Processing and Valorization of Cellulose, Lignin and Lignocellulose Using Ionic Liquids

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A B S T R A C T

Cellulose, lignin and lignocellulose are important bioresources in the nature. Their effective and environmentally friendly utilization not only reduces dependence on fossil resources but also protects the environment. Recently, a class of novel eco-friendly solvents, ionic liquids, is employed to dissolve and process these bioresources. In this mini-review, we summarized the recent advances of processing and valorization of cellulose, lignin and lignocellulose in ionic liquids. It is expected that this up-to-date survey provides a comprehensive information of this field, and accelerates the development and utilization of the renewable plant biomass resources.

1. Introduction

Cellulose, lignin and lignocellulose, the most abundant biomass resources, mainly originate from the natural plants. They are abundantly available, renewable, tremendous, completely biodegradable and excellently biocompatible. Thus, the effective and environmentally friendly utilization of cellulose, lignin and lignocellulose not only reduces dependence on fossil resources but also protects our environment. However, owing to the strong hydrogen-bonding interactions and bio-recalcitrance, natural lignocellulose materials exhibit the poor solubility and processability, which seriously limit their efficient and practical utilization. Recently, the novel eco-friendly ionic liquids (ILs) are found to be able to effectively dissolve cellulose, lignin and lignocellulose, providing an available, versatile and fascinating platform for processing these renewable plant biomass resources. The ILs have excellent dissolving capacities, structure and property tunability, high thermal stability, good chemical inertness, high polarity, negligible vapor pressure, easy recyclability and non-flammability. Hence, the ILs are promising for widespread applications in the regeneration and modification of plant biomass. By using the ILs as the solvents, dispersant or additive, a series of cellulosic, lignin-based and lignocellulosic materials have been fabricated, including films, fibers, beads, gels, composites, derivatives and high-value chemicals. This mini-review will highlight the recent advances of various materials fabricated from cellulose, lignin and lignocellulose with ionic liquids.

2. Cellulose-Based Materials

As the most abundant natural polymer on the earth, cellulose is inexhaustible, available, completely biodegradable and excellently biocompatible, and hence is considered as one of fascinating and renewable raw materials to achieve the sustainability of human...
society. Since an initial success of dissolving cellulose by some ILs in 2002, various cellulose-based materials, including fibers, films, spheres, hydrogels, aerogels, ionic gels, composites and derivatives have been successfully and efficiently fabricated by using ILs as the direct solvents and dissolution-regeneration process (Sen et al., 2013; Zhang et al., 2015; Wang et al., 2017; Zhang et al., 2017a; Kostag et al., 2019). In the last decade, via modulating the micro-morphology and composition of the regenerated cellulose-based materials, a series of high-performance materials were prepared from cellulose.

2.1. Cellulose fibers

Generally, the regenerated cellulose fibers are spun from cellulose/ILs solutions by a dry-jet wet spinning process, including dissolving, filtration, extrusion, drawing, coagulation, washing, drying and winding. The spinning process of cellulose has been examined systematically and comprehensively. Spinning process parameters, such as the structure and properties of ILs, solvent composition, molecular weight and polydispersity index of cellulose, concentration of the spinning dope and drawing ratio in the air gap, have a significant impact on the mechanical properties of cellulose fibers.

Zhang et al. (2017c; 2020) used 1-butyl-3-methylimidazolium chloride (BmimCl) to dissolve a dissolving pulp, and subsequently prepared regenerated cellulose fibers (Figs. 1a–1c). It indicated that an appropriate viscosity was in a range of

![Fig. 1](image-url)

Fig. 1  a: Illustrations of the dry-jet wet spinning system (Zhang et al., 2017c); b: Empirical dependencies of tensile strength (black closed symbols) and maximum winding speed (blue open symbols) on the zero-shear viscosity ($\eta_0$) of the spinning dopes (Zhang et al., 2020); c: Wide-angle X-ray diffraction (WAXD) photograph of regenerated cellulose fibers coagulated at 5 ℃ (Zhang et al., 2017c); d: Illustrations of the wet type solution blow-spinning apparatus (Zhang et al., 2019a); e: Illustration and photograph of solution blowing procedure (Jedvert et al., 2020); f: Scanning electron microscope (SEM) image of cellulose non-woven fabric (Zhang et al., 2019a); g: Schematic diagram of the spinning process of cellulose hollow fibers (Lei et al., 2019); h: SEM image of cellulose hollow fibers (Lei et al., 2018); i: Photograph of carbonized cellulose hollow fibers (Lei et al., 2019); j: Separation performances of CO$_2$/CH$_4$ on carbonized cellulose

2008 reboson upper bound

CMS from cellulose precursor, literature data

CMS from cellulose precursor, literature data

CMS from cellulose precursor, this work

2008 reboson upper bound

CMS from cellulose precursor, literature data

CMS from cellulose precursor, literature data

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CO$_2$ permeability (Barrer)
hollow fiber membranes (CHFMs) (Lei et al., 2019); k: Separation performances of O\textsubscript{2}/N\textsubscript{2} on CHFMs (Lei et al., 2019) 2000–4000 Pa/s (100 °C) for spinning dopes to obtain good spinnability and high tensile strength. Via optimizing the degree of polymerization (DP) and concentration of the cellulose, high-performance cellulose fibers with a tensile strength of 1.15 GPa and a Young’s modulus of 42.9 GPa have been fabricated. Zhu et al. (2016; 2018a) employed the low molecular-weight micro-crystalline cellulose (MCC) as the raw material to prepare stiff regenerated cellulose fibers using a dry-jet wet spinning process. They prepared the high concentrated cellulose/1-ethyl-3-methylimidazolium diethyl phosphate (EmimDEP) and cellulose/EmimDEP/dimethylsulfoxide (DMSO) solutions with anisotropic patterns to improve the alignment of cellulose chains. Meanwhile, a high extrusion/winding ratio was chosen to further improve the alignment of cellulose chains. As a result, the obtained highly aligned cellulose fibers possessed high mechanical properties. The highest tensile strength achieved was 555.9 Mpa, the Young’s modulus was 41.2 GPa, and the specific modulus achieved 27.5 GPa/(cm\textsuperscript{2}-g\textsuperscript{-1}) which was similar to E-glass fibers (27.6 GPa/(cm\textsuperscript{2}-g\textsuperscript{-1})).

