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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.

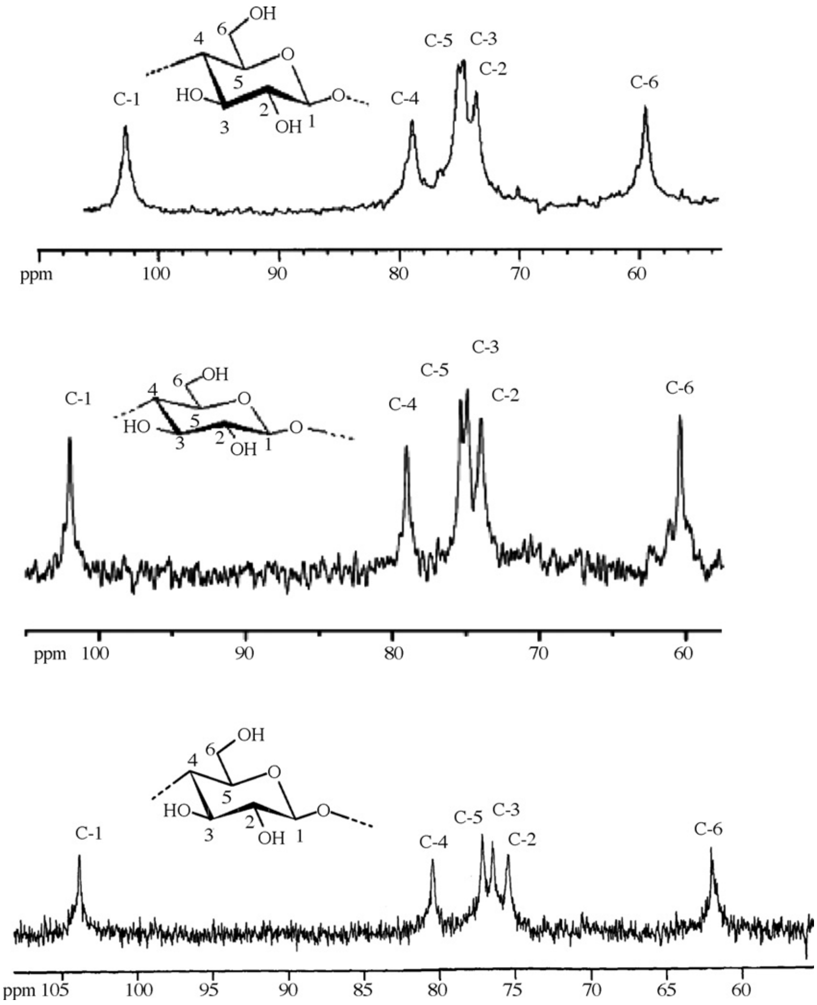
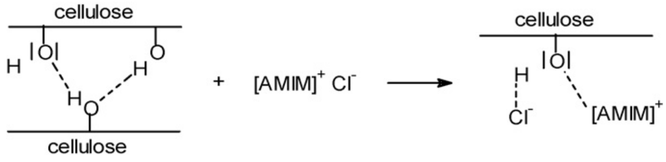


Fig. 1. ^{13}C NMR spectra of cellulose: (a) in BmimCl [12], (b) in AmimCl [9], and (c) in EmimAc [22].

Dissolution of cellulose in RTILs was attributed to their ability to break the extensive network of hydrogen bonds existing in cellulose. In the case of alkylimidazolium chloride, the high chloride concentration in the RTIL enhanced its ability to disrupt hydrogen bonding. We proposed a possible mechanism of cellulose dissolution in AmimCl shown in Scheme 1 as follows [9]: above the critical temperature, the ion pairs in AmimCl dissociated to individual Cl⁻ and Amim⁺ ions. Then free Cl⁻ ions associated with cellulose hydroxyl proton, and free cations complexed with cellulose hydroxyl oxygen, which disrupted hydrogen bonding in cellulose and led to the dissolution of cellulose. Although some simulation studies [23,24] suggested that little or weak interaction between cations of RTIL and the glucose of cellulose existed, we believed cations of RTIL were involved in the dissolution process and their role in the dissolution mechanism should not be neglected.



Scheme 1. Possible dissolution mechanism of cellulose in AmimCl [9].

3. Regeneration of cellulose from RTIL solutions

Nowadays, the regenerated cellulose fibers predominantly produced by the well-known viscose process lasting for 100 years. The viscose fibers (Rayon) have excellent properties for a wide range of products from wet-strength cotton like textile fibers (Modal fibers) to technical fibers as the cord in high-performance tires. The viscose route, however, is technologically complex, and brings about problematic environmental burdens with the use of CS_2, heavy metal compounds (in the precipitation process), and by-products. Therefore, the development of viscose process is greatly restricted because of these serious environmental problems [1,2].

