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Comparison on properties of lignocellulosic flour/polymer composites by using wood, cellulose, and lignin flours as fillers

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ABSTRACT

In this study, cellulose flour (CF) and lignin flour (LF) were separated from wood flour (WF) by nitric acid–ethanol method and ball-milling coupled with dioxane extraction method, respectively. The separated CF, LF, and the original WF were blend with two types of polymers, namely, polypropylene (PP) and poly (lactic acid) (PLA) to make composites. The physical, mechanical, and thermal properties of the thus-filled composites were tested. The results showed that: (1) both CF and LF had significant influence on physical, mechanical, and thermal properties of PP or PLA composites; (2) CF benefited to most mechanical properties of the composites, while LF reduced water uptake and improved thermal stability. WF was more hydrophilic and was easier to thermal degrade than CF and LF. However, the flexural modulus was high in WF groups; (3) for different polymer matrix, the interface bonding between WF components and polymer was different. The interaction between LF and PP was stronger, while it was more compatible for CF and PLA, which showed totally contrary influence on the crystallization behavior of PP and PLA.

1. Introduction

Lignocellulosic materials such as wood flour/fiber (WF) are attractive fillers because of their low cost, high specific strength, large availability, and renewability. The lignocellulosic fibers-based polymer composites have been widely applied for decks, railings, and automotive parts in recent years [1–3]. The main components of wood flour are cellulose, hemicelluloses, and lignin, which are known to present a very complex structure in WF cell wall [4]. Cellulose is a linear condensation polymer consisting of β(1-4) linked D-anhydroglucopyranose units. Hemicelluloses comprise a group of polysaccharides that remain associated with cellulose. Lignin is a complex polymer made up of phenyl propane unit. However, these components differ between species and may affect the intrinsic properties of wood–plastic composites (WPCs). For example, Fabiyi and Mcdonald [5] obtained that composites made of WF from hardwoods were more thermal stable than those made of softwoods, which was related to their different components.

The usual approach to study the effects of WF chemical components on properties of WPCs is to remove certain components from WF. Hemicelluloses are the most hydrophilic, amorphous, and unstable constituents in WF, which have negative effects on properties of WPCs. Therefore, various treatments to remove hemicelluloses from WF have been developed and used, including hot-water extraction [6–8], alkali treatment [9], enzyme modification [10], heat treatment [11], and steam explosion [12]. Lignin is the most hydrophobic constituent of WF. Owing to its cohesion and cross-linking structures, it has been synthesized to adhesives [13]. Therefore, some researchers used lignin as coupling agents to improve the interfacial adhesion between WF and polymer matrix, and thermal stabilities of the composites [14–16]. However, the impact properties of the resulting composites decreased due to the embrittlement of the composites. Besides, lignin is the most sensitive constituent among the main components of WF to ultraviolet rays, which can accelerate the weathering of WPCs, causing serious surface cracking and color fading [17]. Some researchers investigated the effects of delignified WF on properties of WPCs. According to their results, delignification of WF improved the mechanical characteristics [18], photodegradation resistance [19], and processability [20] of the resulting composites but reduced the water repellency [21]. Cellulose benefits mostly the mechanical strength of WF and the polymer composites [22]. However, due to the existence of numerous hydrophilic hydroxyl groups on cellulose surface, it displays two major limitations when used as reinforcing elements in composites, namely, the elevated moisture content and poor compatibility with hydrophobic polymers. These drawbacks lead to the increase in water uptake, hydro-expansion, and further cause fungi decay on the composites [23].

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As mentioned above, a lot of investigations have been performed on effects of WF components on properties of WPCs by removing one or two components of WF. However, few investigations have been done on using separated WF components as fillers and comparing the properties of thus-prepared composites with original WPCs. Several techniques can be used to separate CF and LF, but hemicelluloses are impossible to be completely separated at present. By using different methods, the structures of the resulting CF or LF are all different. CF can be separated by acid or alkali, but alkali causes changes in the natural crystal structure of CF [9]. In nitric acid–ethanol solution, most of lignin can be nitrified or oxidized, and then dissolved in ethanol, while hemicelluloses are hydrolyzed. Thus, this method is able to retain the natural crystal structure of CF. As for LF, the structure of milled lignin is considered to be the most approximate one to natural WF [24]. Bodîrlău et al. [25] separated CF and LF from WF and studied their effects on thermal properties of poly(vinyl chloride). However, their study was insufficient in providing other information such as the physical and mechanical properties. Meanwhile, they obtained LF by using sulfuric acid, which changed its original structures greatly. Besides, the influences of WF components on different polymer matrix have not been investigated yet. Thus, this study proposed to separate CF and LF from WF by nitric acid–ethanol method and ball-milling coupled with dioxane extraction method, respectively. And then, they were respectively blended with two types of polymers, namely, the traditional polymer PP and the biodegradable polymer PLA, to produce lignocellulosic flour/polymer composites. The separated components were characterized by FTIR and XRD analyses to ensure the natural structures that were closed to natural WF. The comparisons on physical, mechanical, and thermal properties of WF, CF, and LF filled composites were made to show their effects on two different main chain polymers (PP and PLA). Furthermore, the interaction between the WF components and polymers was investigated by SEM analysis.