A Ioncell-F process was developed to dissolve and spin cellulose by utilizing a superbase derived ILs, 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]Ac) (Hauru et al., 2014; Michud et al., 2015; Hauru et al., 2016; Nanasekara et al., 2016; Kuzmina et al., 2017; Asaadi et al., 2018). The effects of cellulose samples, solution properties, draw ratio, extrusion velocity, spin bath temperature and spinneret aspect ratio on the mechanical properties of the regenerated cellulose fibers were explored in detail. Ioncell-F fibers exhibited good mechanical properties and high orientation of cellulose chains at high draw ratios. High molecular-weight cellulose chains combined with a low share of short-chain fraction (DP < 100) were favorable when aiming at high strength cellulose fibers. Via the Ioncell-F process, waste paper and unrefined cardboard were fabricated into high-strength cellulose composite fibers (Ma et al., 2015; Ma et al., 2016; Ma et al., 2018a; Ma et al., 2018b; Haslinger et al., 2019).

Combining the melt-blowing technique with twin-screw extruder, Song et al. (2014) fabricated cellulose nonwoven fabric with a high quality as a change of cellulose concentration, extrusion temperature and air pressure. When the cellulose concentration was below 15 wt%, more uniform nonwoven fabrics were obtained. The fiber diameter decreased as the extrusion temperature and air pressure increased. For example, when the extrusion temperature increased from 130 °C to 160 °C, the fiber diameter of the samples at 10 wt% cellulose solution decreased from 25 μm to 8 μm. Zhang et al. (2019a) employed a wet type solution blow spinning system with a water-mist coagulation chamber to fabricate cellulose non-woven fabric with an average diameter of (0.98 ± 0.62) μm (Figs. 1d and 1f). Jedvert et al. (2020) claimed that the high temperature or low flow rate resulted in thinner regenerated cellulose fibers (Fig. 1e).

Ma et al. (2013) and Lei et al. (2018) selected DMSO as co-solvent to adjust the viscosity of the cellulose/ILs solutions. Meanwhile, they used the non-solvent of cellulose as the bore liquid (Fig. 1g). Via a dry-wet spinning method, the cellulose hollow fibers have been obtained (Fig. 1h), and presented a great potential in separation and purification. Subsequently, the cellulose membranes consisting of these hollow fibers were fabricated by treating with glycerol aqueous solutions and drying at room temperature (Lei et al., 2019). After a carbonizing process, novel carbonized cellulose hollow fiber membranes (CHFMs) were obtained, and exhibited superior gas separation capabilities, which were above the Robeson upper bounds of CO\textsubscript{2}/CH\textsubscript{4} and O\textsubscript{2}/N\textsubscript{2}. The CHFMs showed a high CO\textsubscript{2} permeability of 239 barrer and a high CO\textsubscript{2}/CH\textsubscript{4} selectivity of 186 (Figs. 1i–1k).

The addition of nano-fillers has a significant impact on the properties of cellulose fibers. Luo et al. (2014) claimed that the addition of halloysite nanotubes (HNTs) into cellulose/1-allyl-3-methylimidazolium chloride (AminCl) solutions was beneficial to forming liquid crystalline phase (Figs. 2a–2f). Subsequently, via a liquid crystalline spinning method, high-performance cellulose/HNTs composite fibers with improved thermal stability, tensile strength and moisture barrier were successfully prepared. Zheng et al. (2014) fabricated cellulose nanofibers coated with Mg(OH)\textsubscript{2} nanoparticles by a dry-jet wet electrospinning process (Figs. 2g–2j). Cellulose nanofibers are wet electrospun from cellulose/1-ethyl-3-methylimidazolium acetate (EmimAc) into an aqueous suspension of Mg(OH)\textsubscript{2} nanoparticles to obtain flame-retardant cellulose@Mg(OH)\textsubscript{2} nanofibers. The placing of the nanoparticles exclusively on the surface of the cellulose fibers dramatically impacts the functionality of the fibers. In addition, montmorillonite (MMT), carbon black, graphene nanoplatelets and multiwalled carbon nanotubes (MWCNTs) have also been compounded with cellulose to improve the thermal stability, tensile strength and conductivity (Härdelin and Hagström, 2015; Mahmoudian et al., 2015; Liu et al., 2019).

### 2.2. Cellulose aerogels and ionogels

After dissolving cellulose in the ILs and regenerating with water or alcohol, cellulose hydrogels or alcogels can be obtained. Then, via freeze-drying or supercritical CO\textsubscript{2} drying method, cellulose aerogels were fabricated (Buchtová et al., 2019). Aerogels are a family of ultra-lightweight solid materials with a 3D network skeleton. Owing to the highly interconnected porous structure, they have many attractive advantages, such as large specific surface area, high porosity, and low thermal conductivity. By the selection of the appropriate conditions for dissolution, regeneration and drying processes, the porous structure of the regenerated cellulose aerogels can be conveniently controlled. Mi et al. (2016) and Wan et al. (2017) reported a facile and effective method to...
prepare flexible and transparent cellulose aerogels (Fig. 3a), which overcame unfavorable brittleness and opacity of common aerogels simultaneously. By controlling the composition and temperature of the regeneration bath, the obtained cellulose aerogels possessed uniform nanoporous structures, high porosity and small pore size, they thereby displayed high transparency, remarkable bending deformability, low densities of the order of 0.01 g/cm$^3$ and low thermal conductivity at 0.033 W/(m·K). Subsequently, the micro-morphology and physical properties of cellulose aerogels were further regulated by changing the initial concentration of the cellulose solution. The obtained cellulose aerogels could quickly absorb liquid electrolytes to form gel polymer electrolytes, due to the presence of high porosity, nanoporous network structure and numerous polar hydroxyl groups. Lithium-ion batteries assembled with the gel polymer electrolytes composed of cellulose aerogels exhibit excellent electrochemical stability and battery performance. More importantly, the thermally stable cellulose aerogels endow the cells with a superior thermal resistance. The cells run well even at a high temperature of 120 °C. Consequently, the cellulose aerogels have promising applications in the development of highly safe, cost-effective and high-performance lithium-ion batteries (Wan et al., 2017). Plappert et al. (2018) found specific diffusion and phase separation phenomena occurring during decelerated infusion of an antisolvent into isotropic supercooled cellulose/ILs solutions. Based on a slow coagulation process, cellulose aerogels with onion-like structure were fabricated (Fig. 3b). Zhao et al. (2017) prepared flexible and transparent mesoporous cellulose membrane (mCel-membrane) featuring uniform mesopores of ≈ 24.7 nm and high porosity of 71.78%. Then, KOH-saturated mCel-membrane is used as a polymer electrolyte to fabricate solid-state electric double layer capacitor and highly integrated planar-type micro-supercapacitor (Fig. 3c).

