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Ionic liquids assisted processing of renewable resources for the fabrication of biodegradable composite materials

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In recent years, the utilization of renewable resources, particularly lignocellulosic biomass based raw materials, to replace synthetic materials/polymers for the manufacture of green materials has gained increased worldwide interest due to growing global environmental awareness, concepts of sustainability and the absence of conflict between food and chemical/materials production. However, structural heterogeneity and the presence of networks of inter- and intra-molecular interactions in biopolymer matrices remain unsolved challenges to clean pretreatment for biocomposite processing. A number of techniques including physical, physico-chemical and chemical methods have been investigated for the pretreatment of renewable resources. Most of these methods require high temperatures and pressures, as well as highly concentrated chemicals for the pretreatment process. Fortunately, ionic liquids (ILs) – potentially attractive "green" recyclable alternatives to environmentally harmful organic solvents – have been increasingly exploited as solvents and/or (co)solvents and/or reagents for biopolymer processing. Compared to conventional approaches, ILs in processing biodegradable composites exhibit many advantages such as being noncorrosive and nonvolatile, having excellent dissolution power under relatively mild conditions and high thermal stability. Presently, a wide range of different approaches have been explored to further improve the performance of ILs processing of biobased polymers for composites manufacturing. The main goal of this review is to present recent technological developments in which the advantages of ILs as processing solvents for biopolymers for the production of a plethora of green composites have been gradually realized. It is hoped that the present article will inspire new ideas and new approaches in ILs-assisted processing of renewable resources for green composite production.

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1. Introduction

Ionic liquids (ILs), liquids that are entirely composed of ions that can be liquids at ambient or below ambient temperatures, have been widely utilized as promising alternatives to hazardous, toxic, volatile and highly flammable organic solvents.[1,2] In fact, various attractive and unique physicochemical properties of ILs such as extremely low vapor pressures,[3,4] high solvation interactions with inorganic and organic compounds,[5,6] excellent thermal and chemical stabilities,[7] good ionic conductivities and broad electrochemical windows make ILs attractive candidates for the replacement of volatile organic compounds (VOCs) for polysaccharides processing.[8] Furthermore, the physicochemical properties, such as densities, viscosities, hydrophobicities and solute solubilities of ILs can be tailored by appropriate selection of different combinations of anions and cations as well as attached substituent groups to manipulate these for particular demands. Hence, ILs have been called "designer solvents".[9] The combination of all these unique properties opens new avenues to an extensive range of applications, including, organic synthesis and catalysis,[10–12] extraction,[13,14] inorganic synthesis,[15] nanomaterial synthesis,[16] separation,[17] biocatalysis[18,19] pharmaceuticals[20,21] and polysaccharide dissolution.[22,23] Particularly, the utilization of environmentally benign ILs as dissolution media for lignocellulose and various biopolymers has received tremendous attention in the last few years.[23–26]

The use of petroleum based non-biodegradable plastics and composites and their existing processing techniques have become recognized as a threat to the environment and consume much limited fossil resources.[27] The UN conference

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on climate change in Copenhagen December 2009 evoked a fierce public debate about the future of the earth and the need for a transition towards a CO_2 neutral biobased economy (bioeconomy) was emphasized.[28] This situation has led people from both academia and industry to focus on the development of new eco-friendly materials based on biobased renewable resources. In contrast to the field of renewable energy, in which biobased energy resources are in competition with wind and solar energies, the only renewable alternative to materials based on carbon petrochemistry is biobased raw materials. To this end, polymeric carbohydrates, *e.g.*, cellulose, starch, chitin, inulin, chitosan, lignin *etc*. are found abundantly in nature as structural building elements.[29] Agricultural industries generate a substantial amount of lignocellulosic agricultural waste every year, which is mainly composed of cellulose, hemicellulose and lignin. The typical percentages of dry weight of these wastes are 35–50% cellulose, 20–35% hemicellulose and 5–30% lignin.[30] Thus, the utilization of non-food lignocellulosic waste from various agro-industries for the production of high value composite materials could be an attractive approach instead of creating pollution problems.[31]

Sustainability in composites science depends upon not only the assortment of renewable, or environmentally benign raw materials for their manufacture, but also on the development of mild pretreatment methods that avoid the use and production of hazardous substances to minimize their environmental impact.[32] The critical challenge to extend the novel applications of biopolymers and lignocellulose for manufacturing biocomposite materials is to overcome the strong inter- and intra-molecular hydrogen bonding which lead to its recalcitrant nature.[26] These attributes assure the excellent chemical and physical stability of polysaccharides but also prevent their widespread utilization.[33,34] Consequently, considerable efforts have been devoted to enhance the processability of these carbohydrate polymers and lignocellulosic materials. For example, the '*Viscose* process' is a 100 year old technique for cellulose processing which involves derivatizing the cellulose with carbon disulphide to cellulose xanthate followed by dissolution in sodium hydroxide.[35] Alternatively, the '*Lyocell* process' employs the solvent *N*-methylmorpholine *N*-oxide (NMMO) for direct dissolution of cellulose in an industrial fiber-making process.[36] Nevertheless, each of these technologies carries a significant drawback; considerable byproduct formation in cellulose/NMMO/water systems can cause detrimental effects such as degradation of cellulose, temporary or permanent discoloration of resulting fibers, pronounced decomposition of NMMO,[37] and the *Viscose* process generates two kilograms of waste per kilogram of cellulose obtained.[38] In addition, various pretreatment technologies have been developed for lignocelluloses which apply hydrothermal or chemical treatments after mechanical comminution. Hydrothermal techniques include steam explosion,[39] carbon dioxide explosion,[40] and hot water treatment,[41] whereas chemical processes can be dilute-acid treatment,[42] alkali treatment, the organosolv process using organic solvent,[43] ammonia fiber explosion and ozonolysis.[44] However, most of the above mentioned pretreatment methods feature several drawbacks. They have to be tailored to the specific biomaterial source and can cause significant decomposition of biopolymer components to side-products, which can severely inhibit further processing of the biocomposite.[45] Additionally, some pretreatment methods require extreme conditions of temperatures and pressures or strong acids or bases for which special equipment are necessary. The perceived adverse effects of such processes combined with their safety and environmental issues, has resulted in increased pressure to minimize their use, particularly in the light of recent regulations that have aggressively targeted the reduction of the emission of

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industrial pollutants.[46] Thus sustainability, green chemistry, and eco-efficiency are not just newly coined buzzwords, but are forming the principles that are directing the development of the next generation of industrial chemical operations. Subsequently, novel processing technologies for widespread potential applications of biobased polymeric carbohydrates and lignocellulosic agricultural waste are being extensively investigated.[47,48]

The technological utilization of natural polymers and lignocellulosic materials for biocomposite manufacturing can potentially be enhanced significantly by their dissolution in ILs rather than in traditional organic solvents because of ILs' unusual solvent properties.[26,49] Studies on the dissolution of different polysaccharides in ILs over the last 10–15 years have shown that by using these solvents efficient selective extraction of the components is possible.[50] In addition, many biopolymers and lignocellulosic fibers after regeneration from their IL solutions exhibited high thermal and operational stability.[51,52] Therefore, ILs are receiving increased interest as new and highly effective dissolution media for a wide range of biodegradable polymers and lignocellulosic materials. The main objective of this review is to present a brief overview of the current state-of-the-art on the role of ILs as dissolution media for various polysaccharides for engineered green materials applications.

2. Ionic liquids and their selective properties for dissolution of biopolymers

Typical ILs are comprised of an organic cation (most commonly an alkyl-substituted imidazolium, quaternary ammonium or pyridinium ion) with an inorganic or organic anion. While it is not a rigorous definition the term, ionic liquid is commonly used to infer a melting point below 100 °C. Many ILs are liquid at, or below room temperature and remain in the liquid state within a wide temperature window (typically <400 °C). The chemical, physical and biological characteristics of ILs generally depend on the cationic structure (*e.g.*, class of cation, the length and the symmetry of substituent groups) as well as on the structure and extent of charge delocalization of the anion.[53] The specific physicochemical properties of ILs can easily be tailored through suitable structural changes in the cation and anion. Thereby, ILs are a class of solvents that incorporate a wide range of properties and one should avoid overgeneralized statements. Some comprehensive databases of physical properties of ILs such as viscosity, melting point, density *etc*. have been compiled.[54–56]

Ionic liquids are generally considered to be capable of having a broad range of intermolecular interactions such as hydrogen bonding, dipolar, dispersive and ionic.[57,58] Therefore, various compounds are remarkably soluble in ILs. Moreover, many compounds which are insoluble or only partially soluble in other organic solvents can be efficiently dissolved in ILs possessing coordinating anions such as $[OAc]^-$, Cl^-, $[NO_3]^-$ that are strong hydrogen bond acceptors.[59,60]

Based on their solvation capabilities, ILs are classified generally as highly polar solvents. Various methods have been employed to understand the polarity of ILs such as partition,[5] fluorescence probe methods[61] and solvatochromic dyes.[62] In addition, a number of empirical and semi-empirical polarity scales such as COSMO-RS,[63] the Hansen solubility parameters,[64] and the Kamlet–Taft polarity method[5] have been applied to predict and correlate the solubility of biopolymers and biomolecules in ILs with their polarities. In the Kamlet–Taft system, the parameter describing the hydrogen-bond basi-

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Tom Welton

Tom Welton is the Dean of the Faculty of Natural Sciences and Professor of Sustainable Chemistry at Imperial College London. He has been working with ionic liquids for over 30 years and is interested in all aspects of the science of ionic liquids, form their fundamental physical properties to their applications in biomass conversions. He received his BSc and DPhil from the University of Sussex, UK.

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city is expressed by β, whereas α represents the hydrogen-bond acidity and π* is the measure of interactions through polarisability and dipolarity effects. In ILs having non-functionalised cations like dialkylimidazolium, the β value is primarily affected by the anion.[65] For cellulose dissolution in ILs, it was found that dissolution capabilities of ILs are characterized by their high values of hydrogen-bond basicity parameters.[24]

Ionic liquids are usually miscible with polar solvents such as ketones, lower alcohols and dichloromethane, but immiscible with non-polar organic solvents including ethers and alkanes. Furthermore, on the basis of solubility of ionic liquids in water they can be classified into hydrophilic (water miscible) and hydrophobic (forming a biphasic system with water). It was found that water miscibility of an IL also generally depends on its anion.[66]

ILs have higher viscosities as compared to those of most common molecular solvents. In general, the viscosities of ILs depend on their interionic interactions, such as Coulomb forces, hydrogen bonding and van der Waals interactions. Therefore, viscosities of IL vary considerably with composition, temperature and chemical structure. The higher viscosities of ILs significantly hinder the dissolution of lignocellulose and other biopolymers in these. In order to reduce viscosities, organic co-solvents including dimethylsulfoxide, dimethylformamide and 1,3-dimethyl-2-imidazolidinone *etc*. have also been successfully used.[67] Fig. 1 provides structures of some ILs that have been used for processing of various biopolymers and lignocellulosic materials for biocomposite manufacturing.

2.1. Dissolution of biopolymers in ionic liquids: a comparison study with conventional solvents

In addition to the green aspects and the unique physicochemical properties of ILs, some important advantages of ILs that make these promising as potential solvents for cellulose and a wide range of other biopolymers are as follows.

As ILs are tunable solvents, they can be designed by appropriate combination of cations and anions for a particular biopolymer, which is not possible using conventional organic solvents. In fact, since ILs can undergo a wider spectrum of intermolecular interactions, they are capable of dissolving a vast range of biopolymer compounds that are insoluble in organic solvents.[68] For example, ILs can be used for dissolution of starch,[69] chitin,[70] chitosan,[71] polylactic acid,[72] lignin,[73] cellulose,[22] or for even complete dissolution of lignocellulosic materials.[24,74] ILs can also be employed for selective dissolution and extraction of any desired or undesired component from a mixture or matrix solution.[75]

In comparison to molecular solvents, the remarkable benefit of using ILs for dissolution of lignocellulose and various biopolymers is that they can dissolve these under relatively mild operating conditions and at normal atmospheric pressure. Fukaya *et al.*[76] reported the dissolution of cellulose at the temperature of 45 °C for 30 min by utilizing alkylimidazolium based ILs with a methyl phosphonate anion.

