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Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization

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ABSTRACT

Recent studies on the application of room temperature ionic liquids (RTILs) in cellulose chemistry have made great progresses. This has been providing a new and versatile platform for the wide utilization of cellulose resources and creation of novel functional materials. In this paper, the research progress in the field of dissolution, regeneration and derivatization of cellulose with RTILs are reviewed. And the perspective of RTIL application in cellulose industry is also discussed.

1. Introduction

Cellulose is the most common organic polymer on the Earth, with an estimated annual natural production of 1.5×10^{12} tons, and is considered as an almost inexhaustible source of raw materials [1]. Hence, effective utilization of cellulose not only reduces the consumption of our limited fossil resources but also protects the environment of the Earth. Starting with dissolving pulp as a purified raw material, cellulose is converted by large-scale industrial processing into regenerated materials (fibers, films, food casings, membranes, sponges, and among others) and cellulose derivatives (ethers and esters). However, processing and derivatization of cellulose are difficult in general, because this natural polymer is neither meltable nor soluble in conventional solvents due to its hydrogen bonded and partially crystalline structure. Therefore, present industrial production of regenerated cellulose and cellulose derivatives are in long time dominated by polluting viscose process and heterogeneous processes, respectively [2]. With increasing governmental regulations in industries, the need to implement "green" processes for cellulose processing and to explore alternative routes for the functionalization of cellulose with simpler reagents and less steps is getting increasingly important.

Over the past decades, several solvent systems have been developed for manufacturing regenerated cellulose materials and cellulose derivatives. Typical examples of these solvents include lithium chloride (LiCl)/*N*,*N*-dimethylacetamide (DMAc), LiCl/*N*-methyl-2-pyrrolidine (NMP), LiCl/1,3-dimethyl-2-imidazolidinone (DMI), dimethyl sulfoxide (DMSO)/tetrabuthlammonium fluoride trihydrate (TBAF), DMSO/paraformaldehyde, *N*-methyl-morpholine-*N*-oxide (NMMO), aqueous solutions of NaOH, some molten salt hydrates, such as $LiClO_4{\cdot}3H_2O$, and $LiSCN{\cdot}2H_2O$, and some aqueous solutions of metal complexes [3]. However, the above solvent systems are limited to their dissolving capability, toxicity, high cost, solvents recovery, uncontrollable side reaction, and instability during cellulose processing and/or derivatization.

Current interests in room temperature ionic liquids (RTILs) stem primarily from the heightened awareness of their potential applications in "Green Chemistry" and the associated emphasis on clean manufacturing processes. Due to their unique properties such as chemical and thermal stability, non-flammability and immeasurable low vapor pressure, RTILs seem to be an attractive alternative to conventional volatile organic solvents. RTILs show promises for a variety of applications in chemical industry including chemical synthesis, catalysis, separation, and preparation of materials. Therefore, RTILs have attracted considerable attentions from both the academic and industrial communities in recent years [4].

Since Swatloski et al. [5] reported the dissolution of cellulose in alkyl substituted imidazolium RTILs, it has attracted considerable attention in this area [6,7]. Recent studies on the application of RTILs in cellulose chemistry have made great progresses. Some new advances in this field include dissolution of cellulose in some new RTILs, the mechanism of cellulose dissolution in RTILs, preparation of some new functional cellulose materials by using RTIL, syntheses of more kinds of cellulose derivatives in RTILs, regenerated cellulose fibers with outstanding mechanical properties spun

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Abbreviations: AdmimBr, 1-*N*-allyl-2,3-dimethylimidazolium bromide; AmimCl, 1-*N*-allyl-3-methylimidazolium chloride; BmimCl, 1-*N*-butyl-3-methylimidazolium chloride; BmimBr, 1-*N*-butyl-3-methylimidazolium bromide; BmimSCN, 1-*N*-butyl-3-methylimidazolium sulfocyanate; BmimAc, 1-*N*-Butyl-3-methylimidazolium acetate; BdmimCl, 1-*N*-butyl-2,3-dimethylimidazolium chloride; EmimAc, 1-*N*-ethyl-3-methylimidazolium acetate; EmimCl, 1-*N*-ethyl-3-methylimidazolium chloride.

