Cellulose processing in ionic liquids from a materials science perspective: turning a versatile biopolymer into the cornerstone of our sustainable future

László Szabó, Romain Milotskyi, Gyanendra Sharma and Kenji Takahashi

Shaping cellulose into functional materials entered a new era with the introduction of ionic liquids as novel, green solvents about 20 years ago. As non-volatile solvents with high thermal and chemical stability, ionic liquids can provide an environmentally more benign tunable platform for cellulose processing, compared to existing technologies. The past decades have seen fruitful efforts devoted to the development of materials based on ionic liquid/cellulose processing systems. In this review we discuss the experiences gained, and highlight the emerging applications. In particular, coatings and thin film applications for structural materials (e.g., for packaging), thin film filtration membranes, immobilisation of enzymes, and catalytically active nanoparticles, separator membranes and conductive composites for energy storage and other electronics applications, cellulose/biopolymer green biocomposites, cellulose-based ionogels, hydrogels and aerogels, and cellulose-based or composite fibres will be discussed in detail. We will also take a critical look at the perspectives of this field. The use of a certain grade of technical cellulose, and the purity of the prepared materials should be more carefully justified in the future, as they have an influence not only on the properties of the fabricated material, but also on the economics of the process. Furthermore, to make ionic liquids truly green solvents, and competitive alternatives to existing technologies, more studies are needed on recyclability after material fabrication, and on ways to minimise the energy consumption of such processes, among other issues.

1. Introduction

Cellulose has been with us in various forms since ancient times, as it is the most abundant biopolymer available on Earth. Materials made from wood, cotton and cellulose fibers have shaped our way of surviving, thriving and living (to generate heat and energy, to construct buildings and tools); and determined our cultural and societal development (e.g., think about the use of paper, clothing/fashion). In fact, thinking of the modern age – the first thermoplastic polymer ever made was also derived from cellulose (called celluloid, a nitrocellulose-based plastic containing camphor). Unfortunately, the momentum that cellulose once had in our life has been greatly suppressed by the emerging synthetic polymer industry utilising fossil fuels. Our society became heavily dependent on these finite resources, and our anthropogenic impact grew to its extremities. This brought about irreversible changes on Earth, such as environmental pollution by microplastics, and climate change among other unusual ecological phenomena. While many may think that humanity is already doomed to fail, we argue that it is still not too late to change our way of living: this means turning away from fossil-fuel centred life and shifting to a material-based society centred around bio-based solutions. In this regard, cellulose may come again to our rescue, as it shaped our history time and time again.

Material scientists have long been interested in shaping cellulose into functional materials. The processing and shaping of cellulose entered a new era with the introduction of ionic liquids as novel solvents, first reported in the work of Swatloski et al.20 years ago. Ionic liquids (IL) are a type of molten salts, defined here as those with melting point below 100 °C. They are extensively recognised as green solvents mainly due to their non-volatile nature together with thermal and chemical stability. These solvents gained popularity partly due to their exceptional solvating power and unpre-
cedented tunability, as a number of cation–anion combinations exist leading to various physicochemical properties. The past two decades have seen a number of valuable works devoted to ionic liquid/cellulose processing systems to develop materials for a variety of applications. Nevertheless, there has been no systematic review published so far that would discuss material fabrication and structure in detail with a clear focus on applications. Therefore, it is time to summarise the experiences gained and highlight valuable discoveries in this field. Our aim is to discuss the emerging applications of cellulose-based advanced materials fabricated using ionic liquids from a materials science perspective, in order to give guidance in this field, and stimulate more research on these green cellulose processing systems. We really hope that this review will be helpful also for those interested in materials, but have not yet necessarily worked with ionic liquids before, to promote this topic among a wider readership and thereby facilitate industrial implementations.

2. Solid-state structure of cellulose

Cellulose is a linear-chain polymer composed of repeating β-D-glucopyranose units linked through glycosidic bonds connecting the C4 and C1 carbon atoms of neighbouring groups (Fig. 1). Due to these β-1,4 linkages, adjacent anhydroglucose (AGU) units are rotated 180° in plane along the chain, preferring a C1 chair conformation. Two rings connected through β-1,4 linkages give the repeating disaccharide cellulose units. The number of glucopyranose units is defined as the degree of polymerisation (DP), which is used to describe the chain length of cellulose that can vary depending on the source and extraction method.

There are three –OH groups per glucopyranose units, which partly determines the reactivity of the polymer. These free hydroxyl groups provide exceptional tunability to the molecule, a wide variety of cellulose derivatives have been synthesised with various properties. The amount of substituents on the hydroxyl groups is described with the degree of substitution (DS), which takes a value of 3 for a fully substituted derivative (all hydroxyl groups are occupied). Chain degradation can take place under acidic or enzymatic hydrolysis of the glycosidic bonds, which can eventually lead to cellulose decomposition into monomeric sugars. In addition, one end of the polymer chain is terminated with a monomeric unit that has the original C1–OH group. This part of the molecule is in equilibrium with the aldehyde form, a phenomenon known as mutarotation, and therefore, it is called the reducing end. Although reactions targeting the reducing end has been known for quite long, end-wise modification has recently gained interest for nanocelluloses that can enable novel routes to their directed assembly.

Cellulose is the most abundant optically active natural macromolecule, the stereoregular sequences in its structure enables chiral recognition. Several cellulose derivatives have found success in enantiomeric separation, for example as chiral separation phases for gas and liquid chromatography.

The hydroxyl groups form complex hydrogen bonding network, determining the supramolecular arrangement of cellulose chains with various identified polymorphs and amorphous domains in the solid state. Cellulose polymorphs are

Fig. 1 Molecular structure of cellulose. n: degree of polymerisation.
grouped into 4 types: cellulose I (there are two subtypes which are present concomitantly: Iₐ and Iₐ₁) which can be found in native cellulose, and thermodynamically more favoured cellulose II, III and IV crystal structures can be obtained irreversibly under certain conditions (Fig. 2A). Cellulose II allomorph is the most stable, and it is also the most important for materials science. It forms from cellulose I after mercerisation (treatment with aqueous NaOH), or after dissolving native cellulose followed by precipitation in an antisolvent – a process often called regeneration. The latter method is widely used to shape cellulose into various materials, such as regenerated films, fibres and numerous composites. As notable difference, in the cellulose I allomorph the chains are oriented parallel in the unit cell, while cellulose II has antiparallel chain polarity.⁹,¹⁰ Furthermore, while for cellulose I the hydroxymethyl groups (–CH₂OH) adopt a trans–gauche (tg) conformation (Fig. 2B), they have a gauche–trans (gt) conformation in cellulose II.¹¹,¹² The hydrogen bonding network also differs in these crystal structures. It was reported that the intramolecular hydrogen bonds in cellulose Iₐ are well defined, while the intermolecular hydrogen bonds connecting sheets are rather disorganised.¹¹ In cellulose II a more ordered, single hydrogen bonding system exists that forms a three-dimensional network.¹² In contrast, cellulose III is obtained by treatment of cellulose I or II with liquid ammonia. Cellulose III prepared from cellulose I is referred to as cellulose IIIₐ in contrast to the allomorph cellulose IIIₐ which is prepared from cellulose II. The detailed structural differences between cellulose IIIₐ and cellulose IIIₐ have not been determined.¹³ It was reported that cellulose IV is formed by heat treatment of both cellulose IIIₐ and IIIₐ in glycerol,¹⁴ although some studies debate the existence of this allomorph.¹⁰ Fig. 3 highlights a schematic representation of the allomorphs of cellulose. It was previously reported that cellulose III exhibits enhanced hydrolysis by cellobiohydrolase I, producing cellobiose at rates more than five times higher than from cellulose I.¹⁵ It was also shown that the surface hydrophilicity/hydrophobicity of the regenerated cellulose films can be controlled by post-treatment with liquid ammonia, or hot glycerol, due to the inherent structural anisotropy of the AGU. These results were supported by contact angle measurements as well.¹⁶

Cellulose can be available as raw material from numerous sources, with varying degree of polymerisation and crystallinity. Plant-based cellulose in its purest form can be found in cotton fibres (nearly 90%), this type of cellulose has high degree of polymerisation (DP) (plant fibres have DP values about 800–10 000 depending on the treatment) and crystallinity (crystallinity index ᵇ (CI) ≈ 50–80%).¹⁹,²⁰ Cellulose can be produced as an exopolysaccharide in very pure form by some bacteria. This type of cellulose is called bacterial cellulose or microbial cellulose, it can have very high degree of polymeris-

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Gyanendra Sharma received his PhD in Chemistry from the Indian Institute of Technology Madras. He joined Kanazawa University as Postdoctoral Fellow and now works as a specially assigned Assistant Professor in the Institute of Science and Engineering department. He has worked 10 years on ionic liquids synthesis and their applications, and co-authored 20 articles that include one Indian patent. From 2019, he started working on polysaccharides dissolution and processing. Currently he is working on modification of polysaccharides and developing biodegradable plastic materials.

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**Kenji Takahashi**

Kenji Takahashi received his PhD in 1994 from Hokkaido University. As a researcher belonging to the Ministry of Education, Culture, Sports, Science, and Technology in Japan, he joined the Radiation Chemistry Group of Dr Charles Jonah at Argonne National Laboratory in USA, where he worked from 1993 to 1996. He was then appointed Associate Professor at Kanazawa University in 2003 and Professor in 2012. His research group is currently working on the use of ionic liquids in reaction and material engineering for biomass refineries. He is now Project Leader of COI-NEXT by JST & MEXT.
dissolving pulp is produced after chemical refining (e.g., sulphite pulping or kraft pulping processes) and bleaching.23 Dissolving pulp is characterised by high cellulose content (>90%) and a relatively uniform molecular weight distribution. It is an important form of technical cellulose used commercially in large quantities to prepare cellulose derivatives, regenerated cellulose and other materials. By acidic hydrolysis, microcrystalline cellulose can be produced from dissolving pulp, this material has relatively low molecular weight (DP 25–300), and gained interest for numerous applications (e.g., pharmaceutical, food industry, etc.).

Another intriguing class of cellulose materials can be isolated after disintegrating the cellulose microfibrils into nanosized domains via chemical, mechanical or enzymatic means. The obtained cellulose nanocrystals (CNCs) or nanofibers (CNFs) have found great scientific and industrial interest. Ionic liquids can be also used for the fabrication of these materials from cellulose microfibrils. This topic has been summarised in a recent work,24 and is excluded from this review.