As well as acting as dissolution medium, recently many ILs, especially with methylimidazolium cations, were found to outperform other conventional plasticizers by significantly disrupting the inter- and intra-molecular hydrogen bonding within polysaccharides, such as starch, and thus can be employed as excellent media for polysaccharide modification and plasticization.[77,78] Sankri *et al.*[79] and Leroy *et al.*[80] have performed pioneering work using the IL 1-butyl-3-methylimidazolium chloride ([C_4C_1im]Cl) as a novel plasticizer in melt processing of starch-based polymers with remarkable improvements in plasticization, hydrophobicity and electrical conductivity being reported.

Pretreatment is an essential unit operation in a polysaccharides based biorefinery and for sustainable material applications, but is considered to be of one the most cost intensive operations. The production of valuable products from lignocellulose or starch has a narrow profit margin. Various acidic, alkaline, hydrothermal and ammonia fiber expansion (AFEX) pretreatment technologies have been examined under high biomass loadings (>15%).[81,82] Lately, ILs have been shown to be highly efficient dissolution media for lignocellulosic materials under solid biomass loads of as high as 50%.[83]

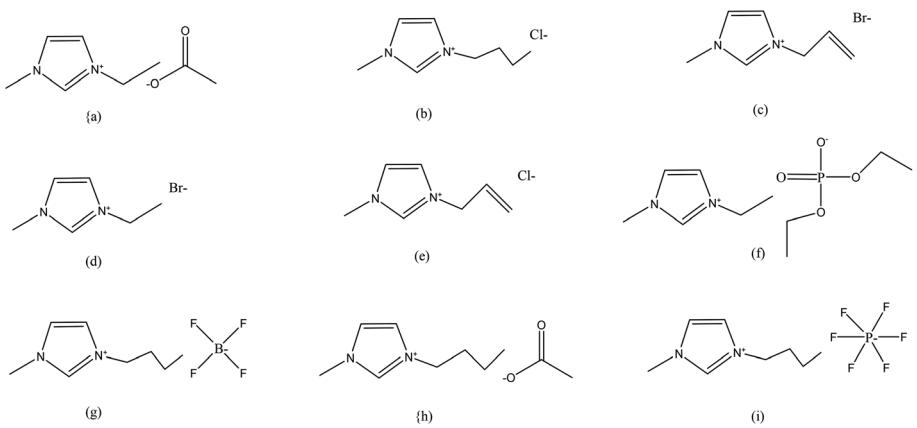

Fig. 1 Structures of the ILs used for dissolution of biopolymers and lignocellulosic materials for fabrication of biocomposites: (a) [C_2C_1im][OAc], (b) [C_4C_1im]Cl, (c) [(C_1=C_2)C_1im]Br, (d) [C_2C_1im]Br, (e) [(C_1=C_2)C_1im]Cl, (f) [C_2C_1im][Et_2PO_4], (g) [C_4C_1im][BF_4], (h) [C_4C_1im][OAc], (i) [C_4C_1im][PF_6].[24,93]

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Recently, we have explored high solids loading, because of lower overall cost, improved efficiency and environmental benefits.[51] Thus, the possibility of high-throughput pretreatment in a continuous process could improve the potential for the use of ILs as a cost-effective and extremely promising technology for manufacturing sustainable composites from various polysaccharide raw materials. The most important advantages of ILs as dissolution media for the fabrication of polysaccharides based biocomposites is the possibility of ILs recycling and product recovery schemes which are not viable with conventional organic solvent systems.[74,84]

It should be noted that biopolymer dissolution is often controlled by kinetics rather than by thermodynamics. Sescousse *et al.*[85] performed a comparative study for the dissolution and regeneration of cellulose in the ILs 1-butyl-3-methylimidazolium acetate [C_2C_1im][OAc] and [C_4C_1im]Cl with conventional cellulose solvent systems, *i.e.*, NaOH and *N*-methylmorpholine *N*-oxide (NMMO). Kinetic study of the cellulose regeneration process from cellulose–IL solution revealed that this was a diffusion-controlled process. Gavillon and Budtova[86] also predicted that the cellulose regeneration steps from cellulose–NaOH–water and cellulose–NMMO solutions were diffusion-controlled. For complete dissolution of a biopolymer, the solvent must diffuse into the structure of polymeric chain to affect both the amorphous and the crystalline regions. Therefore, high diffusivity and the capability of chain disentanglement are necessary attributes for an effective solvent.[87] At a given cellulose concentration, the diffusion coefficient for 1-ethyl-3-methylimidazolium acetate [C_2C_1im][OAc] and [C_4C_1im]Cl were four to five times lower than the diffusion coefficient of NaOH and about twice lower than that of NMMO, which might be due to the larger size of the ILs.[86–88] Moreover, compared with the NMMO process, the direct dissolution of cellulose in IL is more easily controlled and the process is inherently safer. It has been described that cellulose fibers prepared using ILs displayed similar properties in terms of elasticity and tenacity compared to the fibers manufactured by the Viscose and Lyocell processes. In addition, the process can be designed such that both fibrillating and non-fibrillating fibers can be fabricated specially for textile applications.[89,126,127]

Ionic liquids exhibit a far lower degradation potential compared to the NMMO. The study of Wendler *et al.* showed that a [C_2C_1im][OAc]–cellulose solution exhibited a T_{onset} (temperature corresponding to the point of intersection of tangents to two branches of the thermogravimetric curve) of 180 °C compared to the value of 146 °C for a NMMO–cellulose system. Apart from T_{onset}, numerical estimation of pressurization rates from pressure curves of cellulose–solvent mixture showed that compared to NMMO the pressure rise during the exothermic event for cellulose–IL solution was much less, which evidently suggested the ILs as solvents with much higher thermal stability.[90]

The dissolution of cellulose in acidic solvents is accompanied by a substantial hydrolysis of cellulose and causes depolymerization, which consequently limits its use in some applications.[91] On the contrary, for cellulose dissolution in 1-allyl-3-methylimidazolium chloride [(C_1=C_2)C_1im]Cl at 60 °C, a well resolved ^{13}C NMR spectrum of all the six anhydroglucose units was observed, indicating that the cellulose dissolved in a similar manner in [(C_1=C_2)C_1im]Cl as in other familiar solvents for cellulose including sodium hydroxide–carbon disulfide solution.[92] Allyl- and *n*-alkyl-imidazolium based ILs with Cl^-, Br^- and $[OAc]^-$ anions showed 5–14.5% cellulose solubility over a temperature range of 80–110 °C.[93] In comparison, an aqueous mixture of NaOH/urea/thiourea that could readily dissolve cellulose exhibited a maximum cellulose solubility of only 7.2%.[94] Moreover, thermal gelation of cellulose in aqueous NaOH/urea/thiourea solution due to self-aggregation of the cellulose chains has also been reported.[95]

Although a great deal of experimental and computational advances have been made, there is no explicit understanding about the specific mechanism of biopolymer dissolution in ILs compared to other solvents. Currently, two main models for the ILs' interactions with cellulose prevail: (1) the dissolution process is controlled by the interaction of the anion with the biopolymer with no particular role for the cation; and (2) the principal driving force for cellulose dissolution originates from the H-bond interactions of the cellulose hydroxyl group with both the cation and the anion of the IL.[96] Conversely in the case of the NMMO solvent, the proposed mechanism presumes the cleavage of intermolecular bonds of cellulose *via* the creation of a soluble complex of stronger hydrogen bonds between the NO group of NMMO and the cellulosic hydroxyl groups.[97] For mixed inorganic/organic solvents such as lithium chloride/dimethylacetamide (LiCl/DMAc), the dissolution mechanism is suggested to go through an intermediate involving the interaction of Cl^- (due to its basicity) with cellulose.[98] This type of interaction can be considered as a polyelectrolyte effect, in which polymer molecules are forced apart because of charge repulsion. A similar polyelectrolyte effect has been suggested for the tetrabutylammonium fluoride/dimethyl sulfoxide (TBAF/DMSO) solvent system.[99]

2.2. Ionic liquids as an effective tool for biopolymer processing

Certain ILs can dissolve lignocellulose by disrupting the hydrogen bonding network of the natural composite of cellulose, hemicellulose and lignin, as studied by ^{13}C-NMR and $^{35/37}$Cl-NMR spectrometric results.[100] Recently, cellobiose (the repeating unit of cellulose) solvation was investigated in [C_2C_1im][OAc] by *in situ* and variable-temperature NMR spectroscopy.[101] The study suggested that the principal reason for cellobiose solvation was hydrogen bonds formed between the hydroxyl groups of cellobiose and both the anion and cation of [C_2C_1im][OAc]. The excellent dissolution capabilities of this IL for lignocellulosic materials under relatively mild conditions, its ease of synthesis and its potential for recycling have led to many researchers selecting this solvent to be a promising green processing medium for polysaccharide research in a future biorefinery. However, there are concerns regarding the reactivity of this and other closely related ionic liquids with cellulose (see below).

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3. Composites based on ionic liquid assisted processing of biopolymers

Composites are engineered materials fabricated from two types of constituents *viz*. reinforcement and matrix, which maintain their distinct characteristics within the finished structure.[102] However, in the case of polysaccharide based composites, the final product properties could be achieved without keeping the strict classification for reinforcement and matrix.[103] For conversion of various biopolymers and lignocellulosic materials into biodegradable composite products, biomaterial is typically dissolved in the IL in the temperature range of 65–110 °C with dissolution times of 10 min to 22 h.[24,93] The resulting IL–polymer solution can be processed *via* different fabrication techniques such as electrospinning, casting, molding, gelation *etc*. to form numerous types of biocomposites. Conversely, the dissolved material in IL can be regenerated by addition of certain anti-solvents such as water, acetone, ethyl alcohol *etc*. The regenerated cellulosic material may be utilized in a broad range of applications including textiles, cosmetics, biomedical, fiberboard composites, fiber-reinforced polymeric composites, all-cellulose composites, wood-plastic composites *etc*. Fig. 2 provides a schematic view of manufacturing methodologies for numerous biocomposite products using ILs as the solvent. Here we describe ILs based manufacturing of various composites prepared solely from polysaccharides or their sources.