Recently, as an industrial breakthrough, regenerated cellulose fibers made from NMMO solution (Lyocell-type fiber) are competing with viscose-type fibers. Compared with conventional viscose fibers, Lyocell fibers spun from NMMO solution exhibit outstanding properties in certain respect such as strength in both wet and dry states, modulus of elasticity, sorption behavior, wearing properties, gloss, and touch. And a particular feature of the NMMO process is its essentially physical characteristic, so that no chemical reaction involved and no chemical by-product formed. Otherwise, these by-products must be disposed off as wastes or transformed back to the initial substances by chemical methods. Therefore, the NMMO process fundamentally ranks among the very environmentally friendly processes.

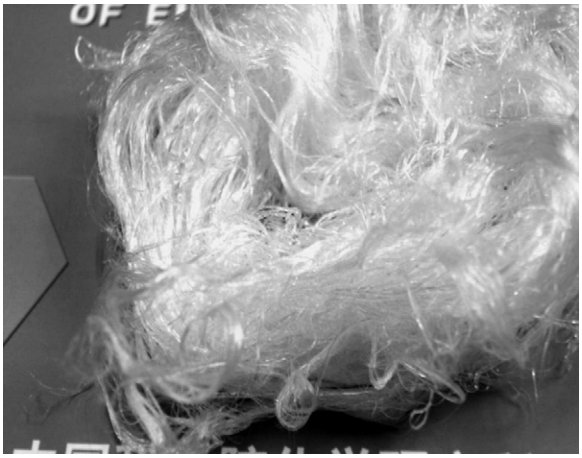


Fig. 2. Cellulose fibers manufactured by dry jet-wet spinning process from AmimCl solution [22].

Despite so many advantages, the Lyocell process still cannot replace viscose process to date, because there are some disadvantages associated with its use, like the activation of cellulose before dissolution, the need for high temperature to dissolve cellulose, the degradation of cellulose, the side reactions of the solvent itself without antioxidants, and its high cost as well [25]. Therefore, in the past several years, intense research efforts have been made to develop new efficient and environmental friendly cellulose solvents.

Due to the unique properties and superior dissolving capability for cellulose, RTILs used for manufacturing regenerated cellulose materials have received much attention from both academic and industrial interests. Using RTIL AmimCl, we prepared regenerated cellulose films and fibers [9,26]. As AmimCl was completely miscible with water in any ratio, the regenerated cellulose materials were easily obtained by coagulation. To obtain cellulose films, AmimCl/cellulose solution was cast onto a glass plate and then coagulated in water. After removing AmimCl and drying completely, a transparent cellulose film was obtained. SEM micrographs showed that both the free surface and fracture surface of the regenerated films display a uniformity, indicating a dense texture from the interior to the surface. The tensile strength of the regenerated cellulose film with a DP of 480 was as high as 138 MPa. The cellulose fibers regenerated from AmimCl can be prepared easily by either wet spinning or dry jet-wet spinning process and coagulated with water. The cellulose fibers spun from AmimCl solution by dry jet-wet spinning method exhibited a smooth surface (see Fig. 2) [22]. The fractured surface of cellulose fibers displayed a fibrillar morphology, which was very similar as the cellulose fibers from NMMO process (Fig. 3) [27]. The RTIL process for production of regenerated cellulose fibers is illustrated in Fig. 4.

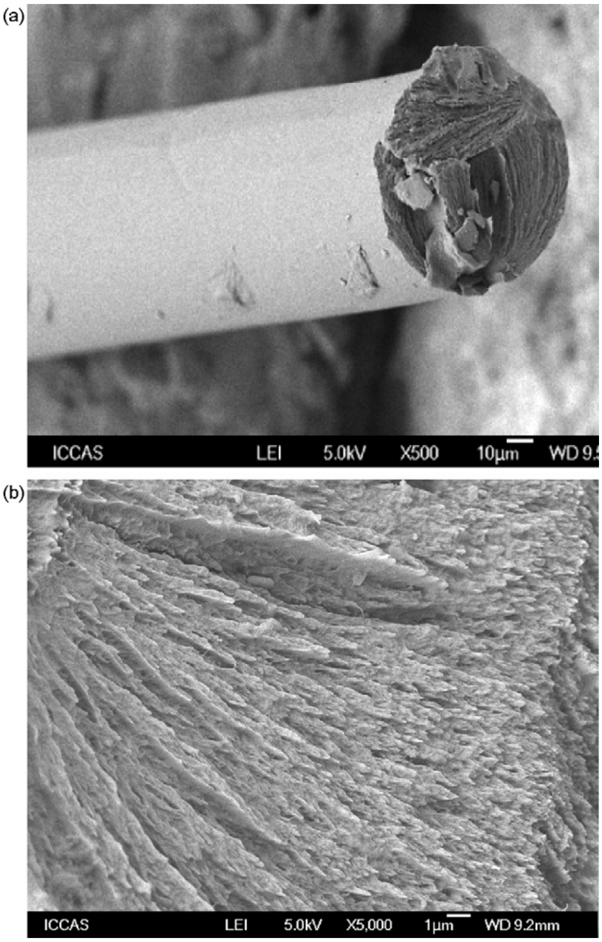


Fig. 3. SEM micrographs of fracture surface of regenerated cellulose fiber from AmimCl [22].

