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Strategies for the inhibition of cellulose degradation in the valorization of lignocelluloses for the fabrication of functional materials

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Synthetic fibers in the market are mainly derived from fossil resources. The depletion of these resources and the accompanied environmental issues have stimulated interest in the utilization of renewable materials. Cellulose, which is widely available in lignocelluloses, is a type of abundant and renewable biopolymer in nature. It has been ascending as a promising feedstock for the manufacture of functional materials to replace fossil-based synthetic fibers. Pretreatment of lignocelluloses is a requisite step for the production of cellulosic materials since this biopolymer is embedded in a matrix composed of lignin and hemicellulose in the plant cell wall. However, cellulose degradation usually occurs during the pretreatment and subsequent material preparation processes, affecting the properties of the fabricated materials. In this study, we provide a comprehensive review of the strategies to inhibit cellulose degradation in the valorization of lignocelluloses for the fabrication of functional materials. It is demonstrated that the interactions between the solvent (including organics, ionic liquids, and deep eutectic solvents) and cellulose are closely related to its degradation. Specifically, too strong interactions would lead to the degradation of this biopolymer, resulting in a decrease in the degree of polymerization of cellulose, which leads to inferior properties (including mechanical properties) of the corresponding materials. Introducing additives, co-solvents, and radical scavengers or the selection of appropriate solvents affect the interactions between the solvent and cellulose, thereby inhibiting degradation and facilitating the fabrication of functional materials with excellent properties. The challenges and future perspective (e.g., understanding the inhibition mechanism at the molecular level) in the development of more efficient technologies to prevent cellulose degradation are also highlighted. This study can provide guidance for the design of systems to obtain cellulosic materials with excellent properties, encouraging more researchers to engage in this field to promote relevant progress.

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Sustainability spotlight

Synthetic materials, such as plastics, play important roles in the daily life of people. However, the available synthetic materials on the market are mainly obtained from fossil resources. Their threats to the environment and the depletion of fossil resources have motivated researchers to develop materials based on renewable sources. Cellulose, as a widely available natural biopolymer, has the potential to replace synthetic materials, but its potential has not yet been fully utilized. One of the reasons for this is that cellulose degradation usually occurs during its fractionation from lignocelluloses (the main source of cellulose) and material fabrication processes. This review paper summarizes the strategies to prevent cellulose degradation and highlights the challenges as well as the future perspectives in this specific field.

1. Introduction

Synthetic fibers are man-made textile materials created *via* chemical synthesis, typically derived from fossil resources like petroleum and coal. The growing demand for light-weight and unique composite materials increases the need for synthetic fibers due to their excellent properties, including low cost, good chemical resistance, processing possibility, transparency, and strength.¹ However, their threats to the environment (caused by their non-biodegradability, expensive recycling process, and greenhouse gas emissions) and depletion of fossil fuels have

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motivated the development of materials based on renewable sources for applications in the aviation, automobile, marine, construction, and textile industries.^{2,3} In recent years, natural materials have attracted increasing attention as eco-friendly and inexpensive alternatives for the synthetic ones due to their attractive properties including biodegradability, low cost, and renewability.^{4–6}

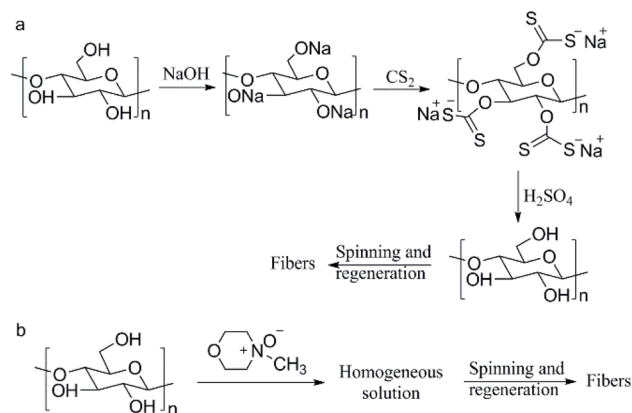
Cellulose is a type of abundant and renewable natural biopolymer. It is not easily dissolved in conventional solvents due to the strong hydrogen bond interactions among its hydroxyl groups,⁷ while this unique property enables cellulose to be a potential material in processes such as filtration that requires solvent resistance.⁸ Natural cellulose-based fibers have been considered alternatives to synthetic ones because of their low cost and density, abundant availability, and ecofriendly nature.^{9,10} Moreover, cellulosic textiles can be grafted with functional groups to exhibit desirable properties, like antimicrobial activity, drug delivery capability, and flame resistance.^{11,12} There are several studies that report cellulose-based films, fibers, beads, hydrogels, and filaments, their excellent water adsorption and drug delivery properties, and their uses as flexible electrodes and nanogenerators.^{13–17}

Cellulosic materials have the potential to replace synthetic ones, but this has not been realized to date, where the reason for this is closely related to the source of cellulose and its fabrication process. Cellulose is widely available in lignocellulosic biomass, where it is surrounded by a matrix of lignin and hemicellulose. Lignocelluloses principally consist of cellulose (30–50 wt%), hemicellulose (19–45 wt%), and lignin (15–35 wt%),¹⁸ and their composition depends on the environmental conditions under which the biomass grows and type/species of the plants. Mechanical strength is an important property of cellulose-based materials, where the presence of lignin and hemicellulose significantly affects this property. It was found that fibers containing more cellulose exhibit better mechanical properties than those with a lower cellulose content.^{19,20} Therefore, a pretreatment step to separate cellulose from the three-dimensional tight bonds of the three main constituents in lignocelluloses is necessary.²¹ Currently, pretreatments such as physical (chipping, milling, and grinding), chemical (alkaline, acid, and organic solvents),^{22–25} biological (enzymes),²⁶ and their combination (*e.g.*, steam-auto hydrolysis, alkali-enzymatic delignification, and hydrothermolysis-wet oxidation)^{27–29} are mainly used to separate cellulose from lignin and hemicellulose.³⁰ Mechanical routes could reduce the biomass particle size and disrupt its crystalline structure,³¹ but are less efficient and need more energy than chemical processes. Alternatively, severe conditions (*e.g.*, high acidity or basicity) are required for chemical processes, and under these conditions, the biomass usually decomposes into undesired products,³² which affect the properties of the corresponding cellulosic materials. Also, biological pretreatment is expensive and time-consuming, where a certain environment is usually needed to activate the enzymes.³³

After the cellulose-rich material is separated from lignocelluloses (also called the pulping process), effective dissolution of the pulp enriched in cellulose is necessary for the fabrication of

materials with certain shapes. In the typical Viscose process for manufacturing fibers, cellulose is firstly converted to cellulose xanthate in carbon disulfide and NaOH (Scheme 1a), which is then transformed back into cellulose in an H₂SO₄ coagulation bath, making the preparation of cellulosic materials possible.³⁴ However, hazardous compounds, such as CS₂ and H₂S, are used or formed in this process, posing a threat to the environment.³⁵ Additionally, the conventional solvents, including carbon disulfide, sulfuric acid, sodium hydroxide, and concentrated orthophosphoric acid, have been gradually phased out owing to their severe pollution.^{36,37} The more eco-friendly Lyocell process dissolves cellulose in *N*-methylmorpholine-*N*-oxide (NMMO), which is then regenerated to make fibers/films (Scheme 1b). NMMO is illustrated as a more environmentally friendly and non-derivatizing solvent for cellulose.³⁸ However, this process also faces drawbacks such as cellulose decomposition and occurrence of side reactions with NMMO due to its thermal instability,^{39,40} resulting in an inferior barrier and affecting the mechanical properties of the obtained films or fibers. Based on the above-mentioned analysis, it is clear that cellulose should undergo physical processing and chemical reactions during its manufacturing process, which can alter its structure, leading to a certain degree of degradation, and thus inferior properties. In contrast, synthetic fibers do not easily degrade during their preparation. Thus, the challenge of the degradation of cellulosic materials is attracting more and more attention from academic and industrial experts.

