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Ionic liquids: Promising green solvents for lignocellulosic biomass utilization

Chang Geun Yoo[a,b], Yunqiao Pu[a,b] and Arthur J. Ragauskas[a,b,c,d]

Ionic liquids are effective solvents/media for the utilization of lignocellulosic biomass. The unique properties of ionic liquids enable them to effectively dissolve and/or convert the biomass into various types of products. This review aims to cover the latest progress achieved in applications of ionic liquids on biomass conversion and analysis. Specifically, several recently developed approaches on how to overcome current challenges on the use of ionic liquids in the biomass conversion were highlighted. Recent studies addressing the potential applications of ionic liquids for the production of novel biomass-derived chemicals and materials were also discussed.

Addresses
[a] BioEnergy Science Center and Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] UT-ORNL Joint Institute for Biological Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[c] Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA
[d] Center for Renewable Carbon, Department of Forestry, Wildlife, and Fisheries, University of Tennessee, Knoxville, TN 37996, USA

Corresponding author: Ragauskas, Arthur J. (aragausk@utk.edu)

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Introduction

Ionic liquids (ILs) have been investigated as a viable substitute for conventional volatile organic solvents over the last few decades. IL is defined as a liquid entirely composed of ions that are fluid at relatively low temperature, from ambient temperature to 100 °C [1]. The strong electrostatic forces between ions in the ILs impart low volatility/flammability and high chemical and electrochemical stability [2]. ILs are classified as “green solvents” because of their low vapor pressure. In addition, ILs have distinct features as “designer solvents,” due to the properties of ionic liquids that can be tuned by a combination of selected cations and anions [3]. While IL cations are organic, for instance, imidazolium, pyridinium, aliphatic ammonium, alkylated phosphonium and sulfonium ions, both inorganic and organic ions can be used as IL anions [4]. Fig. 1 presents a number of typical cations and anions in ILs.

ILs have been used in a variety of applications such as catalysis [5], biocatalysis [6], analytical applications [7], electrochemical applications [8] and other applications [1,9]. Along with the growing interest in lignocellulosic biomass, the application of ILs was expanded to the conversion and characterization of biomass [10–12]. Lignocellulosic biomass has been highlighted as a promising resource because of its abundance and sustainability. It contains complicated and rigid structures composed mainly of cellulose, hemicellulose and lignin. These structural characteristics of biomass are involved in the biomass recalcitrance; therefore, the efficient conversion and analysis of biomass are still challenging. It is reported that ILs can effectively dissolve the plant cell walls and/or selectively remove hemicellulose and lignin under mild reaction conditions in many biomass-related applications including pretreatment and characterization. Herein, the recent progresses on the utilization and characterization of biomass using ILs are reviewed, with a particular focus on the advancement during the past two years.

Applications of ILs for biomass dissolution and conversion

For the successful utilization of biomass, partial or entire dissolution of biomass is an important step. However, dissolution of biomass is not easy because of its rigid and complicated structure. ILs have been introduced as an effective medium for chemical modification and/or dissolution of biomass and its components. Cellulose, the most abundant carbohydrate fraction in biomass, is an important resource for many biomass-related applications such as fiber, paper, membrane, ethanol, and furan-based products. It is composed of linear glucose polymer chains and is insoluble in water and most common organic solvents. Cellulose can be dissolved in

