



## Research paper

## Highly translucent all wood plastics via heterogeneous esterification in ionic liquid/dimethyl sulfoxide



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## ABSTRACT

Wood-based plastics obtained via chemical modifications are usually dark and opaque, which limits their potential applications. All-wood plastics (AWPs) derived from ball-milled mulberry wood (BMMW) via an efficient heterogeneous esterification for 2 h in dimethyl sulfoxide (DMSO)/1-butyl-3-methylimidazolium chloride (BMIMCl) with the molar ratios of DMSO to BMIMCl at 5.9:1 exhibit a highly translucent appearance. With desirable thermoplasticity and tensile strength, AWPs can be processed into light-permeable specimens and transparent film. FT-IR and solid-state <sup>13</sup>C NMR spectra provide evidence for successful substitution of hydroxyl groups of BMMW by carboxybenzoyl groups. The darkness of AWPs arising from the oxidation of phenolic lignin into benzoquinone indicates that reaction time plays a critical role for controlling the transparency of AWPs. AWPs represent composite structures, including cellulose I and cellulose II. Different degradation mechanisms are observed among AWPs differently esterified. Moreover, the SEM and AFM images demonstrate the self-reinforcement of AWPs specimens and the heterogeneous surface of a transparent AWP film, respectively.

## 1. Introduction

With the increasing awareness of the fact that fossil raw materials are finite resources, researchers have paid attention to develop bio-based plastics that can replace petro-based plastics in the future. As one of the most-studied bio-based plastics, poly(lactic acid), which is synthesized from lactic acid by micro-organisms using glucose from food resources, has been widely applied in packaging, automotive applications, tissue engineering and drug delivery (Iwata, 2015; Gupta et al., 2007; Tsuji 2014). In addition, extracted components from plant biomass, such as starch (Belhassen et al., 2014; Jaramillo et al., 2016), proteins (Félix et al., 2016), and plant oil (Gandini et al., 2016) were used as raw materials to produce bio-based plastics. Nevertheless, non-food resources are more reasonable for developing bio-based plastics, given that it is possible for human beings to encounter food crises in the future. Currently, wood has become an abundant resource for biofuels, chemicals and new materials. However, it has not yet been fully utilized for practical proposes (Hill, 2006). A typical example is that in southern China, there are hundreds of thousands of tons of mulberry branches

burned in fields every year after mulberry leaves are harvested for feeding silk-worms. The conversion of waste mulberry wood into bio-based plastics is of great interest in China (Su et al., 2015).

Wood is naturally a composite material mainly composed of cellulose, hemicelluloses, and lignin. Specifically, lignin binds hemicelluloses and cellulose to form a rigid three-dimensional network, which affects the thermoplasticity of wood components upon heating. Moreover, cellulose, featuring an intensive hydrogen bonded structure, has a melting temperature much higher than its decomposition temperature (Schroeter and Felix, 2005). Therefore, wood cannot be melted and molded directly. Plasticization of wood fibers can be accomplished by chemical (Zhang et al., 2005; Mohammadi-Rovshandeh and Sereshti, 2005; Chen et al., 2014) and physical (Shibata et al., 2013; Huber et al., 2012) modifications. In our previous work, we have developed all-wood plastics (AWPs) by kneading mulberry wood in DMSO/ILs (Chen et al., 2015). However, from a practical application point of view, wood-based plastics obtained via the aforementioned methods usually exhibited a dark and opaque appearance, which limit their potential applications. The darkness of wood-based plastics arising from the

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oxidation of phenolic lignin into benzoquinone is an intrinsic barrier to dyeing plastics for either aesthetic purposes or weathering resistance (Stärk et al., 2010; Badamali et al., 2013). In the study of flexible electronics, plastic substrates hosting electronic devices require high optical transparency. (Hu et al., 2010)

Recent developments of transparent cellulose-based materials have attracted much attention. For example, there are some excellent reviews dealing with the concept of optically transparent paper and its applications (Zhu et al., 2014; Zhu, Luo et al., 2016; Zhu, Song et al., 2016; Koga et al., 2013). Significantly, transparent wood has been successfully developed by first removing lignin and filling the porous woody matrix with a transparent polymer of matching refractive index (Zhu, Luo et al., 2016; Zhu, Song et al., 2016). For the first time, transparent wood has been used as building materials with several advantages over glass in terms of unique light guiding effect and excellent thermal insulation (Li et al., 2016). So far, very little information is available about the preparation of transparent bio-based plastics, and only in cellulosic materials, not in wood whole components.

Ionic liquids (ILs), well known as green solvents, can effectively dissolve cellulose (Swatloski et al., 2002) and wood (Kilpeläinen et al., 2007). ILs used as homogeneous media for producing cellulose-based plastics have been intensively studied (Liu et al., 2006; Yuan et al., 2013). Transparent plastic films were prepared with cellulose-graft-poly (L-lactide) copolymers in 1-allyl-3-methylimidazolium chloride (Yan et al., 2009). Sugarcane bagasse was homogeneously modified in an IL for preparing films (Chen and Shi, 2015). Compared with neat IL, a binary solvent combining IL and an organic solvent was reported to be far more powerful to dissolve cellulose (Rinaldi, 2011). Accordingly, an IL-containing solvent might be able to disrupt the robust woody nanostructure and thus promote the modification of wood in solution meanwhile controlling the production of benzoquinone in order to obtain transparent wood-based plastics.