2. Materials and methods

2.1. Materials

WF of poplar (*Populus tomentasa* Carr.) with mesh size of 40 to 60 was kindly donated by Xingda Wood Flour Company, Gaocheng, China. It has an average length of 1.5 mm and average diameter of 0.2 mm. PP (K8303; Sinopec Chemical Products Sales Company, China) with a density of 0.9 g/cm^3 was purchased from Beijing Yanshan Petrochemical Co. Ltd., China. It had a melt point around 165 °C and a melt flow index of 1.5 to 2.0 g/10 min at 230 °C. PLA (AI-1001) (L content) was obtained from Esun, Shenzhen Bright-China Industrial Co., Ltd., Guangzhou, China. It has a density around 1.25 g/cm^3 and a melt flow index about 10–20 g/10 min at 190 °C. The M_n of PLA was about 80,000 g/mol. The reagents used in this study were all bought from Tianjin Jinke Fine Chemical Institute, China.

2.2. Separation of WF components

Prior to separation, WF was extracted in a Soxhlet extractor with a mixture of 1:2 ethanol and toluene (v/v) for 6 h, followed by a second extraction with ethanol for 4 h to remove extractives. The extracted WF was dried in an oven at 103 ± 2 °C to reach a constant weight. The yield of the extracted WF was about 97%.

The CF was separated as follows: 5 g of extracted WF was placed in a 1000-mL beaker, in which 25 mL HNO_3 (68%) and 100 mL of ethanol were added. The mixture was refluxed under shaking in a water bath at 100 °C for 60 min. After that, samples were filtered using a G2 sand core funnel. The 60-min refluxing cycle was repeated 4 times. Finally, the sample was washed with hot water until reaching neutral pH and then washed with ethanol. The sample was dried at in an oven at 103 ± 2 °C until the weight was constant. The yield of the CF was about 40%.

The LF was separated as follows: extracted WF was emerged in toluene and subjected to 48 h of milling at 250 rpm using agate balls by frequency conversion dual planetary ball-mill equipment (Chunlong Instrument SHQM-2L, China). The milled WF was extracted with a mixture of 1,4-dioxane and water (v/v) at a ratio of 9:1. After filtration, the liquor was collected and dried in an oven at 35 ± 2 °C. The residue obtained was dissolved in a solution of acetic acid and water (9:1, v/v) and then precipitated with water. The precipitated residue was separated by centrifugation. The residue was then dissolved in 1,2-dicloromethane and ethanol (1:2, v/v) and precipitated with diethyl ether to obtain the purified LF. The sample was dried at in an oven at 35 ± 2 °C to reach a constant weight. The yield of LF was about 8%.

The visual images of WF, CF, and LF are shown in Fig. 1. Their particle size distribution was tested by laser scattering particle distribution analyzer (Mastersizer 2000, Malvern, UK). The results are listed in Table 1.

2.3. Preparation of lignocellulosic flour/polymer composites

The composites contained 50 wt% of WF, CF or LF and another 50 wt% PP or PLA. They were mixed in a high speed blender at about 2900 rpm for 4 min. The mixture was then dried at 103 ± 2 °C for 2 h. After drying, the mixture was extruded via a co-rotating twin-screw extruder (KESUN KS-20, Kunshan, China) with a screw diameter of 20 mm and a length-to-diameter ratio of 36/1. The corresponding temperature profile along the extruder barrel was 150/160/180/180/150 °C, and the screw speed was 180 rpm. The extrudates were ground into small particles with diameters about 2 mm, and then the particles were dried again at 103 ± 2 °C for 2 h and taken out for hand matting. A hot press (SYSMEN-II, China Academy of Forestry, Beijing, China) was used to produce the composites by compressing the mat at 180 °C with a pressure of 4 MPa for 6 min. The target density of the PP and PLA composites was 1.00 and 1.28 g/cm^3, respectively at size of 270 × 270 × 3 mm^3. Prior to demoulding, the formed mat was cooled down at 4 MPa for another 6 min at room temperature. After then, all the mats were cut into required dimensions for further tests according to the related standards.

2.4. Characterization of WF and WF components

The chemical groups of pure WF, CF, and LF samples were examined by FTIR analyses (BRUKER Vertex 70v, Germany). The samples were mixed with Potassium bromide (KBr) in a weight ratio of 1:100 before spectrum collection. All spectra were displayed in wavenumbers ranging from 400 to 2000 cm^{-1} with 40 scans at a resolution of 4 cm^{-1}.

XRD analyses of the pure WF, CF, and LF samples were carried out on an X-ray 6000 (Shimadzu, Japan) instrument. The X-ray beam was Cu Kα (λ = 0.1540 nm) radiation, operated at 40 kV and 30 mA. The scanning rate was 2°/s and 2θ ranged from 2° to 40° with the rotational speed of 30 rpm.

2.5. Physical, mechanical, and thermal tests

The water absorption or uptake (WA) test was carried out according to Chinese standard GB/T 17657-1999. Samples with of 50 × 50 × 3 mm^3 were completely immersed into water at 20 ± 2 °C. WA was calculated based on the weight percent gains after 6, 24 and 48 h and thereafter at 48 h intervals. The weights were taken after removal of excessive water on the sample surface.