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Short communication

Preparation of microfibers from wood/ionic liquid solutions

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ABSTRACT

Two types of ionic liquids, 1-ethyl-3-methylimidazolim acetate and 1-ethyl-3-methylimidazolium lactate, were employed for the direct processing of pine wood into microfibers. The concentration of 5 wt.% of wood in ionic liquids was rated as the most appropriate for electrospinning. The fibers were electrospun into the collector water bath. The final structure varied from individual microfibers to fiber bundles. It was demonstrated that 1-ethyl-3-methylimidazolium lactate is a powerful solvent and provides the direct transformation of pristine pine wood into the non-wovens.

1. Introduction

Bio-fibers generated from annually renewable biomass feedstock are regarded as promising materials that could replace synthetic reinforcements in polymer composites (John & Thomas, 2008).

In this context, wood belongs to one of the most important renewable resources of fiber forming biopolymers. Cellulose, hemicellulose and lignin rank among the most contained carbohydrate polymers in wood. While cellulose has linear fibrous structure that is assembled by a large amount of intra- and intermolecular hydrogen bonds, lignin is an irregular polymer forming three-dimensional network in which cellulose and hemicellulose fibers are embedded (Brandt, Hallett, Leak, Murphy, & Welton, 2010; Hendriks & Zeeman, 2009; Zavrel, Bross, Funke, Büchs, & Spiess, 2009).

Due to this complex structure wood has a remarkable chemical resistance that makes this material very attractive for various applications which, on the other hand, limits processing, possibility of shape and morphology modification and separation of individual components. Thus, various chemical and biological approaches to modify and process raw wood still represent a significant scientific challenge (Fort et al., 2007; Hendriks & Zeeman, 2009; Muhammad, Man, & Bustam Khalil, 2012; Sun et al., 2009).

In this respect, ionic liquids (ILs) gained in interest, since some of them possess high efficiency to dissolve lignocellulose biomass. Ionic liquids represent new class of solvents that consist entirely of ions with melting point below 100 °C. In comparison to traditional molecular solvents ILs have negligible vapour pressure and broad thermal stability. The combination of cation and anion affects the final properties of ILs as melting point, viscosity, hydrophobicity and overall stability (Cao et al., 2009; Swatloski, Spear, Holbrey, & Rogers, 2002; Zhu et al., 2006). Therefore, a wide spectrum of ILs can be tailored toward the specific properties for certain application (Zhu et al., 2006).

Dissolution of wood in ILs has been studied and at least partial dissolution has been obtained for both hard and soft wood. Thus far, 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride have been the choice in majority of these studies (Cao et al., 2009; Fort et al., 2007; Xie, King, Kilpelainen, Granstrom, & Argyropoulos, 2007; Zavrel et al., 2009). Recently, environmental aspects are also taking into account and less corrosive and toxic anions than chloride are preferred. Imidazolium based ILs containing acetate anion providing satisfactory

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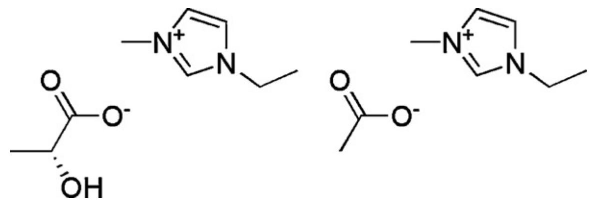

Fig. 1. Chemical structure of [Emim][Lactate] (left) and [Emim][oAc] (right).

results in the case of wood dissolution (Cao et al., 2009; Lovell et al., 2010; Sun et al., 2009). Sun et al. and Zavrel et al. found high dissolution capability of 1-ethyl-3-methylmidazolium acetate for wood after mild grinding without any side derivatizing effects (Sun et al., 2009; Zavrel et al., 2009). Wood that is dissolved in such ILs can be precipitated by addition of anti-solvents like water which enables the separation of cellulose from lignin and hemicellulose and formation of structural forms like fibers (Bagheri et al., 2008; Zavrel et al., 2009).