The RTIL BmimCl has also been used to dissolve cellulose over a wide range of molecular weights [28]. Fibers and films have been produced from solutions, and some with their properties have been measured. The fiber spinning was conducted on a lab-scale apparatus with a promising result. Table 1 shows some properties of regenerated cellulose fibers spun from BmimCl. The mechanical properties of cellulose fibers were comparable with Lyocell fibers, and much higher than viscous fibers.

Recently, Kosan et al. [17] reported regenerated cellulose fibers spun from four kinds of RTILs, BmimCl, EmimCl, 1-*N*-butyl-3-methylimidazolium acetate (BmimAc), and EmimAc. Their study showed that all these RTILs exhibited good dissolving capability and were suitable for the preparation of cellulose dopes in concentration ranges exhibiting highly technical importance. And the cellulose solutions in these RTILs exhibited a good spinnability. Using a dry-wet spinning process, cellulose fibers with good textile-physical properties were obtained. Table 2 summarized some textile-physical properties of the regenerated cellulose fibers from BmimCl, EmimCl, BmimAc, and EmimAc. For the sake of comparison, the properties of cellulose fibers spun from NMMO process are also listed. It can be seen that the tenacity of all cellulose fibers spun from solutions of these four RTILs is even slightly higher than that of fibers from NMMO. Interestingly, using the same pulp as cellulose source, cellulose solutions in RTILs with chloride anions

Table 1
Some properties of regenerated cellulose fiber spun from BmimCl [28].

Cellulose source	Rayon	Rayon	Rayon	Pulp	Pulp	B1 Cot	B1 Cot
Sample ID	54-1	54-2	As recd.	66-1	65-2	69-1	69-2
Fiber property							
Linear density (g/9000 m)/SD	59.3/9.2	38.6/4.3	6.63/0.44	35.5/–	27.3/3.5	15.3/2.4	11.3/0.42
Tenacity (g/den)/SD	2.44/0.38	3.43/0.42	1.89/0.20	3.78/–	4.41/0.46	3.32/0.67	3.38/0.31
Breaking elong. (%)/SD	18.7/4.6	14.4/2.8	30.9/7.45	8.8/–	7.6/1.7	4.1/1.7	3.8/0.52
Ave. modulus (g/den)	13.0	23.8	6.1	42.9	58.0	77.3	88.9

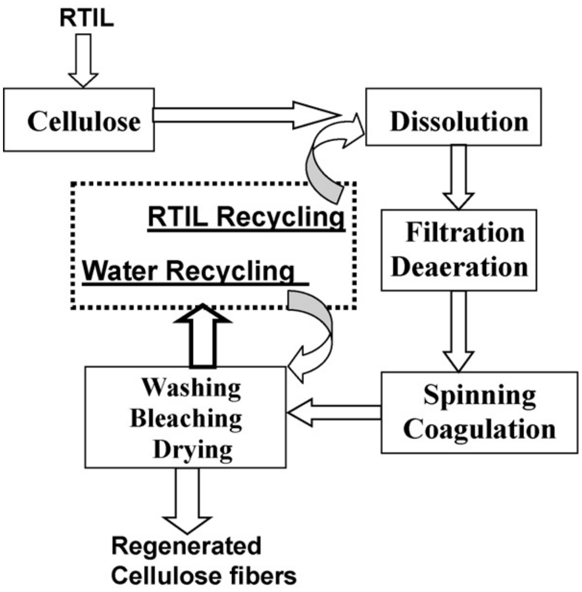


Fig. 4. RTIL process for regenerated cellulose fibers [22].

(BmimCl and EmimCl) led to fibers with somewhat higher tenacity, higher loop tenacity values and lower elongation values than fibers spun from acetate anion (BmimAc and EmimAc) containing solutions and NMMO solutions. However, compared to the chloride solutions, significant lower viscosities of acetate anion solutions favor higher cellulose concentrations. Therefore, the RTIL EmimAc is expected to be much more efficient and flexible in cellulose dissolution and shaping processes.

In addition, regenerated cellulose composites with special properties can be prepared by introducing different kinds of additives into the RTIL/cellulose solutions, either dissolved or suspended, prior to reconstitution.

Using a cellulose-in-ionic-liquid dissolution and regeneration process, bioactive cellulose membranes, film, and beads have been prepared [29,30]. Enzymes can be encapsulated in cellulose matrix and covalently attached onto the surface of cellulose materials.

