability products, their degradation in outdoor environments is still a concern [7]. Lignocellulosic fibers are reported as one group of materials with a well-known reputation for susceptibility to degradation, especially when exposed to combined conditions of ultraviolet (UV) light, heavy impacts, strong chemicals, and cyclic wetting. Since WF is one of the most common lignocellulosic materials, the durability of wood–plastic composites (WPCs) has been widely studied [8–14]. Fabiyi et al. [10] observed the visual appearance and chemical changes in WPCs during weathering, suggesting that longer exposure time increased the degree of color change, carbonyl concentrations, and wood loss on weathered surfaces. The discoloration of WPCs was mainly because of the photodegradation of lignin and wood extractives during weathering [11,12]. Other studies reported that color change is highly related with wood species used in WPCs, resulting from their different lignin content [13]. Among all components of wood, lignin absorbs 80–95% of the total amount of UV light absorbed by wood. The groups of α-carbonyl, biphenyl, and ring-conjugated double bond structures in lignin can react with oxygen to form

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Table 1
Compositions and labeling of the studied formulations.

Labels	WF (wt%)	Cellulose (wt%)	Lignin (wt%)	PP (wt%)
Control (C)	40	0	0	60
PP	0	0	0	100
CL	0	40	0	60
L1	0	30	10	60
L2	0	20	20	60
L3	0	10	30	60

chromophoric groups such as carbonyl and carboxyl groups, which lead to discoloration of WPCs [14].

Except for WF, the chemical compositions of other kinds of lignocellulosic materials are also important factors that affect the aging properties of the reinforced composites. In our previous studies [15], WF, lignin, and cellulose were chosen to blend with polypropylene (PP) matrix at different loading levels, and then the composites were exposed in an accelerated UV weathering tester. Previous work revealed that the discoloration of composites was accelerated by lignin, especially at high content [15,16]. However, composites containing lignin showed less loss of flexural strength and modulus, and less cracks on weathered surface, owing to the antioxidation effect of lignin [17]. On the contrary, cellulose-based composites exhibited better color stability but more significant deterioration in flexural properties after weathering [15].

Apart from the effects of weathering on the wood component in WPCs, polymer matrix also undergoes a series of changes during weathering such as chain scissions and recrystallization [7]. Fabiyi et al. [18,19] reported that longer exposure time resulted in an increase of the crystallinity of polypropylene (PP) and high-density polyethylene (HDPE) in WPCs. Changes in the degree of crystallinity have been shown to have pronounced effects on the mechanical behavior of WPCs [18].

Despite the extensive studies on the weathering of WF-based polymer composites, little work has been done to provide insights into the effects of weathering on PP composites reinforced with cellulose and lignin, especially their surface chemistry changes during weathering. In this study, we determined the surface characteristics of the composites by atomic force microscope (AFM), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Moreover, in order to have a better understanding of the changes in composites mechanical properties, the behavior of matrix crystallinity during weathering was monitored by differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Materials

Wood flour (WF) of poplar (*Populus tomentasa* Carr.) with size of 60–80 mesh was kindly donated by Xingda Wood Flour Company, Gaocheng, China. Alkali lignin was purchased from Shan Feng Chemical Co., Ltd., Changzhou, China. Cellulose with an average fiber length of 300 μm was supplied by Ying Jia Industrial Development Co., Ltd., Shanghai, China. PP powder (K8303) with a density of 0.9 g/cm^3 was purchased from Beijing Yanshan Petrochemical Co. Ltd., China. It had a melting point around 165 °C and a melting flow index of 1.5 g/10 min at 230 °C.

2.2. Preparation of lignocellulosic flour/PP composites

According to different lignin contents in different plants (lignin content in wood: 20–30%, in gramineous plants: 15%) [20], WF, lignin, cellulose, and PP powder were weighted at specific ratios as described in Table 1. All the three lignocellulosic materials (WF, lignin, and cellulose) were oven-dried at 103 ± 2 °C until the weight was constant. They were mixed in a high-speed blender at a mixing speed of 2900 rpm for 4 min and then dried at 103 ± 2 °C for 2 h. After drying, the mixture was melt-blended in a co-rotating, twin-screw extruder (KESUN KS-20, Kunshan, China) to produce composite pellets. The corresponding temperatures in the extruder barrel were 165/170/175/180/175 °C from hopper to die zones and the screw speed was 180 rpm. The extrudates were cut into small particles about 5 mm and then dried again before being taken out for hand matting. A hot press (SYSMEN-II, made by Chinese Academy of Forestry) was used to produce the composites by compressing the mat at 180 °C with a pressure of 4 MPa for 6 min. After hot pressing, the formed mat was cooled down at room temperature in a cold press, following methods reported in our previous literature [12]. The dimension of WF/PP composites was 270 mm × 270 mm × 3 mm with a target density of 1.0 g/cm^3. After that, all the composites were cut into required dimensions for further tests.

2.3. Artificial weathering test

Composite samples were placed in a QUV accelerated weathering tester (QUV/Spray, Q-Lab Co., USA) according to ASTM G154 [21] for a total of 960 h. Each 12 h weathering cycle consisted of 8 h of UV exposure at 60 °C and 4 h condensation at 50 °C.

2.4. Atomic force microscope (AFM)

The surface morphologies of the samples before and after weathering were tested by a scanning probe microscope (Shimadzu SPM-9600, Japan). The scanned area for all samples was 2 μm × 2 μm and five different locations were measured on each sample. Sample roughness has been estimated on the base of 10-point height of irregularities (R_z parameter).

2.5. ATR-FTIR spectral measurements

The surface chemical changes in composites during accelerated weathering were monitored by an FT-IR spectrometer (BRUKER, Vertex 70v, Germany) equipped with an attenuated total reflection (ATR). Composite surfaces were put in contact with the ZnSe crystal at a 45° angle of incidence.

For the quantitative analysis, the spectra were normalized and the absorbance of the peak of interest was obtained. The concentrations of the carbonyl (C=O) and hydroxyl (OH) groups (degradation products) were estimated based on the Lambert–Beer Eq. (1) [10].

$$c = \frac{A}{2d_p \cdot \varepsilon} \tag{1}$$

where c is the molar concentration of the functional group (mol/L), A is the absorbance of the functional group band in the infrared spectrum, d_p is the ATR depth of penetration, and ε is the molar absorptivity (L/mol/cm). Values for the molar absorptivity ε used in this study were taken from the work reported by Fabiyi et al. [10] from the spectra of model carbonyl groups (1740 cm^{-1}) and hydroxyl groups (1635 cm^{-1}), which are 590 and 121 L/mol/cm, respectively.

2.6. X-ray photoelectron spectroscopy (XPS)

Small composites chips (10 mm × 10 mm of exposed surface) before and after 960 h weathering were prepared. The XPS measurements were performed on Escalab 250Xi (Thermo Scientific, USA). The base pressure in the analytical chamber was between 10^{-9} and 10^{-8} Torr with a pass energy of 29.35 eV and a take-off angle of 45°.