Scientists have devoted great efforts to developing new technologies for the fractionation of cellulose from lignocelluloses and the processing of pulp for the manufacture of cellulosic materials with excellent properties. Stabilizers (*e.g.*, propyl gallate and oxa-chroman derivatives) have been used to keep the cellulose chains intact, and thus inhibit the degradation of cellulose in traditional solvent systems.⁴¹ Optimization of the operating conditions could also restrain its degradation to some extent. The emergence of designable solvents, such as ionic liquids and deep eutectic solvents, provides new opportunities for the valorization of lignocelluloses and fabrication of cellulosic materials.^{42–44}



Scheme 1 Chemical reactions of Viscose (a) and Lyocell (b) processes.



This review paper aims to provide a comprehensive review of the strategies to stabilize cellulose and to prevent its degradation during its separation from lignocelluloses and subsequent material fabrication processes. (Fractionation of lignocellulosic biomass using various techniques and the improved efficiency have been extensively reviewed by others;^{45–48} in addition, processing of cellulose/lignocelluloses and functional biopolymers in ionic liquids or deep eutectic solvents has also been summarized.^{49–51} Alternatively, our focus herein is on the methods for the inhibition of cellulose degradation.) Furthermore, the challenges and perspectives in this specific field are proposed based on the existing problems in the fabrication of cellulose-based advance materials. It is intended that this review will provide guidance for future researchers in the relevant field, especially beginners.

2. Inhibition of cellulose degradation

A flow chart for the preparation of functional cellulosic fibers from lignocelluloses is shown in Fig. 1. In the valorization of lignocelluloses, cellulose should first be separated from the biomass to obtain pulp enriched in cellulose (Step 1). In this process, the pulverized raw material (usually used for laboratory research, but not very practical in industry) is treated in acid, base or organic solution to separate cellulose, which is then washed to remove any residual chemicals or other impurities. To further increase the purity and whiteness, the obtained product is bleached (Step 2). For the fabrication of materials with certain shapes, the pulp should be dissolved in certain solvents to form homogeneous solutions (Step 3), which is then molded into fibers, beads, films, *etc.* (Step 4). It has been reported that the crystallinity and strength of the material are greatly affected by the solvent–polymer interaction during wet spinning.⁵² Cellulose degradation mainly occurs in Steps 1, 2 and 3, and in this section, strategies to inhibit it are discussed.

2.1 Production of pulp enriched in cellulose

2.1.1 Acid/base treatment. Acid or base pretreatments are widely used for the separation of lignocelluloses to obtain pulp. The effects of alkaline, acid and hydrothermal pretreatments on the property of the regenerated cellulose fibers from eucalyptus was explored by Xu *et al.*⁵³ The degree of polymerization (DP) of cellulose from hydrothermal treatment was 3250, which is much lower than the DP of the sample obtained from the NaOH (4829) or H₂SO₄ treatment process (4745), owing to the severe conditions (180 °C, 30 min) in the hydrothermal process. The excellent capability of hydrothermal treatment in separating cellulose microfibrils resulted in a reduction in the molecular

weight. Afterwards, the cellulose samples were each dissolved in the ionic liquid 1-butyl-3-methylimidazolium acetate ([C₄mim][OAc]) for fiber spinning.⁵³ It was found that the DP of the obtained fibers ranged from 1043 to 2907, exhibiting an obvious decreasing trend compared with that of the samples obtained right after the above-mentioned pretreatments. This observation implied the partial degradation of cellulose induced by the relatively high temperature (100 °C) and long time of the ionic liquid dissolution process. The morphologies of the cellulose fibers indicated that the regenerated fibers from hydrothermal treatment contained more small apertures due to the degradation of part of the cellulose during treatment, while the surface of the fibers from NaOH- or H₂SO₄-treated cellulose was more compact. Therefore, the selection of a suitable medium for the pretreatment process could alleviate the degradation of cellulose.

In a study by Kumar and co-workers, it was demonstrated that when cellulose from filter paper was treated with aqueous solution containing acetic acid and sodium chlorite, the average degree of polymerization of cellulose decreased from 1500 (for raw filter paper) to 410,⁵⁴ implying that the solvent could affect the polysaccharides. Later, the effects of free lignin on the pretreatment of Avicel PH-101 and Whatman filter paper by the acid-chlorite method were revealed by measuring the molecular weight distribution and DP of the obtained cellulose.⁵⁵ The Avicel samples with the absence of lignin showed a reduction in DP of ~5% during the processing (from 309 to 294), while the DP reduction decreased to 1% in the presence of 30% lignin. It was illustrated that the filter paper cellulose was more sensitive to the acid-chlorite treatment process than the Avicel sample due to the difference in their crystallinity. The DP of the filter paper cellulose decreased from 2046 to 1347 after processing, with a reduction of nearly 35%. When 30% lignin was present in the system, the drop in DP value was reduced to <12%. Even in the presence of 1% lignin, the average DP value was found to be 1706, decreasing by 17%. Therefore, the presence of a small amount of free lignin could inhibit the degradation of cellulose to some extent in the acid-chlorite treatment, which was attributed to the fact that lignin in the system could be preferentially degraded before cellulose, protecting cellulose to some extent.

Lactic acid and microwave irradiation were combined to treat kenaf bast for the fabrication of cellulose fibers,⁵⁶ and for comparison, this biomass was also treated with the conventional sulfate method. The results indicated that the lactic acid-involving process exhibited a higher lignin removal percentage (94.7% vs. 88.3%). The GPC analysis showed that the DP of the fibers obtained in the lactic acid treatment process at 130 °C for 30 min was 7250, which was much higher than that of the fibers

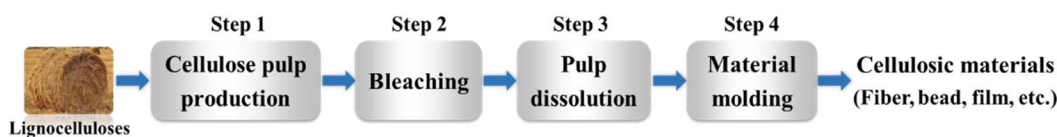


Fig. 1 Process for the fabrication of cellulosic materials from lignocelluloses.



(i.e., 3749) in the traditional process, indicating obvious cellulose degradation in the latter case. Interestingly, the DP of the cellulose fibers obtained in the lactic acid-microwave coupled process (130 °C, 30 min) was slightly higher than that of the raw kenaf (6927), given that cellulose with a low DP in the plant was removed, maintaining the integrity of the cellulose chains during the treatment using less corrosive solvent under gentler conditions.