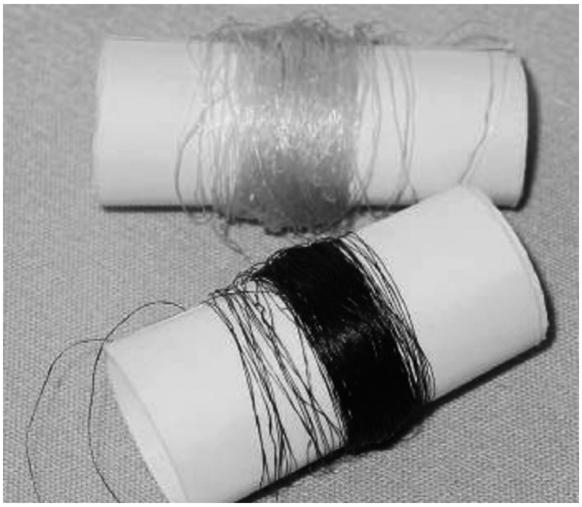


Fig. 5. Photograph of the regenerated cellulose (white) and cellulose/MWCNT composite fibers (black) [26].

By co-dissolution of cellulose and related substances in RTIL BmimCl followed by regeneration, cellulose films containing entrapped analytical reagents have been prepared for metal-ion detection [31]. Cellulose films containing 1-(2-pyridylazo)-2-naphthol has been used for colorimetric determination of divalent zinc, manganese, and nickel with the detection limits at the 10^{-6} mol/L level.

Using dry jet-wet spinning method, cellulose/multiwalled carbon nanotube (MWCNT) composite fibers were successfully spun from cellulose/MWCNT/AmimCl solutions containing different MWCNT loadings [26]. Well-dispersed and -aligned MWCNTs were observed in cellulose fibers. The composite fibers exhibited improved mechanical properties and thermal stability because of the good interaction between cellulose and MWCNTs (see Table 3). This simple method of preparing regenerated cellulose/MWCNT composite fibers could lead to the production of carbon fibers from a renewable resource (cellulose). Fig. 5 shows regenerated cellulose (white) and cellulose/MWCNT composite (black) fibers.

Table 2
The textile-physical properties of the obtained fibers spun from cellulose solution in BmimCl, EmimCl, BmimAc, and EmimAc in comparison to a cellulose solution in NMMO [17].

Solvent	NMMO	BmimCl	EmimCl	BmimAc	BmimAc	EmimAc
Solution and spinning parameters						
Cellulose concentration (%)	13.5	13.6	15.8	13.2	18.9	19.6
Zero shear viscosity (85 °C) (Pa s)	9914	47,540	24,900	9690	63,630	30,560
Spinning mass temperature (°C)	94	116	99	90	98	99
Fiber properties						
Tenacity, cond. (cN/tex)	43.6	53.4	53.4	44.1	48.6	45.6
Elongation cond. (%)	16.7	13.1	12.9	15.5	12.9	11.2
E-modulus (0.5–0.7%) (cN/tex)	942	682	903	712	715	682
Fiber-DP	520	514	493	486	479	515

Table 3
Mechanical properties of regenerated cellulose/MWCNT composite fibers at different MWCNT loading [26].

MWNTs concentration (wt%)	Tensile strength (MPa)	Storage modulus E' (25 °C) (GPa)	Storage modulus E' (150 °C) (GPa)	E' (150 °C)/E' (25 °C)
0	204	5.1	1.4	0.27
1	222	6.7	3.8	0.57
3	256	12.1	7.7	0.64
4	335	17.6	13.6	0.77
5	280	13.9	12.4	0.89
6	265	11.1	8.6	0.77
8	211	7.6	6.4	0.85
9	210	7.4	6.7	0.91

Sun et al. [32] prepared magnetically active cellulose fibers with the help of RTIL EmimCl. Cellulose from different sources with various DP values was used for making fibers by first dissolving the cellulose in the EmimCl, dispersing particles of magnetite in the solution, and then spinning and coagulating fibers in a water bath under appropriate conditions.

It has been shown that some RTILs can be used to produce cellulose solutions of concentration as high as 20 wt% by means of a simple dissolution without pre-treatment, indicating their very strong dissolution capability for cellulose [16]. The reported results showed that regenerated cellulose fibers spun from RTILs solutions displayed the similar properties in terms of tenacity and elasticity compared with fibers manufactured by the NMMO and viscose processes. Therefore, RTIL process has the potential for wide-scale use in future textile and technical applications. Compared with NMMO process, RTILs are more stable so that it can be stored at room temperature for several months without mixing with water; and the spinning dopes are even stable up to storage temperature of 120 °C for 48 h without obvious degradation and decomposition. Usually, after the spinning process, only RTILs and water are left in the coagulation bath, so that recycling of the RTIL can be accomplished by evaporation of water and be reused without further purification. The properties of fibers spun from recycled RTILs remain intact even after a number of process cycles with RTILs.