In this study, in order to develop AWP with desirable transparency and processability, we have prepared AWP via heterogeneous esterification of mulberry wood in DMSO/IL under different reaction conditions. AWP endowed with sufficient plasticity have been processed into specimens and film, respectively. The properties of AWP, including transparency, morphologies and mechanical strength, were studied in addition to structural and thermal analysis.

## 2. Materials and methods

### 2.1. Materials

Mulberry wood as agricultural wastes was obtained from Jiangsu province, China. The mulberry wood was dried in sunlight, peeled and pulverized into 40 mesh size and oven-dried at 60 °C, and further pulverized by a planetary ball mill for 2 h in a stainless steel vessel (QM-3SP2, Nanjing University Affiliated Instrument Factory, Nanjing). 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-butyl-3-methylimidazolium acetate (BMIMAcO) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. DMSO of analytical grade purity was purchased from Nanjing Chemical Reagent Company, China. Acetone, phthalic anhydride (PA), and 4-dimethylaminopyridine (DMAP), *N,N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Company.

### 2.2. Methods

#### 2.2.1. Heterogeneous esterification of BMMW in ILs/DMSO

The flow diagram for preparing AWP derived from mulberry wood is illustrated in Scheme 1. Mulberry wood was first subject to a ball-milling treatment. Heterogeneous esterification of the ball-milled mulberry wood (BMMW) in DMSO/IL was carried out under various conditions, as listed in Table 1. BMMW was suspended in DMSO/IL (50 g) at various molar ratios of DMSO to IL ( $R_{DMSO}$ ). PA and DMAP

were first dissolved in DMSO and then added into the BMMW/ILs/DMSO mixture. AWP were precipitated by pouring this mixture slowly into 100 mL of acetone with agitation. The resultant precipitates were centrifuged, filtered, and washed with ethanol twice to remove the IL, unreacted PA and other chemicals. After that, the AWP were weighed to determine the weight percent gain (WPG) calculated using Eq. (1):

$$WPG = \frac{M_1 - M_0}{M_0} \times 100\% \quad (1)$$

where  $M_0$  is the initial oven-dried weight of BMMW and  $M_1$  is the weight of oven-dried AWP. Each experiment was performed in triplicate under the same conditions, and each WPG listed in Table 1 represents the average value.

#### 2.2.2. Injection molding process

The dumbbell-shaped AWP specimens shown in Scheme 1 were prepared through an injection molding process with a stainless mold to obtain the specimens whose dimensions correspond to the ISO 527-2-A5 standard specifications for the tensile strength test. Before the injection molding process, the AWP were homogenized with a twin screw extruder (minilab, Thermo) at 155 °C and extruded under a screw speed set at 50 rpm. The extrudate was granulated using a mill (A11, IKA) and then oven-dried at 80 °C for 24 h. The injection molding at 170 °C and under 550 bar was performed using an injection molding machine (Mini-jet, Thermo).

#### 2.2.3. Preparation of AWP film

AWP (0.6 g) were dissolved in 10 mL of DMF under stirring for 4 h at room temperature. The resultant solution was cast onto a polytetrafluoroethene mold and oven dried with air circulation at 50 °C for 6 h to obtain the AWP film.

### 2.3. Characterization

#### 2.3.1. Fourier transform infrared (FT-IR)

The chemical structures of BMMW and AWP samples were characterized by FT-IR spectrophotometer (Nicolet 6700, USA) with finely ground samples (1%) in KBr pellets. 16 scans were collected for each sample recorded in the range of 4000–500  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

#### 2.3.2. Solid-state $^{13}\text{C}$ NMR

Solid-state  $^{13}\text{C}$  NMR spectra of BMMW and AWP were characterized on an AVANCE III 600 MHz NMR spectrometer using MAS rates of 6 kHz at a frequency of 150.90 MHz.

The spin rate of the 4-mm rotor was 8 kHz for the CP/MAS experiments. The acquisition time was 0.0127 s. The delay time was 2 s.

#### 2.3.3. X-ray diffraction (XRD)

X-ray diffraction patterns of the BMMW and AWP were characterized by a wide angle X-ray diffractometer (DX-2000X Shimadzu, Japan). The measurements were performed using Cu-K $\alpha$  radiation at 40 kV and 30 mA in the range of  $8^\circ \leq 2\theta \leq 40^\circ$  with step size at 0.02°.

#### 2.3.4. Thermal flow behavior

The thermal flow behavior of the AWP was observed by an Olympus BX5.2 POM (Polarizing optical microscope) (Olympus, Japan) equipped with a Linkam THMS 600 hot-stage device. A small amount of the AWP sample (0.02 g) was sandwiched between two cover glasses and heated from 30 °C to 120 °C at a rate of 20 °C/min, holding for 1 min, and then heated from 120 °C to a sufficient temperature to melt and begin to collapse at a heating rate of 5 °C/min.

#### 2.3.5. Thermal analysis

Thermogravimetric analysis (TGA) was performed on the BMMW and AWP using a thermogravimetric analyzer (DTG-60AH Shimadzu,

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