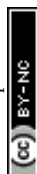
2.1.2 Organosolv treatment. Pretreatment of lignocelluloses by organic solvents (such as a mixture of dioxane and ethylene glycol or glycerol), namely organosolv treatment, is another method to fractionate the three biopolymers.⁵⁷ The conditions, especially temperature, time, and pH value, could obviously affect the separation efficiency as well as degradation of the biopolymers.⁵⁸ For instance, poplar wood particles were pretreated using a mixture of dioxane and ethylene glycol (2/1, v/v) as the medium and H₂SO₄ as the catalyst under microwave irradiation.⁵⁹ An increase in the temperature from 100 °C to 160 °C resulted in a continuous decrease in the amount of recovered cellulose, indicating the degradation of this biopolymer. Schmetz and colleagues reported the extraction of lignin from tall fescue using aqueous ethanol solution (with an ethanol content of 92%) in the presence of H₂SO₄ (0.32 M) under heating conditions (heating at a rate of 5 °C min⁻¹ for 30 min and stabilizing at 148 °C for 5 min).⁶⁰ It was found that these conditions were too harsh, resulting in the obvious degradation of cellulose. By choosing the appropriate conditions and solvents, cellulose degradation could be prevented to some extent. Dimethyl formamide (DMF) could inhibit cellulose degradation in the pulping of wheat straw,⁶¹ and the addition of morpholine to 1,1,3,3-tetramethyl guanidine promoted the dissolution of lignin and reduced the degradation of cellulose in the delignification of eucalyptus wood.⁶²

2.1.3 Pretreatment with ionic liquids. Ionic liquids (ILs), a type of fantastic material with designable structures and properties, have attracted attention from experts in academy and industry since the 1990s because of their unique properties and wide applications in various fields.^{63–67} In 2002, Rogers' group discovered that imidazolium-based ILs (e.g., [C₄mim]Cl) were excellent solvents for cellulose,⁶⁸ which opened up a new generation of solvents for the processing of cellulose-based biopolymers.⁶⁹ Since then, various functional ILs, such as 1-allyl-3-methylimidazolium chloride ([Amim]Cl),⁷⁰ 1-ethyl-3-methylimidazolium dimethylphosphate ([C₂mim] [(MeO)₂PO₂]),⁷¹ and [C₂mim][OAc],⁷² have been developed for the dissolution and processing of cellulose. Also, a series of 1-alkyl-3-methylimidazolium ILs, which incorporated organic anions with varying alkalinity including phenolate ([OPh]⁻), 1,2,3- and 1,2,4-triazolates, benzotriazolate, oxazolate, and imidazolate, was shown to be excellent solvents for cellulose.⁷³ Moreover, extensive efforts have been devoted to the dissolution and fractionation of the three main components in lignocelluloses using ionic liquids. For instance, Sun *et al.* demonstrated that lignocelluloses, such as southern yellow pine and red oak, can be readily dissolved in [C₂mim][OAc] at 110 °C.⁷⁴ Lignin and cellulose-rich materials (CRMs) can be regenerated from IL solution by the addition of an appropriate solvent such as

a mixture of acetone and water (1 : 1, v/v). Protic ammonium ILs were used to treat pineapple crown, and the obtained CRM contained reduced contents of lignin and hemicellulose compared to the raw biomass.⁷⁵

However, when the lignocellulosic biopolymers were treated with ILs at relatively high temperatures (e.g., ≥130 °C) for a long time, degradation of the solubilized polymers would occur. When raw cotton was solubilized in [C₄mim][OAc] or [Amim]Cl at 80 °C, DP of regenerated cellulose was 650, which decreased to ~230 when the temperature increased to 130 °C.⁷⁶ Gel permeation chromatography analysis of the solubilized wood components after treatment with [C₂mim]Cl illustrated that components with a low DP were formed an increase in the treatment time.⁷⁷ Compounds of sugars from cellulose degradation, such as 5-hydroxymethylfurfural, were detected in the ionic liquid. Furthermore, the presence of water and oxygen would accelerate the degradation process. Additionally, the degradation behaviors of the biomass components vary with a change in the structure of ILs. For example, it was proven that less degradation occurred in the system containing 1-ethylpyridinium bromide compared with that in [C₂mim]Cl.⁷⁸ Besides, the use of an external field, such as microwave, could not only enhance the dissolution of cellulose in ILs but also cause a significant decrease in its DP.⁷⁹

Ishida investigated the dissolution and degradation mechanisms of cellulose fibers in [C₂mim][OAc] by molecular dynamics simulation.⁸⁰ It was found that the number of inter- and intra-chain hydrogen bonds in cellulose was reduced sequentially when the ionic liquid and cellulose were mixed. The roles of the cation and anion in this process were also revealed. The intercalation of acetate anions into the cellulose fibers favored the formation of hydrogen bonds between the anion and cellulose, and the intrachain hydrogen bonds in cellulose were broken prior to the interchain interactions due to the presence of IL anions. The cations could interact with cellulose and stabilize its detached chains through van der Waals interaction. The breakage of the intrachain hydrogen bonds in cellulose facilitated the flexibility of the rigid cellulose chains, accompanied by dissolution as well as degradation of this biopolymer in IL. In fact, mechanism of cellulose dissolution in ILs is subjected to debate, especially for the role of their cations. Most of the researchers demonstrated that the hydrogen bonds between the IL anion and cellulose were the driving force in the dissolution process.^{81,82} Lu *et al.* tried to reveal the interactions between the IL cations and cellulose through ¹³C NMR by dissolving cellulose in ILs composed of different cations and the same acetate anion.⁸³ The results indicated that the cations could form hydrogen bonds with the hydroxyl oxygen in cellulose, but the chemical shift was not significant. However, some researchers doubt whether hydrogen bonds can be formed between cations and cellulose.⁸⁴ Moreover, the Raman analysis by Ferreira *et al.* indicated that the imidazolium and pyridinium cations, with aromatic features, exhibited strong polarization to enhance the dissolution of cellulose in ILs.⁸⁵ Li *et al.* summarized the dissolution mechanism in more detail.⁸⁶



In this subsection, the methods to prevent the degradation of cellulose in ILs are summarized, while the reports only mentioning cellulose degradation without providing any strategy to prevent its degradation are not mentioned.^{87–92}

2.1.3.1 The use of typical neat IL solvent. Ma and coworkers used 1,5-diazabicyclo[4.3.0]non-5-ene-1-ium acetate ([DBNH][OAc]) to dissolve waste paper and cardboard,⁹³ which were refined under mild conditions to destroy the lignin-carbohydrate complexes to prepare cellulose dope for dry-wet spinning. The properties of the obtained fibers were shown to be comparable to or better than that produced by the Lyocell process. Interestingly, the authors found that no obvious cellulose degradation and losses in the spinning process were observed due to the low processing temperature (80 °C) and the high inertness of [DBNH][OAc]. Raut *et al.* demonstrated that *N*-allyl-*N*-methylmorpholinium acetate ([AMMorp][OAc]) is an efficient solvent for cellulose dissolution.⁹⁴ At 120 °C, this acetate-based IL could dissolve 25 wt% native cellulose without any pre-processing, resulting in a DP of 2082 in 20 min. When the DP was 789, more cellulose (30 wt%) could be dissolved. Further analysis by size exclusion chromatography (SEC) illustrated that the DP of the cellulose after regeneration remained almost unchanged, and [AMMorp][OAc] is a non-degradative solvent to dissolve cellulose. Therefore, the degradation of cellulose in ILs with certain structures could be neglected, indicating the importance of the IL structure.