This review will focus on material fabrication processes that are mostly based on the dissolution of cellulose in ionic liquids, except some special cases (ionogels based on gel-forming cellulose derivatives, bacterial cellulose and nanocellulose in combination with non-dissolving ionic liquids, see section 4.7.1).

3. Dissolution of cellulose in ionic liquids

On account of its high molecular weight, and the existence of strong intra- and intermolecular hydrogen bonding network with highly ordered crystalline domains, cellulose has low solubility in common single-component solvents, and is not melt processable. These features posed considerable obstacles for materials scientists aimed at shaping cellulose into functional structures. For long time, heterogeneous systems have been applied to chemically modify cellulose without complete solubilisation,4 in order to prepare readily soluble and melt-processable derivatives (such as thermoplastic cellulose esters soluble in a range of organic solvents). There have been great efforts towards developing solvent systems able to directly dissolve cellulose, facilitating its direct shaping into various materials (fibres, films, composites, etc.), and enabling greener and controllable homogeneous chemical modification. Several aqueous (aqueous inorganic metal complexes, such as cuprammonium hydroxide; molten inorganic salt hydrates, such as LiCl·5H2O; aqueous solution of alkali hydroxides, such as NaOH/urea/H2O; N-methylmorpholine N-oxide (NMMO) monohydrate), non-aqueous (e.g., N,N-dimethylacetamide (DMA)/LiCl; dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF)), and derivatising (e.g., the viscose process through cellulose xanthate; N,N-dimethylformamide (DMF) or DMSO with N2O4) solvent systems have been studied. These solvent systems all have some demerits (e.g., toxicity/non-recyclability/instability), which have been extensively recognised and critically evaluated in the literature.4,25,26 The introduction of ionic liquids as direct, tunable solvents for cellulose opened new horizons in this field, leading to exciting material discoveries and properties that have not been seen before (e.g., see section 4.7.1).

The first group of ionic liquids to dissolve cellulose with melting points below 100 °C were based on dialkylimidazolium cations (see Fig. 4) in combination with chloride, bromide and thiocyanate anions.3 Among the studied ionic liquids, 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) was the most powerful solvent able to dissolve cellulose at 10 wt% concentration when heated to 100 °C, and up to 25 wt% with the help of microwave heating. Furthermore, 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) and 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) were also reported to dissolve cellulose even at high loading around 100 °C (up to 30 wt%).27–29 These ionic liquids have lower melting points and lower viscosities after cellulose dissolution, making them more attractive for industrial application compared to [Bmim][Cl]. Following these initial reports, the effect of the structure of the anion and cation on cellulose solubility was comprehensively studied.30 It appeared that ionic liquids with strong dissolution power contain anions with strong hydrogen bond basicity, such as chloride,1 carboxylate (e.g., formate, acetate, lactate),31–35 amino acid,36 phosphate or phosphonate anions.37 Likewise, ionic liquids containing anions with poor ability to form hydrogen bonds with the hydroxyl groups of cellulose can be classified as non-solvents, anions of hexa-
fluorophosphates ([PF₆]⁺), tetrafluoroborate ([BF₄]⁻), dicyanamide ([N(CN)₂]⁻), and bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻) are some of the examples. Some non-solvents of cellulose containing [MeSO₄] and [HSO₄] anions can dissolve hemicellulose and lignin, these ionic liquids gained appreciable interest for the pretreatment of lignocellulosic biomass.38–40 Effect of the structure of imidazolium cations on the solubility of cellulose was also addressed in several works.41,42 Long alkyl chain substituents, and moieties that increase the hydrogen bond acidity, have in general a negative effect on cellulose dissolution. It should be noted that, although dialkylimidazolium carboxylic ionic liquids, such as [Emim][Ac], may be favourable for industrial application (low melting point and viscosity compared to other cellulose dissolving ionic liquids), they are not inert media for cellulose solubilisation as reaction can take place at the reducing end of the polymer.43 Nevertheless, such side reaction does not take place in [Bmim][Cl].

Pyridinium-based ionic liquids (Fig. 4) that are capable of dissolving cellulose, such as 1-butyl-3-methylpyridinium chloride ([BmPyr][Cl]),44 along with other analogues,45 were also reported. Depolymerisation of cellulose, and other side reactions were recognised in pyridinium-based ionic liquids, e.g., in 1-ethylpyridinium chloride ([EtPyr][Cl]),46 limiting their applications.

Some quaternary ammonium-based ionic liquids (Fig. 4) containing carboxylate anions were also reported as efficient solvents of cellulose. Ammonium ionic liquids with cyclohexyl substituent,47 with dialkoxy functional groups,48 with PEG side chains,49 and derivatives with long alkyl chains50 are some of the reported examples. Benzyl alkylammonium ionic liquids containing acetate anion were also reported to dissolve cellulose.51 The aromatic structure in the latter work was derived from lignin monomers.

Ionic liquids based on the morpholinium cation (Fig. 4) proved also efficient to dissolve cellulose. It was reported that 4-benzyl-4-methylmorpholinium formate ([BMmorf][HCOO]) or acetate ([BMmorf][Ac]) can dissolve cellulose; the advantage of this type of ionic liquid is the moderate to low toxicity as evaluated by Pernak et al.52 Later, N-allyl-N-methylmorpholinium acetate ([AMMorf][Ac]) was introduced as an excellent solvent able to dissolve up to 30 wt% of cellulose at 120 °C without degradation of the polymer.53,54

An intriguing class of ionic liquids to dissolve cellulose are derived from superbases (Fig. 4). First reported examples are based on cations derived from polycyclic amine bases,55 such as 1,5-diazacyclo[4.3.0]non-5-ene ([DBN]) and 1,8-diazacyclonon[5,4,0]undec-7-ene ([DBU]). When paired with carboxylic acids, such as acetate or propionate, cellulose solutions with relatively low viscosities could be obtained.56 Another intriguing example is based on 1,1,3,3-tetramethylguanidine ([TMG]) organic base in combination with short-chain carboxylic acids (formic, acetic, propionic).57 The advantage of superbase-derived ionic liquids, besides their relatively low cost and simple preparation, is that they can be readily distilled and recycled with high purity (e.g., in some cases at much higher pressures than [Emim][Ac], affording more cost-effective recovery of the ionic liquid).58

It should be noted that cellulose solubility in ionic liquids greatly depends on the degree of polymerisation of the starting material, the temperature and method of heating (e.g., microwave-assisted heating can greatly enhance solubility59), the amount of water and other impurities (e.g., for tetrabutylammonium acetate/DMSO system some alkali metal ion impurities have negative effect on the dissolution process58) present in the solvent.60 Furthermore, the addition of aprotic co-solvent to ionic liquids, such as DMSO, DMF, etc., can enhance their dissolution power for cellulose.61–63 This phenomenon might be explained by the decreasing viscosity of the system, which increases the mass transport while not affecting the forming hydrogen bonding network in the solution involving the ionic liquid and the polymer.60 Furthermore, other additives, such as solid acids (e.g., Amberlyst® 15 and Cs₂H₅₋₃PW₁₂O₄₀ in [Bmim][Cl]) or metal chlorides (e.g., ZnCl₂, LiCl, or NaCl in [Amim][Cl]) were reported to enhance cellulose dissolution (i.e., higher cellulose loading/shorter dissolution time/lower temperature). In a report by Yang et al.,64 the addition of an amino acid, L-arginine could prevent cellulose degradation in [Bmim][Cl],
[Emim][Cl] and [Amim][Cl] ionic liquids when dissolution was performed at 130 °C for long time (24 h).

The dissolution mechanism of cellulose in ionic liquids has been the subject of intense discussions and debates over the years. Interested readers are directed to the comprehensive review of Li et al.65 It may be of interest for the reader to understand some of the selection criteria to obtain suitable ionic liquid for dissolving cellulose. It has been known that the difficulties of cellulose dissolution in common organic solvents resides in the strongly concentrated hydrogen bonds present in cellulose, as we mentioned above. There are two major factors that most of the studies consider: a solvent with high hydrogen bond basicity is needed to break down the hydrogen bonding network, and it should be considered that water impurities can negatively affect the dissolution ability of such systems.30,66 Nevertheless, this is not the case for organic onium/inium hydroxide aqueous solutions (OHAS), an intriguing class of ionic liquids that needs the presence of water (upon drying they would decompose). For example, tetrabutylphosphonium hydroxide ([P4444][OH]) and tetrabutylammonium hydroxide ([N4444][OH]) can dissolve cellulose with presence of 40 wt% water.67 It was reported that a weaker hydrogen bonding network around the H2O and [OH] is preferred in these cases (i.e., strong self-associating behaviour of the IL is unfavourable), as followed by the chemical shift of the protons of water molecules.68 It is of utmost importance to develop ionic liquids that can tolerate water content, which is naturally present in biomass.

4. Cellulose-based materials using ionic liquids as processing media

4.1. Coatings and thin films

4.1.1. Conventional processing systems. Cellulose esters, such as cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are excellent additives in coating and ink formulations for a wide range of substrates, including metals, plastics, wood, leather, paper, cloth, etc.69 They are considered superior compared to nitrocellulose that can yellow over time, and is flammable. As an advantage, by properly selecting the degree of substitution and molecular weight of these esters, their properties can be customised for specific applications. Nevertheless, serious environmental concerns surround the application of volatile organic compounds (VOCs) as solvents for preparing the coating formulations. VOCs emissions are subject to strict regulations both in the EU (under the VOC Solvents Emissions Directive29), and in the US (National Volatile Organic Compound Emission Standards under the Clean Air Act21). In order to comply with these requirements, efforts have been made to develop water-dispersible, and radiation-curable (these formulations contain non-volatile monomers acting as both solvent and reactant) cellulose esters as greener alternatives.72–74 Some cellulose esters with high hydroxyl content exhibit enhanced hydrophilicity, and show good properties in waterborne coating formulations. Furthermore, water-dispersible/soluble derivatives can be obtained by introducing carboxyl group to the cellulose ester structure via e.g., grafting acrylic acid onto cellulose esters, reacting them with succinic/phthalic anhydrides, oxidising the corresponding cellulose ester (e.g., using O3 as oxidant), or by preparing cellulose acetoacetate esters.74 In addition, esterification of carboxymethyl cellulose was shown to represent another option to obtain water-dispersible esters for coating applications (e.g., carboxymethyl cellulose acetate butyrate75).