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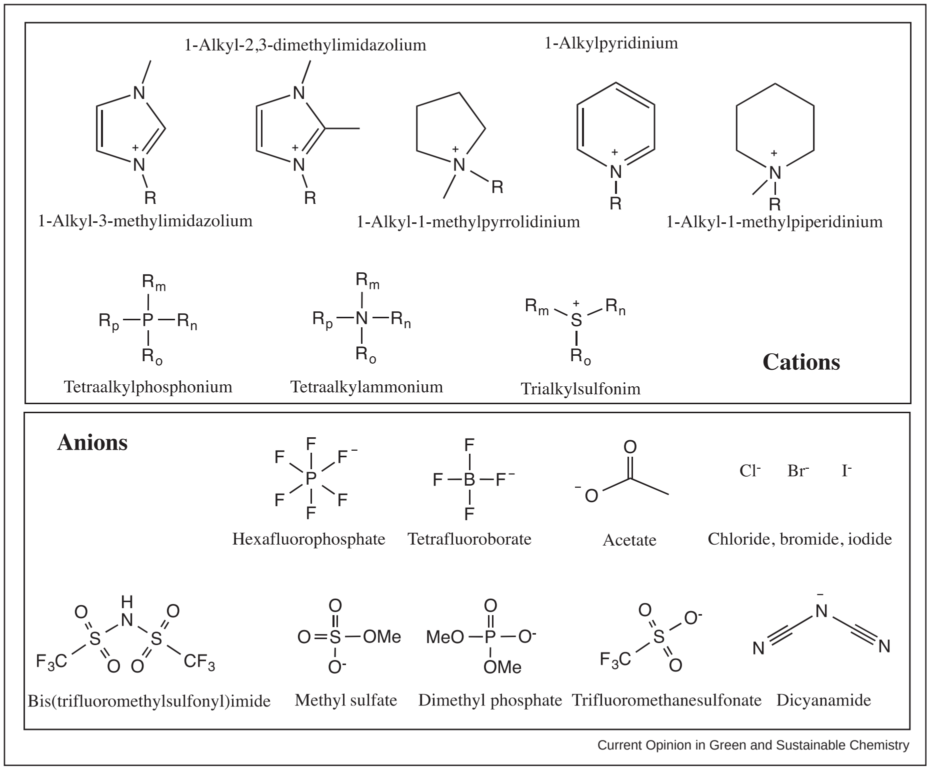
Figure 1

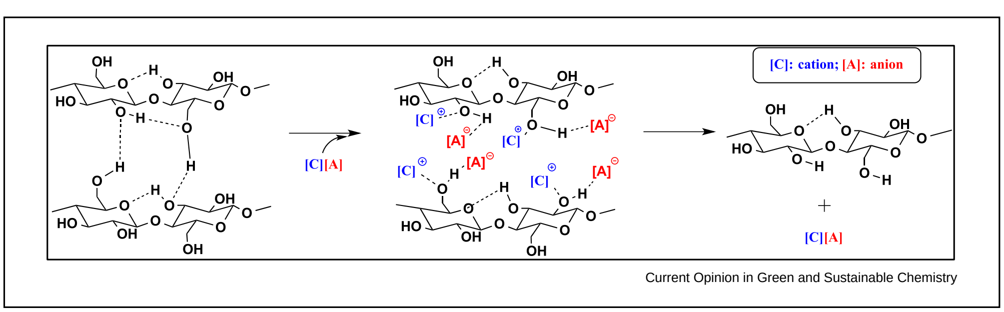


Common cations and anions in ionic liquids [4].

solvents by disrupting its inter- and intra-molecular hydrogen bonding [13], as presented in Fig. 2. Payal et al. indicated that among room temperature ILs, a good solvent for cellulose solubilization contains a strong hydrogen bond acceptor and a moderate hydrogen bond donor [14]. Both the calculated solvation free energy and experimental results consistently showed cellulose solubility in ILs as $[OAc]^- > [Cl]^- > [BF_4]^- \sim [PF_6]^-$ [14–16]. These results proved a crucial role of IL anions in cellulose dissolution. The effects of IL cations for cellulose dissolution were also investigated. Zhao et al. discussed the heterocyclic structure and alkyl chains in the cations that possibly increase the steric inhibition for the binding of anions to cellulose [17]. The addition of electron-withdrawing groups in the alkyl chain of the cations enhanced the cellulose solubility in the ILs.

Lignin is the largest non-carbohydrate fraction in the biomass. It contributes to the biomass recalcitrance in the form of physical and chemical barriers; therefore, the isolation and dissolution of lignin is one of the key steps for biomass utilization. Pu and his coworkers tested dissolution of lignin with the isolated lignin from pine kraft pulp using selected aprotic ILs [18]. They

Figure 2



Dissolution of cellulose in ILs [13].