Fig. 2  a–d: Polarized optical micrographs of 9 wt% MCC/AmimCl/HNTs solutions with 0.63 wt% HNTs (a, before shear; b, under shear at a shear rate of 5 s$^{-1}$; c, after shear for 30 min; d, after shear for 4 h. The white scale bar represents 200 μm and is applicable to all the micrographs) (Luo et al., 2014); e: Moisture absorption curves of regenerated MCC/HNTs composite fibers with different contents of HNTs (Luo et al., 2014); f: Schematic indicating the moisture barrier function of HNTs (the dark blue circles depict water molecules) (Luo et al., 2014); g: Schematic of the electrospinning route for preparing cellulose@Mg(OH)$_2$ nanofibers (Zheng et al., 2014); h: Schematic of the
distribution of Mg(OH)₂ nanoparticles on the cross-section of cellulose@Mg(OH)₂ nanofibers (Zheng et al., 2014); i: SEM image of cellulose@Mg(OH)₂ nanofibers (Zheng et al., 2014); j: Flame test of cellulose@Mg(OH)₂ nanofiber composite (Zheng et al., 2014)

In addition, silica and aluminum hydroxide nanoparticles were introduced into cellulose gels via an in-situ two-step impregnation-gelation process (Figs. 3d–3h). Then, after a supercritical CO₂ drying process, transparent and flame-retardant cellulose-based nanocomposite aerogels were readily prepared (Tsioptsias et al., 2008; Demilecamps et al., 2015; Yuan et al., 2016; Yuan et al., 2017). The silica and aluminum hydroxide nanoparticles homogeneously distribute within the matrix without any aggregation behavior. The nanoparticles do not affect the homogeneous nanoporous structure and morphology of regenerated cellulose aerogels, while they significantly improve the mechanical performance and flame retardancy of cellulose aerogels, which achieves self-extinguishment after ignition.

Recently, Scott et al. (2011) synthesized zwitterionic 1,3-dialkylimidazolium-2-carboxylates ILs, which served as by-productless foaming or blowing agents for cellulose dissolved in ILs. Upon contacting with dilute aqueous acid solutions, 1,3-dialkylimidazolium-2-carboxylates release CO₂ gas to foam cellulose. The foamed cellulose products are lightweight open cell materials, which can include added fillers to increase strength and rigidity or to endow the cellulose foam with new characteristics.

Owing to the strong interactions between hydroxyl groups in cellulose and ILs, cellulose/ILs ionogels were fabricated and used in electronic devices. Thiemann et al. (2014) prepared a new class of ionogels based on cellulose and various methylphosphonate-based ILs. The cellulose ionogels exhibit many advantages, including transparency, flexibility, transferability, and high specific capacitances of 5–15 μF/cm². Thus, they act as high capacitance dielectrics for inorganic (spray-coated ZnO and colloidal ZnO nanorods) and organic (poly[3-hexylthiophene], P3HT) electrolyte-gated field-effect transistors (FETs), which is operated at very low voltages (∼2 V) (Figs. 4a–4d). Khammirzaei et al. (2015) used hydroxypropyl cellulose (HPC) and 1-methyl-3-propylimidazolium iodide (MpipI) to prepare non-volatile gel polymer electrolyte for dye-sensitized solar cell. After introducing 100% of MpipI with respect to the weight of the HPC, the highest ionic conductivity of 7.37 × 10⁻³ S/cm was achieved, and the best energy conversion efficiency of the solar cell was 5.79% with short-circuit current density, open-circuit voltage and...
fill factor of 13.73 mA/cm², 610 mV and 69.1%, respectively. Zhao et al. (2020) constructed cellulose/BmimCl/H₂O ionogels by a hydrogen-bond topological network-regulation strategy. The prepared ionogels exhibited good stretchability, robust toughness, high ionic conductivity and self-healing ability, thus they were used as electronic skins and intelligent devices (Figs. 4e–4g).

Fig. 4  a: Chemical structures of methylphosphonate-based ILs and cellulose (Thiemann et al., 2014); b: Schematic of ZnO-FETs (Thiemann et al., 2014); c: Schematic of P3HT-FETs (Thiemann et al., 2014); d: Schematic of ZnO nanorod FETs (Thiemann et al., 2014); e: Schematic of cellulose/BmimCl/H₂O ionogels as e-skin device (Zhao et al., 2020); f: Current waveforms measured for e-skin during sensing of air flow (Zhao et al., 2020); g: Current waveforms measured for e-skin during sensing of touching (Zhao et al., 2020)

2.3. Cellulose composite materials

As a novel class of organic molten salts, the ILs have many favorable advantages, such as excellent solvating capacities, structure and property tunability, high thermal and chemical stabilities, negligible vapor pressure, easy recyclability and non-flammability, they thus show promise for widespread applications in fabricating cellulose composite materials and functional cellulose materials by using the ILs as the solvent, dispersant or additive.

