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A green and efficient method for preparing acetylated cassava stillage residue and the production of all-plant fibre composites

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ABSTRACT

Cassava stillage residue (CSR), a kind of agro-industrial plant fibres, was directly acetylated and converted into thermoplastic material by mechanical activation-assisted solid phase reaction (MASPR) in a stirring ball mill without the use of organic solvent and additives. As combining mechanical activation and chemical modification in the same equipment, the destruction of hydrogen bonds and crystalline structure of CSR induced by intense milling improved the reactivity of CSR, leading to the effective acetylation of CSR. After acetylation by MASPR, the modified CSRs possessed thermoplasticity, ascribing to the introduction of acetyl groups and the destruction of high crystallinity structure of cellulose. The self-reinforced all-plant fibre composites (APFC) were successfully produced with the modified CSRs as both matrix and reinforcement by hot pressing technology. The direct acetylation of CSR and successful production of APFC suggested that MASPR was a simple, efficient and environmentally friendly method for chemical modification of agro-industrial lignocellulose biomass.

1. Introduction

Cassava stillage residue (CSR) is the agro-industrial solid residue generated in the still bottoms following fermentation and distillation during the production process of cassava-based bioethanol, and a main component of this residue is plant fibre [1,2]. A large amount of CSR is generated every year, and most of this residue has not been effectively used, or is even discarded as waste. The decay of so much solid residue will cause serious environmental pollution, so it is a significant issue to properly dispose the CSR. Recently, a new class of plant fibre-based biocomposites, defined as all-plant fibre composites (APFC), is prepared by using plant fibres as both the matrix and reinforcement [3,4]. Without the use of petroleum-based materials, the self-reinforced APFC are fully bio-based and fully biodegradable [5]. Besides, the interfacial adhesion is expected to be improved by using the same molecular level materials as matrix and reinforcement [6]. Thus, the effective utilization of CSR for the preparation of APFC can help to avoid environmental pollution and increase the added value of this lignocellulosic biomass. It is well known that plant fibres mainly consist of cellulose, hemicellulose and lignin. Due to the high degree of crystallinity of cellulose and the three-dimensional net structure of lignin, plant fibres cannot be processed like thermoplastic polymers [3,7]. It has been demonstrated that plant fibres can be converted into thermally formable materials through chemical modifications, such as etherification and esterification [8,9]. As a result, the self-reinforced plant fibre composites can be prepared by hot pressing, in which the plasticized parts serve as matrix and the unplasticized parts as reinforcement. However, the conventional chemical modifications often involve the use of organic solvents [10–12], which result in high cost for solvent recycling and the reduction of the possibility for industrial scale-up. So, it is important to develop a simple, efficient and environmentally friendly method for chemical modification of plant fibres.

With the increasing concerns on environmental protection, solid phase reaction (SPR) has attracted much attention for the advantages of the simplification of reaction process and product separation without the use of solvent, specificity of reaction, high selectivity and efficiency, and saving resources, and it is considered as an efficient procedure for green chemistry [13–15]. However, the contact between reagents and plant fibres is poor under SPR conditions because of the highly-ordered and recalcitrant structure of cellulose–hemicellulose–lignin complex and high crystallinity of cellulose in plant fibres [16]. In order to improve the reactivity of plant fibres and enhance the efficiency of SPR, it is necessary to

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adopt assisted means for chemical modification of plant fibres. Mechanical activation (MA), which refers to the use of mechanical actions to change the crystalline structure and physicochemical properties of the solids carried out by high-energy milling, is considered as a simple, efficient and environmentally friendly method for the pretreatment of solid materials attributing to the use of simple and cheap equipment and the operations without the use of solvents, intermediate fusion, etc. [17–19]. The destruction of stable hydrogen bond and crystalline structure induced by MA could effectively enhance the reactivity of plant fibres [20]. Generally, MA is used for the pretreatment of solid materials, and then the reaction of the pretreated materials is carried out in other equipment. However, during the process of MA, a part of mechanical energy can be converted into internal energy of the milled solids and thus generates many metastable active sites, which may rapidly reduce after removing the solids from the equipment of MA [21]. In order to make full use of the mechanical energy induced by MA and improve the conditions of chemical modification by SPR, we combine the MA pretreatment and chemical modification of plant fibres in the same equipment, and this MA-assisted SPR (MASPR) method can also simplify the technological process and improve the production efficiency. In this study, CSR was directly acetylated and converted into thermoplastic material by MASPR in a stirring ball mill without the use of organic solvent and additives, and then the modified CSR was used to produce APFC by hot pressing technology.