By investigating cellulose degradation in three quaternary ammonium ILs, including *N,N,N*-triethyl-*N*-hexyl-1-ammonium acetate ([N₆₂₂₂][OAc]), tetrahexylammonium acetate ([N₆₆₆₆][OAc]), and *N,N,N,N',N',N'*-hexaethyldecane-1,10-diammonium acetate (C₁₀(N₂₂₂OAc)₂; Fig. 2), Tseng *et al.*⁹⁵ found that the DP of cellulose regenerated from [N₆₂₂₂][OAc] with a polymer content of 12% decreased from 309 (for original cellulose) to 269. Moreover, it was proven that with an increase in the biopolymer content in the solution, the DP of cellulose regenerated from [N₆₂₂₂][OAc] increased (Fig. 3). This is because an increase in cellulose content would make the solution more viscous, retarding the degradation of cellulose. When comparing the DP of cellulose regenerated from different ILs (the cellulose content was fixed at 5%), the one from C₁₀(N₂₂₂OAc)₂ exhibited the lowest DP, which was only 62 (*vs.* 146 for cellulose from [N₆₆₆₆][OAc] *vs.* 174 for the one from [N₆₂₂₂][OAc]). One carbon chain in C₁₀(N₂₂₂OAc)₂ was long, and

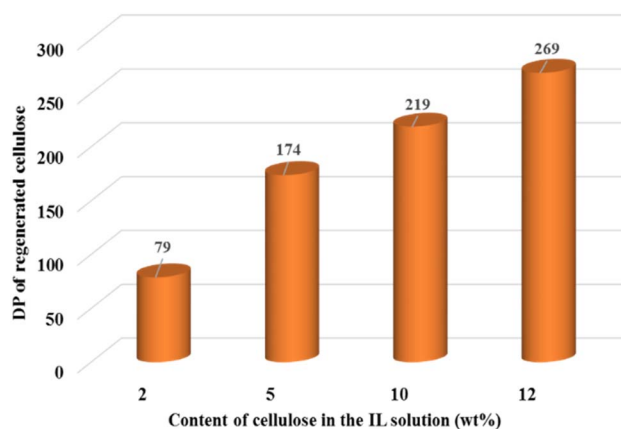


Fig. 3 DP of regenerated cellulose from [N₆₂₂₂][OAc] solution as a function of cellulose content (this figure was drawn based on data provided in ref. 95).

both ends of this long chain were bonded with the triethylammonium group, resulting in high viscosity. When the ions in the IL penetrated cellulose, the retention time of the ions in this biopolymer was long because of the high viscosity of the IL. Thus, C₁₀(N₂₂₂OAc)₂ can destroy more glycosidic or hydrogen bonds, resulting in severe degradation of the regenerated cellulose.

Sun *et al.* dissolved bagasse in [C₂mim][OAc] at 110 °C for 16 h, and fibers could be directly produced from the biomass/IL solution.⁹⁶ However, when southern yellow pine was treated under the same conditions, fibers could not be obtained from the solution. To shorten the dissolution time to 0.5 h, the dissolution temperature was enhanced to 175 °C, and it was interesting to find that fibers could be spun from the pine/IL solution. It was also illustrated that fibers spun from the bagasse solution obtained at 175 °C for 0.5 h were stronger than that obtained under 110 °C for 16 h. This is because treating the biomass at 110 °C for this long time would lead to severe degradation of the biopolymer. The above-mentioned phenomena indicated that proper treatment conditions could also inhibit the degradation of the biopolymer in IL systems. Generally, decreasing the temperature, pressure and the treating time could inhibit the degradation of cellulose. Of course, in real operation, a balance should be made between the

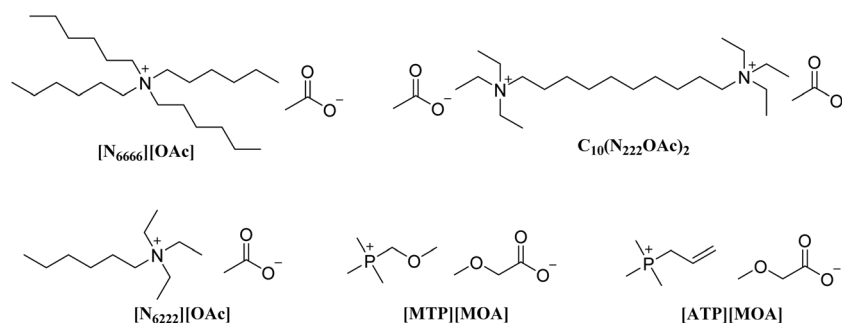


Fig. 2 Structures of [N₆₆₆₆][OAc], C₁₀(N₂₂₂OAc)₂, [N₆₂₂₂][OAc], [MTP][MOA], and [ATP][MOA].



treatment temperature and time, as illustrated in the work by Sun *et al.*,⁹⁶ *i.e.*, 110 °C/16 h *vs.* 175 °C/0.5 h. Although 175 °C was higher, the time needed for the complete dissolution of biomass was significantly shortened, under which the degradation of the biopolymer could be relieved to some extent.

2.1.3.2 Addition of cosolvent to the IL. A computer-aided methodology was proposed by Mai *et al.* to screen ILs for cellulose dissolution.⁹⁷ A quantitative structure–activity relationship (QSAR) model was developed to predict the solubility of cellulose using the group contribution and artificial neural network methods, and a genetic algorithm was employed to solve the mixed integer nonlinear programming problem to maximize the solubility of cellulose. It was demonstrated that the solubility of cellulose in the designed ILs was at least 1.2-times higher than its solubility in the best ILs measured experimentally in the literature. Also, when a mixture of (methoxymethyl)trimethylphosphonium 2-methoxyacetate ([MTP][MOA])/DMSO (or allyltrimethylphosphonium 2-methoxyacetate ([ATP][MOA])/DMSO) (1:1, *v/v*) was used to dissolve cellulose (see Fig. 2 for the IL structures), 74.0 wt% (or 100 wt%) of Avicel could be dissolved at 100 °C. The DP of the regenerated cellulose from the [MTP][MOA] and [ATP][MOA] systems was 232 and 248, respectively, similar to that of the original cellulose (245), implying that a mixture of any of the two ILs with DMSO was an effective solvent for the dissolution of this polymer with no obvious degradation.

Phosphonium amino acid-based ionic liquids, including tetrabutylphosphonium glycine ([TBP][Gly]), tetrabutylphosphonium alanine ([TBP][Ala]), tetrabutylphosphonium valine ([TBP][Val]), and tetrabutylphosphonium *N,N*-dimethylglycine ([TBP][DMGly]), in the presence or absence of a cosolvent, were used to treat cellulose.⁹⁸ It was found that without cosolvent, all these ILs could not dissolve Avicel cellulose, even at 120 °C. The addition of a cosolvent, such as DMSO and *N*-methylimidazole (NMI), could improve the dissolution efficiency for cellulose. Also, among the four ILs, [TBP][Gly] in combination with a cosolvent was the most effective system. For instance, 15% cellulose could be dissolved in [TBP][Gly]/DMSO and [TBP][Gly]/NMI at 30 °C (the content of the cosolvent was not mentioned). The DP of the regenerated cellulose from different systems varied from 194 to 205, which slightly decreased compared to the value of the original cellulose (*i.e.*, 208), indicating that no obvious degradation occurred during the dissolution process. The viscosity of ILs can significantly decrease in the presence of one cosolvent, thus improving the mobility of the ions in ILs and facilitating the interactions between ILs and cellulose. A similar study from the same research group reported that some polar organic cosolvents could prevent the degradation of cellulose in imidazolium-based ILs.⁹⁹ For example, no decrease in the DP of cellulose was observed in a mixture of [C₂mim][OAc] and DMAc in comparison with the 8–9% decrease in the DP for the system with neat [C₂mim][OAc], even at 30 °C, which indicated that some cosolvents could also protect cellulose in the dissolution in ILs.