observed that up to 20 wt% of lignin could be dissolved in 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([Hmim][CF_3SO_3]), 1,3-dimethylimidazolium methylsulfate ([Mmim][$MeSO_4$]) and 1-butyl-3-methylimidazolium methylsulfate ([Bmim][$MeSO_4$]). The lignin solubility was primarily influenced by the nature of the anions. For instance, they discovered that for 1-butyl-3-methylimidazolium salts the order of solubility was $[MeSO_4]^- > Cl^- \sim Br^- \gg PF_6^-$, while ILs containing large, non-coordinating anions were not suitable solvents for lignin dissolution. Since this study, several researchers have investigated the dissolution of lignin using ionic liquids as a green solvent. Very recently, Hart et al. reported that hydrogen bonding strength was not a crucial factor for the lignin dissolution in ILs as it was in the cellulose dissolution, but a minimum hydrogen bonding basicity was still required to solubilize the lignin [19]. They explained the effect of ILs cation on the lignin solubilization by examining the interaction between the cation and the solute. Also, Hallett and his colleagues studied characteristics of isolated lignin and mechanistic insights of lignin depolymerization in acidic ionic liquids [20,21]. They reported that the ionic liquid treatment cleaved lignin-hemicellulose linkages and decomposed the lignin by the cleavage of glycosidic, ester, and β-*O*-4 ether bonds [20]. They also pointed out that anion-cation association plays an important role in determining the solvation reaction rate [21].

ILs have been considered effective solvents and catalysts for biomass utilization because of the aforementioned dissolution effects. In the biological conversion of biomass, pretreatment is an essential step for effective conversion of biomass. It reduces and/or removes the biomass recalcitrance, and results in an increase of cellulose accessibility to enzymes. The 1-ethyl-3-methylimidazolium acetate ([Emim]OAc) and many other ILs have been applied as pretreatment solvents to various feedstocks including agricultural, herbaceous and woody biomass [22–24]. Reina et al. converted *Eucalyptus dunnii* bark into ethanol using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) [22]. Hashmi et al. evaluated the efficiency of 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) pretreatment on sugarcane bagasse and reported an improved digestibility and hydrolysis rates as compared to high severity autohydrolysis pretreatment [21]. Farahani et al. investigated an integrated pretreatment strategy composed of alkaline oxidation with IL ([Emim]OAc) incubation for effective biomass pretreatment at low temperature (50 °C) [24]. These ILs showed remarkable effects on biomass pretreatment; however, there are a number of issues still to be addressed, including inhibitory effects on enzyme activity, toxicity towards microorganisms, extensive water input in the downstream process, and expensive costs of some ionic liquids. Recent studies focus on overcoming these drawbacks in many ways. Hu et al. studied the effects of 1-ethyl-3-methylimidazolium diethyl phosphate ([Emim]DEP) on the activity of *Paenibacillus* sp. LLZ1 cellulases [25]. They reported that increase of [Emim]DEP concentration reduced the enzyme affinity to microcrystalline cellulose. Also, they found that inactivation of endoglucanases was reversible at low concentration of [Emim]DEP (<30%), while it became irreversible at high concentration (>40%). Socha et al. introduced a series of tertiary amine-based ionic liquids from aromatic aldehydes derived from lignin and hemicellulose [26]. They replaced expensive imidazolium-based ionic liquids with biomass-derived ionic liquids and resulted in high sugar release during enzymatic hydrolysis. This study also proposed the potential of a closed-loop process for the biorefinery using the biomass-derived ILs. Another approach to overcome the cost barrier of the ionic liquid-based biorefineries was development of the cost-effective ILs by George et al. [27]. They prepared a series of protic ILs containing the hydrogen sulfate anion with inexpensive chemicals. Among the ILs investigated, triethylammonium hydrogen sulfate IL resulted in the highest saccharification yield through lignin removal without significant reduction of cellulose crystallinity. One-pot biomass conversion process using ionic liquids was another approach to minimize the sugar loss and waste [28]. The proposed process with dilute bio-derived ILs showed significant economical and environmental benefits by reducing IL and water input with minimal waste. Similarly, Sun and coworkers used a biocompatible IL, [Ch][Lys], with CO_2 for controlling pH [29]. This approach integrated the steps between pretreatment to fermentation, but did not need IL-tolerant enzymes and readily recycled the ILs with minimum loss; therefore, it achieved high saccharification and fermentation yields.