More recently, an unconventional mixed cellulose ester with biomass-derived levulinic acid was prepared, and modified to obtain a carboxymethylamino derivative (Fig. 5(a)), and its application in waterborne coating formulations was demonstrated.76 Based on this progress, fully biobased levulinate ester (Fig. 5(b)) was also synthesised by using alpha-angelica lactone in 1.8-diazabicyclo[5.4.0]undec-7-ene ([DBU])/dimethyl sulfoxide/carbon dioxide organocatalytic reaction system.77

The levulinate ester with moderate DS (1.2 for the levulinate group, and 0.13 for the pseudo-levulinate moiety) showed good properties for possible applications in waterborne film preparations and coatings in limited water environments.

Thin cellulose ester films have found applications in a range of devices (e.g., in liquid crystal displays (LCDs)) as protective optical films, based on their high transparency, unique optical characteristics, together with excellent heat resistance, and mechanical properties.73,74,78 Advanced polariser protective films and optical retardation films can be achieved using cellulose esters by chemical modification or by specific additives.78

Various cellulosic films were developed for food packaging applications. The most notable example is cellophane, which is produced through cellulose xanthate (viscose). The viscose process, however, requires high-quality pulp and suffers from its large environmental footprint due to the use and generation of toxic chemicals and byproducts (e.g., sulphur byproducts,79 heavy metals80). Several alternative methods have been developed using cellulose derivatives (cellulose acetate, methyl cellulose, carboxymethyl cellulose81), nanocellulose films,82 and environmentally more friendly processing systems for cellulose dissolution and regeneration (through cellulose

![Fig. 5](image-url)
strongly correlated with the mechanical properties of the regeneration this step, the regenerated cellulose will be discussed later (see section 5). Favoured, its stability is attributed to ring-stacking obtained. Cellulose II is known to be thermodynamically process. The regenerated cellulose film from [Amim][Cl] showed excellent transparency (90% at 550 nm) according to Table 1 shows a list of selected works devoted to the fabrication of regenerated cellulose films for e.g., packaging application using various ionic liquids such as [Amim][Cl], [Bmim][Cl], [Bmim][Ac] and [Emim][Ac]. Transparent films could be obtained (Fig. 6) with optical transmittance values in some cases greater than that of commercial cellophane (optical transmittance: 85%). The barrier properties (oxygen and water vapor permeability) of the regenerated cellulose films can be controlled by additives such as plasticisers, as demonstrated by Furthermore, in the cellulose/ionic liquid solution active agents can be dissolved such as curcumin (using [Amim][Cl]) to prepare antibacterial regenerated cellulose films, or the regenerated cellulose film can be post-modified to obtain films with antibacterial or antioxidant properties for state-of-the-art active food packaging applications.

The degree of polymerisation (DP) and crystallinity index was strongly correlated with the mechanical properties of the regenerated cellulose films in several works. It was suggested that above a certain level of DP (given as ~450), the mechanical properties are dominated mostly by the crystallinity. In addition, other secondary interactions such as intra- and inter-molecular hydrogen bonding, and hydrophobic stacking interactions are also important in shaping the physical properties of the material. In general, the structure of cellulose changes from cellulose I to cellulose II as a result of the regeneration process (Fig. 7). The crystallinity index also decreases compared to the native cellulose, a more amorphous material is usually obtained. Cellulose II is known to be thermodynamically favoured, its stability is attributed to ring-stacking via hydrophobic interactions and to additional hydrogen bonding interactions between sheets (inter-molecular), forming a three-dimensional structure (see section 2).

The crystallinity of the regenerated cellulose can be influenced by several factors, such as the coagulation process. Östlund et al. dissolved pulp in [Emim][Ac], and studied the effect of the coagulation media (water, ethanol and 1-propanol) on the structure of the regenerated cellulose. When water was used as coagulation medium, mainly cellulose II structure was obtained, while other solvents yielded mostly amorphous films. This was explained by the slow diffusion of [Emim][Ac] to ethanol/1-propanol compared to water on account of their lower solubility for [Emim][Ac]. The hydroxymethyl group in cellulose dissolved in [Emim][Ac] is in gauche–trans (gt) conformation, which can be trapped in this stage during fast solvent exchange (in water). This conformation is beneficial for the formation of the cellulose II structure (hydroxymethyl group is in gt conformation in contrast to native cellulose I with trans–gauche conformation, see section 2, Fig. 2). Furthermore, molecular mobility was suggested to be another factor that can have an effect on the crystallinity of the regenerated films. Zheng et al. studied the effect of ionic liquids with increasing dissolution power ([Bmim][Cl] < [Amim][Cl] < [Emim][Ac]) on the properties of the regenerated cellulose. They found that the cellulose regenerated from [Amim][Cl] solution had the highest tensile strength, which was attributed to its highest crystallinity among the samples. They argued that the higher crystallinity was due to the lower molecular weight of the sample compared to the others, resulting in enhanced molecular mobility aiding molecular arrangement during the regeneration process. The regenerated cellulose film from [Amim][Cl] showed excellent transparency (90% at 550 nm) according to their study. Pang et al. compared the properties of regenerated films from different cellulose starting materials (microcrystalline, cotton linter, pine, bamboo celluloses) dissolved in [Emim][Ac]. They found that pine-derived cellulose sample with high DP (559) and crystallinity index (39.58%) gave the highest mechanical performance (tensile strength of 120 MPa), compared to the poorly performing microcrystalline cellulose that had although high crystallinity index (40.58%), its DP was the lowest (143) among the samples.

Several studies point out the importance of dissolution conditions, such as time and temperature on the structure of the regenerated cellulose, and thus on its mechanical properties. Cao et al. prepared regenerated cellulose films from cornhusk cellulose using [Amim][Cl] and [Emim][Ac] ionic liquids. They realised that the DP decreases with increasing dissolution time and temperature, and the latter had greater effect on cellulose degradation (Fig. 8). Chen et al. reached a similar conclusion when dissolving wheat straw cellulose in [Bmim][Cl]. By optimising the dissolution time and temperature to avoid substantial cellulose degradation (i.e., decrease in DP), a regenerated cellulose film with high tensile strength could be obtained (170 MPa).

Regenerated cellulose films can show brittle characteristics, which can be disadvantageous for packaging applications. To overcome this limitation, several studies focused on including plasticisers (sorbitol, glycerol and carboxymethyl cellulose (CMC)) in the ionic liquid/cellulose solution before the regeneration process using [Amim][Cl] and [Emim][Ac] solvent systems. Interestingly, the crystallinity indices of the regener-
Table 1: Regenerated cellulose films from ionic liquids, for applications as structural materials (e.g., packaging). Degree of polymerisation (DP) and crystallinity index (CI in %) of the starting materials, and the regenerated films. Tensile strength in MPa (elastic modulus in GPa).

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>DP</th>
<th>CI</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>DP</th>
<th>CI</th>
<th>Mechanical properties</th>
<th>Note</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn husk-derived</td>
<td>509</td>
<td>59.6</td>
<td>[Emim][Ac]</td>
<td>4 wt%</td>
<td>80 °C (2 h)</td>
<td>370</td>
<td>47.9</td>
<td>47'' (4.11)</td>
<td>--</td>
<td>Water</td>
<td>88</td>
</tr>
<tr>
<td>Agave-derived cellulose</td>
<td>64.4</td>
<td>4 wt%</td>
<td>[Amim][Cl]</td>
<td>80 °C (4 h)</td>
<td>410</td>
<td>49.5</td>
<td>112'' (6.01)</td>
<td>--</td>
<td>Water</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Microfibrils</td>
<td></td>
<td></td>
<td>[Amim][Cl]</td>
<td>4 wt%</td>
<td>55.9</td>
<td>135'' (8.15)</td>
<td>--</td>
<td>--</td>
<td>Water</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Cotton linter fiber</td>
<td>920</td>
<td>54</td>
<td>[Amim][Cl]</td>
<td>5 wt%</td>
<td>90 °C (30 min)</td>
<td>38</td>
<td>50'' (-)</td>
<td>No plasticiser</td>
<td>Remaining undissolved cellulose microfibrils as &quot;self-reinforcing&quot; agents</td>
<td>Water</td>
<td>91</td>
</tr>
<tr>
<td>Softwood pulp</td>
<td>1460</td>
<td>77.3</td>
<td>[Bmim][Cl]</td>
<td>6 wt%</td>
<td>80 °C (8 h) with static conditions, then 95 °C (3 h) with stirring</td>
<td>32.9</td>
<td>52.8'' (-)</td>
<td>No plasticiser</td>
<td>Effect of plasticiser (glycerol)</td>
<td>Water</td>
<td>92</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td></td>
<td></td>
<td>[Bmim][Cl]</td>
<td>4 wt%</td>
<td>85 °C (7 h)</td>
<td>--</td>
<td>1.3'' (-)</td>
<td>Fluorescent sensing composite</td>
<td></td>
<td>Water</td>
<td>93</td>
</tr>
<tr>
<td>Natural luffa fiber-derived</td>
<td></td>
<td></td>
<td>[Bmim][Cl]</td>
<td>14 wt%</td>
<td>50 °C (7 h)</td>
<td>--</td>
<td>12.51'' (-)</td>
<td>Adsorption study</td>
<td>Nanoporous film</td>
<td>Water</td>
<td>94</td>
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<table>
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<tr>
<th>Type of cellulose</th>
<th>DP</th>
<th>CI</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>DP</th>
<th>CI</th>
<th>Mechanical properties</th>
<th>Note</th>
<th>Antisolvent</th>
<th>Ref.</th>
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<tr>
<td>Wheat straw-derived</td>
<td>580</td>
<td></td>
<td>[Bmim][Cl]</td>
<td>5 wt%</td>
<td>90 °C (12 h)</td>
<td>470</td>
<td>170'' (-)</td>
<td>Effect of dissolution time and temperature</td>
<td>--</td>
<td>Water</td>
<td>95</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>240</td>
<td>51.36</td>
<td>[Emim][Ac]</td>
<td>5 wt%</td>
<td>Stirring at 80 °C (0.5 h); then standing at 80 °C for 1 h (for degassing)</td>
<td>145</td>
<td>40.58</td>
<td>69'' (-)</td>
<td>--</td>
<td>Water</td>
<td>96</td>
</tr>
<tr>
<td>Cotton linter</td>
<td>831</td>
<td>54.01</td>
<td>[Emim][Ac]</td>
<td>819</td>
<td>49.02</td>
<td>819</td>
<td>49.02</td>
<td>120'' (-)</td>
<td>--</td>
<td>Water</td>
<td>97</td>
</tr>
<tr>
<td>Pine-derived</td>
<td>625</td>
<td>46.69</td>
<td>[Emim][Ac]</td>
<td>500</td>
<td>73.8</td>
<td>500</td>
<td>73.8</td>
<td>80'' (-)</td>
<td>--</td>
<td>Water</td>
<td>98</td>
</tr>
<tr>
<td>Bamboo-derived</td>
<td></td>
<td></td>
<td>[Amim][Cl]</td>
<td>3 wt%</td>
<td>90 °C (0.5 h)</td>
<td>354</td>
<td>52.4</td>
<td>152'' (-)</td>
<td>--</td>
<td>Water</td>
<td>99</td>
</tr>
<tr>
<td>Coniferous dissolving pulp</td>
<td>500</td>
<td>73.8</td>
<td>[Emim][Ac]</td>
<td>625</td>
<td>46.69</td>
<td>625</td>
<td>46.69</td>
<td>84.5'' (-)</td>
<td>Addition of plasticiser (sorbitol, glycerol and CMC)</td>
<td>Water</td>
<td>100</td>
</tr>
<tr>
<td>Cotton linter</td>
<td>920</td>
<td></td>
<td>[Emim][Ac]</td>
<td>5 wt%</td>
<td>80 °C (5 min)</td>
<td>451</td>
<td>34.8</td>
<td>84.5'' (-)</td>
<td>--</td>
<td>Water</td>
<td>92</td>
</tr>
</tbody>
</table>