From the above, it is concluded that RTILs enhance the efficiency of cellulose processing. RTIL process appears to be more suitable for industrial application in cellulose fiber production than NMMO.

4. Homogeneous derivatization of cellulose in RTILs

Cellulose derivatization under homogeneous reaction conditions offers a distinct advantage over the heterogeneous methods due to its higher reaction efficiency and easy control of the degree of substitution (DS) [33]. The discovery of numerous solvent systems for cellulose has provided new approaches not only for cellulose regeneration, but also for derivatization under homogeneous conditions. The esterification has been extensively studied in the homogeneous cellulose derivatization reactions. But the homogeneous esterification of cellulose was known to be inefficient in those cellulose solvent systems containing free or covalent water component such as molten salt hydrates, because high excess of acylation reagents must be consumed [3,33]. Based on their excellent capability to dissolve cellulose, RTILs are expected to be used as “green” reaction media for homogeneous cellulose derivatizations suitable for synthesis of different cellulose derivatives, such as cellulose esters, ethers and grafted copolymers.

4.1. Acetylation of cellulose in RTILs

Cellulose acetate (CA) is one of the most commercially important cellulose esters with a wide application in the fields of coating, film, membrane, textile, and cigarette industries. CA was first synthesized by Schuetzenberger in 1865 and was industrially produced as early as 1900 [34]. Nowadays, the commercial CA is mainly produced by heterogeneous acetylation of cellulose with excess of acetic anhydrides in the presence of sulfuric acid catalyst. A typical CA production consists of a sequence of two heterogeneous reactions, namely functionalization of the polymer to a DS of ca. 3, followed by partial hydrolysis of the product to the widely applied acetone-soluble CA with a DS of 2.5 [35]. The heterogeneous acetylation process for producing CA has some disadvantages such as complicated two steps, high energy consumption, uneven substitution, poor reproducibility, and poor mechanical properties of the products [33].

RTILs as novel and efficient solvents for cellulose have created opportunities for more diverse synthesis pathways to CA. In our previous study [36], the homogeneous acetylation of cellulose was successfully performed in RTIL AmimCl under mild conditions. Without using any catalysts, CAs with DS values from 0.94 to 2.74 were synthesized by one step. The synthesized CAs were soluble in some organic solvents such as acetone, chloroform, and DMSO, depending on the DS values. Compared with the heterogeneous process, the homogeneous process seems very simple and acetone-soluble CA can be obtained by controlling the reaction time and molar ratio of acetic anhydride/anhydroglucose unit (AGU) of cellulose.

Heinze et al. [12] found that, using BmimCl as reaction medium, it is possible to synthesize CAs with high DS values in good yield within a short time. The acetylating reagents such as acetic anhydride and acetyl chloride have been proven effective in the absence of catalysts. The homogeneous acetylation of cellulose was investigated with RTILs BmimCl, 1-*N*-allyl-2,3-dimethylimidazolium bromide (AdmimBr), 1-*N*-butyl-2,3-dimethylimidazolium chloride (BdmimCl) or EmimCl as reaction media, and acetic anhydride or acetyl chloride as acetylating reagent [37]. CAs with DS values in the range from 2.5 to 3.0 were accessible within 2 h at 80 °C in a complete homogeneous procedure, and the DS of CA could be controlled by varying the molar ratio and the reaction time. The reactivity of cellulose increased in the order of BmimCl < AdmimBr < BdmimCl < EmimCl at the same molar ratio of 3.0 mol acetic anhydride per mol AGU. But different from BmimCl, the application of acetyl chloride in AdmimBr, BdmimCl, and EmimCl resulted in degradation of both RTILs and polymers.

Recently, we [38] found that, using RTIL EmimAc as a reaction medium and with no catalyst, cellulose could be effectively acetylated by acetic anhydride, even at room temperature. CAs with a wide range of DS from 1 to 3 could be synthesized within only 15 min at 25 °C, mainly depending on the reagent ratio of acetic anhydride/AGU. Interestingly, acetone-soluble cellulose acetate with a DS of 2.5 could be obtained within only 5 min at 25 °C and acetic anhydride/AGU ratio of 3. To our knowledge, this is the most effective acetylation of cellulose under homogeneous state.

Table 4 summarized the typical reaction conditions and results of homogeneous cellulose acetylation in some RTILs. It is clear that in these RTILs, the acetylation of cellulose can be accomplished without any catalysts under mild conditions, with low excess of reagent and in a relatively short reaction time.