Olsson *et al.* investigated the effect of *N*-methylimidazole, the starting material used to synthesize [C₂mim][OAc], on the

solvation of microcrystalline cellulose (MCC) by [C₂mim][OAc].¹⁰⁰ It was demonstrated that the presence of this additive accelerated the dissolution process due to its decreased viscosity. The stability of cellulose in a mixture of NMI/[C₂mim][OAc] was evaluated by determining the DP of 10 wt% cellulose solutions at room temperature. After the solution was stored for 31 days, no obvious decrease in DP was detected (DP of 148 for the sample in the NMI/[C₂mim][OAc] solution with IL content of 90% *vs.* 150 for MCC), indicating that *N*-methylimidazole was an inhibitor for cellulose degradation in [C₂mim][OAc].

Later, Cheng and colleagues proved that the degradation of cellulose could be inhibited when it was dissolved in [C₂mim][OAc] with the addition of DMSO.¹⁰¹ The DP of the cotton linter was 920, and after it was dissolved in neat [C₂mim][OAc], the DP of the regenerated cellulose film (control) decreased to 524, indicating the obvious degradation of cellulose. However, the DP of the regenerated films prepared in DMSO/[C₂mim][OAc] with the IL molar fractions (χ) of 0.1–0.6 ranged from 586 to 833, which is higher than that of the control film (Fig. 4). In the presence of DMSO, the cotton linter could be dissolved at a relatively lower temperature (room temperature *vs.* 80 °C) due to the decrease in viscosity. The DP and tensile strength of the film regenerated from the DMSO/IL solution with χ of 0.1 were 728 and 99 MPa, respectively, which were much higher than the corresponding values of the control film.

Solvents containing amino and/or hydroxyl groups were used to enhance the dissolution of lignocelluloses in ILs and restrain cellulose degradation by our research group.¹⁰² 3-Aminopropanol exhibited the best efficiency in improving the dissolution of lignocelluloses and cellulose-rich material yield in [C₂mim][OAc]. Moreover, the presence of this compound could restrain cellulose degradation in the IL. The regenerated cellulose fiber spinning from the 5% 3-aminopropanol/[C₂mim][OAc] solution exhibited better mechanical properties. The elongation at break and the tensile fracture strength of the fiber reached 15.6% and 184.1 N per tex, in comparison with 9.6%

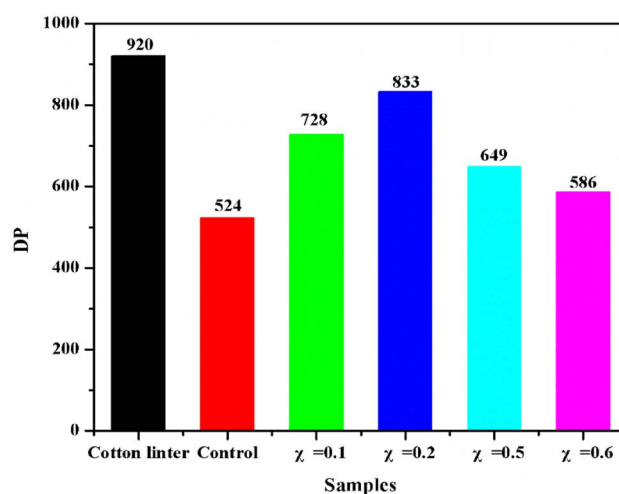
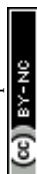


Fig. 4 DP of regenerated cellulose films prepared in mixtures of DMSO/[C₂mim][OAc] with different IL molar fractions (χ). Reproduced from ref. 101 with permission from Springer Nature,¹⁰¹ copyright 2017.



and 99.7 N per tex for the fiber fabricated in neat IL, respectively. Spectroscopic analysis by NMR and IR indicated that 3-aminopropanol and the IL could form hydrogen bonds, which weakened the interactions between the ions and biomass, leading to the inhibition of cellulose degradation.

Waste corrugated cardboards composed of 52.02% cellulose, 6.79% hemicellulose, and 10.43% lignin were treated with [Amim]Cl in the presence or absence of DMSO and CaCl_2 ¹⁰³ to fabricate cellulose films. The tensile strength of the films prepared from the solution by dissolving 4 wt% corrugated cardboard in [Amim]Cl at 90 °C for 4 h was 59.00 MPa. The presence of DMSO (40%) and CaCl_2 (2 wt%) increased the film tensile strength to 85.86 MPa. The authors further demonstrated that DMSO intensified the dissolution of biomass in this IL, and that the Ca^{2+} ion interacted with the molecular chains of this biopolymer (Fig. 5), thus improving the tensile strength of the film, also implying the inhibition of cellulose degradation.

2.1.3.3 Addition of additive to IL. *Eucalyptus urograndis* prehydrolysis kraft was dissolved in $[\text{C}_2\text{mim}][\text{OAc}]$ at 95 °C and the DP decreased by 25.2% after the dissolution step.¹⁰⁴ The solutions were stored at 60 °C, 90 °C, 110 °C, respectively, and DP of the precipitated cellulose from the cellulose/IL solution stored at different temperatures was determined. It was found that cellulose was stable when the prehydrolysis kraft/IL solution was stored at 60 °C, with no polymer chain scission. Cellulose degradation was observed at 90 °C and 110 °C, and more pronounced degradation occurred at 110 °C. The molar mass distribution (MMD) of the regenerated cellulose also shifted to lower values, confirming the degradation of cellulose. Propyl gallate was then proposed as a stabilizer to inhibit the degradation, and it was found that the decreasing extent of cellulose DP reduced from 25.2% to 3.2% in the presence of 2% of this additive (based on dry cellulose). However, the inhibition mechanism was not explored by the authors.

Amino acids, such as L-serine, L-arginine, and L-glycine, were proposed as additives to inhibit cellulose degradation in ILs by Yang *et al.*¹⁰⁵ Among the eleven tested amino acids, L-arginine exhibited the best performance in inhibiting the degradation of cellulose in $[\text{C}_4\text{mim}]\text{Cl}$ (130 °C, 24 h). It was further proven that L-arginine could also restrain the degradation of this biopolymer in $[\text{C}_2\text{mim}]\text{Cl}$ or [Amim]Cl. Further study indicated

that the elongation at break and breaking tenacity of the regenerated cellulose fibers were not apparently affected by the presence of this amino acid at 90 °C. When the temperature was higher than 110 °C, the DP of the regenerated cellulose from the solution with no additive was too small to be measured, and that of the cellulose obtained with the addition of L-arginine remained unchanged. At 130 °C, the fiber elongation at break was enhanced from 4.86% (with no additive) to 9.24% (with 1.25% of L-arginine), and the tensile strength increased from 265.5 MPa to 375.2 MPa. Spectroscopic analysis, including FT-IR and ¹³C NMR, verified that no chemical reaction occurred between L-arginine and cellulose during the processing.