*Degree of polymerisation (DP) and crystallinity index (CI in %) of the starting materials. °Degree of polymerisation (DP) and crystallinity index (CI in %) of the regenerated films. ¦Tensile strength in MPa. °Elastic modulus in GPa.
Fig. 6 (A) Transmittance of cellulose films regenerated from ionic liquids in water as coagulant (the film from [Amim][Cl] has transparency of about 90% at 550 nm). Reproduced from ref. 97 with permission from Elsevier, copyright 2018. (B) Transparent regenerated cellulose film for food packaging application (cotton linter cellulose dissolved in [Emim][Ac], containing 25% glycerol as plasticiser). Reproduced from ref. 98 with permission from Springer Nature, copyright 2013.

Fig. 7 X-ray diffraction (XRD) patterns of native cellulose (coniferous dissolving pulp), exhibiting typical cellulose I structure, and that of the films regenerated from different ionic liquids in water with XRD profiles typical for a cellulose II structure. Crystallinity index: [Amim][Cl] > [Bmim][Cl] > [Emim][Ac]. Reproduced from ref. 97 with permission from Elsevier, copyright 2018.

Fig. 8 Effect of dissolution time and temperature on the tensile strength and degree of polymerisation (DP) of regenerated cellulose (dissolved in [Bmim][Cl], regenerated in water). Reproduced from ref. 95 with permission from Wiley, copyright 2012.
(water, ethanol and 1-propanol). In all cases, pores with radius below 15 nm were observed (spherical pore geometry model). It was also possible to obtain uniform porous structure with pore radius centred around 3 nm, using 1-propanol as coagulant, through repeated drying cycles.

_Ultrathin regenerated cellulose films_ could also be prepared from an [Emim][Ac] solution containing 0.1 wt% cellulose (microcrystalline) that was spin-coated on a silicon wafer substrate, and regenerated using ethanol as antisolvent. AFM image of the ultrathin film indicated the presence of fine nanofibrillar cellulose structure on the surface (Fig. 9).

Radiation-curable coating was also developed using ionic liquid monomers that can dissolve cellulose, this approach is considered a green alternative to coating systems that apply volatile organic solvents. Isik et al. synthesised 2-cholinium lactate methacrylate monomer that dissolved 5–10 wt% cellulose. Photopolymerisation at 368 nm in the presence of 2,2-dimethoxy-2-phenylacetophenon photoinitiator afforded a transparent coating film from the 5 wt% cellulose/ionic liquid solution (Fig. 10). Cholinium-based cellulose-dissolving ionic liquids are advantageous due to their low toxicity, biodegradability, and low cost.

The cellulose/ionic liquid system can be used to form regenerated cellulose coating also for controlled drug release. Song et al. fabricated chitosan hydrogel beads that could be coated with regenerated cellulose by dropping the hydrogels in the cellulose/[Emim][Ac] solution. Regenerated cellulose coating was formed by the diffusion of water from the hydrogel. The fabricated material showed good properties for controlled drug release applications.

### 4.2. Thin film filtration membranes

Cellulosic materials have long history in separation science dating back to ancient times (e.g. just think about cotton cloth for filtering particles). Both natural and physically/chemically modified cellulose were shown to be efficient as adsorbent for water, organic solvents, metal ions and organic substances (such as dyes). Furthermore, cellulose can be converted to various forms of activated carbons with high surface area, extending its efficiency and application to other adsorbates (e.g., gases). Among the chemically modified cellulosic derivatives, cellulose esters proved particularly successful as membranes in the separation field, basically covering all range of the filtration spectrum including micro-, ultra- and nanofiltration, reverse osmosis and dialysis applications.

The introduction of ionic liquids as solvent of cellulose opened the gates for the preparation of novel thin film membranes directly from the natural polymer.

#### 4.2.1. Regenerated cellulose filtration membranes via phase inversion using ionic liquids

Regenerated cellulose films from ionic liquids found applications also in *membrane science*, where *phase inversion* is a well-known way to prepare thin film membranes via immersion precipitation. Table 2 shows selected works devoted to the fabrication of regenerated cellulosic membranes using ionic liquids. The first regenerated cellulose membrane was made by Xing et al. using cellulose acetate dissolved in [Bmim][SCN]. The choice of the ionic liquid was based on its low melting point (≤20 °C) and low viscosity (54 cP at 20 °C), enabling fast dissolution and processing of the cellulose derivative at room temperature. They recognised that the morphology of the resulting membrane is very different from membranes prepared using conventional solvents (such as N-methyl-2-pyrrolidone (NMP) and acetone in their work). While using the latter systems results in macrovoid formation, the membranes regenerated from ionic liquids have a dense structure full with nodules (Fig. 11A). They hypothesised that the mechanism of phase inversion is different when ionic liquids are used, the sequence of events possibly being nucleation growth and gela-

---

**Fig. 9** Atomic force microscopy (AFM) image of cellulose ultrathin film regenerated from [Emim][Ac] solution (0.1 wt% cellulose), using ethanol as coagulant. Reproduced from ref. 100 with permission from Walter de Gruyter GmbH, copyright 2018.

**Fig. 10** Photopolymerisable cellulose coating using a cholinium-based ionic liquid methacrylic monomer as both solvent and crosslinker. Reproduced from ref. 107 with permission from the American Chemical Society, copyright 2013. A part reproduced from ref. 108 with permission from Wiley, copyright 2014.
Table 2 | Regenerated cellulose separation membranes based on the phase-inversion method using various ionic liquids as solvents

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Membrane properties</th>
<th>Membrane thickness</th>
<th>Membrane performance</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate (39.8% acetyl content)</td>
<td>[Bmim][SCN]</td>
<td>10 wt%</td>
<td>50 °C (5 h)</td>
<td>Dense, macrowood-free, self-standing membrane with low porosity (~6%)</td>
<td>8.72 μm</td>
<td>Pure water permeability: 114.14 L m⁻² h⁻¹ bar⁻¹ (at 0.15 MPa), Mean pore size ~39 nm based on neutral solute rejection experiment (PEG/PEO solute)</td>
<td>Water</td>
<td>113</td>
</tr>
<tr>
<td>α-Cellulose (DP 300)</td>
<td>[Amim][Cl]</td>
<td>8 wt%</td>
<td>90 °C (25 min)</td>
<td>Dense, macrowood-free, layered structure. Film casted on PET non-woven fabric</td>
<td>10.5 μm</td>
<td>Pure water permeability: 128.5 L m⁻² h⁻¹ at 0.4 MPa. Antifouling membrane could be developed for filtration of organic dyes with a MWCO less than 700 Da, and for BSA in PBS</td>
<td>Water</td>
<td>114</td>
</tr>
<tr>
<td>Wheat straw-derived (DP 580)</td>
<td>[Bmim][Cl]</td>
<td>5 wt%</td>
<td>90 °C (12 h)</td>
<td>Self-supporting asymmetric porous membrane. Dense thin surface layer with small holes, inner layer with bigger holes. Tensile strength of 170 MPa (6.4% breaking elongation)</td>
<td>~15 μm</td>
<td>Pure water flux 238.9 L m⁻² h⁻¹ at 0.3 MPa. Rejection of BSA ~97%</td>
<td>Water</td>
<td>95</td>
</tr>
<tr>
<td>Bamboo fiber-derived</td>
<td>[Bmim][Cl]</td>
<td>3, 5, 10 wt%</td>
<td>80 °C (8 h)</td>
<td>Self-supporting membranes. Dense, nodular, macrowood-free structure. Denser membrane fabricated from concentrated solution (10 wt%), showing higher rejection towards organic dyes (best performance)</td>
<td>—</td>
<td>Best performance: pure water-flux 150 L m⁻² h⁻¹ (0.4 MPa); about 100% flux recovery ratio, good antifouling performance; maximum organic dye rejection: 89% (for crystal violet)</td>
<td>Water</td>
<td>115</td>
</tr>
</tbody>
</table>