ILs are also effective in other catalytic biomass conversions, including hydrolysis and dehydration for the production of platform chemicals, such as furans and aromatic compounds. da Costa Lopes and Bogel-Łukasik introduced diverse catalytic conversion methods using ILs from biomass to various products, such as fermentable sugars, hydroxymethylfurfural (HMF), furfural, levulinic acid, and other value-added compounds [10]. Xiao and coworkers reported the conversion of cellulose into HMF in a one-pot conversion process consisting of dimethylsulfoxide (DMSO)-[Bmim]Cl mixture and $AlCl_3$ as a catalyst [30]. Carvalho et al. applied acidic 1-butyl-3-methylimidazolium hydrogen sulphate IL to selectively fractionate hemicellulose and further convert it into xylose or furfural depending on the reaction severity [31].

While lignin is a major inhibitor for biomass utilization, it has a great feedstock potential in producing value-added products including phenolic compounds and dicarboxylic acids. ILs have been used as a solvent and catalyst in lignin dissolution and depolymerization. Some ionic liquids act as both an acidic catalyst and a solvent, thus they promote acidolytic cleavage of β-*O*-4 linkages. The nucleophilicity of the IL anion is considered more crucial, because the anion can possibly attack highly electron deficient protonated C–O bonds [32]. Sathitsuksanoh et al. investigated characteristics of the lignin obtained from ionic liquid pretreatment [33]. They reported that the lignins from wheat straw, Miscanthus, and Loblolly pine were depolymerized by the cleavage of β-*O*-4 linkages without formation of condensed structures during the ionic liquid pretreatment; therefore, these lignins may be more amenable to upgrade to value-added products. Depolymerization of organosolv and Klason lignins in the ILs by oxidation using a Cu/EDTA complex in a presence of monomeric phenol was also studied [34]. Two ILs ([Emim][ABS] and [Bmim][$MeSO_4$]) promoted chemical depolymerization of lignin with phenol via the redistribution mechanism, which proposed that the generated monomeric phenoxy radical attacks the phenoxy radical of polyphenol and form the carbon-oxygen bond and dissociate the polyphenols under oxidative condition. Recently, 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide efficiently cleaved β-*O*-4 linkage in the lignin model compound by promoting the generation of •OOH free radicals under metal-free condition in the presence of O_2 [35]. This metal-free oxidation method using IL successfully depolymerized other lignin model compounds and organosolv lignin.

The results in the recent studies showed that ILs are not only useful dissolution and fractionation solvents for biomass pretreatments, but they can also act as solvents/catalysts for the further deconstruction/conversion of biomass components to valuable products. Therefore, ionic liquids have great potential to help make the biomass conversion process more economical, environmental-friendly, and viable.

Applications of ILs for biomass characterization

Elucidating the structural properties of plant cell walls is essential to understanding the biomass. Traditional biomass characterization methods involve separation and isolation steps prior to the analysis of each component. However, these degradative methods are time-consuming and possibly alter the native structure of biomass components. Effective dissolution of biomass is important in the analysis of biomass and biomass-derived products, as in the utilization of biomass, because it allows better spectra and more accurate results from homogeneous solutions. On the other hand, dissolution of samples should not significantly change the original properties. ILs can dissolve individual biomass components, including cellulose and lignin, and even whole plant cell walls under mild conditions with minimal changes on the original chemical structure. Therefore, these liquids are considered as a “non-degradative solvent.”