Based on the phenomenon that BmimCl can well disperse graphite powder (GP) flakes, Chen et al. (2015a) fabricated the cellulose/GP/polyaniline (PAni) films by regenerating cellulose/GP films then in-situ chemical polymerization of PAni nanoparticles on the film surface (Figs. 5a–5c). The obtained cellulose/GP/PAni films exhibited high thermal stability, good electrical conductivity and excellent electromagnetic interference shielding effectiveness, so they were considered as a potential candidate for the lightweight electromagnetic interference shielding materials in electronics, radar evasion and aerospace. Liu et al. (2012) fabricated magnetic Fe₃O₄/cellulose/chitosan hydrogel microspheres by a coprecipitation process (Figs. 5d and 5e). The resultant hydrogel microspheres exhibited high adsorption capacities for different heavy metal ions (Cu²⁺, Fe²⁺ and Pb²⁺), moreover they could be efficiently recycled and reused. Peng et al. (2014a; 2014b) prepared multi-functional magnetic Fe₃O₄/cellulose/chitosan composite microspheres (Fig. 5f) by a combination of the emulsification procedure and cellulose/chitosan regeneration from BmimCl. Subsequently, enzymes were then immobilized in the composite microspheres by glutaraldehyde to achieve easy recycling and enhance their stability and catalytic activity. In addition, the Fe₃O₄/cellulose/chitosan microspheres exhibit efficient adsorption capacity of Cu²⁺ from aqueous solution. The maximum adsorption capacity for Cu²⁺ reaches 65.8 mg/g when the initial concentration of Cu²⁺ is 150 mg/L within 20 h. Additionally, the common coexisting ions almost have no
negative effect on the Cu$^{2+}$ adsorption. Moreover, the Fe$_3$O$_4$/cellulose/chitosan microspheres are easily regenerated with HCl and reused repeatedly for Cu$^{2+}$ adsorption. Thus, the hybrid microspheres are expected to be promising candidates for enzyme immobilization and heavy metal ions removal.

The ILs are also the efficient solvents of natural and synthetic materials, including silk, lignin, starch, chitin, chitosan, feather, wool, curcumin, polycaprolactone (PCL), polyurethane (PU), PPy, polycrylonitrile (PAN) and polyvinyl alcohol (PVA), thus various cellulose-based blends were obtained by a dissolution-regeneration process without any chemical modifications (Zhou et al., 2013; Lorenzo et al., 2016; Tran et al., 2016; Abou-Saleh et al., 2018; Hadadi et al., 2018; Becherini et al., 2019; Berton et al., 2019; Villar-Chavero et al., 2019). For example, Singh et al. (2013) found that the scaffold prepared from cellulose/silk blends could direct stem cell chondrogenic fate. Growing mesenchymal stem cell on a specific blend combination of cellulose and silk in a ratio of 75:25 significantly upregulated the chondrogenic marker genes SOX9, aggrecan, and type II collagen in the absence of specific growth factors. Duri and Tran (2013) fabricated the cellulose/chitosan/cyclodextrin composites containing α-, β-, and γ-cyclodextrin, respectively. The cellulose/chitosan/cyclodextrin composites can effectively adsorb pollutants such as endocrine disruptors (e.g., chlorophenols and bisphenol A). They also found that the cellulose/chitosan composite with a ratio of 50:50 exhibited remarkable enantiomeric selectivity toward the adsorption of amino acids (Duri and Tran, 2014). Luo et al. (2012) introduced water-insoluble curcumin into cellulose/AmimCl solution. Then, after a solution-mixing and casting process, anti-bacterial and transparent cellulose/curcumin films were obtained, and had a huge potential in food packaging and medical fields since the raw materials were entirely from natural resources.

Via controlling the dissolution process of cellulose in the ILs or adding cellulose crystals as the reinforcing phase, all-cellulose composites with the single cellulose components were fabricated (Huber et al., 2012; Mashkour et al., 2014; Zhang et al., 2016). The as-prepared all-cellulose composites display superior mechanical, optical and barrier properties compared with those of common cellulose-based materials. More importantly, they are featured by the good interfacial compatibility, biocompatibility
and biodegradability because of the same cellulosic composition of the matrix and reinforcing phase. Therefore, they are becoming the most promising all-biomass materials, which have a great potential in structural and packaging materials, photoelectric devices, filtration materials and biomedical engineering.

Taking advantage of the excellent hydrogen-bonding capability of the ILs to break hydrogen-bonding and crystal structure of cellulose, Wu et al. (2015) and Utomo et al. (2020) demonstrated that BmimCl was better than water to improve the mobility of cellulose chains. Thus, the BmimCl was used to plasticize cellulose by direct thermal processing. The obtained cellulose/BmimCl composite materials with 25 wt%–70 wt% BmimCl showed only one glass transition terrace and could be processed repeatedly. Moreover, the nonvolatility and high stability of BmimCl broadened the processing temperature window, which was helpful to the thermal processability of cellulose. Haq et al. (2019) regenerated cellulose from cellulose/BmimCl solution in a small amount of H₂O to get cellulose/BmimCl/H₂O iongels. Then, during drying process, water was removed while BmimCl was retained. The retained BmimCl not only acted as a plasticizer of cellulose, but also significantly influenced the arrangement of the cellulose chains during drying of the iongels. Therefore, the retained BmimCl with an enough content in the cellulose/BmimCl induced the flexibility and thermoplasticity of cellulose/BmimCl composite films.

Based on the design flexibility of the ILs, Byrne et al. (2014) designed and synthesized various ILs containing phosphate or sulfate anions. The protic or aprotic ILs containing phosphate anions were used as effective impregnating compounds, which resulted in a 50% improvement of the carbon yield and a 70 °C reduction in the onset of the depolymerization temperature, during carbonization of cellulose.