tion in the beginning followed by spinodal decomposition. Furthermore, they thought that macrovoid formation can be avoided on account of the slow water inflow into the system together with the high viscosity of the ionic liquid. Similar membrane morphologies were observed later by others using [Amin][Cl] \textsubscript{114} [Bmim][Cl] \textsubscript{95,115} and [Emim][Ac] \textsubscript{116-119} ionic liquids. The first ionic liquid-assisted regenerated membrane from native cellulose was made by Li et al.\textsuperscript{114} using [Amin][Cl]. They fabricated the \textit{regenerated cellulose membrane} on a polyethylene terephthalate (PET) non-woven fabric as a support. In membrane science, it has been a common strategy to prepare \textit{multilayer membranes} by using a porous material that provides mechanical support without negatively affecting the flux. Nevertheless, it was difficult to prepare multilayer regenerated cellulose membranes in such a way before the discovery of the ionic liquids, due to the lack of cellulose solvent that would not damage the structure of the porous support. Livazovic et al.\textsuperscript{116} prepared regenerated membranes using [Emim][Ac] on a range of porous substrates including the frequently used polysulphone (PSU); polyetherimide (PEI) and polyester nonwoven supports, demonstrating the versatility of ionic liquids in fabricating \textit{multilayer asymmetric membranes} (Fig. 11B). Furthermore, they showed that the prepared regenerated membrane has excellent solvent resistance against tetrahydrofuran (THF), hexane, DMF, NMP and DMA. Note that \textit{self-supporting membranes} could also be fabricated by others,\textsuperscript{95,111,115,116,118,119} similarly to the initial work of Xing et al.\textsuperscript{111} in some cases with excellent mechanical characteristics \textit{(e.g.,} the membrane developed by Chen et al.\textsuperscript{95} had a tensile strength of 170 MPa, and 6.4% breaking elongation). In several works it was observed that by increasing the cellulose concentration in the ionic liquid, denser membranes can be fabricated providing the highest rejection values, and the lowest permeance in organic dye filtration,\textsuperscript{115,118} in case of the neutral solute polyethylene glycol/polyethylene oxide,\textsuperscript{116} and for oil-in-water emulsions.\textsuperscript{117} Furthermore, Sukma and Culfaz-Emecen\textsuperscript{118} found that dye rejection is also correlated with membrane affinity (sorption), attributed to hydrogen-bonding and electrostatic interactions.

### 4.3. Enzyme immobilisation using cellulose/ionic liquid systems

Cellulose, owing to its biologically compatible and nontoxic nature, has received significant interest as a support material for enzyme immobilisation. Table 3 shows selected works on enzyme immobilisation using regenerated cellulose films/beads through ionic liquid processing media. Turner \textit{et al.}\textsuperscript{120} was the first who studied enzyme encapsulation in regenerated cellulose films using [Bmim][Cl] solvent \textit{(via a cold pressing method to avoid thermal denaturation)}, and laccase from \textit{Rhus vernicifera} as a model enzyme \textit{(an oxidoreductase responsible for the biodegradation of e.g., lignin\textsuperscript{122}}). They observed a significant decrease in laccase activity (18% of the activity compared to the free form) for the enzyme-encapsulated regenerated film. They also realised that a hydrophobic ionic liquid \textit{([Bmim][NTf\textsubscript{2}])} "precoating" enables the formation of a more stable microenvironment in the regenerated cellulose film that results in an enhanced enzymatic activity (29% compared to the native form in aqueous solution). It is known that Cl\textsuperscript{−} in neat ionic liquids can form H-bonds with proteins, which can disturb their secondary structure, leading to denaturation. In addition, several enzymes show higher activity in more hydrophobic ionic liquids.\textsuperscript{122} Following the initial experiences on entrapping enzymes in a regenerated cellulose film, Turner \textit{et al.}\textsuperscript{123} investigated enzyme immobilisation on the surface of the substrate, a strategy known to increase enzyme stability. They prepared regenerated cellulose/poly(oxalkeneamine) composites by directly mixing the amine-containing polymer
<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Immobilised enzyme</th>
<th>Immobilisation strategy</th>
<th>Enzyme activity</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>4.75 wt%</td>
<td>Microwave pulse heating</td>
<td><em>Rhus vernicera</em> laccase</td>
<td>Dispersion in the ionic liquid/cellulose solution (at R.T.). A “precoating” step using a hydrophobic ionic liquid improved enzyme activity in the regenerated film. Immobilisation on the surface using pendant amine groups present in the regenerated cellulose/primary-amine polymer composite film. Glutaraldehyde crosslinker</td>
<td>29% (&quot;precoating&quot; strategy) compared to the native form in aqueous solution</td>
<td>Water</td>
<td>120</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>5 wt%</td>
<td>Microwave pulse heating</td>
<td><em>Rhus vernicera</em> laccase</td>
<td>Regenerated cellulose film with polyamidoamine (PAMAM) dendrimer. The crosslinked (using 1,3-phenylene disiocyanate) generation 1 PAMAM dendrimer (lowest amount of amino groups) provided the highest enzyme activity. Covalent attachment via crosslinker using glutaraldehyde resulted in a lower enzyme activity</td>
<td>Close to 50% activity retained compared to the native form in aqueous solution</td>
<td>Water</td>
<td>123</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>6.5 wt%</td>
<td>Microwave pulse heating</td>
<td><em>Rhus vernicera</em> laccase</td>
<td>Co-dissolution of the protein with cellulose and the ionic liquid at 85 °C. Immobilised in the regenerated film</td>
<td>Enhanced enzyme activity compared to the free form</td>
<td>Water</td>
<td>124</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>3.5 wt%</td>
<td>85 °C (6 h)</td>
<td>Horseradish peroxidase and soybean peroxidase</td>
<td>Covalent attachment via crosslinker using glutaraldehyde resulted in a lower enzyme activity</td>
<td>Retained more than 50% of their original activity in the regenerated films</td>
<td>Water</td>
<td>125</td>
</tr>
<tr>
<td>Dissolving pulp</td>
<td>[Bmim][Cl]</td>
<td>7 wt%</td>
<td>100 °C (30 min)</td>
<td><em>Aspergillus niger</em> glucose oxidase</td>
<td>Cellulose-chitosan microspheres as hydrogels coated on magnetic nanoparticles. Enzyme immobilisation by covalent attachment (via chitosan amine group) using glutaraldehyde</td>
<td>Enhanced thermal and storage stability, wider pH optima</td>
<td>Oil with surfactant, addition of ethanol</td>
<td>128</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>[Bmim][NTf2]</td>
<td>Around 6 wt% cellulose acetate in acetone; addition of the ionic liquid (around 20 wt% in the final solution)</td>
<td>No heating</td>
<td><em>Kluveromyces lactis</em> β-galactosidase</td>
<td>Immobilisation of β-galactosidase via triethylenetetramine anchors on the film using glutaraldehyde crosslinker. Improved flexibility and formability compared to cellulose acetate</td>
<td>60% of the initial enzyme activity could be retained after immobilisation</td>
<td>No antisolvent, acetone was evaporated</td>
<td>126</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Ac]</td>
<td>6 wt%</td>
<td>70-80 °C (3 h)</td>
<td><em>Trametes versicolor</em> laccase</td>
<td>Crosslinked regenerated cellulose beads. Covalent surface attachment of laccase via epoxy groups or catechol moieties (dopamine)</td>
<td>Improved thermal stability and pH tolerance compared to the free form</td>
<td>Water</td>
<td>127</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Porcine pancreatic lipase</td>
<td>Magnetic carboxymethyl cellulose nanoparticles functionalised with an imidazolium ionic liquid bearing carbonyl function (PF6− counterion). Enzyme attachment using EDC/NHS activator</td>
<td>Enzyme activity 2.83 folds higher than free lipase (1.43 folds higher without ionic liquid functionalisation)</td>
<td>—</td>
<td>129</td>
</tr>
</tbody>
</table>

Abbreviations: EDC: 1-ethyl-3-(3-dimethylaminopropyl)carboodiimide; NHS: N-hydroxysuccinimide
with the cellulose/[Bmim][Cl] solution. When laccase was attached to the surface using glutaraldehyde crosslinker, for one of the examined primary amine-containing polymers the enzyme retained about 50% of its activity. This increase was attributed to the improvement in the flexibility of the enzyme attached to the surface. Further improvement was achieved with regenerated cellulose films by using polyamidoamine (PAMAM) dendrimers dissolved together with cellulose in [Bmim][Cl]. Interestingly, the highest enzyme activity was observed when the cellulose-PAMAM matrix was crosslinked with 1,3-phenylene diisocyanate, and surface attachment was done by incubating the enzyme with the regenerated film. This strategy outperformed even the frequently applied method of surface attachment via glutaraldehyde crosslinker. Several works prepared bioactive films through similar strategies by directly including horseradish peroxidase/soybean peroxidase in the cellulose/[Bmim][Cl] solution, or by surface attachment of β-galactosidase on regenerated polyanine/cellulose composite films (hydrophobic [Bmim][NTf2] as solvent – note that cellulose acetate was used here instead of cellulose which does not dissolve in this ionic liquid) postmodified using glutaraldehyde as crosslinker. Regenerated cellulose beads proved also efficient in laccase immobilisation as demonstrated by Gu et al. They fabricated crosslinked cellulose beads by dropping a cellulose/[Emim][Ac] solution containing crosslinkers and reactive functions (epoxy and catechol) into water by means of a syringe, and immobilised laccase by simply incubating the enzyme with the prepared beads. Furthermore, magnetic micro/nanoparticle composites gained interest in enzyme immobilisation as they can be separated easily from the reaction media using a magnet. Liu et al. prepared cellulose-chitosan magnetic microspheres (as hydrogels with about 92% water content) using Fe₃O₄ magnetic support in [Bmim][Cl]. The regeneration procedure was different from others in that the [Bmim][Cl] solution was added to an oil-surfactant mixture, followed by the addition of ethanol. The enzyme glucose oxidase (from Aspergillus niger) was anchored on the surface of the microspheres through the amine group of chitosan using glutaraldehyde. Enhanced thermal and storage stability, and wider pH tolerance window was reported as a result of the enzyme immobilisation. Recently, Suo et al. modified carboxymethyl cellulose-coated magnetic nanoparticles with an imidazolium ionic liquid containing carboxyl function and PF₆⁻ counterion. The porcine pancreatic lipase enzyme was immobilised via the pendant carboxyl group on the surface of the nanoparticles by applying EDC/NHS coupling protocol. By investigating the structure of the immobilised enzyme, they proposed that the lid of the enzyme active site is open to a higher degree (low α-helix content), and the enzyme has a more rigid structure (high β-sheet content) compared to the free enzyme or enzyme immobilised without the ionic liquid anchor. They concluded that these features can be responsible for the high enzyme activity and stability.

The structure of ionic liquids has a profound impact on enzyme activity, the dominating factors have been comprehensively studied. In case of cellulose/ionic liquids systems, the ionic liquid needs to be both a good solvent of cellulose, and should have ideally a positive effect on enzyme activity and stability. There has been great interest in designing novel biocompatible, cellulose-dissolving ionic liquids.