The mechanism of inhibition of cellulose degradation by amino acids in $[\text{C}_4\text{mim}]\text{Cl}$ was revealed by NMR, ESI-MS, and MD simulation.¹⁰⁵ It was demonstrated that the $[\text{C}_4\text{mim}]^+$ cation and Cl^- anion could simultaneously form hydrogen bonds with the -OH groups in cellulose when no additive was present in the system (Fig. 6), inducing the degradation of cellulose. When L-arginine was present in the system, some interactions between cellulose and IL were replaced by hydrogen bonds between the amino acid and cellulose (*e.g.*, O-H...N and N-H...O interactions), preventing the simultaneous formation of several hydrogen bonds between $[\text{C}_4\text{mim}]\text{Cl}$ and the -OH groups in cellulose, leading to the inhibition of cellulose degradation.

In a follow-up study, Yang *et al.* fabricated cellulose fibers directly from solutions obtained by dissolving corn stalk in L-arginine/ $[\text{C}_4\text{mim}]\text{Cl}$.¹⁰⁶ The results indicated that with an increase in the amino acid content in the solvent, the dissolution percentage of this biomass and regenerated cellulose-rich material (CRM) yield increased, and the undissolved residue contained less cellulose. Further analysis by HPLC indicated that increasing the temperature to 170 °C and extending the dissolution time (9 h) did not cause obvious degradation of cellulose. DP analysis showed that the DP of the material obtained in the amino acid-containing system was slightly lower than that in the raw biomass (620 *vs.* 650), and it was much higher than the DP of CRM obtained in neat IL with no additive (450). The mechanical properties of the spinning fibers obtained under different conditions are summarized in Table 1. When L-arginine was added, the lignin removal percentage reached 92.0% by dissolving corn stalk in $[\text{C}_4\text{mim}]\text{Cl}$ at 150 °C

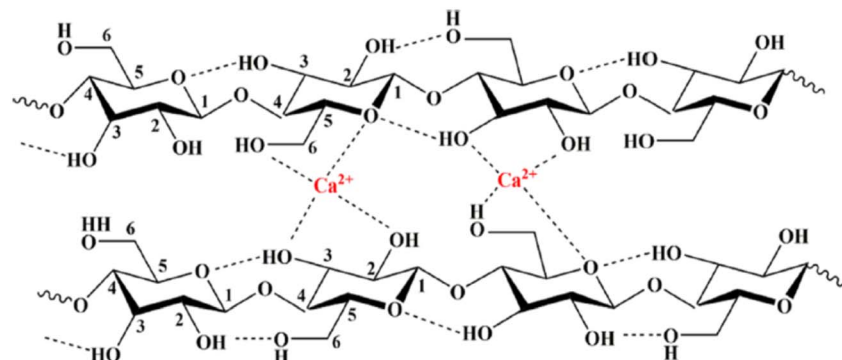


Fig. 5 Interactions of Ca^{2+} with cellulose molecules. Reproduced from ref. 103 with permission from the American Chemical Society,¹⁰³ copyright 2020.



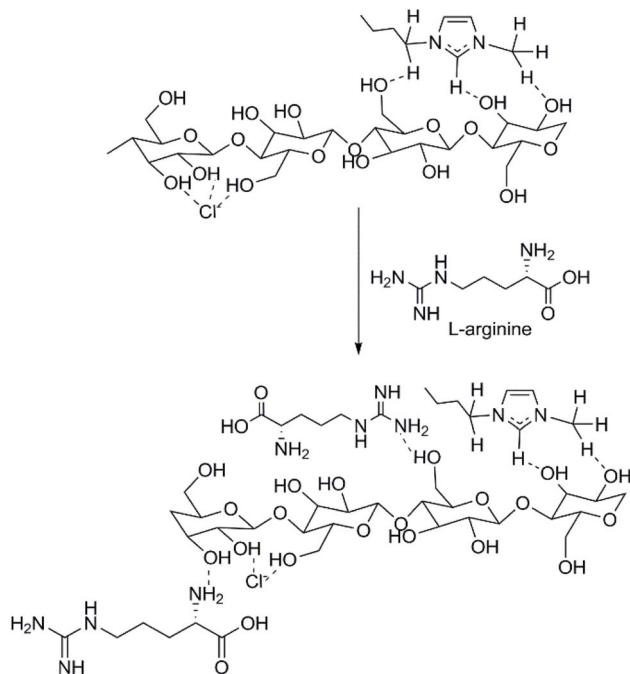


Fig. 6 Cellulose degradation and the mechanism of inhibition of cellulose degradation in $[C_4mim]Cl$ by L-arginine. Reproduced from ref. 105 with permission from The Royal Society of Chemistry,¹⁰⁵ copyright 2019.

Table 1 Mechanical properties of the spinning fibers obtained in L-arginine/ $[C_4mim]Cl$ by wet spinning. Reproduced from ref. 106 with permission from Elsevier,¹⁰⁶ copyright 2020

No.	T (°C)	t (h)	Content (%)	Delignification		DP	σ^a (MPa)	ε^b (%)
				(%)	(%)			
1	110	6	0.0	10		410	150	3.15
2	140	6	0.0	40		290	120	2.45
3	150	11.5	2.5	92		600	420	10.12

^a Tensile strength. ^b Elongation at break.

for 11.5 h. The tensile strength of the corresponding fiber was 420 MPa, with an elongation at break of 10.12%, in comparison with 150 MPa and 3.15% for the fiber spun from the solution (with no additive) by dissolving corn stalk at 110 °C for 6 h, respectively. Therefore, L-arginine as the additive could efficiently facilitate the isolation of cellulose from lignocelluloses in $[C_4mim]Cl$, and also inhibit cellulose degradation, making it possible to fabricate materials with excellent mechanical properties for extensive applications.

2.1.4 Pretreatment with deep eutectic solvents. Deep eutectic solvents (DESs) are considered another class of “designable solvents”, which can be easily synthesized by mixing at least one hydrogen bond acceptor and one donor in different molar ratios.¹⁰⁷ DESs have been widely used as solvents for biomass processing because of their easy synthesis, low price, and good biocompatibility (if the parent materials for their synthesis are from nature).^{108–110} It was reported that the

hydrogen bond acceptors in DES, e.g., Cl, O and N atoms, can form hydrogen bonds with the hydroxyls in cellulose ($O-H\cdots Cl$, $O-H\cdots N$, and $O-H\cdots O$), disrupting the hydrogen bonds in the interlayers of cellulose, resulting in the separation of cellulose into multiple single layers. Then, the DES continued to react with the cellulose chains, disrupting the intramolecular hydrogen bonds of cellulose, which resulted in the dissolution of cellulose.^{111,112} The DES formed by mixing choline chloride and imidazole could remove lignin from *Acacia dealbata* more efficiently than an aqueous solution of 1-butyl-3-methylimidazolium methyl sulfate, with lower cellulose loss and less cellulose degradation (however, the reason to prevent degradation was not mentioned).¹¹³ Sirviö *et al.* synthesized DESs by mixing tetraethylammonium hydroxide with urea, methylurea, dimethylurea or ethylurea, which were used as solvents to fabricate cationic wood nanofiber (CWNF) films using sawdust as the raw biomass, in the presence of the cationization agent glycidyltrimethylammonium chloride.¹¹⁴ The sawdust was not pretreated for component removal, and thus lignin was still present in the system. The cationic group was incorporated to improve the disintegration efficiency and antimicrobial property. The obtained CWNF films were yellow and transparent, with good mechanical robustness, and their average tensile strength was 60 ~ 71 MPa. The mechanical properties of the CWNF films were reported to be comparable to that of the advanced lignocellulose-based materials. It is more interesting to find that the tensile strength of the CWNF films outperformed many synthetic plastics used for packaging, such as polyethylene and poly(vinyl chloride).¹¹⁵ The excellent mechanical properties of the CWNF films implied the negligible degradation of the biopolymer during the fabrication process.