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from RTILs, and so on. RTILs have been providing a new and versatile platform for the wide utilization of cellulose resources and preparation of novel cellulose-based materials with special properties. In this paper, a relatively comprehensive review of research progress on dissolution, regeneration and derivatization of cellulose in RTILs is presented. And the perspective of RTIL application in cellulose industry is also discussed.

2. Dissolution of cellulose in RTILs

The first example of cellulose dissolution and processing using ionic liquids might be dated back to 1934. In a patent, Graenacher [8] discovered that molten *N*-ethylpyridinium chloride, in the presence of nitrogen containing bases, could dissolve cellulose. Unfortunately, this did not attract significant attentions due to the lack of knowledge on this kind of substances at that time and relatively high melt points of the pyridinium salts. In 2002, Swatloski et al. [5] reported that some alkyl substituted imidazolium RTILs could be used to dissolve and process cellulose. The effect of the chemical structure of anions and cations of imidazolium RTILs on their dissolving capability for cellulose has also been studied. Among the RTILs they studied, 1-*N*-butyl-3-methylimidazolium chloride (BmimCl) exhibited the best dissolving capability that up to 10 wt% cellulose solution can be obtained by heating. Cellulose could also be soluble in 1-*N*-butyl-3-methylimidazolium bromide (BmimBr) and 1-*N*-butyl-3-methylimidazolium sulfocyanate (BmimSCN) but with less than half solubility of BmimCl. Whereas, RTILs containing “non-coordinating” anions, including $[BF_4]^-$ and $[PF_6]^-$ were found to be nonsolvents for cellulose. In the case of alkylimidazolium chlorides with cations from $[C_4mim]^+$ to $[C_8mim]^+$, their solubility of cellulose decreased with increasing length of alkyl group substituted on the imidazolium ring.

In our previous study [9], a RTIL, 1-*N*-allyl-3-methylimidazolium chloride (AmimCl), was also found to be a powerful solvent for cellulose. Untreated or inactivated cellulose could be dissolved in this RTIL rapidly. For example, cellulose with a degree of polymerization (DP) of 650 could be dissolved in AmimCl in only 30 min at 80 °C. A solution containing up to 14.5 wt% cellulose with a DP as high as 650 in AmimCl was also readily prepared. In comparison with other imidazolium chloride RTILs such as BmimCl and 1-*N*-ethyl-3-methylimidazolium chloride (EmimCl), the synthesis of AmimCl was performed readily. In a typical synthesis, the conversion ratio of the imidazolium reached up to 80% after a reaction time of 3 h and almost 100% after 6 h, respectively, which was the result of the high reactivity of allyl chloride. More interestingly, AmimCl showed a lower melting point at ca. 17 °C and a considerably lower viscosity of 685 MPa s at 30 °C, while BmimCl had a melting point at 65 °C and viscosity of 11,000 MPa s at 30 °C [10]. The lower melting point and viscosity of AmimCl were attributed to its suppressed crystallization by an allyl group on the *N*-position [11]. Heinze et al. [12] tested the dissolving capability of different RTILs such as BmimCl, 3-methyl-*N*-butylpyridinium chloride and benzyldimethyl(tetradecyl) ammonium chloride for cellulose. Their study also showed that BmimCl was the most appropriate cellulose dissolving solvent for two primary points: (1) its strong ability to dissolve cellulose with DP in the range from 290 to 1200 up to very high concentrations; (2) almost no degradation of cellulose after the dissolution. In their experiments, BmimCl can dissolve the cotton linter (DP = 1198) with the concentration of 10 wt%, and DP is only slightly degraded to 812, which might be caused by mechanical shearing during stirring.