### 4.4. Catalytically active cellulose-based composite materials using ionic liquids

Ionic liquids received great interest as tunable platform for the synthesis of various metal nanoparticles with controlled size and shape, sometimes with superior properties compared to those fabricated via conventional methods. Furthermore, ionic liquids are flexible media in catalysis in that they can not only act as solvents, but also as stabilisers, supports and ligands in various multiphase catalytic transformations.

The first work that described the use of an ionic liquid/metal nanoparticle/cellulose system was from Li et al. They studied the thermally-induced formation of gold nanoparticles from an Au(III) salt in BmimCl using cellulose as the reducing agent.

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**Fig. 12.** Enzyme (porcine pancreatic lipase (PPL)) immobilisation on carboxymethyl cellulose-coated magnetic nanoparticles via an ionic liquid-derived anchor. Reproduced with some modification from ref. 129 with permission from Elsevier, copyright 2020.
agent. Gold microparticles with various sizes and shapes could be obtained by modulating the temperature, owing to the cellulose template and the ionic liquid.

It was Gelesky et al. 139 who first recognised the use of cellulose to prepare catalytic polymeric membranes through the immobilisation of metal nanoparticles in combination with an ionic liquid. The polymeric support can reduce the loss of the nanoparticles in the course of the process, provides porous contact in gas/liquid multiphase reactions, and prevents agglomeration of the nanoparticles. The latter phenomenon is a well-known limitation when ionic liquids are used in transition metal nanoparticle catalysis. 134,137 Gelesky et al. 139 dispersed Pt(0) and Rh(0) nanoparticles in cellulose acetate substrate using [Bmim][NTf2]/acetone solvent system, and obtained films of various thicknesses (10–40 μm) by evaporating acetone. The cellulose/ionic liquid/Pt(0) 20 μm thick composite film showed much higher catalytic activity (turnover frequency (TOF): 7353 h⁻¹) for the hydrogenation of cyclohexane than the nanoparticles alone in the ionic liquid (TOF: 329 h⁻¹). This phenomenon was attributed to the stabilisation of the nanoparticles in the cellulose substrate, and to the presence of porous regions conducive to the effective gas/liquid contact. They also noted that the presence of ionic liquid confers higher flexibility and formability to the membrane. Since this initial work, several studies have been reported on the fabrication of cellulose/metal nanoparticle composite films/spheres for catalytic applications, a list of selected works.

Since this initial work, several studies have been reported on the fabrication of cellulose/metal nanoparticle composite films/spheres for catalytic applications, a list of selected works can be found in Table 4.

Wittmar et al. 140 prepared TiO2-doped regenerated cellulose films using [Bmim][Ac]/[Bmim][Cl] ionic liquids (Fig. 13A). The prepared film showed good photocatalytic efficiency in degradation of organic dye when impregnated on the cellulose substrate. However, the process was less effective in bulk solution of the organic dye, which the authors have attributed to the poor solute diffusion owing to the low porosity of the film. In order to improve the performance of the material, in another study from the same group, TiO2-doped porous films were prepared via a freeze-drying process using [Bmim][Ac] solvent 141 (Fig. 13B). They noted the beneficial effect of DMSO as co-solvent to decrease the viscosity of the ionic liquid, and thereby improve the processability. Interestingly, when irradiated with sunlight, dye decomposition was efficient in case of dye-impregnated films. This feature is promising for application as “self-cleaning” material under sunlight. Furthermore, Fe3O4–TiO2 co-doped regenerated porous cellulose film could be also prepared. 142 In this case, it was noted that the presence of magnetite nanoparticle did not affect the photocatalytic activity of TiO2 (although the activity decreased an order of magnitude compared to TiO2 powder). The magnetic, photocatalytically active film can be easily separated from the reaction solution using a magnet (Fig. 13C), and can be also readily heated by alternating magnetic field (AMF, Fig. 13D). Furthermore, in order to aid the recyclability of the photocatalytic regenerated cellulose material, it was further shaped into porous macrospheres in a recent study. 143 In this case, the superiority of [Bmim][Ac]/DMSO medium was reported, as it provided a material with higher porosity, and it also dispersed TiO2 nanoparticles better. In another work by Jo et al., 144 carrageenan, a polysaccharide with sulphate moieties, was added to the TiO2-doped regenerated films ([Emim][Ac] solvent) that resulted in increased adsorption capacity for the cationic organic dye, and lead to an improved degradation efficiency in the photocatalytic reaction. The compatibility of the cellulose/ionic liquid system for other photocatalytically active nanoparticles, such as Bi2WO6, was also demonstrated. 145

These studies clearly show that ionic liquids provide versatile platform for the fabrication of catalytically active cellulose-based composites with tailored structures and properties.

4.5. Cellulose-based separator membranes and conductive composite films for electronic devices, using ionic liquid processing media

4.5.1. Separators for supercapacitors and batteries.

Cellulose has long been used as an insulating separator material in various energy storage devices. 146,147 Separators provide ion diffusion paths between the opposite electrodes through their porous structure while help avoiding short-circuit issues owing to their insulating nature. They are essential components to improve operation safety, lifetime and performance of battery and capacitor devices. The first semi-permeable cellulose membrane was applied in commercial alkaline batteries which still represents a dominating market within the battery industry. 146 In lithium-ion batteries, polyolefin-based separators (e.g., polyethylene (PE), polypropylene (PP)) gained dominance, although efforts have been made to develop cellulose-based membranes for this application. As an environmentally friendly, renewable material with advantageous properties, such as chemical and thermal stability, there has been revived interest in using cellulose materials for developing efficient separators for high-performance energy storage devices.

Ionic liquids provide a versatile platform to prepare nanoporous membranes for energy storage devices from cellulose via the phase inversion method (which we have already mentioned in section 4.2.1). Zhao et al. 148 prepared regenerated cellulose film (22 μm-thick) from cellulose/[Bmim][Cl] solution (4 wt% cellulose content) using water as coagulant. They obtained a film (Fig. 14A) with good flexibility and mechanical properties (tensile strength of 171.5 MPa, elastic modulus of 8.93 GPa). The tensile strength is among the highest reported in the literature (see Tables 1 and 2), this may be attributed partly to the starting cellulose that had a high DP of 1484, and to the processing conditions. The regenerated membrane exhibited high porosity (71.78%) with uniformly distributed mesopores having diameters in the range of 5–30 nm (Fig. 14B). The thermal stability, which is an important parameter in separator applications, remained comparable (thermal degradation starts around 275 °C) to commercial cellulose-based separators. The thermal stability of cellulose membrane is superior compared to commercial polyolefin-based separators (structural changes above 100 °C). 146 Furthermore, high ion-con-
### Table 4  Catalytically active regenerated cellulose/metal nanoparticle films/spheres prepared using ionic liquids

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Nanoparticle</th>
<th>Film properties, observations</th>
<th>Catalytic activity</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>[Bmim][NTf₂]</td>
<td>Around 6 wt% cellulose acetate in acetone; addition of the ionic liquid (around 20 wt% in the final solution)</td>
<td>No heating</td>
<td>Pt(0)/Rh(0)</td>
<td>Metal nanoparticle catalyst immobilisation inside the cellulose acetate-IL composite. Synergistic effect was observed on the catalytic activity of Rh(0) and Pt(0) nanoparticles</td>
<td>Higher catalytic activity of IL/cellulose/nanoparticle composite (TOF 7353 h⁻¹; 20 μm thick film, Pt(0)) than IL/nanoparticle system (TOF 329 h⁻¹, Pt(0)) in hydrogenation of cyclohexane</td>
<td>No antisolvent, acetone was evaporated</td>
<td>139</td>
</tr>
<tr>
<td>Microcrystalline cellulose (DP 200)</td>
<td>[Bmim][Ac]</td>
<td>8, 10, 12, 14 wt%</td>
<td>70 °C (1 h)</td>
<td>TiO₂</td>
<td>Higher viscosity results in a more compact film. Dispersion of nanoparticles is negatively affected by increasing viscosity</td>
<td>Photocatalytic activity demonstrated on films impregnated with methylene blue/ rhodamine B dye solutions (UV irradiation at 365 nm). Less effective in degradation of dye in solution</td>
<td>Water</td>
<td>140</td>
</tr>
<tr>
<td>Microcrystalline cellulose (DP 210–230)</td>
<td>[Bmim][Cl] [Bmim][Ac] (DMSO co-solvent)</td>
<td>8 wt%</td>
<td>90 °C (1 h) 70 °C (5 h)</td>
<td>TiO₂</td>
<td>Porous film could be fabricated via freeze-drying. Macrospheres via drop-wise addition to the coagulation medium</td>
<td>Wet porous films showed the best photocatalytic activity in dye degradation. Dye adsorbed on porous film could be eliminated by sunlight irradiation in 15 min – self-cleaning surfaces</td>
<td>Water</td>
<td>141</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Nanoparticle</th>
<th>Film properties, observations</th>
<th>Catalytic activity</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose (DP 180)</td>
<td>[Bmim][Ac] [IL/DMSO 3/1]</td>
<td>8 wt%</td>
<td>70 °C (5 h)</td>
<td>TiO₂ + Fe₂O₃</td>
<td>Magnetite nanoparticles are more stable in [Emim][Ac]/DMSO system compared to [Bmim][Ac]/DMSO system. Agglomerate size is smaller in the latter one Less macroporosity, denser film</td>
<td>Films have lower photocatalytic activity (about one order of magnitude) compared to TiO₂ powder. Addition of magnetite did not have negative effect on the photocatalytic activity. Degradation of organic dyes</td>
<td>Water</td>
<td>142</td>
</tr>
<tr>
<td>Microcrystalline cellulose (DP 180)</td>
<td>[Emim][Ac] [IL/DMSO 3/1]</td>
<td>6 wt%</td>
<td>70 °C (–)</td>
<td>TiO₂ + Fe₂O₃</td>
<td>Porous macrospheres. Superior TiO₂ dispersion, higher porosity of the resulting spheres in [Bmim][Ac]/DMSO</td>
<td>Higher photocatalytic activity of the spheres from [Bmim][Ac] solutions. Additional adsorption property for heavy metals (demonstrated on Cu²⁺)</td>
<td>Water</td>
<td>143</td>
</tr>
<tr>
<td>Microcrystalline cellulose (DP 180)</td>
<td>[Emim][Ac] [IL/DMSO 3/1]</td>
<td>7 wt%</td>
<td>80 °C (–)</td>
<td>TiO₂</td>
<td>Cellulose/carrageenan/TiO₂ composite film</td>
<td>The negatively charged composite has high adsorption capacity for a cationic dye. Photodegradation efficiency is higher than TiO₂/cellulose composite</td>
<td>Ethanol, water</td>
<td>144</td>
</tr>
<tr>
<td>Waste cotton fabric</td>
<td>[Amim][Cl]</td>
<td>~2 wt%</td>
<td>65 °C (1 h)</td>
<td>Bi₂WO₆</td>
<td>IL/cellulose solution added to Bi₂WO₆/DMA solution prior to the regeneration. Good compatibility between cellulose and the nanoparticle. Layered porous film</td>
<td>Good adsorption and photocatalytic activity to remove organic dyes under visible light irradiation</td>
<td>Water</td>
<td>145</td>
</tr>
</tbody>
</table>