3.1. Biopolymer films

Currently, researchers from both academia and industry are increasingly focusing their interests onto the exploitation of natural biopolymers as potential alternatives to non-biodegradable plastic products. As the most important skeletal component in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties.[104] However, processing of cellulose is extremely difficult because, in general, it does not melt nor dissolve in common solvents. Recently, the dissolution capabilities of ILs for cellulose provoked a remarkable interest in cellulose processing for biobased polymer films.[24,105]

The IL $[(C_1{=}C_2)C_1im]Cl$ was used as a single component solvent for cellulose to fabricate the regenerated cellulose material with good mechanical properties by a solution casting method.[106] The cellulose samples (cotton linters) were cut into smaller pieces and dried at 70 °C for 3 h in a vacuum oven. A specific mass of cellulose was dispersed into 20 mL of ($[(C_1{=}C_2)C_1im]Cl$) to get 4% polymer concentration, and the mixture was continuously heated and stirred until the material was completely dissolved. Finally, the solution was cast onto a glass plate to achieve a thickness of about 0.50 mm, air bubbles were removed in a vacuum oven and then a transparent regenerated cellulose film was formed in a water bath. The thickness of the film was controlled to within 0.5 mm to avoid curls in the cellulose films. The regenerated cellulose film was washed with plenty of distilled water and dried at 60 °C in a vacuum oven. Thus, $[(C_1{=}C_2)C_1im]Cl$ based processing of cellulose was proposed to be a promising "green process" for the fabrication of regenerated cellulose films, which can solve the inherent environmental problems of the generation of waste toxic gases formed during the current industrial processes. Dissolution and regeneration of cellulosic biofilm from $[C_4C_1im]Cl$ was also reported by Liu *et al.*,[107] where cotton pulp was used as the raw cellulose source. The authors observed that $[C_4C_1im]Cl$ was a direct solvent for cellulose and its solubility could reach up to 13 wt% at 90 °C in 7 h, but at the same time the degree of polymerization was remarkably reduced. Takegawa and coworkers[108] prepared the bi-component biopolymer film containing cellulose and chitin each dissolved separately in $[(C_1{=}C_2)C_1im]Br$ and $[C_4C_1im]Cl$ respectively at 100 °C for 24 h with continuous stirring to give clear solutions of chitin and cellulose. The stress–strain curves were also measured under tensile mode and it was concluded that the biofilms became more elastic with decreasing the ratio of chitin to cellulose in the final product. Meng *et al.*[109] successfully dissolved and regenerated the native skin collagen

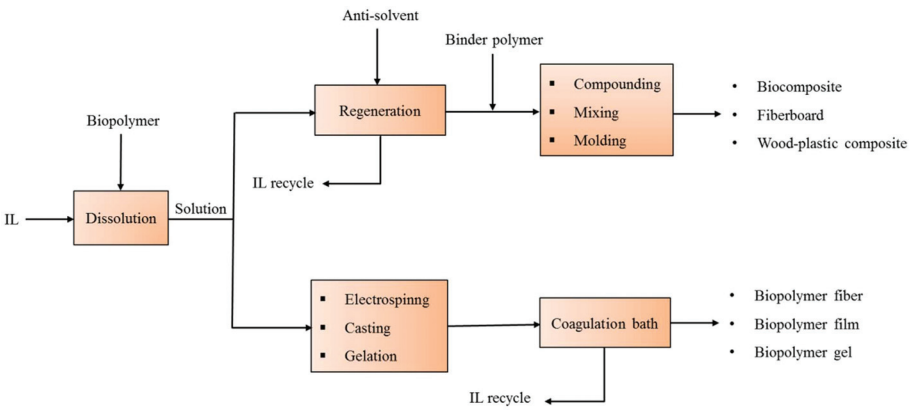

Fig. 2 Schematic representation of the manufacture of various biodegradable composites based on ILs dissolution of biopolymers and lignocellulose.

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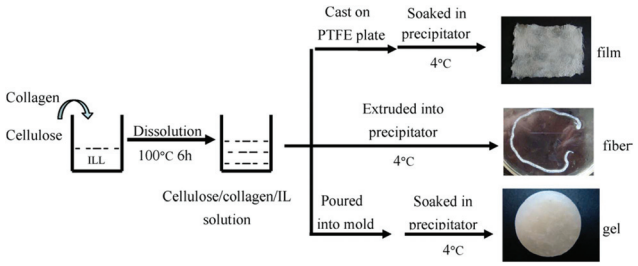

Fig. 3 Schematic representation of collagen/cellulose composite materials preparation using IL $[C_4C_1im]Cl$.[109]

in $[C_4C_1im]Cl$ (Fig. 3). However, the triple helical structure of the collagen had been partly destroyed during the dissolution and regeneration process. A possible mechanism of dissolution and regeneration of collagen in IL was also proposed and it was deduced that the IL dissolved the collagen fibers by mainly breaking the hydrogen bonds and the ionic bonds in collagen macromolecules. Regenerated wool keratin films were prepared from wool keratin/ionic liquid solutions through the addition of water, methanol or ethanol as coagulation solvents.[110] It was suggested that $[(C_1{=}C_2)C_1im]Cl$ had higher solubility for wool keratin fibers than that of $[C_4C_1im]Cl$. XRD data also confirmed that the regenerated films exhibited a β-sheet structure and the disappearance of the α-helix structure. Further, Byrne *et al.*[111] reported the fabrication of regenerated film of three natural polymers, raw cotton, silk and wool using $[(C_1{=}C_2)C_1im]Cl$ at 105 °C. The new biocomposite films showed enhanced thermal stability compared to single component films, which was attributed to the increase in intra molecular hydrogen bonds for the biofilms. Similarly, Rahatekar *et al.*[112] successfully combined the biocompatible properties of chitin with the high electrical conductivity of carbon nanotubes (CNTs) by mixing these using an imidazolium-based ionic liquid as a common solvent/dispersion medium. The IL allowed the uniform dispersion of CNTs and dissolution of chitin to create a biocompatible, electrically conducting scaffold permissive for mesenchymal stem cell function. Recently, Byrne and coworkers[113] presented an exciting example of using $[(C_1{=}C_2)C_1im]Cl$ for the preparation of a novel regenerated cotton/duck feather composite film. The new blended films showed enhanced elastic properties as well as thermal stability in comparison to the single component films regenerated from the same IL. The amount of α-helix in the composite film was responsible for improvement in the elastic properties of the fabricated films.

The novel hybrid green composite films comprising of cellulose, starch and lignin have been prepared by respective dissolution in $[(C_1{=}C_2)C_1im]Cl$.[69] The experimental results showed that the relative contents of cellulose, starch and lignin had a significant impact on the mechanical properties of composite films. The composite films exhibited good thermal stability and high gas barrier capacity with a $CO_2 : O_2$ permeability ratio close to 1.

3.2. Biopolymer fibers

Electrospinning of polymer materials has emerged as a powerful technology for the manufacture of fibrous materials with controllable compositions, high specific surface area and high porosities for a broad range of applications such as reinforcement in nano-biocomposites, as tissue engineering scaffolds, in wound dressing and as protective clothing.[114,115] The electrospinning of natural polymers for biopolymer fiber fabrication is of particular interest, not only because of the renewable resources, but also due to the beneficial properties of these biomacromolecules, such as biodegradability, biocompatibility and excellent specificity.[116] Electrospinning typically employs volatile organic solvents to prepare the polymeric spinning solution which evaporate in the course of fiber formation. This process can release high levels of harmful volatile compounds into the environment and it is unsuitable for effective recovery and recycling of the solvents.[117] Electrospinning from ILs represents an interesting solution to this problem since these non-volatile solvents remain in the fibers as they are cast and are removed by means of a coagulation/washing bath, allowing their effective recovery using an array of strategies.[118] A typical electrospinning scheme based on ILs assisted dissolution and regeneration of cellulose is illustrated in Fig. 4. The setup consists of a high-voltage power supply connected to a spinneret containing the IL–polymer solution and to a grounded conductive collector. The spinneret is often a syringe, controlled by a pump through which the IL–biopolymer solution can be fed with a specific flow rate to get a pendant droplet at the tip of the needle. An electrical charge is accumulated in the surface of the IL solution droplet after a voltage difference is created between the spinneret and the collector. The solution is electrospun under a certain threshold voltage to form a thin, charged IL–polymer jet which is ejected from the tip of the cone and is drawn towards the grounded collector. The residual IL in the fiber is removed using ethanol or water and the fiber is washed by deionized water and dried at 50–60 °C for a day.[118]

Polaskova *et al.*[119] used a wet electrospinning technique for the transformation of raw pine wood into microfiber (1–4 μm) by dissolution in $[C_2C_1im][OAc]$ or $[C_2C_1im][lactate]$. It was

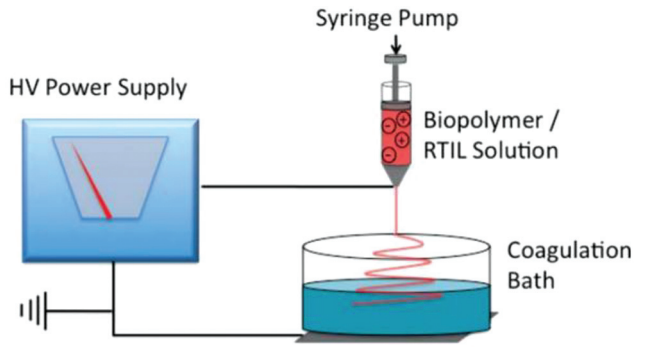

Fig. 4 An illustration of a typical electrospinning apparatus for biofiber processing by ILs.[118]

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reported that 5% wood concentration in the IL was most appropriate for electrospinning and an increase in the biomass loading up to 10% complicated the process due to drastic increase in the viscosities of the solutions. Raw delignified lignocellulose biomass (hemp) was successfully electrospun using ([C_2C_1im][OAc]) as the spinning solvent by Ahn *et al.*[120] As expected, the spinning efficiency and fiber morphology strongly depended on the lignin contents of the raw biomass. It was observed that when the lignin content was higher than 6%, no fiber was formed and the solution was converted into large droplets at the end of the nozzle. Jiang *et al.*[121] studied the microstructure and crystalline properties of the commercial cellulose fibers regenerated and processed with different solvents and technologies with synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). On the basis of their findings, the IL was expected to be much more efficient and flexible in cellulose dissolution and fiber-forming processes.

Quan *et al.*[122] prepared nonwoven nano-scale fibers of cellulose regenerated from [C_4C_1im]Cl using electrospinning and successfully obtained a minimum diameter of the continuous electrospun cellulose fibers in the range of 500–800 nm. Qin *et al.*[123] observed that high molecular weight and high purity chitin powder could be recovered after complete dissolution of raw crustacean shells in [C_2C_1im][OAc] with the yield as high as 94% (Fig. 5). Furthermore, they reported the direct fabrication of chitin fibers and films from the extract solution. High tenacity chitosan fibers with excellent strength and initial modulus were generated from dissolved chitosan in binary IL mixtures of glycine hydrochloride [Gly·H]Cl and [C_4C_1im]Cl with a dry-wet spinning technology.[124] Fig. 6 shows that the same binary system of acidic and neutral IL ([Gly·H]Cl and [C_4C_1im]Cl) was used to fabricate chitosan-cellulose composite fiber with 9.4 wt% chitosan.[125] The hybrid-type biopolymer fiber not only had good mechanical strength but also excellent thermal stability with T_{onset} of 305.1 °C.

Fig. 5 Fabrication of chitin fiber from an IL solution of crustacean shells.[123]

The suitability of several chloride containing ILs was tested for their cellulose dissolving and subsequent fiber-making properties by spinning the IL–cellulose solutions into water.[126] The resulting fibers were asserted to belong to the class of Lyocell-fibers and showed the same or comparable characteristics to fibers obtained from NMMO solutions. Recently, cellulosic fibers were spun in a dry-jet wet spinning process from a solution in the IL 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) into water, resulting in properties equal or better than that made from the conventional Lyocell process (tensile strength 37 cN per tex or 550 MPa).[127] A spinneret aspect ratio L/D (length to diameter ratio of fiber) of 2.0 gave a better orientation than L/D of 0.2 and allowed higher draw ratios.

Another report describes the multiwall carbon nanotube (MWCNT)/cellulose composite fibers processed from solutions in [C_2C_1im][OAc].[128] At 0.05 mass fraction of MWCNT, the fiber tensile strength increased by about 25%, strain to failure increased by 100% and modulus essentially remained unchanged. Later, Rahatekar and co-workers[129] further extended the work by evaluating the effect of fiber extrusion speed and fiber winding speed on the degree of alignment and electrical properties of MWNTs/cellulose composite fiber processed by [C_2C_1im][OAc]. A decrease in degree of alignment was noted when fibers were spun with higher winding speed using a constant extrusion speed. More recently, the work of Rahatekar[130] corroborated the manufacture of highly aligned cellulose fibers spun from optically anisotropic microcrystalline cellulose solutions in 1-ethyl-3-methylimidazolium diethylphosphate ([C_2C_1im][Et_2PO_4]). Fibers with an average diameter of ~20 μm, a high Young's modulus up to ~22 GPa and moderately high tensile strength of ~305 MPa were successfully spun from an 18 wt% cellulose solution in the IL. Similarly, in the interesting study of Byrne *et al.*[131] composite fiber comprising of cellulose and duck feather was extruded from a solution of the biopolymers in the IL [(C_1=C_2)C_1im]Cl *via* a wet spinning operation. The mechanical properties of the composite fiber was shown to be better than regenerated cellulose fibers alone with a 63.7% improvement in tensile strain. The hybrid composite fiber comprising regenerated raw lignocellulosic biomass (yellow pine and bagasse) from [C_2mim][OAc] with a dry-jet wet spinning process under short dissolution times (10–30 min) and temperatures above the glass transition temperature of lignin was reported by Rogers *et al.*[132] Fibers spun using the higher temperature/shorter time method were stronger than those obtained using the lower temperature/longer time method (Fig. 7).