2.4. Cellulose derivatives

Cellulose has many regularly distributed hydroxyl and hence, possesses an outstanding chemical modification capability. As new kinds of aprotic polar solvents, the ILs are thermally stable, chemically inert, and highly polar; as a result, they are ideal media for the homogeneous modification of cellulose. In the past two decades, almost all conventional cellulose derivatives were controllably and precisely synthesized by the homogeneous reactions in the ILs. Recently, after a modularization modification process, many novel and functional groups were introduced onto cellulose chains, which endowed cellulose materials with various new properties, including excellent solubility and processability, melt processing capability, optical performance, stimuli responsiveness, flame-retardant capability, super-hydrophobicity, adsorption and separation capabilities.

A series of cellulose esters bearing different substituents, degree of substitution (DS), and substituent distribution were homogeneously synthesized in AminimCl to understand the chiral recognition mechanism (Fig. 6a) (Chen et al., 2015c; Chen et al., 2015b; Chang et al., 2018; Yin et al., 2019a; Yin et al., 2019b). Then, novel high-performance cellulose-based chiral stationary phases were constructed. Xiao et al. (2014) and Chen et al. (2018) reported that introducing ester substituents containing both bulky moieties and soft segments could significantly improve the mobility of the cellulose chain. The obtained thermoplastic cellulose esters as bioplastics can be processed into transparent disks, dumbbells, fibers and flexible films by traditional injection molding, melt extrusion, and hot pressing without any external plasticizers (Fig. 6b).

Due to the aggregation caused by quenching (ACQ) behavior, the fluorescent emitting property of the conventional lumino gens in the solid state generally quenches. Tian et al. (2016) found that solid fluorescent materials from the conventional lumino gens realized via covalently bonding the ACQ luminogens onto the cellulose chains and subsequently ionizing process. The synergy of the anchoring and diluting effect of cellulose skeleton and the electrostatic repulsion effect of the ACQ luminogens efficiently inhibits the ACQ behavior of luminogens. Based on this strategy, a series of solid and responsive fluorescent materials were fabricated (Nawaz et al., 2018; Tian et al., 2018; Nawaz et al., 2019; Nawaz et al., 2020).

Cellulose-based ratiometric fluorescent materials with superior amine-response were designed and prepared via utilizing the reactive hydroxyl groups along cellulose chains (Jia et al., 2019a). The as-prepared materials were readily processed into different material forms, including printing ink, coating, flexible film, and nanofibrous membrane. The electrospun nanofibrous membrane has been successfully employed as a low-cost, high-contrast, quick-responsive fluorescent trademark for visual monitoring the freshness of shrimp and crab (Fig. 6c). In addition, by introducing protoporphyrin IX groups onto the cellulose backbone, Jia et al. (2019b) fabricated a sunlight-driven wearable and robust antibacterial coating to protect humans from the threats of drug-resistant bacteria (Fig. 6d).

Yang et al. (2014) designed a switchable ionic liquid, [DBUH][O₂COCH₃], consisting of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), methanol and CO₂. The [DBUH][O₂COCH₃] mixing with DMSO is a new solvent capable of dissolving up to 8 wt% of cellulose. The as-prepared cellulose solution could be used to homogeneously synthesize various cellulose esters, such as cellulose acetate, cellulose propionate and cellulose butyrate (Fig. 6e). Subsequently, they found that, in DMSO, the reversible
reaction of cellulose pulp with CO\textsubscript{2} and DBU formed rapid and effective derivative solutions of cellulose (Fig. 6f). In the obtained cellulose solution, the subsequent homogeneous derivatization of cellulose was successfully achieved to get a series of cellulose esters, including cellulose acetate, cellulose methyl carbonate and cellulose levulinate (Yang et al., 2015; Du et al., 2018; Onwukamike et al., 2018; Pei et al., 2020).

Liu et al. (2016) synthesized cellulose acetoacetate in AmimCl and then, via a Schiff base reaction, self-healing polysaccharide hydrogels with redox/pH dual responsive behavior were fabricated (Liu et al., 2017a; Liu et al., 2017b; Liu et al., 2018). Granström et al. (2011) synthesized cellulose stearoyl esters to fabricate highly water repellent aerogels in AmimCl. Cellulose stearoyl esters with low DS enable the spontaneous formation of aerogels, in which the long stearoyl tails combined with the porous aerogel structure results in a significant increase in hydrophobicity from an aqueous contact angle of 0°–124°. Vo et al. (2012) synthesized a water-soluble ionic cellulose by means of the dissolution of cellulose in dimethylimidazolium methylphosphite at elevated temperatures over 120 °C. The water-soluble phosphorylated cellulose consists of a dialkylimidazolium cation and a phosphite anion bonded to cellulose.

3. Lignin-Based Materials

Lignin, a kind of renewable aromatic biopolymer, is the second most abundant biomass resource in the nature (Zakzeski et al., 2010; Zhu et al., 2019). It is an extremely complex, amorphous, three-dimensional, cross-linked heteropolymer consisting of three main phenylpropane units, guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H), at different proportions depending on biological factors and separation processes (Fig. 7a). These three units are connected to each other mainly via carbon-carbon linkages such as β-1, β-5, β-β, 5-5, and aryl ether linkages including β-O-4, α-O-4, 4-O-5 and dibenzodioxocin. Among them, the
β-O-4 bond, which accounts for 45%–50% of the whole linkages, is the predominant linkage type. In paper-making industry, lignin is discharged as a waste in the sewage, which could cause serious environmental pollution. Only few (1%–2%) of 50–70 million tons of lignin produced by papermaking industries could be utilized each year (Sanderson, 2011; Ragauskas et al., 2014). How to prepare high-valued materials from lignin sources is thus of great significance to fully utilize this natural biopolymer and minimize the contamination.