It should be noted that, imidazolium-based RTILs containing halide anions, especially chloride anion, seem to be more effective for dissolving cellulose. In addition, these RTILs are cheaper than most well-known RTILs obtained by anion-exchange reactions using imidazolium halide salts as starting materials. However, the relatively high melting points and viscosities of RTILs containing chloride anion possibly limit their practical application in cellulose processing or homogeneous cellulose derivatization. Relatively high dissolution temperatures (often above 80 °C) are often required for dissolving cellulose, which possibly results in thermal decomposition of RTILs [13], and produce some organohalogenides [14], which have uncertain toxicity and hazardousness to zoology and ecosystems after ineluctable release into the environment. The corrosion of imidazolium chloride RTILs was also thought as a potential limitation to the future industrial application. From the aforementioned points of view, it will be of great interest to seek for powerful, halogen-free cellulose solvents with low melt point and low viscosity.

In our earlier work [15], 1-*N*-ethyl-3-methylimidazolium acetate (EmimAc) was found to be good cellulose solvent. In addition to its very low melt point (<−20 °C) and viscosity (∼140 cPs at 25 °C), it showed a much higher capability for cellulose dissolution. Recent studies showed that the preparation time for a 10 wt % cellulose spinning dope was about 45–60 min [16], and a cellulose concentration as high as 20 wt% in EmimAc was reached [17]. Moreover, EmimAc was considered to be less toxic and corrosive than comparable chlorides and even biodegradable [18]. These features make EmimAc a promising solvent for the processing and homogeneous derivatization of cellulose.

Recently, Fukaya et al. [19] found a series of 1,3-dialkylimidazolium formate RTILs exhibited superior solubility for a wide range of polysaccharides including cellulose. These RTILs had significantly lower viscosities than previously reported halogenated imidazolium RTILs, for example 1-allyl-3-methylimidazolium formate had viscosity of 66 cP at 25 °C and 1-allyl-3-ethylimidazolium formate 67 cP at 25 °C. Comparing with RTIL AmimCl, 1-allyl-3-methylimidazolium formate dissolved cellulose at lower temperatures and reached larger concentrations.

A series of alkylimidazolium RTILs containing dimethyl phosphate, methyl methylphosphonate, or methyl phosphonate was synthesized by a facile, one-pot procedure [20]. These RTILs also have the potential to solubilize cellulose under mild conditions. Especially, 1-*N*-ethyl-3-methylimidazolium methylphosphonate enabled to prepare a 10 wt% cellulose solution by keeping it at 45 °C for 30 min with stirring, or to dissolve 2–4 wt% cellulose even without any pre-treatments and heating.

By the aid of energy irradiations, such as high-intensity ultrasound and microwave, the dissolution of cellulose in RTILs can be significantly enhanced. Mikkola’s study showed that the dissolution process of cellulose in RTILs BmimCl and AmimCl could be considerably enhanced by means of high-intensity ultrasound [21]. In comparison with conventional heating, the dissolution time decreased profoundly. For example, in order to obtain a 5 wt% cellulose solution in AmimCl using conventional heating, 1 h (or even more) was needed, whereas only 2 min was used to reach complete dissolution upon ultrasound-enhancing. A solution containing up to 27% of microcrystalline cellulose was easily obtained in AmimCl under periodic ultrasound pulses (1 min of sonication followed by a 1 min pause). Swatloski et al. [5] found that BmimCl could dissolve up to 25 wt% of cellulose under heating supported by short microwave pulses, while only a 10 wt% under conventional heating.

It should be noted that the presence of residual water in RTILs was found to reduce the solubility of cellulose significantly, probably by forming competing hydrogen bonds to the macromolecular chains of cellulose [5]. Therefore, before dissolving cellulose, it is needed to remove water from RTILs thoroughly.

Cellulose solutions in RTILs have been investigated. Fig. 1 shows the ^{13}C NMR spectra of cellulose in BmimCl (spectrum A), AmimCl (spectrum B), and EmimAc (spectrum C), respectively. The NMR studies clearly showed that these three RTILs were nonderivatizing solvents for cellulose.