We studied homogeneous acetylation of cellulose in AmimCl at relatively high cellulose concentrations (8, 10, and 12 wt%) [39], which showed that CAs with DS values in a range from 0.4 to 3.0 could be synthesized under mild conditions. The effects of reaction time, temperature and molar ratio of acetic anhydride/AGU in cellulose on the DS value of CAs were investigated. The obtained CAs had very good solubility and mechanical properties, the tensile strength of CAs synthesized in 12 wt% cellulose/AmimCl solution reached as high as 57.0 MPa, which was even higher than that of commercial CA films (DS 2.44, tensile strength 51.0 MPa). The synthesized CA exhibited the similar thermal stability as the commercial CAs. After the acetylation, AmimCl was easily recycled and reused.

It has been demonstrated that homogeneous cellulose acetylation in RTILs showed some regioselectivity. Fig. 6 shows a ^{13}C NMR spectrum of CA synthesized in AmimCl [40]. The partial DS values of CAs synthesized in RTILs are shown in Table 5. It can be seen that the order of partial DS values of most CAs synthesized in AmimCl was C6 > C3 > C2, which is different from the order with acetic anhydride/pyridine system in AmimCl C6 > C2 > C3. Schlufter et al. [41] found the similar distribution of acetyl moieties in the order C6 > C3 > C2, when they acetylated the bacterial cellulose with a high DP of 6500 in RTIL BmimCl. And our group found the same

Table 4
Reaction conditions and results of homogeneous cellulose acetylation in different RTILs.

RTIL	Acetylation reagent		Time (min)	Temperature (°C)	DS	Reference
	Type	mol per mol AGU				
BmimCl	Acetic anhydride	5.0	120	80	2.72	[12]
BmimCl	Acetic anhydride	3.0	120	80	2.92	[37]
BmimCl	Acetyl chloride	3.0	30	80	3.0	[37]
EmimCl]	Acetic anhydride	3.0	120	80	3.0	[37]
BdmimCl	Acetic anhydride	3.0	120	80	2.92	[37]
AdmimBr	Acetic anhydride	3.0	120	80	2.67	[37]
AmimCl	Acetic anhydride	5	15	80	0.94	[36]
AmimCl	Acetic anhydride	5	480	80	2.49	[36]
AmimCl	Acetic anhydride	3	180	100	1.99	[36]
AmimCl	Acetic anhydride	7.5	48h	25	0.64	[36]
AmimCl	Acetyl chloride	5	120	60	2.19	[40]
EmimAc	Acetic anhydride	3	15	25	2.31	[38]
EmimAc	Acetic anhydride	5	15	25	3.00	[38]

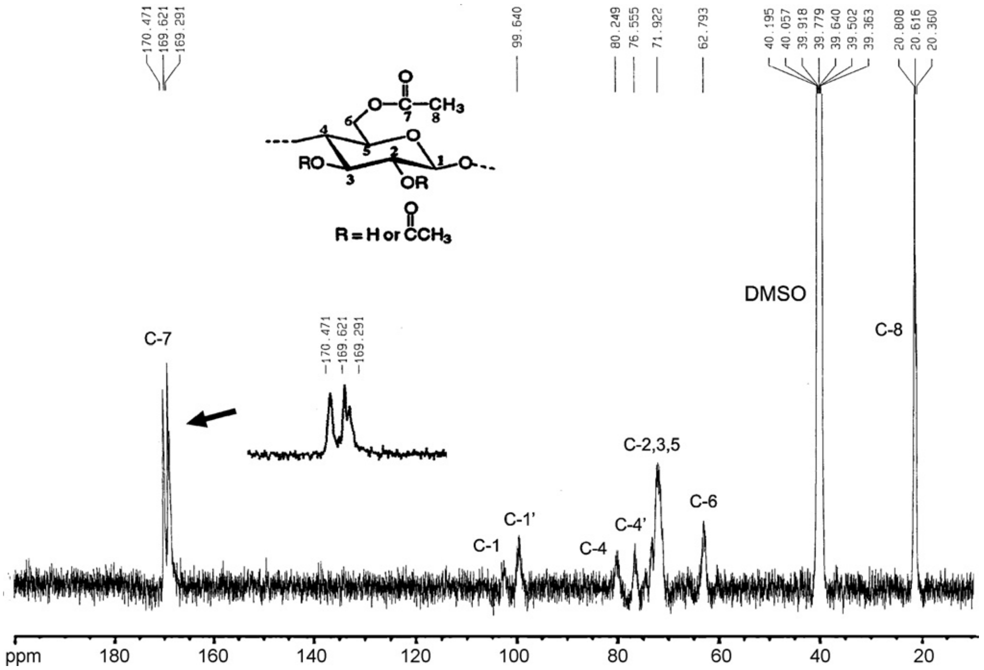


Fig. 6. ^{13}C NMR spectrum of CA synthesized in AmimCl [36].

distribution order in EmimAc. As expected, a preferred acetylation on the primary hydroxyl group at C6 was observed, because this hydroxyl group was the least sterically hindered one of the AGU and was mostly found as a result of homogeneous acylation of cellulose. However, up to now, no simple explanation can be advanced for the difference in the reactivity between C3 and C2. It should be noted that the distribution of acetyl moieties among these three OH groups in the AGU is quite different from industrial CA samples through heterogeneous acetylation–hydrolysis process, whose partial DS order is C3 > C2 > C6 [42]. The difference in functionalization patterns is considered to be the major reason for the difference in solubility of CA samples synthesized via different paths.