Beside a number of fiber processing technologies, electrospinning seems to be highly promising way to prepare continuous fibers from solution of wood in ILs. In the electrospinning process, a polymer solution is held by its surface tension at the end of capillary. When a sufficiently large electric field is applied, the solution at the tip of capillary elongates to form a cone because of coupled effects of the electrostatic repulsion within the charged droplet and attraction to a grounded electrode of opposite polarity (Barakat, Kanjwal, Sheikh, & Kim, 2009; Bhattarai et al., 2004; Deitzel, Kleinmeyer, Hirvonen, & Beck Tan, 2001; Huang, Zhang, Kotaki, & Ramakrishna, 2003; Kimmer et al., 2009).

Typically, electrospinning involves the evaporation of solvent component of the viscoelastic liquid, resulting in fiber formation. Since ILs are low melting salts having very low vapour pressure, it is impossible to evaporate them. Therefore, the fibers have to be spun into the collector bath where the ionic liquid is washed out causing the solidification of electrospun fibers. Once the ionic liquid is washed out from the fibers it can be almost entirely recovered from collector bath (Quan, Kang, & Chin, 2010; Tsioptsias & Panayiotou, 2008; Viswanathan et al., 2006).

2. Experimental

In present work, natural pine wood flour was dissolved in two types of ILs; 1-ethyl-3-methylimidazolim acetate [Emim][oAc] and 1-ethyl-3-methylimidazolium lactate [Emim][Lactate], both supplied by Solvionic, France, with stated purity of 98%. Their chemical structure is depicted in Fig. 1. ILs used are highly hygroscopic, therefore, they were dried in vacuum oven 24 h at 60 °C before use. At such conditions, the ILs do not exhibit further weight loss; it has been demonstrated that the drying procedure leads to elimination of water content below 0.3 wt.% (Brandt et al., 2010). Beside

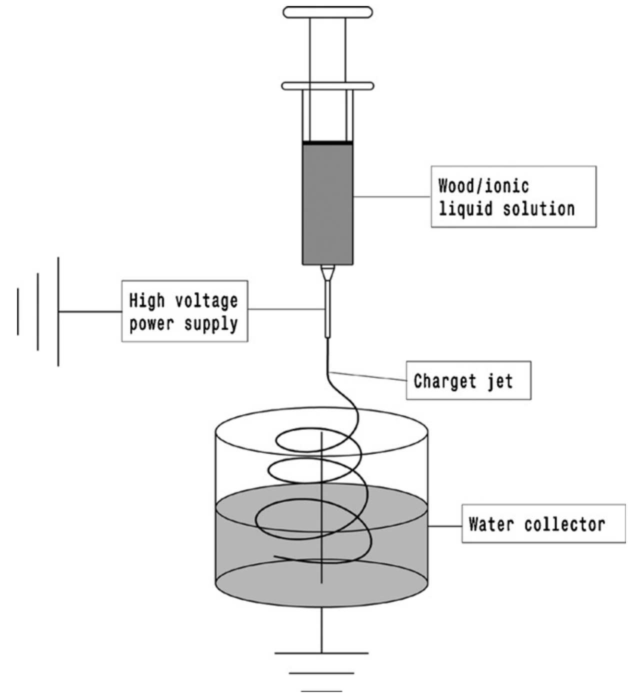

Fig. 3. Scheme of electrospinning process from IL solution.

pristine natural wood flour, pine wood after Soxhlet extraction was utilized in order to evaluate the influence of low molecular waxes contained in natural wood on dissolution capability of ILs. Soxhlet extraction was performed with acetone for 48 h. Natural and Soxhlet wood were kept in vacuum oven for 48 h at the temperature of 40 °C prior dissolution in ILs and electrospinning (Xie et al., 2007).

Structure of wood flour before and after Soxhlet extraction is given in Fig. 2. For these purposes optical microscope Zeiss NU was used. It is obvious that acetone treatment did not significantly change the microstructure of pine wood.