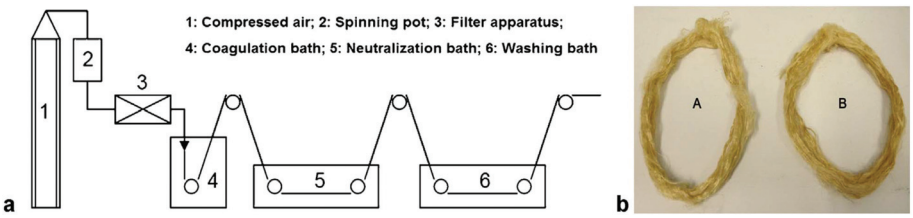

Fig. 6 (a) Schematic representation of the dry-wet spinning technique (b) the obtained chitosan fibers.[125]

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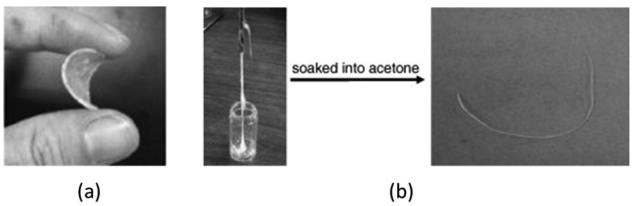

Fig. 7 Cellulose–starch composite gel (a) and fiber (b).[133]

3.3. Aerogels/hydrogels

Aerogels are the class of highly porous synthetic solid materials with extremely low density and low thermal conductivity. Owing to their diverse physical and chemical properties, aerogels have a wide range of applications as engineering materials. These ultra-light materials can be manufactured from a variety of raw materials including silica, carbon, metal oxides *etc*.[134,135] However, due to the rapid diminishment of petroleum reserves and serious environmental problems created by the non-biodegradable material products and their energy intensive syntheses, alternative polysaccharides based resources have attracted a great deal of attention for aerogels.[136,137] Lignocellulose and various biopolymers based aerogels are new highly promising biomaterials that could offer a broad range of potential applications including cosmetics, biomedical (*e.g.* scaffolds, delivery systems), electro-chemical, wastewater treatment and as insulation materials.[138,139]

Li *et al.*[140] reported a facile fabrication method of a lignocellulose aerogel by dissolution of wood in [$(C_1{=}C_2)C_1$im]Cl by a cyclic-freeze–thaw (FT) process, as shown schematically in Fig. 8. It was shown that the IL assisted FT treatment, when used as a physical cross-linking technique, can successfully form continuous 3D network structures. Later, Sescousse *et al.*[141] fabricated an ultra-light and highly porous cellulose material which they called *aerocellulose.* The material was prepared *via* cellulose dissolution in [C_2C_1im][OAc] or [C_4C_1im]Cl and then regenerated and dried under supercritical CO_2 conditions. The density of the aerocellulose was from 0.06 to 0.20 g cm^{-3}. The "bead-like" morphology of aerocellulose from cellulose–ionic liquid solutions was similar to that of samples obtained from cellulose–NMMO monohydrate solutions. A facile preparation of a flexible gel material from a solution of cellulose in [C_4C_1im]Cl (15% w/w) by keeping it at room temperature for 7 days was reported (Fig. 9).[142] Elemental analysis data showed that the fabricated gel was composed of cellulose, the IL, and water. Both XRD and TGA results indicated that the crystalline structure of cellulose was largely disrupted in the material.

Matrices based on silk fibroin show good applicability in the field of regenerative medicine, but the cocoons of *Antheraea mylitta* are underutilized because of the poor ability of traditional organic solvents to dissolve these. Consequently, Silva *et al.* investigated the solubilization and processing of degummed fibers extracted from the cocoons of silkworms into hydrogels using [C_4C_1im][OAc].[143] The degummed silk fibers were dissolved in the IL at 95 °C with 10 wt% solid loading, as shown schematically in Fig. 10. The outcomes of the study suggested that the use of ILs for the dissolution/processing of degummed fibers derived from *A. Mylitta* cocoons into hydrogels could be interesting in cartilage regeneration repair strategies. Lately, a simple method for the preparation of cellulose/graphene composite hydrogels with high toughness was developed.[144] The hydrogel was prepared by regeneration of the mixture of wood pulp and reduced graphene oxide from their IL solution using deionized water as an anti-

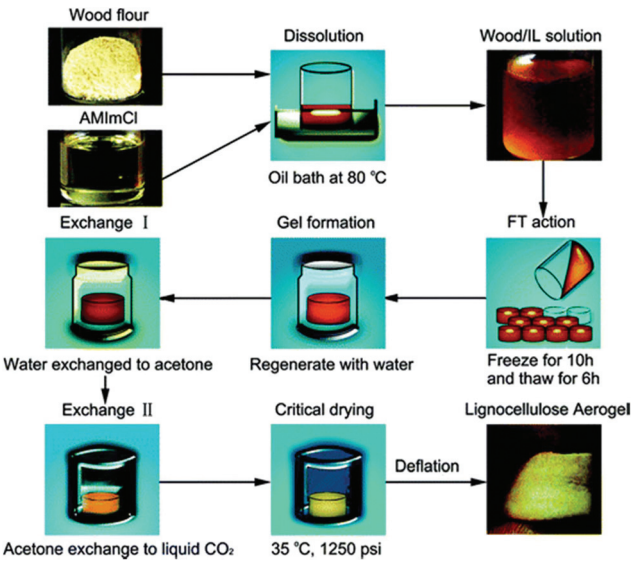

Fig. 8 Schematic presentation of lignocellulose aerogel preparation.[140]

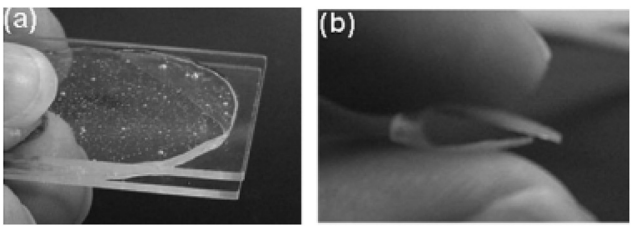

Fig. 9 Photographs of (a) a cellulose–IL solution gelation process, (b) the obtained gel product.[142]

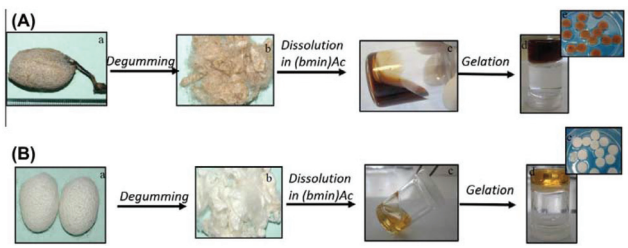

Fig. 10 The fabrication of silk hydrogels from mulberry and non-mulberry silk cocoons using the IL [C_4C_1im][OAc] as solvent. (A): *Antheraea mylitta* cocoons, (B): *Bombyx mori* cocoons.[143]

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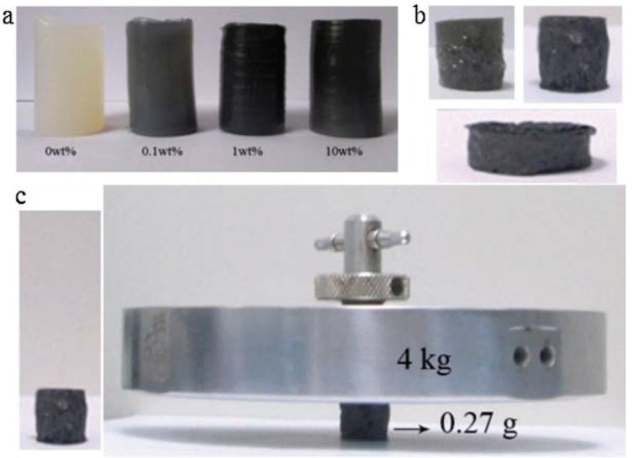

Fig. 11 (a) Images of cellulose and cellulose/graphene composite hydrogels (CGH); (b) the freeze-dried CGH; (c) the freeze-dried CGH with height of 1.50 cm and diameter of 1.40 cm supporting a 4 kg counterpoise which is more than 14 800 times its own weight.[144]

solvent. This approach provides a simple and green method to compound the multifunctional properties of cellulose with the extraordinary performances of graphene based hydrogels (Fig. 11).

Nanofibrillar aerogels were developed from cellulose, spruce wood and from mixtures of cellulose, lignin and xylan by first dissolving in $[C_4C_1im]Cl$ and coagulating from IL solution using aqueous ethanol. These microporous aerogels could be readily disintegrated into fibrous or powder-like material by rubbing between one's fingers. Aerogels made from wood were much harder and possessed much more structural strength than the hybrid aerogels made from cellulose, lignin and xylan (Table 1).[171]

3.4. Self-reinforced all-cellulose composites (ACCs)

Eco-friendly composites can be manufactured by compounding a variety of lignocellulosic fibers such as wood fiber, leaf fiber, bast fiber or regenerated cellulose with a thermoset or thermoplastic matrix.[102,174] However, the mechanical strength of such biocomposites is often limited due to the poor chemical compatibility between the hydrophilic fiber and hydrophobic matrix, which results in weak interfacial stress transfer.[45,84,175] Recently, in order to resolve the interfacial adhesion problem, a new class of composite materials with superior mechanical properties which entirely consist of nonderivatized cellulose have been developed – all-cellulose composites (ACCs).[176,177]

A novel approach to prepare cellulose-based conductive hydrogels was demonstrated by dissolution of microcrystalline cellulose (MCC) in $[C_4C_1im]Cl$ (Fig. 12).[165] The obtained MCC composite hydrogel showed excellent electrical conductivity of 7.83×10^{-3} S cm^{-1}, as measured using a four-probe method. Ma *et al.*[178] utilized the excellent selective solubility of the IL 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[(HO)^2C_2C_1im]Cl$) for microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) to fabricate green all-cellulose composite films. The ACC film was prepared by adding NCC to the MCC–IL solution. The composite film was fully biobased, biodegradable and easily recyclable, and proposed to be useful as biomaterials and food ingredients (Fig. 13b). Huber *et al.*[176] developed a fiber-reinforced all-cellulose composite (ACC) laminate on the basis of a conventional hand lay-up method (Fig. 13a). Four layers of each natural fiber textile (linen) and man-made cellulosic textile (Cordenka rayon) were impregnated with $[C_4C_1im][OAc]$. The layers were heated under pressure to partially dissolve in the IL so that compaction of the single laminate was achieved to form a composite. The formation of the matrix phase was obtained *in situ* by the regeneration of the dissolved fraction of the cellulose fiber, which resulted in a composite with strong fiber–matrix interfacial properties.

Recently, in the interesting work of Reddy *et al.*,[179] the cellulose was extracted from the Agave plant and the extracted cellulose microfibrils were successfully dissolved in $[(C_1{=}C_2)C_1im]Cl$ along with a small amount of microfibrils which remained undissolved as can clearly be observed in Fig. 14. The self-reinforced regenerated cellulose biocomposite films with an average strength as high as 135 MPa were prepared from this solution. Furthermore, a comparison of an IL based all-cellulose composite with an epoxy matrix composite was reported by partial dissolution of flax and Lyocell fiber in $[C_4C_1im]Cl$.[180] It was observed that ACCs fabricated from Lyocell fiber showed similar strength and stiffness but superior extensibility as compared to Lyocell fiber–epoxy composites.