Table 5
The DS and partial DS values of CAs synthesized in RTILs.

RTIL	DS_{total}	DS_{C2}	DS_{C3}	DS_{C6}	Reference
BmimCl	1.66	0.29	0.37	1.0	[41]
BmimCl	2.50	0.71	0.79	1.0	[41]
AmimCl	0.94	0.01	0.14	0.71	[36]
AmimCl	2.63	0.86	0.78	0.99	[47]
EmimAc	1.94	0.50	0.52	0.92	[38]

It should be noted that, in our previous studies, CA samples with DS in a range of 2.3–2.7 synthesized in AmimCl and EmimAc readily dissolved in acetone, a technically important solvent, especially for CA fiber spinning. However, CAs with similar DS values synthesized in BmimCl were reported to be insoluble in acetone [37]. This difference in solubility may be a consequence of different distributions of acetyl groups both within the repeating AGU units and along the cellulose chains.

4.2. *Other esterification of cellulose in RTILs*

Different acylation reagents for the preparation of other kinds of cellulose esters in RTILs were also reported. Barthel and Heinze [37] studied the acylation of cellulose in four kinds of RTILs with fatty acid chloride lauroyl chloride, leading to cellulose laurates with DS from 0.34 to 1.54. The reaction was found to start homogeneously and then continue heterogeneously. The synthesis of cellulose carbanilates was also carried out in the RTIL BmimCl without any catalysts. The new homogeneous path produced pure cellulose carbanilates. All reactions were carried out under mild conditions, with low excess of reagent and in a short reaction time. The RTILs were easily recycled and reused.

Liu et al. [43] successfully carried out the homogeneous phthalation of cellulose in AmimCl without any catalysts. The DS of cellulose derivatives ranged from 0.10 to 0.73 under the given conditions, and it increased with the increase of the molar ratio of phthalic anhydride/AGU in cellulose, reaction time and reaction temperature. Solid-state ^{13}C NMR spectroscopy confirmed that the phthalation at all C6, C2, and C3 positions occurred.

RTIL BmimCl was also studied as reaction medium for the homogeneous acylation of cellulose with 2-furoyl chloride in the presence of pyridine [44]. Cellulose furoates with DS values in the range from 0.46 to 3.0 were accessible.

Granström et al. [45] carried out tosylation reaction for microcrystalline cellulose in AmimCl and obtained a product of DS about 1, which would be useful when considering subsequent selective nucleophilic displacement reaction at position C6 from the tosylated intermediate.

4.3. Other derivatization of cellulose in RTILs

Besides attempts for cellulose esterification, cellulose etherification in RTILs was also tried and reported. In a study by Heinze et al. [12] carboxymethyl cellulose (CMC) with DS of 0.49 at the molar ratio of 1 mol AGU per 1 mol reagent was obtained in BmimCl mixed with DMSO and NaOH as a base. Erdmenge et al. [46] performed the tritylation of cellulose in BmimCl using pyridine as the base. The influences of reaction time and the molar ratio of trityl chloride/AGU on the DS were investigated in detail. A DS of around 1 was obtained after 3 h reaction time using a sixfold excess of trityl chloride.

In summary, it has been demonstrated that RTILs are powerful and promising media for homogeneous functionalization of cellulose. Without adding additional bases, cellulose of high DP dissolved in RTIL can react with acetic anhydride or acetyl chloride. Just controlling the reaction time and temperature, and molar ratio of reactants permits one to obtain CAs with desired DS values. Compared with homogeneous cellulose derivatization in other solvents, the main advantages using RTILs as media include no catalysts, short reaction time, simple separation of products and solvents, no by-product, easy solvent recovery, and so on. It is worth to mention that cellulose dissolved in EmimAc had very high reactivity so that CA with high DS could be obtained at room temperature in tens of minutes, and the product could be soluble in acetone. The acetylation of cellulose in solutions of high cellulose/IL concentrations demonstrates its potential in the homogeneous acetylation for future industrial applications.

5. Recovery of RTILs

For environmental conservation and economy of processes, it is required and important to recover and recycle RTILs after the regeneration or derivatization of cellulose.