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Fig. 7  a: Representative structures of lignin and its monolignol units (Zhu et al., 2019) (b) Solubility of softwood kraft pulp lignin in ILs (Pu et al., 2007); c: Separation protocol of the lignocellulose using N-methyl-N-(2-methoxyethyl)-pyrollidin-1-ium 2,6-diaminohexanoate as an extracting agent (Hamada et al., 2013)

3.1. Dissolution of lignin in ILs

Inspired by the effectiveness of the ILs as the powerful solvents of cellulose by breaking the hydrogen-bondings, many researchers tried to dissolve lignin by the ILs. Pu et al. (2007) used a series of the ILs to dissolve softwood kraft pulp lignin, and found that 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([Hmim][CF₃SO₃]), 1-butyl-3-dimethylimidazolium methylsulfate ([Bmim][MeSO₄]) and 1,3-dimethylimidazolium methylsulfate ([Mmim][MeSO₄]) dissolved up to 20 wt% of
lignin (Fig. 7b). Tan et al. (2009) reported an ionic liquid mixture containing the 1-ethyl-3-methylimidazolium cation and a mixture of alkylbenzenesulfonates with xylenesulfonate was the main anion to extract lignin from bagasse at 170–190 °C. The extraction yield of lignin exceeding 93% was attained. Pinkert et al. (2011) studied the ILs with acsesulfamate ([Ace]) anion to extract lignin from wood without dissolving and degrading cellulose. The extracted lignin showed a larger average molar mass and a more uniform molar mass distribution, compared to the Kraft lignin. Rashid et al. (2016) investigated three kinds of protic ILs, and found that pyridinium formiate was the best ILs which could dissolve more than 70 wt% Kraft lignin at a relatively low temperature of 75 °C. Except imidazolium and pyridinium ILs, phosphonium, pyrrolidinium and ammonium ILs could also dissolve lignin (Fig. 7c) (Keskar et al., 2012; Hamada et al., 2013; Xu et al., 2017; Nagatani et al., 2019). Zhang et al. (2019b) reported that a 35 wt% enzymatic lignin solubility was achieved at 90 °C in ethanolamine acetate. Akiba et al. (2017) found that adding a small amount of water enhanced lignin solubility in many polar ILs. The mechanism of the ILs dissolving lignin is not completely understood. It is generally considered that the hydrogen-bonding basicity of the anions, the hydrogen-bonding acidity of the cations, the π-π interactions and hydrophobic interactions promote the dissolution of lignin in the ILs (King et al., 2009; Hart et al., 2015; Akiba et al., 2017; Zhu et al., 2018b; Chu and He, 2019).

### 3.2. Depolymerization of lignin in ILs

Because of the high carbon content and aromaticity of lignin, researchers depolymerized lignin to fabricate some high-value platform chemicals, such as phenol, benzaldehyde, benzoic acid (Prado et al., 2016a; Zhang et al., 2017d). The traditional methods of lignin depolymerization include pyrolysis, hydrolysis, hydrogenolysis. In the ILs, the conversion of lignin is relatively mild. The strategies of lignin depolymerization in the ILs are mainly divided into four types, acid depolymerization, base depolymerization, hydrosolubilization depolymerization and oxidation depolymerization.

The dominant linkage, β-O-4 bond, in lignin is easily broken by acid, since β-O-4 ether bond is the weakest linkage in lignin. Jia et al. (2011) reported that the model compounds of lignin could be depolymerized by Lewis acid/H2O/BmimCl. All the β-O-4 bonds in guaiacylglycerol-β-guaiacyl ether (GG) were broken, and the guaiacol yield was about 69%–80% at 150 °C for 2 h. Only about 75% of the β-O-4 bonds in veratrylglycerol-β-guaiacyl ether (VG) reacted with water to liberate guaiacol in AlCl3/H2O/BmimCl system at 150 °C for 4 h. This phenomenon is because the phenolic hydroxide group serves as an additional proton donor and interacts with metal chlorides to generate more hydrochloric acid. Therefore, the GG is more easily hydrolyzed. Except Lewis acid system, Brønsted acid system can also depolymerize lignin. The 1-H-3-methylimidazolium chloride was proved to effectively cleave the β-O-4 linkage (Jia et al., 2010a). More than 70% of the β-O-4 bonds of both the GG and the VG reacted with water to produce guaiacol at 150 °C. Moreover, the ionic liquid solvent/catalyst could be reused without extra treatment and appreciable loss of activity.

Due to the instability of most imidazolium-based ILs under basic condition, the reports about the base-catalyzed depolymerization of lignin in imidazolium-based ILs are meager. Jia et al. (2010b) reported a series of organic bases which could be used as the catalyst to cleave the β-O-4 bonds of the GG in 1-butyl-2,3-dimethylimidazolium chloride. Among all the tested organic bases, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is the most active, leading to more than 40% cleavage of β-O-4 ether bonds. The higher activity of the TBD is probably associated with the exposed nature of the nitrogen atoms.

A two-step conversion strategy, which consists of depolymerization and hydrodeoxygenation, can remove oxygen and produce basic chemicals from lignin. Chen et al. (2016) developed a pseudo-homogeneous catalytic system, consisting of uniformly stabilized noble metal nanoparticles in the ILs, for the selective reductive cleavage of C-O and hydrodeoxygenation. Metal nanoparticles including Pd, Pt, Rh and Ru were synthesized in situ and well distributed in the ILs without aggregation. These catalytic systems displayed almost 100% conversion for various monomeric and dimeric lignin model compounds at 130 °C, and were recycled several times without loss of activity. The Pt nanoparticles in 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF6) are identified as the best catalytic system for the transformation of lignin monomeric and dimeric model compounds with an almost 100% conversion and maximum 97% selectivity.