ILs assisted welding of cellulosic fiber. Although ILs have been shown to be powerful solvents for processing biopolymer matrices, the reconstitution process of the dissolved biopolymers in ILs often fails to regenerate the original 'native' structure, and thus full dissolution irreversibly and uncontrollably denatures the original biopolymer structure and can degrade fiber properties.[150] Recently, it has been shown that ILs can offer versatile applications in manufacturing composite materials by partial dissolution and reconstitution of biopolymers in a process so-called '*natural fiber welding*'.[181] In this process, the IL swells and mobilizes biopolymers at the fiber surface as it disrupts native intermolecular hydrogen bonding. Subsequently, mobilized materials from neighboring fibers intermingle and upon removal of the IL form a congealed all-cellulose composite material. Trulove *et al.*[181] demonstrated the IL based welding process for bombyx mori silkworm cocoon silk thread and hemp thread with $[C_2C_1im][OAc]$ (Fig. 15). XRD and FT-IR spectroscopy of the welded cellulosic fibers showed that significant amounts of the native polymer structure were retained after the process was completed. Afterwards, a systematic study of variables that affect the fiber welding process (IL quantity, temperature, time) was presented by Haverhals and co-workers.[182] It was shown that the quantity of IL introduced was the most influential parameter to control the amount and location of biopolymer modification. In addition to material reorganization, natural fiber welding opens biopolymers to possible chemical functionalization at

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Table 1 Dissolution of polysaccharides in ILs for biocomposite processing

Entry	IL	Raw material	Conditions	Loading (%)	Fabrication technique	Product	Ref.
1	$[(C_1{=}C_2)C_1im]Cl$	Cellulose	100–130 °C 40–180 min	4	Solution casting	Film	106
2	$[C_4C_1im]Cl$ $[C_2C_1im]Cl$ $[C_2C_1im][OAc]$ $[C_4C_1im][OAc]$	Cotton pulp	90 °C 7 h	—	Solution casting	Film	107
3	$[C_4C_1im]Cl$	Natural wool Cellulose	100 °C 10 h	5	Solution casting	Film	145
4	$[(C_1{=}C_2)C_1im]Cl$	Cotton Silk Wool	100 °C	10	Solution casting	Film	111
5	$[(C_1{=}C_2)C_1im]Cl$ $[C_2C_1im][OAc]$	Cornhusk Cellulose	80–120 °C 2–12 h	4	Solution casting	Film	146
6	$[C_4C_1im]Cl$	Silk fibroin Cellulose	90 °C 12 h	2	Molding	Film	147
7	$[C_4C_1im]Cl$	Cellulose Montmorillonite	85 °C 28 h	8	Solution casting	Film	148
8	$[(C_1{=}C_2)C_1im]Cl$	Bamboo pulp Soy protein isolate	80 °C	6	Solution casting	Film	149
9	$[C_2C_1im][OAc]$	Crustacean shells	100 °C 19 h	10	Dry-jet wet spinning	Film Fiber	108
10	$[C_4C_1im]Cl$ $[(C_1{=}C_2)C_1im]Br$	Cellulose Chitin	100 °C 24 h	10 5	Solution casting	Film Gel	108
11	$[C_2C_1im][OAc]$	Chitin Carbon nanotubes	60–120 °C 2–12 h	3	Solution casting	Film	112
12	$[C_2C_1im][OAc]$	Cellulose Silk	80 °C 1 h	10	Blending Molding	Film	150
13	$[C_4C_1im]Cl$	Skin collagen Cellulose	100 °C 6 h	5	Solution casting Extrusion Molding	Film Fiber Gel	109
14	$[(C_1{=}C_2)C_1im]Cl$	Wool keratin	100 °C	—	Solution casting	Film	110
15	$[(C_1{=}C_2)C_1im]Cl$	Cotton Duck feather	100 °C	—	Solution casting	Film	113
16	$[(C_1{=}C_2)C_1im]Cl$	Cellulose Starch, lignin	80 °C	6	Solution casting	Film	69
17	$[C_4C_1im][OAc]$	Cellulose Chitosan	85–95 °C 6 h, 3–4 days	6	Solution casting Vacuum freeze drying	Film	151
18	$[C_4C_1im]Cl$ $[C_4C_1im][OAc]$	Cellulose Chitosan	25–110 °C 4 h	—	Solution casting	Film	152
19	$[C_2C_1im][OAc]$	Hemp biomass	—	14	Electrospinning	Fiber	120
20	$[(C_1{=}C_2)C_1im]Cl$	Cotton Duck feather	100 °C	—	Lab spinning set-up	Fiber	131
21	$[C_2C_1im][OAc]$ $[C_2C_1im][lactate]$	Pine wood	80 °C 24 h	5–10	Wet electrospinning	Fiber	119
22	$[C_4C_1im]Cl$	Cellulose pulp	—	—	Dry-jet-wet-spinning	Fiber	121
23	$[C_4C_1im]Cl$	Cellulose	90 °C 30 min	5	Electrospinning	Fiber	122
24	$[C_4C_1im]Cl$	Chitosan	80 °C 1 h	5	Dry-wet spinning	Fiber	124
25	$[C_4C_1im]Cl$	Chitosan Cellulose	80 °C	5 10	Dry–wet spinning	Fiber	125
26	$[C_2C_1im][OAc]$	Hemp biomass	70 °C 24 h	14	Electrospinning	Fiber	153
27	$[C_4C_1im]Cl$	Cellulose, starch Hindered amine light stabilizer	100 °C 20 h	4–10	Dry-jet wet spinning	Fiber	154
28	$[C_2C_1im]Cl$	Silk fibroin	95 °C	10	Extrusion	Fiber	155
29	$[dbmim][BF_4N_2]$	Quantum dots elastomer	70 °C 6 h	1% IL	Electrospinning	Fiber	156
30	$[C_4C_1im]Cl$	Cellulose Heparin	Microwave heating	10 2	Electrospinning	Fiber	157
31	$[(C_1{=}C_2)C_1im]Cl$	Cellulose	80 °C 2 h	1–5	Electrospinning	Fiber	158
32	$[C_2C_1im][OAc]$ $[C_1C_1im][Cl]$	Cellulose	RT	8	Electrospinning	Fiber	159
33	$[C_4C_1im]Cl$	Wood pulp MWCNT	100 °C 45 min	4	Dry-jet wet spinning	Fiber	160

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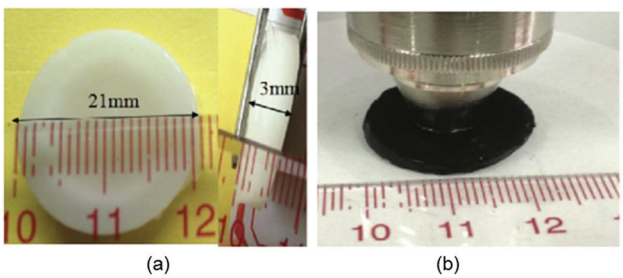
Table 1 *(Contd.)*

Entry	IL	Raw material	Conditions	Loading (%)	Fabrication technique	Product	Ref.
34	$[C_2C_1im][OAc]$	Chitin	—	1.5	Electrospinning	Fiber	161
35	$[C_2C_1im][OAc]$	Cellulose MWCNT	80 °C 2–3 h	4–8	Dry-jet wet spinning	Fiber	128
36	$[C_2C_1im][OAc]$	Cellulose MWCNT	80 °C 2 h	—	Lab-built spinning equipment	Fiber	129
37	$[C_2C_1im][Et_2PO_4]$	Microcrystalline cellulose	95 °C 24 h	7.6–18	Dry-jet wet spinning	Fiber	130
38	[DBNH][OAc]	Birch kraft pulp	80 °C 75 min	13	Multi-filaments piston-spinning	Fiber	162
39	$[C_2C_1im][OAc]$	Yellow pine Bagasse	175 °C 30 min	5	Dry-jet wet spinning	Fiber	132
40	$[C_4C_1im]Cl$ $[(C_1{=}C_2)C_1im]Cl$	Cellulose	100 °C 2–4 h	3	Spinning into water	Fiber	126
41	[DBNH][OAc]	Cellulose	80 °C 3 h	13	Dry-jet wet spinning	Fiber	127
42	$[C_4C_1im]Cl$	Cellulose Starch	100 °C 24 h	10	Solution sandwiched between glass plates, raising by spatula	Fiber Gel	133
43	$[C_2C_1im][OAc]$	Cellulose Xylan, lignin	—	—	Electrospinning	Synthetic wood fiber	163
44	$[(C_1{=}C_2)C_1im]Cl$	Pineapple peel	100 °C 12 h	2.5–7.5	Heating–cooling–freezing–thawing–washing process	Hydrogel	164
45	$[C_4C_1im]Cl$	Microcrystalline cellulose	80 °C 12 h	1.5–5.5	Chemical crosslinking	Hydrogel	165
46	$[C_4C_1im]Cl$	Cellulose Collagen	100 °C	6	Dropping solution from syringe needle	Hydrogel beads	166
47	$[C_4C_1im]Cl$	Cellulose	100 °C 24 h	15	Keeping in RT for 7 days	Hydrogel	142
48	$[C_4C_1im][OAc]$	Silk fibroin from the silkworm	95 °C 8 h	10	Molding followed by gelation overnight	Hydrogel	143
49	$[C_4C_1im]Cl$	Cellulose Graphene	80 °C 24 h	3–5	Degassing the solution by ultrasound	Hydrogel	144
50	$[C_4C_1im]Cl$	Cellulose	70 °C 2 h	—	Solution casting	Hydrogel	167
51	$[C_4C_1im]Cl$	Cotton cellulose	100 °C 24 h	8	Solution casting	Aerogel	168
52	$[(C_1{=}C_2)C_1im]Cl$	Nalita wood	80 °C, 4 h	8	Freeze thaw	Aerogel	140
53	$[C_2C_1im][OAc]$	Cellulose	80 °C 16 h	3	Molding	Alcogels	169
54	$[C_2C_1im][OAc]$ $[C_4C_1im]Cl$	Cellulose	80 °C 48 h	—	Regeneration/drying in supercritical CO_2	Aerocellulose	141
55	$[(C_1{=}C_2)C_1im]Br$	Chitin	100 °C 48 h	7	Dissolution + cooling	Gel	170
56	$[C_4C_1im]Cl$	Spruce wood	130 °C 4 h	7	Solution casting followed by coagulation and high pressure cell	Aerogel	171
57	$[C_4C_1im]Cl$	Cellulose, starch Zein protein, agar	95 °C	3	Molding	Aerogel	172
58	$[C_4C_1im]Cl$	Agarose Chitosan	100 °C	5	Regeneration from IL solution	Ionogel	173



(a) (b)

Fig. 12 (a) Cellulose hydrogel and (b) swollen hydrogel.[165]

fiber surfaces and entrapment of modifiers between neighboring congealed fibers.[183,184]

3.5. All-wood composites

Wood is widely utilized for furniture and building materials. However, most of the waste timbers recovered from demolished wooden buildings and massive deforestation are usually incinerated for energy purposes, which causes severe environmental problems.[185,186] Furthermore, it has also been reported that a massive increase of damaged trees due to various diseases such as *sugi-mizogusare*, which can no more be useful as lumber, is becoming a critical problem in countries such as Chiba and Japan.[187] On the other hand, the requirement for wood based composite materials for furniture and construc-

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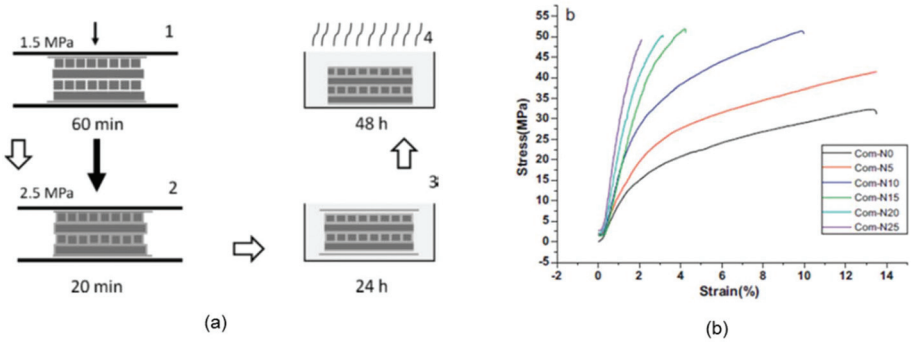