Anthraquinone (AQ) was proposed as an agent to protect cellulose in the degumming of ramie using a DES formed by mixing choline chloride and urea at a molar ratio of 1 : 2.¹¹⁶ It was illustrated that a small amount of AQ could protect carbohydrates from excessive degradation. For instance, when 0.2 g L^{-1} AQ was added to the solution, the degree of polymerization increased by 3.2%, also resulting in fibers with improved mechanical properties. It was considered that the reducing aldehyde terminal group in carbohydrates was oxidized into a carboxyl group by AQ under alkaline conditions in the DES system, which rapidly inhibited the peeling reaction of carbohydrates and prevented the degradation of the carbohydrates during degumming, resulting in an improvement in the yield and mechanical properties of the obtained ramie fibers.

2.2 Bleaching process

To increase the purity and whiteness of pulp enriched in cellulose, the pulp should be further bleached. The principle of bleaching is mainly to oxidize and decompose colored impurities on the surface of cellulose through oxidants, where ozone is a strong oxidizing bleaching agent. However, the rapid decomposition of ozone would cause the problems of low efficiency of lignin oxidization, affecting strength of the final obtained fibers.^{117,118} Besides, there exists a trade-off between brightness improvement and cellulose chain stability, given



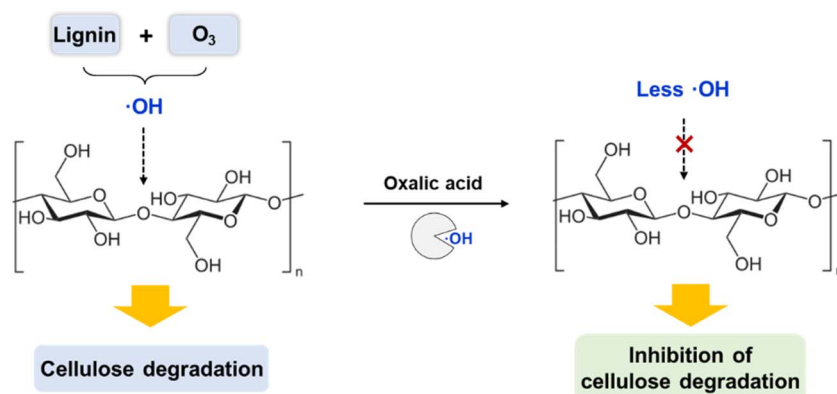


Fig. 7 Schematic of the inhibition of cellulose degradation in ozone treatment with the addition of oxalic acid.

that during the decomposition of the colored impurities, cellulose could also degrade to some extent.¹¹⁹ In this case, the cellulose content in the pulp would be reduced, which could impact the paper strength and other properties. To prevent the degradation of cellulose, Roncero *et al.* studied the ozone treatment of *Eucalyptus globulus* kraft pulp with the addition of oxalic acid.¹²⁰ Ozone as the oxidizing agent primarily reacted with lignin because of the presence of electron-rich groups (*e.g.*, double bonds and aromatic rings), and hydroxyl radicals were formed by the reactions between ozone and lignin. These free radicals would attack the β-1,4-glycosidic bonds and sugar ring structures of cellulose, leading to chain scission and cellulose degradation (Fig. 7). Oxalic acid could be a scavenger for hydroxyl radicals. Meanwhile, oxalic acid could decrease the swelling of cellulose. All the above-mentioned factors contributed to the inhibition of cellulose degradation. DMSO has also been shown to be an efficient hydroxyl radical scavenger, and thus cellulose degradation inhibitor in ozone bleaching; however, the brightness of the obtained cellulose would be influenced to some extent.¹²¹

In the work by He *et al.*,¹¹⁹ an active hydroxylamine intermediate (AHI), containing carbamic acid and *N*-hydroxy-ethyl ester (with the concentration of each compound of 5% w/v), was proposed as an additive in the ozone bleaching process to protect cellulose. The crystallinity of the corresponding fibers prepared in the system with AHI increased from 56.4% (for the sample obtained in the system without AHI) to 63.2%, indicating the protective effect of AHI on cellulose, and the pulp brightness was enhanced by 3.8%. It was further proven that the mass transfer as well as diffusion in the bleaching system were improved, while the decomposition of ozone in the system decreased. Thus, the addition of AHI inhibited the self-decomposition of ozone and oxidative degradation of cellulose triggered by free radicals.

2.3 Pulp dissolution for the fabrication of cellulosic materials

To prepare cellulosic materials such as fibers and films, the pulp needs to be dissolved to form homogeneous solutions. Currently, the fabrication of cellulose fibers or films in the wet

spinning industry is prevalently achieved in NMMO. However, several chemical reactions could occur during the manufacturing, causing the formation of byproducts, inducing decomposition of the solvent, cellulose degradation, and inferior material property.¹²² Propyl gallate and an oxa-chroman derivative (*i.e.*, 2,4,5,7,8-pentamethyl-4H-1,3-benzodioxin-6-ol(3-oxa-2,4,5,7,8-pentamethylchroman-6-ol)) were proven to be efficient stabilizers for the cellulose/NMMO solution,^{122,123} acting as scavengers of radicals, *N*-(methylene)iminium ions and HCHO (the intermediates or byproducts in NMMO degradation). However, the strategies and discussions were based on the prevention of the degradation of NMMO (also leading to inhibition of cellulose degradation in some cases), which is not the focus of this review, and thus not mentioned here in too much detail.

Since Rogers' research group reported that ILs are an excellent solvent for cellulose in 2002, this type of unique medium has been widely used for the dissolution of pulp for the fabrication of materials. Also, it seems that the IL strategy is more efficient for the preparation of cellulosic materials due to their designable structure, excellent dissolving capacity, *etc.* The strategies mentioned in Section 2.1.3 for restraining the degradation of cellulose in ILs are also applicable to the dissolution of pulp. The emergence of functional ILs brings promising opportunities for processing cellulosic materials, and the preparation of Ioncell fibers in IL has been commercialized on a 1000 ton/a plant in China.

The above-mentioned strategies developed for the inhibition of cellulose degradation are summarized in Table 2. It was found that a common aspect in the inhibition of cellulose degradation in different processes could be ascribed to the altering interactions between the solvent and the biopolymer with the addition of an additive/co-solvent or by choosing a suitable solvent. According to Table 2, it is clear that there are more efficient methods for preventing the degradation of this biopolymer in IL-involving processes than in traditional ones. Thus, the treatment of lignocellulosic biomass by ILs, either the fractionation of its components or transformation of biopolymers into high value-added materials, are attracting increasing attention.