Abbreviations: TOF: turnover frequency.
digital watch in plane or bent state (Fig. 14F and G). About twice the current and discharge time), and can drive a supercapacitors in the literature (Fig. 14E). In addition, it was demonstrated that the micro-supercapacitor can be connected in series (giving twice the operating voltage) or parallel (giving higher than the performance achieved with commercial cell-structure. The presence of cellulose conferred exceptional flexibility and structural stability to the microfiber separator, which could be shaped into various forms without fracture even when wetted with electrolyte (Fig. 15B and C). Furthermore, the composite separator exhibited good thermal stability (200 °C), electrolyte wettability; superior electrolyte retention, ionic conductivity and Li⁺ transference number compared to the glass microfiber film as reference. The assembled LiFePO₄-Li battery cell showed lower charge transfer resistance (102.2 Ω), higher discharge specific capacitance (160.6 mA h g⁻¹ at 0.2 C), better rate capability (145.9 mA h g⁻¹ at 2 C) and cycling stability (108.5 mA h g⁻¹ after 1000 cycles at 2 C) compared to the reference (Fig. 15D). A pouch cell was also assembled to demonstrate a flexible Li battery application. It was concluded that the inhibition of Li dendrite growth and rapid ion diffusion through the composite membrane contributed to the excellent rate performance and cycling stability.

**4.5.2. Conductive composite films.** Various works describe the fabrication of conductive regenerated cellulose films by the addition of a conductive filler (Table 5), such as single-walled and multi-walled carbon nanotubes,150–153 graphene,153 graphite154,155 and silver nanowires.156 The first work on conductive regenerated cellulose films was done by Pushparaj et al.150 They impregnated vertically aligned multiwalled carbon nanotubes (MWCNTs; grown on a silicon substrate via thermal chemical vapor deposition (CVD)
Several works prepared conductive filler/regenerated cellulose composite by including the filler in the ionic liquid/cellulose solution prior to the coagulation process. Interestingly, it was observed by Ye et al.\textsuperscript{157} that graphite can be exfoliated directly in a [Bmim][Cl]/cellulose solution under ultrasonication. They recognised that cellulose can help the exfoliation process, probably through hydrogen bonding between –OH groups of cellulose and the π electrons of graphene. Similar phenomenon was noted later by Zhang et al.\textsuperscript{153} using [Amim][Cl]. They also observed the positive effect of the presence of small amount of single/multilayer graphene (0.1–1 wt%) on the mechanical properties of the regenerated cellulose film. In the regenerated cellulose film, cellulose nanofibers were observed, the diameter of these fibres were affected by the amount of graphene in the composite. At the lowest graphene loading, graphene was nicely dispersed resulting in small cellulose nanofibers, meanwhile increasing the graphene content resulted in graphene aggregation and larger cellulose nanofibers. Toughness and tensile strength were the highest when cellulose nanofibers had the smallest diameter. Furthermore, Chen et al.\textsuperscript{154} studied relatively high amount of graphite loading (10–200 wt%) in regenerated cellulose films, which had negative effect on the tensile properties. In this case, graphite flakes were present in the film, exfoliation by e.g., ultrasonication was not done, graphite flakes were only stirred in the ionic liquid. The prepared graphite/regenerated cellulose film coated with a polypyrrole layer showed good properties as an electromagnetic interference shielding material (electromagnetic shielding effectiveness: 30 dB). Relatively small loading of single walled carbon nanotubes (SWCNT) had also positive effect on the tensile strength and elongation at break, with an increase in the elastic modulus.\textsuperscript{152} Furthermore, Wang et al.\textsuperscript{151} prepared regenerated cellulose/poly(butylene succinate) composite with improved toughness and ductility (compared to regenerated cellulose), the presence of multiwalled carbon nanotubes (0.5–4 wt%) could further improve the tensile strength of the material. In respect to electronics applications of the films, it was noted in several cases that electrical conductivity is limited by the discontinuity of the conductive filler at low concentrations. At high concentrations, agglomeration limits the continuity, and thus the electric contact between filler segments. In order to prevent graphene restacking, and improve the contact points throughout the cellulose matrix, Zhou et al.\textsuperscript{153} prepared graphene/MWCNT/cellulose composite using [Emim][DEP] ionic liquid. At optimum graphene/MWCNT/cellulose loading the regenerated film reached a conductivity of 1124 S m\textsuperscript{−1}, which is the highest reported to the best of our knowledge for a conductive regenerated cellulose film prepared via ionic liquid processing.

4.6. Regenerated cellulose/biopolymer green composites using ionic liquids

Since a synthetic petroleum-derived polymer additive would compromise the green nature of cellulose-based materials, in order to tailor their properties, several works focused on
blending cellulose with other biopolymers to obtain tailor-made biocomposites with improved properties (Tables 6–8).

Some ionic liquids that can dissolve cellulose show good ability to dissolve other biopolymers as well, among them are a range of polysaccharides: chitin/chitosan, glycosaminoglycans (e.g., heparin), starch, agarose, carrageenan, etc.; proteins: silk, wool keratin, collagen; and lignocellulosics: xylan and lignins, etc. This provides unique opportunity to prepare homogeneous blends of cellulose with biopolymers, which lead in several cases to advantageous film properties.

4.6.1. Cellulose/chitin and cellulose/chitosan biocomposites. Several studies considered chitin (β-1,4-linked 2-acetamido-2-glucose) as additive (Table 6), being the second most abundant biopolymer on Earth after cellulose. Takegawa et al.159 dissolved cellulose in [Bmim][Cl], and chitin in [Amim][Br] separately, then mixed the two solutions, followed by the common film casting and regeneration step (water coagulation bath) to obtain finally the composite films. They noted that it is difficult to find an ionic liquid that can dissolve both cellulose and chitin at high concentration. They also found that [Amim][Br] can dissolve chitin, a 5 wt% clear solution could be prepared without deacetylation and degra-
<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Conductive filler</th>
<th>Conductivity</th>
<th>Film properties, observations</th>
<th>Application</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified plant cellulose</td>
<td>[Bmim][Cl]</td>
<td>—</td>
<td>—</td>
<td>Vertically aligned multiwalled carbon nanotubes (MWCNTs) in the film. Polyvinylpyrrolidone nanoparticle coating on the film surface</td>
<td>55 S m⁻¹ at 200% graphite loading. Conductivity attributed to the polyvinylpyrrolidone coating (graphite forms discontinuous segments)</td>
<td>Few tens of microns thick film</td>
<td>Ultrathin flexible supercapacitor, Li-ion battery, hybrid supercapacitor-battery</td>
<td>Ethanol</td>
<td>150</td>
</tr>
<tr>
<td>Cotton linter pulp</td>
<td>[Bmim][Cl]</td>
<td>~4 wt%</td>
<td>100 °C (1 h)</td>
<td>Graphite powder in the film. Polyvinylpyrrolidone nanoparticle coating on the film surface</td>
<td>1.3 × 10⁻⁵ S m⁻¹ (4 wt% MWCNTs)</td>
<td>PBS particles and MWCNTs uniformly dispersed in the matrix</td>
<td>Presence of PBS could improve toughness and ductility. Elastic modulus and tensile strength increase due to MWCNT</td>
<td>Water</td>
<td>154</td>
</tr>
<tr>
<td>α-Cellulose (DP 650)</td>
<td>[Amin][Cl]</td>
<td>—</td>
<td>90 °C (2 h)</td>
<td>Exfoliated graphite (single and multilayers of graphene)</td>
<td>2.5 S m⁻¹ (0.3 wt% graphene loading)</td>
<td>Regenerated cellulose nanofibers in the film</td>
<td>Increasing tensile strength and toughness by addition of graphene (0.1–1 wt%)</td>
<td>Water</td>
<td>151</td>
</tr>
<tr>
<td>Coniferous dissolving pulp (DP 500)</td>
<td>[Amin][Cl]</td>
<td>3 wt%</td>
<td>90 °C (0.5 h)</td>
<td>Ag nanofiber deposited on the surface</td>
<td>Sheet resistance of 29 Ω□⁻¹</td>
<td>HNO₃ treatment improved the transmittance. Optimal treatment gave 80% transmittance</td>
<td>Water</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Cl]</td>
<td>6 wt%</td>
<td>90 °C (24 h)</td>
<td>Single-walled carbon nanotubes (SWCNTs)</td>
<td>Maximum electrical conductivity at 2 wt% SWCNT loading (0.3 S m⁻¹)</td>
<td>Thickness about 30 μm. Uniformly dispersed SWCNTs</td>
<td>1 wt% SWCNT increases elastic modulus by 188%, tensile strength by 129%, elongation at break by 51%. Improved oxygen barrier and water absorption resistance</td>
<td>Water</td>
<td>152</td>
</tr>
<tr>
<td>Wood pulp cellulose (DP 900)</td>
<td>[Emim][DEP]</td>
<td>~1 wt%</td>
<td>90 °C (3 h)</td>
<td>Graphene nanoplatelets (GN) + MWCNTs</td>
<td>Highest: 1124 S m⁻¹ (GN : MWCNT : Cellulose 7 : 3 : 2 by weight)</td>
<td>14–83 μm</td>
<td>After carbonisation, application as electrode in Li-ion battery</td>
<td>Water</td>
<td>153</td>
</tr>
</tbody>
</table>
Table 6  Regenerated cellulose/chitin and cellulose/chitosan binary composite films using ionic liquid processing media