Fig. 13 (a)The fabrication process for ACC laminate by hand lay-up method,[176] (b) stress–strain curve of the all-cellulose composites.[178]

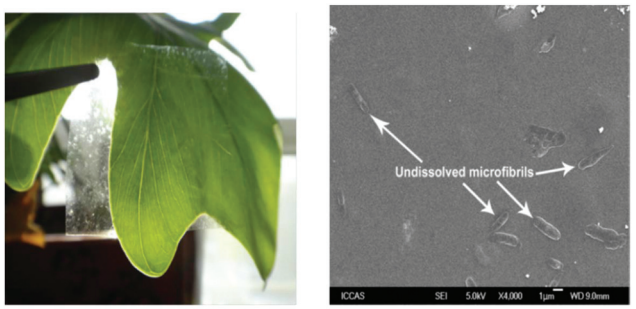

Fig. 14 (a) Photograph and (b) SEM images of regenerated all-cellulose composite film.[179]

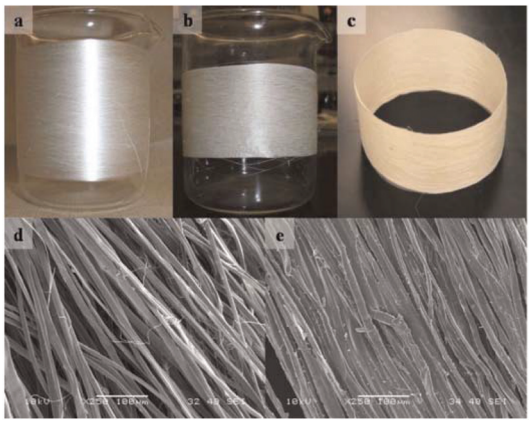

Fig. 15 An example of fiber welding. (a) Raw silk thread, welded with $[C_2C_1im][OAc]$ for 5 min at 60 °C to create a solid, yet flexible band structure, (b) and (c). SEM images of (untreated) desized silk and of the welded silk band are shown in (d) and (e), respectively.[181]

tion industries in the form particleboard, fiberboard, oriented strand board *etc*. is increasing every year.[188] Therefore, there has been a substantial demand for novel technologies that could provide new routes for consumption of the untapped or waste lumber as well as for the production of wood composite materials in a more efficient and environmentally benign manner (Table 2).

Shibata *et al.*[189] developed a new method for waste wood processing based on the partial dissolution of waste wood flour in $[C_4C_1im]Cl$ as depicted in Fig. 16. Wood flour (WF) and bark flour (BF) derived from cedar wood were mixed with 40 wt% $[C_4C_1im]Cl$ at 100 °C and the resulting mixtures were compression-molded at 210 °C in a stainless steel mold. The tensile strength and thermal properties of the biocomposites were significantly improved by the extraction of the IL from the final product and further by the annealing process. In their further work,[190] Shibata and co-workers tried to improve the tensile strength and modulus of all-wood based biocomposites from dipped hinoki lumber (HL) with dimensions 50 mm × 10 mm × 2 mm in the same IL at 100 °C and the IL-impregnated HL was hot-pressed at 210 °C for 30 min (Fig. 17a). Although the tensile strength of the fabricated biocomposite was found to be lower than that of original HL, the tensile modulus of the former was significantly improved. In-depth analysis of the structural and chemical changes of wood during IL interaction is needed to explore the opportunities for using ILs in wood and wood based composite materials.

3.6. Synthetic wood and synthetic wood composites

The main rationale for using ILs in the field of polysaccharide based composites is the excellent dissolving power of some ILs for most of the biopolymers, which can be exploited for the production of highly useful hybrid composites consisting of both biodegradable and non-biodegradable components. In the work of Simmons *et al.*,[194] synthetic wood was fabricated from the three major components of lignocellulosic biomass *i.e.*, cellulose, hemicellulose and lignin, as shown in Fig. 17c. The artificial wood films were obtained by dissolution of individual biopolymer components (cellulose/xylan/lignin, 5/3/2, wt%) in $[C_2C_1im][OAc]$ at 90 °C for 3 h and reconstituting these using water as anti-solvent. As compared to the individual components, synthetic wood showed remarkably improved physicochemical properties. In addition, a wide variety of synthetic wood based composite materials could be fabricated having special properties like mechanical strength, color, conductivity or anti-microbial properties *etc*. Simmons and co-workers[194] also prepared synthetic wood composites by dissolution of different polymers such as chitosan or nanoparticle

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Table 2 All-cellulose and all-wood composites based on partial dissolution in ILs

Entry	Ionic liquid	Raw material	Conditions	Loading (%)	Fabrication technique	Ref.
1	$[C_4C_1im][OAc]$	Linen Rayon	110 °C 80 min	50	Hot press	176
2	$[C_4C_1im]Cl$	Microfibrillated cellulose	80 °C 20–160 min	—	Solution casting	191
3	$[C_2C_1im]Cl$	Microcrystalline cellulose	85 °C 2 h	3	Solution casting	178
4	$[(C_1{=}C_2)C_1im]Cl$	Agave fibers	80 °C	4	Solution casting	179
5	$[C_4C_1im]Cl$	Lyocell fibers Flax fibers	130 °C 1 min impregnation	—	Solution casting	180
6	$[C_4C_1im]Cl$	Rice husk Filter paper	100 °C	5–10	Solution casting	192
7	$[C_4C_1im]Cl$	Cedar wood flour Bark flour	100 °C 10 min	60	Compression molding followed by annealing	189
8	$[C_4C_1im]Cl$	Cotton fabric hinoki lumber	100 °C 30 min	—	Hot press followed by annealing	190
9	$[C_4C_1im]Cl$ $[C_4C_1im][OAc]$	Mulberry wood	80 °C 2–3 h	—	Twin-screw kneader followed by injection-molding	193
10	$[C_2C_1im][OAc]$	Silk fiber Hemp fiber	60 °C 5 min	—	Natural fiber welding	181
11	$[C_2C_1im][OAc]$	Cotton cloth	40–80 °C 0.5–24 h	—	Natural fiber welding	182

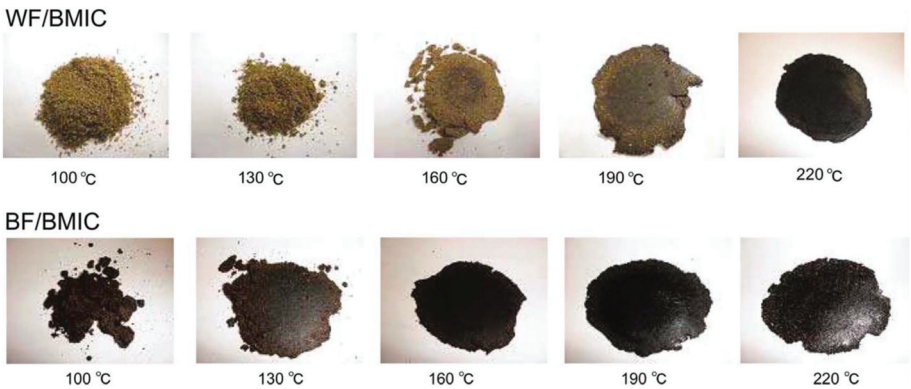

Fig. 16 Photographs of the all-wood biocomposites compression-molded at various temperatures.[189]

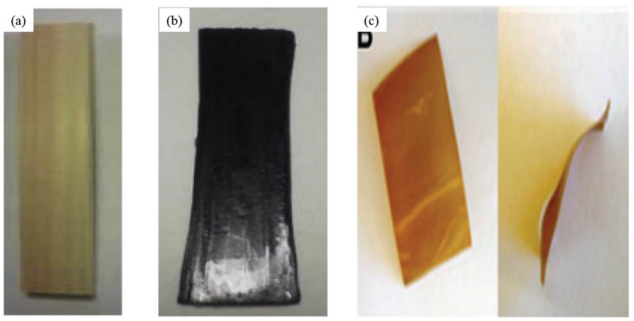

Fig. 17 (a) Original hinoki lumber (HL), (b) HL composite after IL pre-treatment with $[C_4C_1im]Cl$,[190] (c) synthetic wood films.[194]

like multi-wall carbon nanotubes (MWNT) in $[C_2C_1im][OAc]$ along with wood components followed by regeneration with water. This excellent property of synthetic wood MWNTs composites makes them a suitable candidates as flexible high dielectric insulator materials in applications such as batteries and supercapacitors.[195]

3.7. Chemical and surface modification of lignocellulosic materials with ionic liquids

The properties of synthetic fibers can be engineered during their manufacturing process to make them suitable for different end uses.[196] In the case of natural fibers, various pre-treatment steps are highly desirable in order to impart a range of suitable characteristics for different applications as engineered materials.[197] For example, in order to improve the interfacial compatibility between individual components in composites containing natural fibers, the modification of the natural fiber is an extremely important step prior to hybrid injection molding. Thus, the chemical or surface modification of lignocellulose and wood has been extensively studied with the objective of modifying or improving its compatibility with thermoplastics or thermosets, as well as for improving dimensional stability.[84,198] However, to obtain a hydrophobic wood

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matrix by heterogeneous chemical modification so that it could be molded into any desired shape is a very difficult task, due to the poor solubility of its lignocellulosic components in conventional solvents.[199] Recently, the efficient lignoellulose dissolution capabilities of ILs have opened a new platform for novel homogeneous modification of wood and lignocellulose for derivative biopolymers.

In the study of Wen *et al.*,[200] complete dissolution and homogeneous lauroylation of abundantly available hydroxyl groups in ball-milled lignocellulose bamboo meal was carried out in $[C_4C_1im]Cl$ at 130 °C for 6 h. The thermal stability of the esterified derivatives was found to be lower than that of the unmodified bamboo meal and the rough appearance of the bamboo meal changed into a relatively homogeneous and smooth surface morphology after lauroylation. Another work that describes the development of an IL-assisted pretreatment technology for efficient conversion of chemically modified wood material into thermoplastic material was reported by King *et al.*[201] Benzoylation and lauroylation of spruce wood thermomechanical pulp was carried out in the IL solution 4% w/w spruce in $[C_4C_1im]Cl$ followed by the incremental addition of benzoyl chloride and lauroyl chloride, respectively. Subsequently, these highly substituted benzoylated and laurolyated lignocellulosic spruce fibers were used as reinforcement for thermoplastic composites of polypropylene and polystyrene. Excellent dispersion of the IL-modified wood fibers material into the synthetic polymers was achieved throughout the composite material, as highlighted by SEM images. Utilization of $[C_4C_1im]Cl$ for homogeneous benzolyation of wood meal was also reported by Yuan *et al.*[202] The focus of this study was to enhance the compatibility as well as photostability of wood with hydrophobic synthetic polymers for the production of green composites that could be used for outdoor applications. The article describes a highly promising IL based modification of wood fiber with improved properties for photostable green composites applications.