Oxidation depolymerization is another strategy for lignin depolymerization. Prado et al. (2016b) proposed a method for oxidation depolymerization of lignin extracted from willow trees by using triethylammonium hydrogen sulfate as solvent. Lignin was successfully depolymerized under oxidizing conditions either with H2O2 or TiO2/H2O2 treatments. Oxidation of lignin with H2O2 alone leads to an oil rich in sugar derived acids, whereas oxidation of lignin with TiO2 catalysis leads to an oil rich in phenolic derived fragments. Covalent triazine frameworks (CTFs) were proved to be effective in the oxidative cleavage of both the C-C bond and C-O bond in the lignin model compounds and organosolv lignin (Zhao et al., 2018). When the CTFs were applied during the depolymerization of organosolv lignin, nearly 80% of β-O-4 bonds in lignin were converted, producing phenol, benzoic acid, methyl benzoate and methyl benzoyleformate as the major products.
Apart from the above four types of lignin depolymerization methods, there are some new approaches like polyoxometalate-based catalytic system and microwave-assisted method for biomass delignification and lignin depolymerization in ILs (Brandt et al., 2013; Cheng et al., 2014; de Gregorio et al., 2016; Zhao et al., 2018). Cheng et al. (2014) discovered that the southern yellow pine could be completely dissolved with over 90% delignification in EmimAc at 110 °C for 6 h by the catalytic action of polyoxometalate ($\text{H}_5\text{[PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot29\text{H}_2\text{O}$) in the presence of an appropriate $\text{O}_2$ feed. Cellulose, hemicellulose and lignin could be separated by this method, meanwhile lignin could be oxidized into methyl vanillate, acetovanillone, vanillic acid, methyl 3-(3-methoxy-4-hydroxyphenyl) propionate, and methyl 4-hydroxybenzoate. Sun et al. (2019) extracted meanwhile depolymerized lignin by ILs-based microwave-assisted strategy. The lignin depolymerization occurred at different modes during the ILs pretreatment under different microwave irradiation conditions.

### 3.3. Lignin-based materials fabricated in ILs

Owing to numerous phenolic groups and high molecular weight, lignin can be processed as natural wood adhesives (Li et al., 2018), pressure sensitive adhesive (Wang et al., 2018), UV-resistant sunscreen (Qian et al., 2015), thermoplastic elastomers (Zhang et al., 2019c) and so on. When the ILs are employed as the solvent and additive, the lignin has been converted into a series of high value-added materials.

Salanti et al. (2016) synthesized epoxidized and carbonated lignin. Two kinds of commercial lignin were modified by a direct insertion reaction between phenolic groups and epichlorohydrin. The resultant epoxide groups were then converted to cyclic carbonates via a coupling reaction of CO$_2$ with the oxirane rings. Imidazolium based ILs, acting as both solvents and catalysts, were successfully employed in the carbonation reaction. Via a crosslinking reaction between lignin extracted by the ILs and epoxide-terminated PEG (ETPEG) in alkaline solution, Shen et al. (2016) fabricated lignin/ETPEG hydrogels with high water absorbency, antioxidant capacity and antimicrobial activity (Fig. 8a).

Fig. 8  a: Preparation procedure and photographs of lignin/PEG gels by different crosslinking routes (Shen et al., 2016); b: Preparation procedure and photographs of lignin/chitin films from BmimAc-GVL solution (Duan et al., 2018); c: Illustrations and photograph of choline citrate/gelatin/lignin UV-shielding film. (Mehta and Kumar, 2019); d: Illustrations and photographs of IL-lignin/cellulose/gluten composites (Guterman et al., 2019)

Except chemical modification, lignin can be blended with other polymers to fabricate composite films, beads, fibers and bulk materials. Duan et al. (2018) used the mixture of 1-butyl-3-methylimidazolium acetate (BmimAc) and $\gamma$-valerolactone (GVL) as
the solvent of both lignin and chitin (Fig. 8b). Then, the lignin/chitin composite films were prepared for absorbing Fe\(^{3+}\) and Cu\(^{2+}\) ions uptake from aqueous solutions. The maximum adsorption capacity for Fe\(^{3+}\) was 84 wt% and for Cu\(^{2+}\) was 22 wt% within 48 h. The lignin/chitin films could be regenerated by desorption of the Fe\(^{3+}\) and Cu\(^{2+}\) ions. Mehta and Kumar (2019) constructed choline citrate/gelatin/lignin UV-shielding films with excellent antimicrobial and mechanical properties (Fig. 8c). The prepared choline citrate/gelatin/lignin films showed a sun-protection factor of up to 45.0, large elongation of 200%, and tensile strength of 70 MPa. Shen et al. (2019) fabricated cellulose/lignin beads by using IL-extracted cellulose-rich materials as the raw materials. Because of the porous structure and high hydroxyl numbers, the obtained cellulose/lignin beads have a high adsorption capacity for heavy metal ions, with maximum adsorption capacities of 0.144 mmol/g and 0.161 mmol/g for Cu\(^{2+}\) and Pb\(^{2+}\), respectively.

Ma et al. (2015) dissolved Eucalyptus dissolving pulp and kraft lignin in 1,5-diazabicyclo[4.3.0]non-5-енииum acetate with different ratios to prepare cellulose/lignin fibers by dry-jet wet spinning process. Vincent et al. (2018) extracted lignin from willow by using triethylammonium hydroxide sulfate. Then, the cellulose/lignin fibers were prepared in EmimAc as the precursor for the manufacture of carbon fibers. Guterman et al. (2019) fabricated an ionic liquid lignin (IL-lignin) with a low glass transition temperature of –13 °C by a cation exchange reaction between sodium lignosulfonate and diethylene glycol functional cation. Subsequently, IL-lignin/cellulose/gluten composite materials were produced by a hot-pressing process (Fig. 8d).

4. All-Lignocellulose Materials

In natural lignocellulosic biomass, the main components, cellulose, hemicellulose and lignin, couples together to form a complex and rigid 3D structure defined as “biomass recalcitrance”. Therefore, so far, it remains a significant challenge to directly convert lignocellulosic biomass into functional materials with adjustable structures and excellent properties which are comparable to the synthetic polymers.

The ILs have both polar and nonpolar groups which are beneficial to the dissolution of lignocellulosic biomass. It has been widely reported that the ILs with imidazolium cations exhibit good solubility for lignocellulose. The dissolution of wood powder in BmimCl was firstly demonstrated by Fort et al. (2007). Subsequently, Kilpeläinen et al. (2007) found that AmimCl was more efficient than BmimCl in dissolving lignocellulose. Further studies revealed that hydrogen bond basicities of the ILs were important in reflecting their capacities for dissolving lignocellulose. The ILs with the higher hydrogen bond basicity like EmimAc exhibit better capability in dissolving lignocellulose (Sun et al., 2009). The ILs are destructive to the “biomass recalcitrance”, contributing to the complete or partially dissolution of lignocellulose. Thus, lignocellulose feedstock can be processed into high value materials when the ILs are used as the solvents.