Both types of wood were added within the amount of 5 wt.% to the vials with ILs, closed and sealed by Teflon tape. Such vials were placed into an oil bath and heated on a hot plate at the temperature of 80 °C for the time of 24 h. These dissolution conditions have been chosen to prevent any chemical changes of both ILs and wood; preceding experimental study showed strong chemical changes when the dissolution proceeded at the temperatures higher than 100 °C. Then, wood solution was transferred to the syringe and the electrospinning was carried out.

The apparatus for wet electrospinning consisted of a high voltage source and collector water bath (Fig. 3). Electrospinning process was performed under ambient temperature. The syringe with the needle was placed vertically above the bath and 7-cm

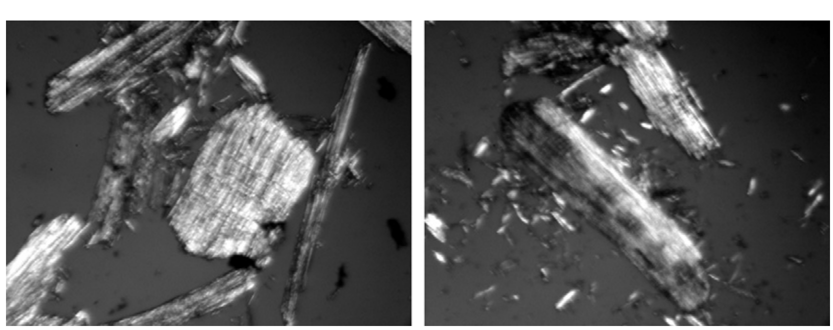

Fig. 2. Optical micrographs of natural wood (left) and Soxhlet wood (right), magnification of 320×.

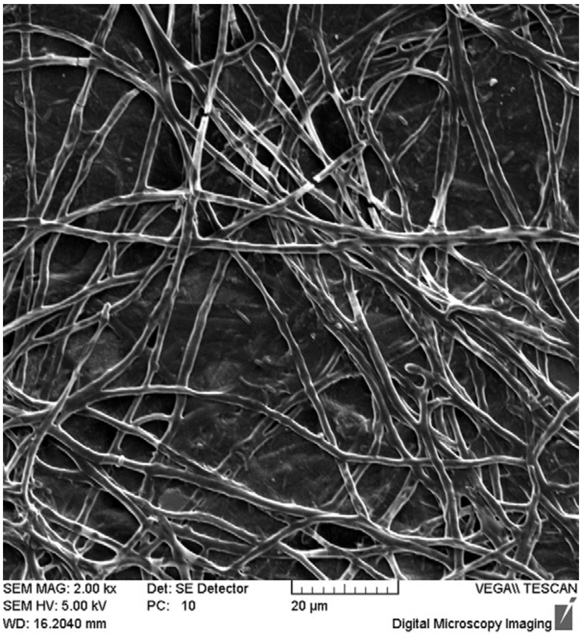

Fig. 4. SEM micrographs of fibers prepared from native pine wood/[Emim][Lactate] solution.

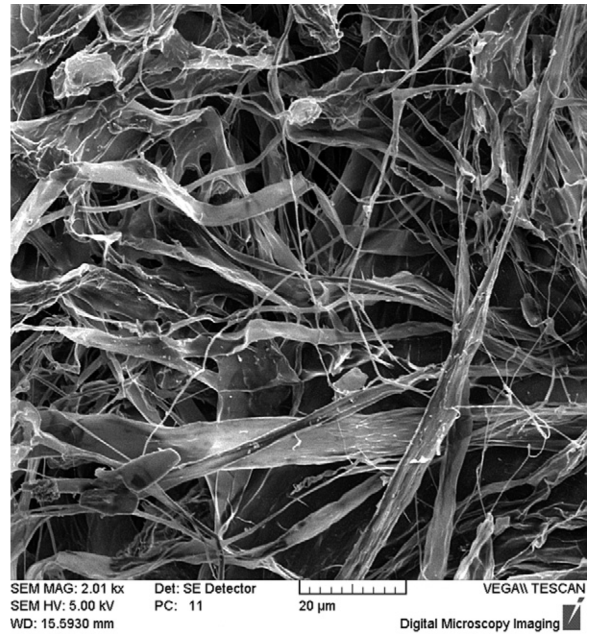

Fig. 5. SEM micrographs of fibers prepared from Soxhlet pine wood/[Emim][oAc] solution.