For the application of ILs in wood based composite materials, most of the studies have been focused on the effect of ILs on the bulk properties of lignocellulosic biomass and wood, and there are only a few reports related to the IL based modification of wood surface properties. In the study by Croitoru *et al.*,[203] the effect of four types of imidazolium-based ILs, namely 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4C_1im][BF_4]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4C_1im][PF_6]$), $[C_4C_1im]Cl$ and 1-butyl-3-methylimidazolium tetrachloroferrate ($[C_4C_1im][FeCl_4]$), on the various surface properties of poplar wood veneers was studied in terms of contact angle, electrical conductivity measurement and photographic image analysis and compared with those of untreated wood. It was found that IL treatment improved the flexibility of the cellulose matrix and decreased its crystallinity. Indeed, the workability of wood could be remarkably enhanced by IL surface pretreatment, which decreased its rigidity as well as preventing the accumulation of static electric charges on the surface of the wood during finishing. The changes that occurred in the structure and surface properties of maple wood veneers treated with three different types of IL, $[C_4C_1im][BF_4]$, $[C_4C_1im][PF_6]$ and 1-hexyl-3-methylimidazolium chloride ($[C_6C_1im]Cl$) were studied after being subjected to an electron beam irradiation with a 50 kGy dose.[204] Also, an interesting observation was noted that a higher resistance to water penetration and spreading on the wood surface resulted after the electron beam irradiation, due to covalent bonding of the imidazolium moiety to wood structure (Table 3).

Whether wood is used for interior applications or under exterior conditions, the important properties that could be sig-

Table 3 Ionic liquid assisted modification of lignocellulosic materials for biocomposites

Entry	Ionic liquid	Raw material	Conditions	Modification reaction	Ref.
1	$[C_4C_1im]Cl$	Bamboo meal	130 °C 6 h	Lauroylation	200
2	$[C_4C_1im]Cl$	Southern pine Thermomechanical pulp	70 °C 2 h	Lauroylation	201
3	$[C_4C_1im]Cl$	Wood meal	130 °C 5 h	Benzoylation	200
4	$[C_4C_1im]Cl$ $[C_4C_1im][PF_6]$ $[C_4C_1im][BF_4]$	Poplar veneers	22 °C 15 min	Surface treatment	203
5	$[C_4C_1im]Cl$ $[C_4C_1im][PF_6]$ $[C_4C_1im][BF_4]$	Poplar veneers	22 °C 15 min	Electron beam irradiation	204
6	$[C_4C_1im]Cl$ $[(C_1{=}C_2)C_1im]Cl$	Spruce thermomechanical pulp	130 °C 4–6 h	Acylation Carbanilation	205
7	$[C_4C_1im]Cl$	Poplar wood	125 °C 1 h	Acylation	206
8	$[(C_1{=}C_2)C_1im]Cl$	Cellulose	80 °C 1 h	Acetylation	183
9	$[C_4C_1im]Cl$	Poplar wood	130 °C 5 h	Benzoylation	202
10	$[C_4C_1im]Cl$ $[C_4C_1im][PF_6]$ $[C_4C_1im][BF_4]$	sspen veneer	22 °C 15 min	Surface treatment	207

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nificantly affected are its texture, color, wettability and roughness. Patachia *et al.*[207] studied the effect of four types of imidazolium-based IL on the chemical modification and photodegradation of the surface of wood veneers. The ILs treated wood showed some useful properties including enhanced wettability that could increase the compatibility of the wood with adhesives in fabrication of wood based composite materials.

3.8. Ionic liquids as plasticizers for biodegradable thermoplastic polymers

In nature, most vegetal structures are based on matrices of various biopolymers. In terms of the vocabulary of polymer material scientists, one could state that nature has developed extremely efficient composites of biopolymers.[208] The glass transition temperature (T_g) of a polymeric material is an important parameter in determining its mechanical performance during composite manufacturing and service.[209] Unfortunately, T_g of most of the biopolymers is experimentally inaccessible due to thermal degradation of these polymers at elevated temperatures.[210] Consequently, the plasticization of different biopolymers using various plastisizing agents and employing different mechanical techniques, such as shear mixing, melt-processing, extrusion *etc*., has been demonstrated through the decrease in the T_g of the native biopolymer.[211,212] Recently, ILs have been shown to be efficient thermoplasticizers for different bipolymers leading to significantly different properties, such as water sensitivity and thermomechanical properties, from those of classical plasticizers such as glycerol, glycerine, glycol, urea *etc*.[213,214] ILs are able to disrupt the semicrystalline structure of native biopolymer granules and destroy the intermolecular hydrogen bonding among hydroxyl groups of polysaccharides.[215] Among various biopolymers, starch has been recognized as a promising substrate due to its wide availability, low cost and renewable character.

Sankri *et al.*[79] reported modification of starch with $[C_4C_1im]Cl$ in a microcompounder and a twin screw extruder. To the best of the author's knowledge, this is currently the only article describing a continuous method of starch plasticization using ILs. The remarkable reduction in molecular weight of starch extruded with $[C_4C_1im]Cl$ compared to glycerol-plasticized polysaccharide was assigned to thermo-mechanical treatment rather than interaction with IL. The use of $[(C_1{=}C_2)C_1im]Cl$ as a corn starch plasticizer to fabricate solid biopolymer electrolytes has been described.[215] The films were obtained by solution casting starch plasticized with 10 and 30 wt% IL respectively. Another study[216] showed the plasticization of starch by mixing with same IL in the presence of lithium chloride. It was noted that thermal decomposition of starch was stimulated by high Cl^- ion concentration.

Cellulose acetate is one of the most valuable cellulose derivatives, with a wide range of applications including films, coatings, membrane separation, textile and cigarette filters. Availability from renewable sources, biodegradability, non-toxicity and low cost are the combination of characteristics that make the cellulose acetate a highly promising biopolymer matrix. However, its functionalization and processing for different applications is limited by its properties such as high crystallinity and thermal decomposition temperature, which is very close to its melt processing temperature. Bendaoud and Chalamet[217] utilized a micro-compounding technique to convert cellulose acetate into a thermoplastic polymer using $[C_4C_1im]Cl$. The biocomposites were thermo-molded into dumbbells and disk-shaped plates of dimensions of 30 mm × 10 mm × 2 mm and 25 mm × 2 mm (Fig. 18), respectively. It was noted that the presence of the IL strongly reduced the interactions between cellulose acetate chains as evidenced from mechanical tensile tests and rheology analyses of plasticized cellulose acetate (Table 4).

3.9. Role of ILs in fiber-reinforced polymeric composite (FRC)

Recently, wood plastic composites (WPCs) have attracted significant attention from both industrial and scientific communities due to their increasing applications as engineered materials in automobile components, building materials and infrastructure *etc*. and have achieved commercial success.[219,220] Natural lignocellulosic resources can efficiently be utilized in WPC manufacturing and thus have high potential to reduce the environmental hazard mainly created by waste from non-degradable plastic products.[174] However, in general increasing the wood contents resulted in higher viscosity of the WPC melts. During the processing of WPC, higher viscosity undoubtedly requires high torque for efficient mixing of the blends which will increase the energy consumption. Moreover, this can stimulate high internal friction and can generate local overheated spots, which will ultimately cause the thermal degradation of the wood flour.[221,222] Hence, the overall performance and surface quality of WPC will be remarkably reduced. Also, at high wood contents, the rigid cell wall architecture of wood lacks sufficient plastic deformability during extrusion processing, which under extreme conditions may induce structural damage of lignocellulose particles and consequently poor reinforcing effects.[223,224] Therefore, current technologies such as controlling die stresses or altering the flow of plastics do not work efficiently for high levels of wood flour. Recently, ILs have emerged as alternative and benign

Fig. 18 Visual observations of pressed plasticized cellulose acetate samples.[217]

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Table 4 Plasticization of biobased polymers by ILs

Entry	Ionic liquid	Raw material	Compounding method	Ionic liquid proportion (%)	Conditions	Ref.
1	$[C_4C_1im]Cl$	Maize starch	Melt-processing	15–30	160 °C, 2 min	79
2	$[(C_1{=}C_2)C_1im]Cl$	Corn starch	Mixing	23	75 °C, 20 min	215
3	$[C_4C_1im]Cl$	Cellulose acetate	Micro-compounder	20–40	150 °C, 150 rpm	217
4	$[C_4C_1im]Cl$	Starch, zein	Micro-compounder	23	130 °C, 3 min	80
5	$[C_2C_1im]Cl$	Wood flour	Twin-screw extruder	1–5	150–175 °C	218

processing media for the manufacture of natural fiber reinforced polymeric composites.

Ou *et al.*[218] proposed that improving the thermoplasticity of rigid cell walls of lignocellulose using ILs may be a viable strategy to enhance the processability of wood based thermoplastic composites. They pretreated the wood flour with $[(HO)^2C_2C_1im]Cl$ to different weight percent gains and the pretreatment effect on the rheological properties of the resulting wood flour/high density polyethylene (HDPE) composites was investigated. It was observed that $[(HO)^2C_2C_1im]Cl$ treatment significantly reduced the crystallinity and improved the thermoplasticity of wood fibers and thus broadened the processing window of wood fiber/HDPE composites with stable flow and remarkably smooth product surfaces. It was further concluded that filler–filler interaction had a dominant effect on the extrusion/injection processing of WPCs and that IL pretreatment of wood fiber laid the groundwork for future research in WPCs. A recent report[193] also describes the novel use of ILs in production of WPCs. Ball-milled mulberry wood (BMMW) was firstly kneaded in $[C_4C_1im]Cl$ or $[C_4C_1im][OAc]$ with the help of the cosolvent DMSO. Plasticization of BMMW for injection-moulding was achieved after the structural destruction of the wood cell walls in the presence of ILs (Fig. 19). The thermal flow and mechanical results revealed that the WPC obtained with DMSO/$[C_4C_1im][OAc]$ exhibited better thermal and mechanical properties than those obtained with DMSO/$[C_4C_1im]Cl$, indicating that the thermoplasticity of AWP was related to the ILs' anionic ability to disrupt the hydrogen bond networks in the rigid crystalline region of cellulose.

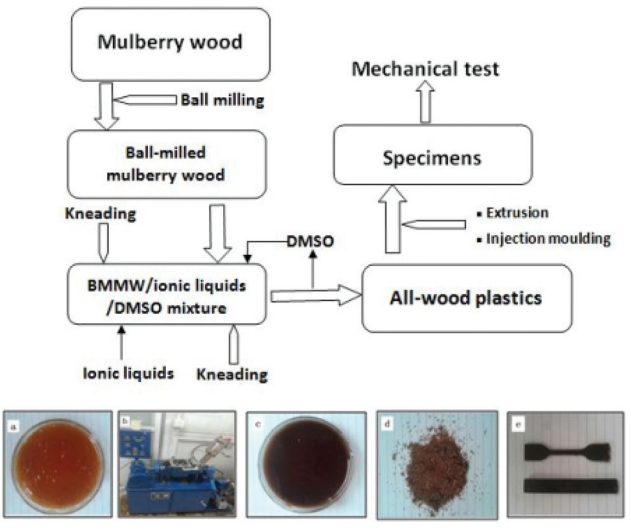

Fig. 19 Process flow diagram of the preparation AWP and appearance of mulberry wood before kneading (a), the kneader (b), mulberry wood after kneading (c), final AWP (d) and injection moulded AWP specimens (e).[193]

4. Could ionic liquids be helpful to provide alternative raw materials for the wood composite industry?

Among the various lignocellulosic resources, woody biomass has been the most promising raw material for widely known and used natural organic fibers for the production of composite panels.[225] However, the massive deforestation, forest degradation and simultaneously increasing demand for wood based composite panels has created a critical raw material issue in the wood composite industry for a long time. Considering these factors, recently research has been focused on the utilization of a wide variety of agro-based renewable lignocellulosic residues as a supplement to, or as a direct substitute for, wood fiber in the production of industrial products such as particleboard, fiberboard, plywood *etc.*[226,227] The availability of these inexpensive lignocellulosic materials in every part of the world together with exclusive advantages in terms of low density, CO_2 neutrality (when burned), non-abrasive nature and safe working environment have fueled their use for composite panels manufacturing in the past few years. Malaysia is one of the most important producers of palm oil in the world. During oil palm fruit harvesting, the pruning of oil palm frond (OPF) generates approximately 44 million tonnes dry weight in the oil palm fields annually. Conversely, considering the international scenario, each year about 184.6 million tonnes of lignocellulosic residue is available worldwide from the palm oil industry alone.[228] The exploration of this lignocellulosic residue as a biobased renewable resource for manufacturing of industrial products will open a new avenue for the efficient utilization of agricultural waste by reducing the need for disposal and environmental degradation and simultaneously add value to the development of agricultural based economies in rural areas.[227]

Recently, we have reported the pretreatment of lignocellulosic oil palm biomass with imidazolium based ILs.[84] The oil palm biomass was ground to a particle size range of 250–300 μm and dissolved in $[C_2C_1im][Et_2PO_4]$ or $[C_4C_1im]Cl$ at 80 °C for 3 h and then regenerated using an acetone–water

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mixture as an anti-solvent. Afterward, the precipitated solid residue was separated by decantation and washed with distilled water 4–5 times to ensure complete removal of any residual IL. The anti-solvent acetone/water was removed from the supernatant using a rotary evaporator to leave an IL/lignin rich phase. The dried regenerated cellulose-rich fiber was compounded with a thermoplastic starch polymer and was thermally pressed at 160 °C for 10 min in a Carver Laboratory compression molding machine (CARVER, INC. USA) to fabricate a 'green' composite board (Fig. 20). The cellulose contents in the regenerated fibers after IL pretreatment were significantly increased, which resulted in a more accessible surface area for binder interaction and improvement in the thermal stability of the fibers. Due to removal of non-cellulosic impurities from the fiber surface as a result of the IL pretreatment, the composite panels fabricated from IL pretreated fiber exhibited superior mechanical and thermal properties. It was clearly indicated that IL-assisted pretreatment could be a new, highly promising and green technology for effective utilization of lignocellulosic biomass in the wood composites and related industries.