2. Materials and methods

2.1. Materials

CSR was kindly supplied by Guangxi State Farms Minyang Biochemical Group, INC. (Nanning, China). The sun-dried CSR was comminuted and further oven-dried at 105 °C for 4 h before use. The dried CSR was designated as original CSR. The components of CSR were crude fibre (35.5 wt.%), crude fat (4.3 wt.%), crude protein (2.6 wt.%), ash (7.2 wt.%) and nitrogen-free extract (50.4 wt.%, mainly low molecular compounds). All chemical reagents were of analytical grade without further purification and were obtained commercially. Deionized water was used throughout the work.

2.2. Acetylation of CSR by MASPR

The chemical modification of CSR was performed in a customized stirring ball mill driven by a commercially available drill press equipped with a speed-tuned motor [22]. A fixed amount of milling balls (500 mL, 5 mm diameter) was first added into a jacketed stainless steel chamber (1200 mL), and then 20.0 g of CSR, 60.0 g of acetic anhydride and 6.0 g of catalyst ($ZnCl_2$) were added into the chamber. The mixture was subjected to milling at the speed of 375 rpm and reacted at a constant temperature of 80 °C by circulating the thermostatic water in the jacket of chamber. When the mixture was milled for different desired reaction time, the balls were removed from the resulting sample, which was then purified through repeated washing-filtration processes with water to remove inorganic salts and with absolute alcohol to remove residues of acetic anhydride and by-products, respectively. Finally, the modified CSR was oven-dried at 60 °C until reached constant weight.

2.3. Determination of weight gain

Due to the complexity of CSR with containing macromolecular and low molecular compounds, the extent of acetylation was measured by percentage weight gain after the chemical modification. The weight gain (W) of modified CSR was calculated by using the following equation [23]:

$$W = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where m_1 is the dry weight of original CSR, and m_2 is the dry weight of modified CSR.

2.4. Activation grade measurement

Activation grade (A_g) is defined as the degree of nonwettability between water and solids, and the higher A_g value indicates the better hydrophobicity of the solids. The A_g of CSR samples was measured according to our previous work [24].

2.5. Preparation of APFC

The modified CSR samples were first comminuted by a high-speed pulverizer (Tianjin Taisite Instrument Co. Ltd., China), and then they were put in the molds with liquid paraffin as lubricant. These CSR particles were compression-molded in an XLB25-D plate vulcanizing press (Huzhou Xingli Corp., China) to produce APFC specimens in a preheated press at 120 °C under a pressure of 8 MPa for 5 min.

2.6. Mechanical properties of APFC

The stress–strain properties of the composites were measured by an Instron DNS-100 universal testing machine (Changchun Testing Machine Research Institute, China). The flexural strength and flexural modulus were measured at a crosshead speed of 2.0 mm/min according to ASTM D790, and the tensile strength and elongation at break were measured at a crosshead speed of 2.0 mm/min according to ASTM D638 [25]. All these tests were performed at room temperature.

2.7. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were acquired on an 8400S Fourier transform infrared spectrometer (Shimadzu, Japan) using the KBr disk technique. For FTIR measurement, the samples were mixed with anhydrous KBr and then compressed into thin disk-shaped pellets. The spectra were obtained with a resolution of 4 cm^{-1} and a wavenumber range of 4000–400 cm^{-1}.

X-ray diffractometry (XRD) patterns were recorded on a D/MAX 2500 V diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. The scattering angle (2θ) was varied from 10° to 40° with a step width of 0.02°.

Differential scanning calorimetry (DSC) curves of the samples were determined using a DSCQ20 analyzer (TA Instruments, USA) under nitrogen atmosphere with a heating rate of 10 °C/min.

Morphologies of the samples were performed using an S-3400N scanning electron microscope (Hitachi, Japan). The samples were fixed on a sample bench using double-sided tape, and then the samples were coated with a thin layer of gold prior to examination to improve the conductivity. SEM micrographs with different magnifications were obtained to observe the surface morphologies of different samples.

3. Results and discussion

3.1. Synthesis and properties of acetylated CSR

CSR consists of complex components, including macromolecular and low molecular compounds. Chemical modification of CSR