In our previous studies [9,47], the recycling of RTILs in both regeneration and derivatization processes of cellulose was investigated. In the case of AmimCl for the regeneration of cellulose, the residual RTIL in the coagulation bath was recovered by reducing the pressure and subsequently distilling water away. The purity of recovered AmimCl was above 99%, confirmed by ^{1}H NMR spectroscopy. Compared with the fresh RTIL, the recycled AmimCl exhibited the similar dissolving capability for cellulose. In the case of AmimCl for the homogeneous synthesis of CAs, it contained a large excess of water for precipitating the products after cellulose acetylation. The product was filtered out first, and then the residual RTIL in the filtrate was recovered by evaporation, giving a clean AmimCl. The refreshed AmimCl as the acetylation medium could produce CAs with the similar DS values under comparable reaction conditions.

Hermanutz et al. [16] reported that RTILs used as solvents for manufacturing cellulose fibers were almost entirely recovered (99.5%). Recycling of EmimAc was achieved by the collection of used liquids and evaporation of water. The refreshed EmimAc was then reused without further purification. Fiber properties such as the tenacity and elasticity remained intact even by using RTILs recycled several times. Also, the filterability and stability of the spinning dope in the recycled RTILs were still unchanged.

However, for the future industrial applications on a large scale, it has been suggested that other methods for removal of water may be more practical [48,49]. These alternative methods include nanofiltration, reverse osmosis, pervaporation, and salting out of the RTIL. Apparently, the advantages of easy recycling of RTILs will promote their industrial application in this field.

6. Conclusions and remarks

In conclusion, RTILs are promising solvents both for cellulose processing and homogeneous cellulose derivatization, particularly for the esterification. RTILs provide a new and powerful platform for cellulose chemistry and have been taken as the next generation of solvents for cellulose. With the significant progress in their fundamental research, it is needed to focus our attention on their potential industrial applications. Before the large-scale utilization of RTILs in cellulose industry, several urgent questions still remain to be explored:

(1) *Effective synthesis of RTILs*: Emphasis should be put on the exploitation of new and effective routes to synthesis of RTILs, especially new “clean” and “atom efficient” synthesis methods. On the other hand, in order to meet the requirement for clean manufacturing and effective cost-decreasing, it is needed to develop techniques together with corresponding facilities for large-scale production of RTILs, and the integration of producing processes of RTILs with other industrial processes.

(2) *Evaluation of toxicity, safety, biodegradation and bio-accumulation of RTILs, and their impact on human being and environment*: Significant uncertainty still exists regarding the toxicity and potential impact of RTILs on the environment. In their use as solvents in cellulose industry, the toxicity and safety to human health should be evaluated, because of possible trace residual RTILs in the final regenerated cellulose materials and cellulose derivatives. The environmental evaluation of RTILs should be put into the agenda. RTILs as solvents will somewhat release to the environment, so the pollution of the environment, the degradation of RTILs in the nature and the accumulation in organisms should draw widely attentions. Whereas this field is just in the early stage, the accumulation of data about the toxicity, biodegradation and physiological effect is needed urgently.

(3) *Recovery and reuse of RTILs*: From the viewpoint of environmental conservation and economy of processes, effective recycling and reuse of RTILs are required. In previous studies, the recovery of RTILs was performed only by evaporation. This, however, would consume large amount of energy, especially in the case of dilute RTIL/water solutions. Therefore, further efforts to develop effective methods and facilities for RTIL recycling are needed.

(4) *Study on instability of RTILs*: It has been shown that most alkylimidazolium RTILs are thermally stable up to 200 °C. However, the degradation and decomposition of RTILs under long-term heating at about 100 °C have been observed, which will lead to the formation of by-products and the loss of RTILs. Therefore, stability of RTILs at relatively high temperatures/cycled temperatures over extended periods of time, and under shearing conditions should be investigated. Further studies are also necessary both to monitor and to reduce the

accumulation of these by-products caused by thermal degradation during processes. Finally, the study on removing these by-products is absolutely needed.

(5) *Evaluation of obtained products*: For regenerated cellulose fibers spun from RTIL solutions, further investigation on their condensed structure, morphology, and textile-related physical properties, namely tensile properties, dyeability, and moisture absorption, is needed. For cellulose derivatives synthesized in RTILs, due to their different substitution patterns from commercialized products produced by heterogeneous methods, their chemical and physical properties, solution behavior, and processability are needed to be investigated in detail.

(6) *Optimization of process*: Despite of the impressive progresses mentioned above, RTIL processes for cellulose processing and cellulose derivatization must be optimized in the aspects of dissolution, spinning, coagulation, reaction, precipitation, separation, and RTIL recycling.

(7) Cost–benefit and cost-effectiveness analyses for RTIL process: Despite of the recent studies showing great potential of RTILs for their application in cellulose processing and derivatization, cost–benefit and cost-effectiveness and life-cycle analyses for whole RTIL processes will be demanded before their large-scale application.

In all, industrial implementation of RTILs in cellulose industry is attractive. However, the present investigation is still in the preliminary stage, and further study is required. We believe that RTIL processes for cellulose definitely have a prosperous future.

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