5. Parameters affecting the practical applications of ILs for green composites processing

Several criteria must be considered for the large scale use of ILs for pretreatment and dissolution of lignocellulose and other biobased polymers for the manufacture of sustainable biocomposites. The most significant ones include price, toxicity, corrosivity, physical properties, availability, regeneration requirement, biodegradability and water tolerance. Unfortunately, until now these issues have been rarely discussed. Utilization of ILs in manufacturing engineered green composites based on renewable and biodegradable resources is possible only if both ILs and dissolution conditions are properly optimized.[14,24,26,229]

5.1 Toxicity and corrosivity

Toxicity of ILs is one of the most important parameters when considering their practical applications on industrial scale. The toxicological effect on human health must be further evaluated for the implementation of ILs as solvents in the biocomposite industry. The ease of modification and tunability of IL compositions holds great potential to design targeted properties of ILs which may be useful in this regard.[230–232] In addition, IL corrosivity is a very important economic issue while selecting the material of construction for equipment to be used in large scale applications for lignocellulose pretreatment. Halogen-free ILs may be suitable candidates as non-corrosive IL solvents.[233,234]

5.2 Viscosity and water content

Viscosity is another important parameter from the practical point of view, because the higher viscosity of an IL will require a higher dissolution temperature and also more energy for mixing and fluid transfer. Furthermore, this could potentially give rise to other side-effects, such as the generation of unwanted side-reactions.[235–237] One promising approach to reduce the viscosity of ILs is to use a co-solvent such as DMSO, polyethylene glycol *etc.*[67,84] Similarly, the water content of an IL also has an impact on its dissolution efficiency. It has been observed that the presence of water in ILs significantly hampers their cellulose dissolution ability.[8] Therefore, drying of woody material at 90 °C prior to the dissolution experiments

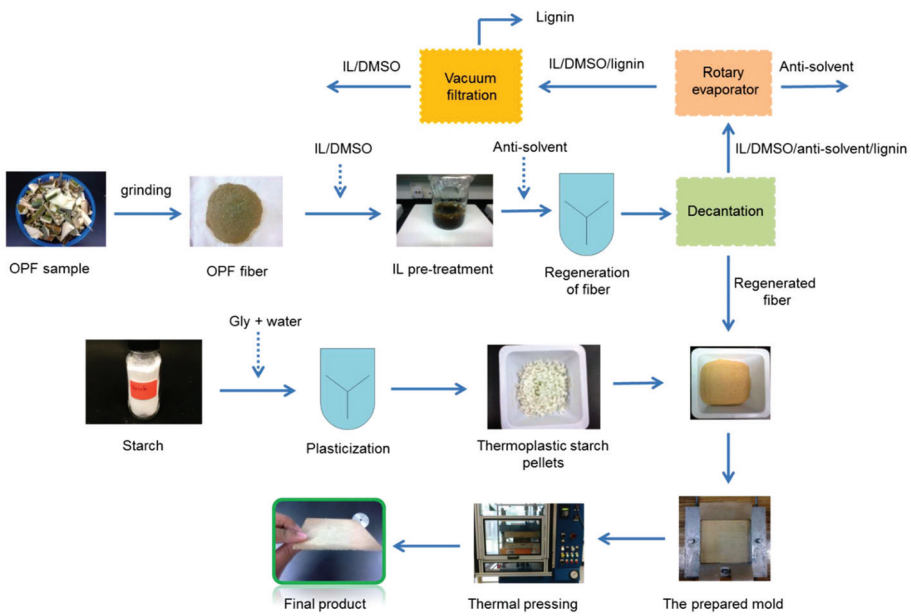

Fig. 20 Manufacturing steps to fabricate composite board from ILs treated oil palm fiber.[84]

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in ILs is strongly recommended to reduce its water content.[74] In addition, the use of water as precipitating solvent for dissolved lignocellulose has also been demonstrated.[84] The dissolved lignocellulosic material can be easily regenerated for subsequent biorefinery applications by precipitating it from an IL through the addition of water as an anti-solvent.[49,74] When water is added as an anti-solvent into the IL and lignocellulose mixture, the IL ions form hydrogen bonds with the water molecules and they become highly hydrated. The interactions between the IL and lignocellulosic particles are hence shielded by the hydration shells formed by the water molecules around the ions of IL, which ultimately provokes the precipitation of the dissolved material.[26]

5.3 Recycling and re-use of ILs

The efficient recycling and reuse of ILs is indeed critical to reduce the cost of pretreatment processes as well as to realize the environmental and economic benefits of ILs. This is an inherent advantage in the IL based processing of biomass that biomass dissolved in IL can be regenerated rapidly using precipitation from solution by addition of various anti-solvents, such as water, acetone *etc*.[49,238,239] The IL used can then be easily recovered upon removal of the non-solvent through evaporation. The selection of suitable anti-solvent is considered to be one of the most important factors that has had a significant impact on the yields of the regenerated material and the recycled IL, which ultimately affects the overall cost of the pretreatment process.

5.4 Unwanted reactions of solvated biopolymers with IL

The side reaction of IL with biopolymer species during dissolution processes to form intermediate products could not only cause IL recycling and product separation issues but also deteriorate the quality of regenerated material for downstream applications. The reactivity of carboxylate ILs towards carbohydrates was first demonstrated by Ebner *et al.*[184] and later thoroughly explored by Welton and co-workers.[240] Mixtures of $[C_2C_1im][OAc]$ with carbohydrates were found to undergo reaction of the C^2 carbon of the imidazolium ring yielding a terminal adduct species 1-ethyl-2-(hydroxymethyl)-3-methylimidazolium acetate by elimination of successive formaldehyde units from the sugar adduct. Such unwanted side reactions of solvated biopolymers with IL presents potential problems for both laboratory and industrial processes, due to the influence of new chemical species on both the physical and rheological properties of the mixture. It is crucial, therefore, to understand factors contributing towards unwanted side reactions, and how they might be prevented or controlled.[240]

5.5 Batch *vs.* continuous pretreatment

Disregarding its various advantages, currently IL-assisted pretreatment is not feasible for industrial-scale operations due to many reasons, including the large initial biomass loading requirements. The considerable number of studies that investigated IL-mediated pretreatment operations with low biomass loadings (5–10%) could be because of the effective mixing obstructions of conventional stirred reactors for 'semi-solid' high biomass loads systems (>20 wt%).[241,242] Recently, continuous pretreatment of lignocellulosic material with $[C_2C_1im][OAc]$ mediated by a *twin-screw extruder* was reported at biomass loadings as high as 50 wt%. The extrusion process can be carried out continuously and is suitable for industrial-scale lignocellulose processing allowing higher throughputs and reactant concentrations, improved mixing rates as well as more uniform products as compared to batch operations.[83]

6. Future prospects

While there is a growing literature of the use of ionic liquids in the processing of renewable resources for the fabrication of biodegradable composite materials, this remains an underdeveloped field of research. The literature is characterized by a large number of initial proof of concept studies. For the future success of ionic liquids in this endeavor, deeper mechanistic understanding of the processes involved is required to enable the optimization of these processes, since their application will only be achieved if the advantages of ILs outweigh their drawbacks, most prominently the prices of ILs relative to the value of the material processed by these.[243] Generally the development of pretreatment processes and selection of suitable conditions for efficient processing requires a compromise between conflicting objectives which can be overcome by applying multi-objective optimization techniques in pretreatment process design and selection.

Modeling of the process is essential to estimate the energy requirement and cost for dissolution processes, so that the comparison with other pretreatment methods will be possible. The first techno-economic analysis of IL based processing system was carried out and the following order of importance/sensitivity among the investigated variables was reported: IL price > biomass loading > recycling rate.[243] Furthermore, molecular level simulation should be employed for better understanding the interaction mechanism of ILs with biobased molecules.[244] Additionally, an optimized selection of both cations and anions as well as processing conditions may allow the design of IL systems with unique physicochemical characteristics that could lead to more effective utilization of ILs in lignocellulosic and biopolymer based composite industries.[53]

Despite all of these advantages and potential applications, ILs currently suffer from clear and significant disadvantages of their high cost that stand in the way of many commercial applications. It is believed that ILs normally fall in the range of 5–20 times more expensive than molecular solvents.[245] The most common criticism of ILs that the authors encounter is that of the 'severe' limitations placed upon their large-scale deployment by their high cost. But are ILs inherently expensive, or is this opinion a consequence of the specific ILs that are historically prominent (dialkylimidazolium cations with polyfluorinated anions)? To answer this question, Welton and co-workers evaluated the economic feasibility and determined the cost price of two ILs synthesized from cheap raw

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materials.[246] The cost prices of triethylammonium hydrogen sulfate and 1-methylimidazolium hydrogen sulfate were estimated as \$1.24 kg^{-1} and \$2.96–5.88 kg^{-1}, respectively, which compares favourably with organic solvents such as acetone or ethyl acetate, which sell for \$1.30–\$1.40 kg^{-1}. These results indicate that ionic liquids are not necessarily expensive, and therefore large-scale IL-based processes can become a commercial reality. In addition, organic electrolyte solutions containing a small fraction of ILs with potential dissolution capabilities for large amounts of cellulose can lead in the future to very interesting developments.[247] Dissolution and depolymerization of cellulose in organic acid-catalyzed 30 wt% aqueous solution of NaCl under mild reaction conditions (100–125 °C) and some pressure (10–30 bar) has also been observed.[248] It was proposed that such salt solutions disrupt the hydrogen-bond matrix among cellulose fibrils in a mechanism similar to that of ILs. Development of such ILs based solvent systems, in the future, might open new pathways in the field of biopolymer processing in which environmental concerns can be tackled, while simultaneously keeping process costs (energy, substrates, catalysts, *etc.*) at an acceptable level.

It must also be emphasized that conventional dissolution processes employ various solvent systems under extreme conditions and also are limited due to their dissolving capability, solvent recovery, toxicity, uncontrollable side reactions and high cost during biomass processing and derivatisation, the following list summarizes the major aspects for IL based processing of natural fibers and polymers that should receive attention for future research.[24]

- Low cost of ILs and co-solvents (typically less than \$2.50 kg^{-1})
- Decreased IL loading
- Short dissolution time
- Applicability to a wide range of raw materials
- End of use IL recovery
- Optimized recycling to reduce ILs losses
- Reduced influence of residual IL on downstream processing
- 'Greenness' of ILs (environmental and health impact).

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