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Ionic liquid mediated technology for fabrication of cellulose film using gutta percha as an additive

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ABSTRACT

A great paradigm for state-of-the-art biomaterials is to use renewable lignocelluloses with ionic liquid-based green regimes. Novel transparent films were successfully prepared from the purified eucalyptus cellulose by the moderate incorporation of gutta percha (GP, 5–15%) using 1-butyl-3-methylimidazolium acetate ([bmim]OAc) as a versatile solvent. The refined GP was obtained from *Eucommia ulmoides* Oliver after hot-water extraction, alkaline treatment, enzymatic hydrolysis, and extended petroleum ether purification. The cellulose/GP films exhibited a well-distributed and smooth structure, and the crystalline structure of composite films was transformed from cellulose I to II. The incorporation of 5–10% GP obviously improved the tensile strength of films (129–139 MPa) as compared to the pure cellulose film (81 MPa). Moreover, the novel hybrid films showed excellent thermal stability and oxygen barrier property as a result of the reinforcement by GP. The cellulose/GP films with prominent tensile strength, thermal stability and oxygen permeability could be tuned via varying the ratio of GP to cellulose matrix, which can be exploited as a potential candidate of pollution-free, biodegradable and renewable cellulose-based composites for the substitute of petroleum derived packaging materials.

1. Introduction

The recent upsurge of research interest has been dedicated on the development of biodegraded and green biomaterials from lignocellulosic biomass as a potential alternative of fossil-derived materials to reduce environmental pollution resulted from non-biodegradable plastic films (Cao et al., 2010; Fernandes et al., 2009). Crystalline polysaccharides of biomass are auspicious for noteworthy and rapidly growing applications ranging from advanced energy storage, electronics, and catalyst or enzyme supports to tissue engineering and biological devices (Huang et al., 2017). Among them, cellulose is the most abundant polysaccharide in lignocelluloses, which possesses unparalleled physicochemical properties such as biodegradability and biocompatibility and has a large number of current and potential applications (Siró and Plackett, 2010). There is no doubt that cellulose-based materials have attracted vast research interests in the fields of fibers, films, food casings, and membranes (Qi et al., 2009; Turner et al., 2004). However, cellulose has often suffered from solubility problems due to the presence of hydrogen bonds, hindering the improvement of their processability, fusibility, and functionality (Pinkert et al., 2009). To date, only a limited number of cellulose solvent systems have been found, for example, LiCl/N,N-dimethylacetamide (DMAc), N-methylmorpholine-N-oxide (NMMO) (Zhang et al., 2005). As the best one of amine-oxides, NMMO system is the solely industrialized solvent for the manufacture of regenerated cellulose fibers and films. However, these solvents have some limitations such as volatility, toxicity, unsafety, difficult recovery, and instability in application (Zhang et al., 2005). Ionic liquids (ILs), the low-melting point salts that are liquids at temperature below 100 °C, have recently found to be used as excellent solvents for cellulose (Wang et al., 2012; Zhang et al., 2014). As the novel and multifaceted media, ILs have a series of superior properties, such as admirable thermal stability, negligible vapor pressure, and tunable properties with respect to hydrophobicity, polarity, and solvent miscibility through appropriate combination of anions and cations (Brandt et al., 2013; Petkovic et al., 2011). Thanks to these unique properties of ILs, the IL-mediated technology has been considered as an efficient method to produce novel cellulosic hybrid composites. ILs with acetate anions have been expounded to exhibit excellent solvating power, low melting points and viscosities, low toxicity and corrosivity, and high hydrogen bonding acceptor abilities (Sun et al., 2009). An impressive recyclability of 1-butyl-3-methylimidazolium acetate ([bmim]OAc) was also affirmed (Xu et al., 2017). Representatively, films have been facilely prepared by the regeneration of the biopolymers from solutions in acetate ILs (Abdulkhani et al., 2013; Soheilmoghaddam et al., 2014).

In general, the packaging composites are potentially subjected to a

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variety of external forces that require a certain mechanical properties to resist the outside pressure and scratch. However, cellulose-based materials often suffered from their frangible feature and inferior mechanical strength that impede the exploitation of bio-based composites in a wide range of applications (Orelma et al., 2011). Various types of additives, such as plasticizer and polymers, could be affiliated to cellulose for improving the mechanical strength and specific properties of the regenerated cellulose membrane. Gutta percha (GP), also called balata or Eucommia-rubber, is a thermoplastic crystalline polymer with a molecular structure of *trans*-1,4-polyisoprene from *Eucommia ulmoides* Oliver and an isomer of natural rubber (Sun et al., 2013; Zhang et al., 2008). GP is a hard, fibrous and long-chain natural rubber resource that exhibits properties similar to plastic and is suitable for various industrial uses (Sun et al., 2013; Zhang et al., 2011). In addition, GP can be extracted from the whole of certain tissues or organs (such as seed coats 12–18%, barks 6–12% and leaves 1–3%) of *Eucommia ulmoides* Oliver tree and is resistant or agglomerate to acids and alkalis, which is used extensively in electrical insulation and filling material. *Trans*-1,4-polyisoprene is easy to crystallize due to its regular macromolecular chain structure. Two crystalline forms, α-form and the β-form, can be obtained by crystallizing at room temperature from the molten state which directly affects macroscopic mechanical behavior (Zhang et al., 2011). Because of the *trans*-configuration and high degree of polymerization of GP, it has distinct properties and functions with the duality of flexibility and plasticity. With these properties, GP can blend with natural polymers to obtain mixtures exhibiting special functions which do not present in individual rubbers, plastic, and polymers (Takeno et al., 2008; Zhang and Xue, 2011; Zhang et al., 2008). Therefore, GP is a potential additive to improve the unique features, such as mechanical strength and fabricability, with a wide range of applications in the fields of polymer, pharmaceutical, and thin film materials.