Table 2 Summary of the methods for the inhibition of cellulose degradation in different processes

Process	Reagents	Methods for inhibition of cellulose degradation	Ref.
Acid, alkali or hydrothermal treatment	Aqueous solution of H ₂ SO ₄ or NaOH or water	Selection of the suitable solvent system (acid or alkali)	53
	Aqueous solution of CH ₃ COOH (acetic acid) and NaClO ₂ (sodium chlorite)	Introducing free lignin	55
Organosolv treatment	Lactic acid	The solvent itself	56
	DMF	The solvent itself	61
IL treatment	1,1,3,3-Tetramethyl guanidine	Addition of morpholine	62
	[DBNH][OAc]	The IL structure and the mild conditions	93
	[AMMorp][OAc]	The IL itself	94
	[N ₆₂₂₂][OAc], [N ₆₆₆₆][OAc], or C ₁₀ (N ₂₂₂ OAc) ₂	The IL structure and cellulose content in the IL	95
	[MTP][MOA]	The IL structure and addition of DMSO	97
	[ATP][MOA]	The IL structure and addition of DMSO	97
	[TBP][Gly], [TBP][Ala], [TBP][Val], or [TBP][DMGly]	Addition of cosolvent, <i>e.g.</i> , NMI, DMSO	98
	[C ₂ mim][OAc]	By controlling treatment temperature and time	96
		Addition of DMAc	99
		Addition of <i>N</i> -methylimidazole	100
		Addition of DMSO	101
		Addition of 3-aminopropanol	102
		Addition of propyl gallate	104
		Addition of DMSO and CaCl ₂	103
Deep eutectic solvent treatment	[Amim]Cl	Addition of amino acid	105
	[C ₄ mim]Cl, [C ₂ mim]Cl or [Amim]Cl	The solvent system and the addition of glycidyltrimethylammonium chloride	114
	Tetraethylammonium hydroxide and carbamides		
Bleaching	Choline chloride and urea (1 : 2)	Addition of anthraquinone	116
	O ₃	Addition of oxalic acid	120
		Addition of DMSO	121
		Addition of active hydroxylamine intermediate	119
Pulp dissolution for material fabrication	NMMO	Propyl gallate or oxa-chromanol derivative as the additive	122

3. Conclusions and perspectives

Cellulose is increasingly important for the preparation of functional materials that have the potential to replace synthetic materials. Lignocelluloses are the main source of cellulose, and mainly contain cellulose, lignin, and hemicellulose. Pretreatment is necessary for the fabrication of value-added materials from lignocelluloses, given that the presence of other compounds (*e.g.*, hemicellulose and ash) in cellulose would affect their properties. Besides, the mechanical properties of cellulose-based materials is closely related to the DP of this biopolymer. Several pretreatment methods, including treatment with acid, alkali, or organics, have been developed for separating lignin- and cellulose-rich fractions. Unfortunately, these traditional fractionation methods are destructive, which would degrade the biopolymers during processing, resulting in reduced value of the resource. The addition of additives (*e.g.*, oxalic acid and AHI) or proper selection of the media and

treatment conditions would alleviate its degradation to some extent. However, the development of more efficient methods, besides simply changing the processing conditions, to protect cellulose from degradation in these pretreatment processes deserves more efforts. Perhaps, understanding the fractionation of lignin, hemicellulose from cellulose as well as degradation of cellulose by the above-mentioned solvents (*e.g.*, organic solvent, water, alkali or acid) at the molecular level would help the design of related systems.

The concerns of the hazards and corrosivity of conventional solvents motivated researchers to turn their attention to IL-involving processes. Hydrogen bonds between the biopolymer and ILs facilitate the dissolution and fractionation process. However, biopolymer degradation also occurred in ILs to some extent during the pretreatment, as indicated by the decrease in the DP of the biopolymer after treatment. In some ILs, such as *N*-allyl-*N*-methylmorpholinium acetate and allyltrimethylphosphonium 2-methoxyacetate, no discernible degradation of



cellulose was observed under the tested conditions, indicating the importance of the IL structure in this process. Decreasing the temperature and shortening the treatment time could also inhibit biopolymer degradation in ionic liquid media. However, a decrease in temperature or time would reduce the efficiency of dissolving and separating lignocellulosic components. Introducing a co-solvent or additive (e.g., DMSO, NMI, and amino acid) in the IL would reduce the viscosity of the medium, facilitating the mass transfer. Importantly, this method was shown to be efficient in inhibiting the degradation of cellulose by changing the ion-cellulose interactions.

Although progress has been made in separating cellulose from lignocelluloses and preparing fibers, films, beads, and hydrogels, challenges exist in improving the mechanical properties of the products from this process, and more work needs to be done in the future.

(1) The relationship between cellulose degradation and IL structure should be revealed based on the fact that the degradation of cellulose in some ILs with certain structures could be prevented, while it occurred in others. The degradation mechanism at the microscopic level should be clarified with the aid of *in situ* spectroscopic characterization and molecular simulation for the control of its degradation. Revelation of the difference in hydrogen bonds between cation-cellulose from that between anion-cellulose and how the hydrogen bonds govern the cellulose orientation in the processing might facilitate understanding of the degradation mechanism. These insights could guide the design of novel ILs for cellulose processing and fabrication of materials.

(2) The cost for the fabrication of cellulosic materials needs to be further reduced, especially for ionic liquid-based processes given that the cost of ionic liquids is much higher than conventional solvents.¹²⁴ Although this type of solvent is recyclable, the recycling energy is high, especially for the separation of ionic liquids and water. Efficient methods have been developed for the recovery of ionic liquids, such as the use of a falling film evaporator¹²⁵ and membrane-based strategy.¹²⁶ However, none of the IL-based pretreatment methods for the fractionation of lignocelluloses are considered to be cost-effective.¹²⁴ Even if 99.6% of the IL (with the price of \$50 kg⁻¹) was recycled, the cost was still higher than the ethanol-involved process.¹²⁷ The price of deep eutectic solvents is lower than that of ionic liquids, but a techno-economic analysis of the fabrication of cellulosic materials using DES has been rarely reported.

(3) Besides, it is important to consider the biodegradability and biocompatibility of the solvents, especially when the cellulosic materials are used for food or medical purposes, to ensure the safety, sustainability and circular economy of the route. Also, the environmental impact of the different strategies (IL, DES, and organosolv treatment) should be comprehensively evaluated based on a pilot study.

(4) Moreover, the real composition of lignocelluloses as well as the lignin structure are dependent on the species, area and season where the biomass grows. Thus, the development of a universal approach to efficiently fractionate the three major biopolymers from various lignocelluloses and inhibit cellulose

degradation is important. This would improve the universality of the proposed technology, avoiding its limitation on certain biomass species.

This article could provide some hints towards developing methods for the fabrication of functional cellulosic materials, which would promote the full utilization of lignocellulosic biomass and alleviate the dependence on fossil resources. We hope more researchers would join this specific field to make dramatic breakthroughs and to put related technologies into practical applications.

Conflicts of interest

There are no conflicts to declare.

Data availability

No new data were generated in this review.

Acknowledgements

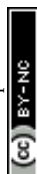
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