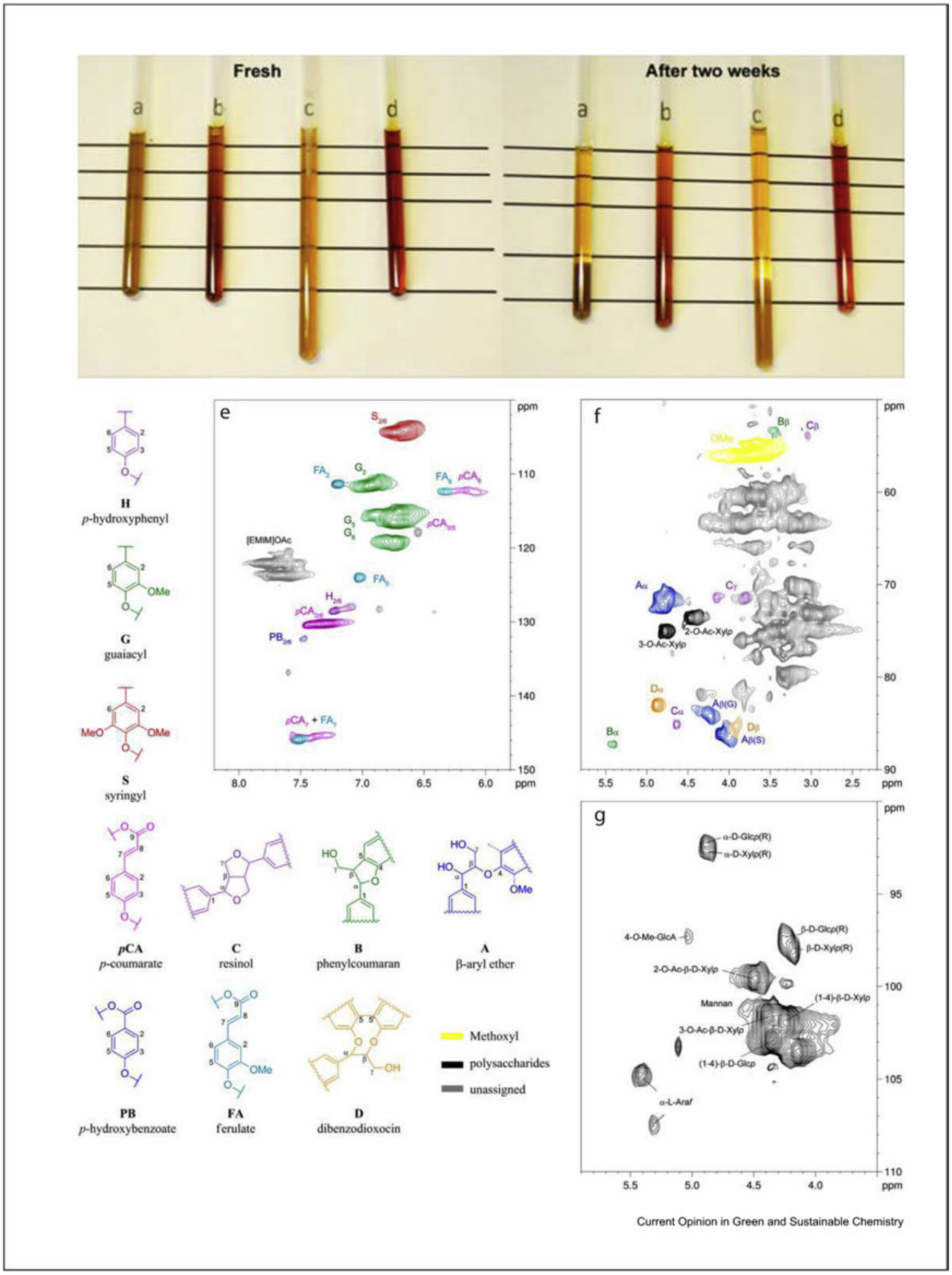
Solution state nuclear magnetic resonance (NMR) analysis has been applied to characterize biomass including lignin subunits, hydroxycinnamates, lignin inter-unit linkages, hemicelluloses and part of cellulose structures, and lignin-carbohydrate complex (LCC) linkages. ILs showed effective dissolution of biomass primarily by disrupting the intermolecular hydrogen bonds in cellulose. Some ionic liquids like 1-methylimidazole ([C4min]Cl-d_6)-DMSO-d_6 and pyridinium chloride ([Hpyr]Cl-d_6)-DMSO-d_6 mixtures were introduced as a NMR solvent for cellulose and whole cell wall biomass in the previous studies [36,37]. More recently, Cheng and coworkers introduced a new solvent composed of DMSO-d_6 and [Emim]OAc for high-resolution 2D HSQC NMR spectra of whole plant cell walls [38]. Fig. 3 shows that the dissolution of plant cell walls, especially cellulose, was more effective with [Emim]OAc-DMSO-d_6 than other previous NMR solvents like DMSO-d_6/TBAF and DMSO-d_6/[Hpyr]Cl-d_6, and gave better resolution of NMR spectra.