Utilizing the ILs with the efficient dissolving capacity for lignocellulose, the pristine lignocellulose can be directly converted into regenerated materials in various forms, such as films, fibers and gels. Fort et al. (2007) indicated that the untreated wood shaving dissolved in BmimCl could not be regenerated into films. The presence of lignin and hemicellulose was considered to be a principal obstacle. By improving the dissolution conditions and increasing the solubility of lignocellulose, it is possible to produce regenerated lignocellulosic materials. Extending the dissolution time or increasing the temperature will contribute to the increased solubility of lignocellulose. After being treated at 110 °C for 16 h or 185 °C for 10 min, bagasse was able to be dissolved and spun into lignocellulose composite fibers in EmimAc (Sun et al., 2011). Regenerated lignocellulose materials prepared in the ILs with a higher dissolving capacity exhibit better mechanical property. The regenerated hydrogels from poplar and sorghum bagasse in EmimAc have the compressive strengths of 0.123 MPa and 0.05 MPa, respectively (Kalinoski and Shi, 2019). They also exhibited excellent antibacterial property with 80% Escherichia coli colonies inhibited, which could be attributed to the retained lignin.

After a pretreatment with ball milling, the poplar wood could be dissolved in BmimCl and regenerated into lignocellulose composite film (Abdulkhani et al., 2013). Hot water pretreatment of lignocellulose can partially hydrolyze hemicellulose and enhance the solubility of the resulting biomass. Hybrid poplar after a hot water pretreatment at 160 °C for 1 h could be easily dissolved in EmimAc, and then regenerated into lignocellulose film with a tensile strength of up to 70 MPa and a promising UV-resistant property (Wang et al., 2017). After an autohydrolysis in hot deionized water at 160 °C for 1 h, the resultant poplar could be spun into lignocellulose fiber with a tensile strength of up to 122 MPa using EmimAc as solvent (Nguyen et al., 2019). Another effective strategy is to firstly separate components of lignocellulose and then blend them together in the ILs for making lignocellulose composite materials. Cellulose/xylan composite film obtained by blending xylan with cellulose in EmimAc had a higher modulus than pure cellulose film due to the enhancement of xylan (Sundberg et al., 2015).

The construction of physical cross-linking points can help to form stable regenerated materials in lignocellulose/ILs solutions. After five cycles of freezing-thawing processes of spruce/AmimCl solution, spruce hydrogel was obtained by solvent replacement (Roata et al., 2018). The obtained lignocellulose hydrogel exhibited a high adsorption capacity for heavy metal ions.
and dyes in water. By adjusting the freezing-thawing conditions, mesoporous lignocellulose aerogels with a specific surface area of up to 80 m$^2$/g were obtained by liquid nitrogen freezing-thawing process (Lu et al., 2012). Moreover, the co-solvent addition can reduce the viscosity of solution and improve the solubility of lignocellulose. Using the DMSO as the co-solvent, lignocellulose aerogel prepared from the lignocellulose/AmimCl/DMSO solution with a high concentration of 11 wt% showed a higher specific surface area of 103 m$^2$/g (Mussana et al., 2018).

All-biomass composite obtained by compositing pristine lignocellulose and other biomass can achieve high performances. Reinforcing by in-situ retained cellulose nanocrystals, the corn leaf was successfully fabricated into all-biomass composite film (Fig. 9a) (Zhang et al., 2017b). The tensile strength of the obtained film is as high as 67 MPa. Li et al. (2019) demonstrated a simple strategy to enhance the wheat straw by adding cellulose with a high DP (Fig. 9b). The tensile strength of the obtained wheat straw/wood pulp all-biomass film reached 62 MPa. In addition, due to retention of most of the lignin, the obtained all-biomass film showed a high UV-shielding property.

The ILs can be used as pretreatment solvents for lignocellulose to improve accessibility. In this process, only a small fraction of lignocellulose is dissolved by the ILs. Composite boards were successfully prepared through hot-pressing oil palm leaf pretreated by the ILs together with starch (Fig. 9c) (Mahmood et al., 2016a; Mahmood et al., 2016b; Mahmood et al., 2017). The fracture strength of composite boards reaches 12–25 MPa. Partially dissolving the surface of lignocellulose fibers to generate matrix, by which the undissolved parts are welded together, is an approach to fabricate lignocellulose composites. The lignocellulose yarn with a high thermal stability was fabricated by using EmimAc as welding “ink” (Durkin et al., 2019). Via the same process, Durkin et al. (2016) prepared lignocellulosic yarn loading Pd and Pd-Cu nanoparticles from flax and bamboo yarn powders. Zhu et al. (2016) used BmimCl to partially dissolve and weld wood fibers. As a result, highly transparent and hazy papers were obtained (Fig. 9d).

Cellulose nanocrystals (CNC) as bio-based nanomaterials have a huge potential in papermaking, food, electronics, medicine and other fields. Some acidic ILs like 1-butyl-3-methylimidazolium hydrogen sulphate (BmimHSO$_4$) have been used as catalysts for cellulose hydrolysis to prepare CNC (Man et al., 2011). Lignocellulose is a promising raw material instead of pure cellulose to prepare the CNC in EmimAc (Abushammala et al., 2015; Ewulonu et al., 2019).

**5. Summary and Perspective**

The up-to-date advances have demonstrated that the ILs have a huge potential in efficient, multifarious and environmentally-friendly utilization of cellulose, lignin and lignocellulose. Via using the ILs as the solvent, dispersant or additive, more and more...
high-performance materials from these plant biomass resources are being designed, fabricated and attempted to apply in various fields. The development and utilization of biomass-based materials are beneficial to protecting our environment, because the environmental degradability of the biomass-based materials is far superior to the petroleum materials. For the future practical application of cellulose, lignin and lignocellulose, more efforts should be made to prepare high-performance, high-value, low-cost and eco-friendly materials by a facile, easy-to-operate and pollution-free process.

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