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Effects of dissolution of some lignocellulosic materials with ionic liquids as green solvents on mechanical and physical properties of composite films

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ABSTRACT

In this study two imidazole-based ionic liquids (ILs), namely 1-butyl-3-methyl-1-imidazolium chloride ([BMIM]Cl) and 1,3-methyl imidazolium dimethyl sulfate ([DiMIM][$MeSO_4$]), were used to dissolve ball-milled poplar wood (PW), chemi-mechanical pulp (CMP), and cotton linter (CEL). A set of comparative experiments was carried out, and physical and mechanical properties of the composite films from three different raw materials were determined by means of optical transparency (OT), scanning electron microscopy (SEM), water absorption (WA), thickness swelling (TS), water vapor permeability (WVP), and tensile strength (σb). The overall evaluation indicates the inability of [DiMIM][$MeSO_4$] in complete dissolution of lignocellulosic materials, and sample treatment with this solvent did not lead to water soluble degradation products. However, dissolution trials using [BMIM]Cl were able to dissolve all used lignocellulosic materials by destroying inter and intramolecular hydrogen bonds between lignocelluloses. The OT, WA, TS, and σb of regenerated CEL films were much higher than those of CMP and PW composites. In addition, CEL film showed the lowest WVP compared to WF and CMP composite films. This work demonstrated a promising route for the preparation of biodegradable green cellulose composite films.

1. Introduction

The use of lignocellulosic biomass based materials in various sectors (e.g. automotive and aerospace) instead of petro-materials has received increased attentions due to the growing global environmental awareness, and concepts of sustainability and industrial ecology (Hamzeh, Ashori, Mirzaei, Abdulkhani, & Molaei, 2011; Moniruzzaman & Ono, 2012). Wood is a renewable source for cellulose, lignin, hemicelluloses and extractives (Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010). A lignocellulosic material contains 35–50% cellulose, up to 35% hemicelluloses, 5–30% lignin as well as a few percent of extractives (Lynd, Weimer, Van Zyl, & Pretorius, 2002). Cellulose is the most abundant biopolymer on the Earth and, thus, it is a valuable source of raw materials (Mäki-Arvela et al., 2010). It is formed via 1,4-β-D-glucose linkage of anhydroglucose units, and contains several inter- and intramolecular hydrogen bonds (Zhang, Wu, Zhang, & He, 2005), which should be broken during the dissolution of cellulose. Furthermore, native cellulose is considered as a rigid semi-crystalline material (Pinkert, Marsh, Pang, & Staiger, 2009). Lignin is a complex polymer composed of phenylpropanoid units consisting primarily of coniferyl, sinapyl and *p*-coumaryl alcohols. These components are assembled in a complex three-dimensional structure, remarkably resistant against chemicals and microbial attack that makes it very difficult to hydrolyze. The insolubility of wood in common solvents has severely hampered the development of new methods for the efficient utilization of wood and its components (Kilpeläinen et al., 2007). An effective dissociation of these components and their subsequent separation is needed for the production of high value products from lignocellulosic biomass (Hamzeh, Ashori, Khorasani, Abdulkani, & Abyaz, 2013). On the other side, if the biopolymers could be cleanly and easily separated from any lignocellulosic biomass source, they could serve as ready feedstock for not only polymeric composite materials, but also for base chemicals and fuels that are now obtained primarily from oil. The true biorefinery would not be based on production of only a fuel, but a rich, nearly limitless variety of chemicals (Fig. 1).

Traditionally, drastic conditions, such as strong base or mineral acids, are used to exploit the lignocellulosic materials. In these processes, the extracted fractions are severely and irreversibly altered, and environmental pollution is also of great concern. Moreover, conventional processes cannot make full use of non-cellulose

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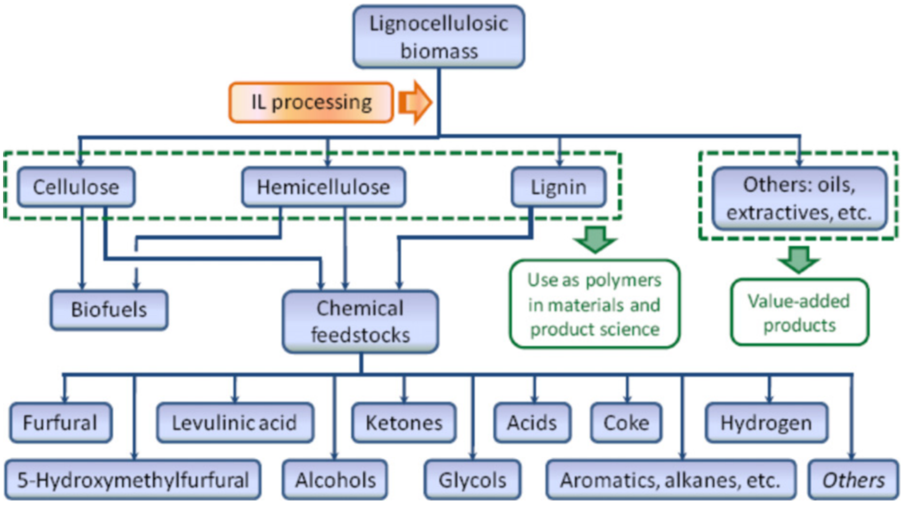