ILs were also used in gel permeation chromatography (GPC) analysis to measure the molecular weight distribution of cellulose and/or whole biomass cell walls. Zoia and coworkers carried out the dissolution of ball-milled biomass in the ionic liquid 1-allyl-3-methylimidazolium chloride ([Amim]Cl) prior to the derivatization of the biomass with benzoyl chloride and pyridine [39]. This method was used to help understand the LCCs interactions between lignin and carbohydrates by using three representative biomass species. Engel et al. developed a new method using dimethylformamide (DMF) containing [Emim]OAc without any pre-swelling, activation, or derivatization treatment [40]. The proposed method employing DMF/[Emim]OAc as cellulose solvent and GPC eluent can measure the cellulose molecular weight distributions with minimal sample preparation. This method is also potentially applicable to measure molecular weight distribution of lignin and whole biomass [39]. These novel GPC analysis methods may play a role for in-depth understanding of enzymatic cellulose hydrolysis too.

Applications of ILs for biomass-derived functional materials

Apart from the application of ILs for alternative fuels and chemicals by deconstructing the biomass, ILs were applied as a medium to generate functional biopolymer products from cellulose or biomass. Esterification, etherification, and polymer grafting are commonly used in cellulose modification methods so far. Cellulose esters (CEs) are widely used in many industrial applications such as coatings, paints, plastics, textiles, membranes, and even in drug delivery

Figure 3



Dissolution of the ball-milled Miscanthus in (a) DMSO-d_6, (b) DMSO-d_6/TBAF, (c) DMSO-d_6/[Hpyr]Cl-d_6, and (d) DMSO-d_6/[Emim]OAc, and 2D ^{13}C–^{1}H HSQC NMR spectra ((e) aromatic; (f) aliphatic; (g) anomeric region) of ball milled Miscanthus biomass dissolved in DMSO-d_6/[Emim]OAc (Adapted with permission from Ref. [38]. Copyright (2016) American Chemical Society.).

technology. Schenzel et al. used 1-butyl-3-methylimidazolium chloride ([C_4min]Cl) as a solvent for catalytic transesterifications of cellulose [41]. The method using the IL as the solvent made a homogeneous catalytic reaction on cellulose, and the solvent could replace toxic and corrosive chemicals typically used for cellulose esterification and is reusable for the reaction.

Grafting method is another approach to modify the surface of polymers. Wang and coworkers designed a novel graft copolymer, cellulose-*graft*-polyisoprene (Cell-*g*-PI) copolymer with opposite physical properties [42]. The IL, 1-allyl-3-methylimidazolium chloride, plays an important role in completely dissolving cellulose for the formation of 2-broisobutyryl bromide modified cellulose as the macro-initiator in the synthesis of the copolymer. The Cell-*g*-PI copolymer shows a great potential in many material applications by combining rigidity and flexibility, hydrophobicity and hydrophilicity all in one macromolecule. This copolymer has great potentials in biomedical applications because of its biocompatible and biodegradable characteristics of cellulose and polyisoprene nanoparticles as an efficient drug carrier.

ILs also showed applications in treatment on biocomposites. Two ILs, [C_4min]Cl and [Emim]DEP were recently used to produce biocomposite board [43]. The ionic liquid pretreatment was reported to not only improve the thermal stability of fibers and composite board but also show superior mechanical properties than the untreated one. Besides the aforementioned applications, the effective cellulose dissolution in ILs also made several new processing technologies available for cellulose-derived materials including blends, composites, fibers, and ion gels [44].

Conclusion and outlook

The recent applications of ILs to the utilization and characterization of lignocellulosic biomass were reviewed in this article. The outstanding features and many varieties of IL make it a powerful solvent/media in many biomass-related applications including characterization of the materials and valorization of biomass for fuel, chemicals, and materials. Up-to-date approaches suggested solutions for the economical and environmental challenges of the biomass utilization using ILs [26–29]. In addition, the effectiveness of the ILs in biomass dissolution allows broadening the conversion of biomass-derived products to chemicals and materials. In particular, the application of ILs in lignin valorization [34,35], cellulose ester [41], and multi-functional copolymer production [42] from biomass provides potential solutions for improving current biomass utilization methods more similar to economically-feasible approaches.

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