Herein, for the first time, the use of ([bmim]OAc) as the solvent was explored to fabricate the hybrid cellulose films in the presence of GP for improving the hydrophobicity tensile strength, thermal stability, and barrier properties of cellulose-based films and thus facilitating their actual commercialization. The physicochemical structure, thermal stability, mechanical properties, and oxygen permeability of the hybrid films with the different cellulose/GP weight ratios were investigated to aid a holistic understanding of the interplay between the structure and performance of hybrid cellulose films and evaluate the feasibility of their applications in the fields of packaging and functional materials. This study offers an effective and facile method to produce cellulose-based biocomposites with excellence performances for green and value-added utilization of woody biomass.

2. Experimental

2.1. Material and chemicals

Eucommia ulmoides Oliver leaves were collected from the forestry station of Northwest A & F University, Yangling, China. The leaves were crushed to powder and then dried in an oven at 40 °C prior to use. Eucalyptus was obtained from the arboretum of Beijing Forestry University (Beijing, China), ground to size below 1 mm and then dried at 60 °C for 24 h to isolate cellulose.

The IL, [bmim]OAc, was purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences, Lanzhou, China). The chemical reagents, including sodium chlorite, sodium hydroxide, chloroform, and light petroleum, were of analytical purity and purchased from Sigma Chemical Co. (Beijing, China). The commercial enzyme Cellulase 1.5 L was purchased from Novozymes Biochemical Co. Ltd. (Shanghai, China).

2.2. Isolation of gutta percha

Twenty grams of *Eucommia ulmoides* Oliver leaf powder was firstly extracted with 400 mL of distilled water at 60 °C for 3 h. After filtration, the residue was freeze-dried and then extracted with 1 M aqueous NaOH with a solid to liquid ratio of 1:20 g/mL at 75 °C for 3 h, and then the mixture was filtrated and freeze-dried to obtain crude GP containing impurities prior to cellulose hydrolysis. In order to remove the cellulose associated with crude GP, the enzymatic hydrolysis of leaf pieces treated by hot-water and alkali was conducted at 250 mL flask containing 2 wt% substrate in 0.05 M sodium citrate buffer (pH 4.8) shaking in a thermostatic water bath at 50 °C for 96 h. The commercial enzymes of Cellulase 1.5 L were added at a bioactivity loading of 60 FPU/g of substrate. After hot-water extraction, alkaline treatment and enzymatic hydrolysis of leaf pieces, the isolation of refined GP was performed in a round flask using petroleum ether as purified solvent at 80 °C with a solid to solvent ratio of 1:15 g/mL for 2 h. The resulting mixture was filtered by Buchner funnel to remove the insoluble fractions. Then, the filtrate was cooled down to room temperature and refrigerated at below 0 °C for 1 h to regenerate the pure GP. The refined GP was obtained by filtration of the cooled petroleum ether through 100 mesh stainless steel sieve. The contents of purity and residual impurity were determined by dissolving GP in the hot petroleum ether.

2.3. Extraction of eucalyptus cellulose

In order to obtain holocellulose, the delignification of dried eucalyptus meal was performed with sodium chlorite in acidic solution (pH adjusted to 3.8–4.0 by acetic acid) at 75 °C for 2.5 h. The obtained holocellulose was then treated with 10% NaOH to remove hemicelluloses with a solid to liquid ratio of 1:20 (g/mL) at 80 °C for 4 h. The resulting solid was filtrated and washed thoroughly with distilled water until the pH of filtrate was neutral, then it was freeze-dried in a lyophilizer for 48 h to obtain the original cellulose from eucalyptus. The results of molecular weight distribution and chemical composition of eucalyptus cellulose sample are illustrated in Fig. S1. The molecular weight of the cellulose was calculated using degree of polymerization (DP) multiplying by the molecular weight of an anhydroglucose (162 g/mol).

2.4. Preparation of cellulose/gutta percha film

In a typical procedure, 2 g of eucalyptus cellulose powder was added into 40 g [bmim]OAc in a 50 mL sealed reaction flask with the cellulose loading of 5 wt% and then the mixture was heated in an oil bath under magnetic stirring at 100 °C for 3 h to prepare the cellulose/IL homogeneous solution. In addition, 5%, 10%, and 15% of GP with regard to the dry weight of eucalyptus cellulose were dissolved in 2 mL chloroform respectively to get transparent solution. Then, the GP/chloroform solution was poured into the cellulose/IL mixture after cooling down to ambient temperature, and then continually heated at 80 °C for 2 h. The hybrid films were regenerated by casting the blended gels orderly with oriented draw on a glass plate, followed by soaking in distilled water and drying at ambient conditions. The hybrid cellulose films in the presence of 5%, 10%, and 15% GP were defined as F5, F10 and F15, respectively. As a comparison with the hybrid films, the regenerated cellulose film was also fabricated without the addition of GP as control and labelled as F0. The preparation scheme of cellulose/GP films was depicted in Fig. 1.

2.5. Analytical methods

The gel permeation chromatography (GPC, Agilent 1200, USA) equipped with a PL gel column and an RID detector was applied to measure the weight-average (M_w) and number-average (M_n) molecular weights, and polydispersity index (M_w/M_n) of GP. The mobile phase