Fig. 1. Possible applications of the three major components from lignocellulosic biomass (Sun, 2010).

biopolymers, i.e. lignin and hemicelluloses. In order to overcome these obstacles, some mild processes and pretreatment are proposed, e.g. enzymatic hydrolysis, steam explosion, organic solvent, and ammonia fiber explosion (Öhgren, Bura, Saddler, & Zacchi, 2007; Yang, Zhong, Yuan, Peng, & Sun, 2013). However, this issue is still pending due to the high crystallinity of cellulose, relatively high reactivity of carbohydrates, insolubility of cellulose in conventional solvents and heterogeneity of lignocelluloses (Remsing, Swatloski, Rogers, & Moyna, 2006). Therefore, new technologies should be developed for the green bio-refinery of biomass resources.

In 2002, Swatloski et al. were the first to demonstrate that ionic liquids (ILs) are able to dissolve cellulose. However, in recent years the dissolution of lignocellulosic biomass in ILs has drawn a great deal of attention. ILs are organic salts entirely composed of cations (usually organic) and anions (usually inorganic) with generally low melting temperatures ($\leq 100\,^{\circ}$C). They are green solvents, which are characterized by negligible vapor pressure as well as excellent thermal and chemical stability. The use of ILs as solvents has increased recently as a result of a globally growing interest toward green chemistry. Their unique properties make them attractive alternatives to conventional organic solvents in many chemical processes. Their use can provide a concrete solution to the problem of formation of volatile organic carbons (VOCs) in conventional solvents, which are detrimental to the environment (Anderson, Ding, Welton, & Armstrong, 2002). Many factors, e.g. species of biomass, particle size, water content, affect the dissolution of lignocellulosic materials in ILs (Li, Asikkala, Filpponen, & Argyropoulos, 2010; Sun, 2010). In addition, when the dissolving temperature is higher than the glass transition of lignin, the dissolution and fractionation of lignocelluloses can be more efficient (Li, Wang, & Zhao, 2008). The ILs have attracted increasing interest as media for dissolving cellulose from lignocellulosic biomass in the pretreatment step (Fukaya, Hayashi, Wada, & Ohno, 2008; Zavrel, Bross, Funke, Büchs, & Spiess, 2009). The dissolved cellulose in IL can be easily regenerated with the addition of an anti-solvent, such as water, ethanol or acetone (Zhu et al., 2006). As reported in the literature, apart from extracting cellulose from the primitive resources, regenerated cellulose exhibits significantly reduced crystallinity and increased porosity, which enhance the digestibility of the material and subsequently result in a higher yield for the overall conversion process (Li et al., 2011).

The aim of this work was to explore the influences of IL treatments on the fractionation process under mild conditions. The ILs [BMIM]Cl and [DiMIM][$MeSO_4$], which have been proved to be good solvents for lignocellulosic materials (Huddleston et al., 2001; Zhang, Deng, Li, & Chen, 2008), were used to directly dissolve the ball milling fibrous materials. Consequently, the resulting mixtures were used to make composite films, where they were characterized in terms of physical and mechanical properties.

2. Materials and methods

2.1. Raw materials and chemicals

The lignocellulosic materials (LMs) used for this study were poplar wood (*Populus deltiodes*) (PW), chemi-mechanical pulp (CMP) of poplar, and cotton linter (CEL) containing 99% α-cellulose. The air-dried wood and pulp samples were ground in a 1 gal porcelain jar (rotary ball mill) using alumina balls under a nitrogen atmosphere. Consequently, they were oven-dried at 105 °C for 8 h and kept inside a sealed plastic bag. All the above-mentioned materials were procured from the local market.

Two imidazole-based ILs, namely 1-butyl-3-methyl-1-imidazolium chloride ([BMIM]Cl) and 1,3-metyl imidazolium dimethyl sulfate ([DiMIM][$MeSO_4$]), were synthesized according to the literature (Huddleston et al., 2001; Zhang et al., 2008). Fig. 2 shows the ^{13}C NMR spectra of laboratory synthesized ILs. All other chemical reagents were purchased from Merck, Germany.

2.2. ^{13}C NMR analysis

The NMR spectra of synthesized ILs were recorded on a JOEL JNM-ECX50 500 MHz spectrometer. IL solvents were placed in a 5-mm diameter NMR tube: a 75 pulse width, 1.4 s acquisition time, and 4 s relaxation delay were used. A total of 2000 scans were collected.

2.3. Dissolution process

Since water competes with the IL to establish hydrogen bonds, the presence of water in the solution water may decrease wood solubility in the ILs. Each lignocellulosic material and IL were placed in a flask under nitrogen filled environment and heated at 70–90 °C on a hot plate with magnetic stirring (200–500 rpm). The treatment conditions used for the respective prepared mixes are given in Table 1. The dissolution procedure of the materials was monitored using an optical microscopy with 10× magnification.