distance between the nozzle and the surface of water bath remained constant. Sample of wood/ionic liquid solution was transferred to a syringe and voltage of 30 kV was applied to the needle of the syringe. Flow rate of spinning solution solely depended on free fall in the electric fields without additional control. As soon as the electrospun wood fibers fell into the water bath, ionic liquid used was dissolved in water quickly and wood fibers were formed. The fiber solidification was influenced by the feed rate and the rate of washing out the solvent. The fibers in the form of tangled web were washed with distilled water and then dried in vacuum to remove the residual water.

The morphology of the prepared fibers was characterized by a scanning electron microscope (SEM) Vega II LMU (Tescan, Czech Republic). Prior to the SEM observation the fibers were sputter coated with a palladium gold alloy to form a conductive monolayer film on the surface of fibers. Imaging was carried out at an accelerating voltage of 5.0 kV.

3. Results and discussion

It is interesting to note that the dissolution capacity of [Emim][Lactate] for wood has not been studied yet. The present study revealed that this ionic liquid possesses high potential for wood processing; while the Soxhlet extraction in acetone has been rated as an essential step for wood dissolution in [Emim][oAc], [Emim][Lactate] dissolved the natural wood in concentration of 5 wt.% without any pre-treatment. Recently, the effect of introduction of OH-group on imidazol cation on cellulose dissolution was studied by Luo, Li, and Zhou (2005). They suggested that the hydroxyl groups on cation side chain of ILs additionally interact with hydroxyl groups of cellulose which further weakens hydrogen bonding among the cellulose fibers and promotes its dissolution (Luo et al., 2005; Muhammad et al., 2012). Indeed, the introduction of OH-group on ionic liquid anion could similarly strengthen the dissolution capability. In present study, the pronounced solubility of cellulose in [Emim][Lactate] supported experimentally this presumption.

Fibers electrospun from the native pine wood/[Emim][Lactate] solution are depicted in Fig. 4. As can be seen, the fibers are rather uniform and their diameter varies between 1 and 4 μm. Experiments with higher wood concentration (10 wt.%) have been complicated by dramatic increase in viscosity. At such a high viscosity instability of spinning jet occurred. The spinning solution initially formed a bead at the tip of the needle that grew up and finally fell into the bath significantly faulting the electrospinning process and fiber formation. On the other hand, the structure of electrospun fibers from Soxhlet wood/[Emim][oAc] is diverse. As shown in Fig. 5, beyond the fibrous structure also some kinds of blocks and fiber bundles were formed. This can be attributed to the unbalanced spinning vs. washing out rate. Slow washing out of ionic liquid from the fibers may results in their coalescence on the water bath surface where they are collected and accumulated. In addition, in wood/ionic liquid solutions also no fiber forming polymers are dissolved. These types of polymers precipitated in the form of film or blocks during electrospinning.

4. Conclusions

In this work, a concept of direct fiber processing from raw wood has been introduced for the first time. Cellulose fibers from pine wood/ionic liquid solutions were prepared using electrospinning technique. Both types of chosen ionic liquids, [Emim][Lactate] and [Emim][oAc], appeared to be powerful solvents for pine wood. Concentration of wood/ionic liquid solutions seems to have a crucial influence on fiber forming capability. Thus, proper concentration study should be done. Then, the effect of voltage applied and the distance between the electrodes should be investigated for further optimization of whole electrospinning process.

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