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Biopolymer additive</th>
<th>Film properties, observations</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>10 wt%</td>
<td>100 °C (24 h)</td>
<td>Chitin; 5 wt% [Amin][Br] solution, same dissolution procedure as cellulose</td>
<td>Elasticity of the film decreases with increasing chitin content</td>
<td>Water</td>
<td>159</td>
</tr>
<tr>
<td>Microcrystalline cellulose (DP 124)</td>
<td>[Bmim][Ac]/γ-valerolactone 8/1</td>
<td>8 wt%</td>
<td>90 °C (3 h)</td>
<td>Chitin; 2 wt% solution prior to mixing with cellulose/solvent system</td>
<td>Chitin contributes to the elasticity of the composite; hydrophobicity increases with increasing chitin content</td>
<td>Ethanol, soaking for 4 h, then Soxhlet extraction for 24 h</td>
<td>162</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Dmim][Cl]</td>
<td>4 wt%</td>
<td>75 °C (15 min)</td>
<td>Chitosan; 4 wt% using [Dmim][Cl]/[Hmim][Cl] 9/1</td>
<td>Composite has no porous structure. Chitosan makes the composite brittle; tensile strength improves with cellulose content</td>
<td>Methanol</td>
<td>164</td>
</tr>
<tr>
<td>Cellulose pulp (DP 670)</td>
<td>[Bmim][Ac]</td>
<td>6 wt%</td>
<td>85–95 °C (12 h)</td>
<td>Chitosan; 6 wt% 85–95 °C (3–4 days)</td>
<td>Good miscibility without phase separation</td>
<td>Methanol/water 50/50</td>
<td>165</td>
</tr>
<tr>
<td>Cellulose pulp (DP 630)</td>
<td>[Amin][Cl] with 1 wt% Gly·HCl</td>
<td>3–5 wt%</td>
<td>80 °C (12 h)</td>
<td>Chitosan; 2–3 wt% relative to cellulose, simultaneous dissolution of the two polymers</td>
<td>Antibacterial films could be obtained</td>
<td>Water</td>
<td>166</td>
</tr>
</tbody>
</table>

dation. Hence a binary [Bmim][Cl][Amin][Br] system was used for the formation of the regenerated cellulose/chitin composite. Increasing the amount of chitin in the film appeared to lead to a decrease in the elasticity. They have further improved the mechanical and thermal properties of the chitin/cellulose composite films by changing the coagulation process (Soxhlet extraction in ethanol and water). The simultaneous dissolution of cellulose and chitin was done using [Bmim][Ac], which can dissolve both biopolymers. The authors used γ-valerolactone as biore sourced co-solvent, in order to improve the environmental footprint of the process. A [Bmim][Ac]/γ-valerolactone 8/1 ratio proved sufficient to dissolve the two polymers within relatively short time at low temperature (90 °C, 3 h) compared to other systems. The authors observed that chitin contributed to the elastic properties of the composites, and made them more hydrophobic. The degree of acetylation of chitin only slightly decreased as a result of processing. Chitosan, the deacetylated derivative of chitin has also received significant interest as an additive to regenerated cellulose (Table 6). Xiao et al. investigated different ionic liquid systems for the dissolution of cellulose and chitosan for the preparation of composite blends. They realised that the addition of 1-H-methylimidazolium chloride ([Hmim][Cl]) to 1,3-dimethylimidazolium chloride ([Dmim][Cl]) facilitates the dissolution of chitosan. Interestingly, they noted that chitosan may not be present in its protonated form (it is not a polyelectrolyte), but the increased Cl⁻ concentration may help the dissolution process. They noted that chitosan renders the composites brittle, and the tensile strength increases with increasing cellulose content. Stefanescu et al. pointed out the use of [Bmim][Ac] as good solvent of cellulose and for even high molecular weight chitosan, which otherwise does not dissolve in [Bmim][Cl]. The authors observed the good miscibility of the polymers without phase separation, the formation of hydrogen bonds between cellulose and chitosan was proposed. The composite film exhibited a more amorphous structure compared to the individual regenerated polymer films. In another study, Fu et al. used [Amin][Cl] with the amino acid based ionic liquid Gly·HCl as co-solvent in order to facilitate chitosan dissolution (with relatively high viscosity average molecular weight of about 630 kDa). It was proposed that at relatively high chitosan loading the chitosan/cellulose film is not homogeneous anymore, which lead to a decline in the mechanical properties and thermal stability. Antibacterial films could be obtained owing to the presence of chitosan, which is known to exert bactericidal/bacteriostatic effects against a range of microorganisms.  

4.6.2. Biocomposites prepared using hemicellulose, lignin (synthetic wood), and starch. Hemicelluloses are also among the most abundant polysaccharides in nature. Hemicelluloses are heteropolymers with branched structure, they are present in the plant cell wall together with cellulose. Several works considered them as additives for regenerated cellulose blends (Table 7). Xyloglucan (1,4-β-glucan backbone with 1,6-α-xylansyl substituents that can be further modified with other monosaccharides) is a major hemicellulose that is known to bind
Table 7  Regenerated cellulose/biopolymer composite films (hemicelluloses, synthetic wood (hemicellulose, lignin), starch, natural rubber, and heparin)

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Biopolymer additive</th>
<th>Film properties, observations</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Ac]</td>
<td>1 wt%</td>
<td>100 °C (1 h)</td>
<td>Xyloglycan</td>
<td>At certain composition nanostructuration was observed, which resulted in increased tensile strength and strain at break</td>
<td>Water</td>
<td>169</td>
</tr>
<tr>
<td>Cellulose from spruce via chlorite delignification</td>
<td>[Emim][Ac]</td>
<td>~4 wt%</td>
<td>80 °C (4 days)</td>
<td>Arabinogluconoxylan</td>
<td>Addition of xylan increased the stiffness of the composite at relatively low humidity conditions</td>
<td>Ethanol</td>
<td>170</td>
</tr>
<tr>
<td>Cellulose solution in [Emim][Ac]</td>
<td>[Emim][Ac]</td>
<td>5 wt%</td>
<td>90 °C (3 h)</td>
<td>Xylan from birch wood; softwood kraft lignin from pine</td>
<td>Synthetic wood composite with enhanced hydrophobicity, thermal stability, tensile strength and UV shielding properties</td>
<td>Water</td>
<td>172</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Ac]</td>
<td>5 wt%</td>
<td>80 °C (3 h)</td>
<td>Xylan from birch wood; Alkali lignin; 80 °C (2 h) mixing with the cellulose/[Emim][Ac] solution</td>
<td>Synthetic wood composite. Biodegradability (cellulase) was increased with xylan content whereas decreased with lignin addition. Water vapor solubility was positively correlated with xylan content By optimising the ratio of cellulose/lignin/starch, the mechanical properties could be maximised. The biopolymers exert synergistic effects. Gas barrier properties promising for food packaging applications</td>
<td>Water</td>
<td>173</td>
</tr>
<tr>
<td>Cellulose bamboo pulp (DP 650)</td>
<td>[Amim][Cl]</td>
<td>~2–5 wt%</td>
<td>80 °C (30 min)</td>
<td>Starch, lignin and cellulose dissolved at a 6 wt% total concentration in [Amim][Cl]</td>
<td></td>
<td>Water</td>
<td>175</td>
</tr>
<tr>
<td>Eucalyptus cellulose (via chlorite delignification)</td>
<td>[Bmim][Ac]</td>
<td>5 wt%</td>
<td>100 °C (3 h)</td>
<td>Guuta percha (natural rubber) from Eucommia ulmoides Oliver leaves. 5–15 wt% relative to cellulose. Dissolved in chloroform</td>
<td>Enhanced tensile strength and elongation at break. Decreasing oxygen permeability. Increasing hydrophobicity. Food packaging applications</td>
<td>Water</td>
<td>192</td>
</tr>
<tr>
<td>Cellulose (not specified)</td>
<td>[Bmim][Cl]</td>
<td>10 wt%</td>
<td>Preheating at 70 °C, then microwave heating</td>
<td>Heparin imidazolium salt dissolved in 1-ethyl-3-methylimidazolium benzoate</td>
<td>Nanoporous, blood compatible membrane for renal dialysis</td>
<td>Ethanol</td>
<td>193</td>
</tr>
</tbody>
</table>
Table 8 Regenerated cellulose/natural protein binary composite films (silk fibroin, wool keratin, collagen)

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Biopolymer additive</th>
<th>Film properties, observations</th>
<th>Antisolvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>2 wt%</td>
<td>90 °C (-)</td>
<td>Silk fibroin from Bombix mori</td>
<td>Enhanced mechanical properties (tensile strength, elongation at break), thermal stability and water resistance. Conformational transition from random coil to β-sheet structure. Detailed solid-state NMR study revealing hydrogen bonding between the biopolymers, cellulose structure and secondary protein structure in the composite.</td>
<td>Methanol</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton linter pulp</td>
<td>[Bmim][Cl]</td>
<td>4 wt%</td>
<td>90 °C (-)</td>
<td>Silk fibroin from Bombix mori</td>
<td>Detailed solid-state NMR study revealing hydrogen bonding between the biopolymers, cellulose structure and secondary protein structure in the composite.</td>
<td>Water</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>[Amim][Cl]</td>
<td>10 wt%</td>
<td>85 °C (-)</td>
<td>Silk fibroin from Bombix mori</td>
<td>Detailed solid-state NMR study revealing hydrogen bonding between the biopolymers, cellulose structure and secondary protein structure in the composite.</td>
<td>Water</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>[Bmim][Br]</td>
<td>10 wt% (total polymer)</td>
<td>80 °C (24 h)</td>
<td>Wool keratin, 5 wt% dissolved at 100 °C for 10 h. The cellulose and keratin solutions added at 100 °C, stirred for 12 h</td>
<td>Positive correlation between cellulose crystallite size (cellulose II) and H2O2 concentration. Protein structure is not much affected by the coagulation process.</td>
<td>0-25% aqueous H2O2 solution</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>[Amim][Cl]</td>
<td>9 wt%</td>
<td>85 °C (24 h)</td>
<td>Silk fibroin from Bombix mori (silk fibroin/cellulose fixed at 1/9 weight ratio; 10 wt% total polymer concentration)</td>
<td>Improved thermal stability and elongation at break compared to the individual biopolymers. Hydrogen bonding interactions between the biopolymers.</td>
<td>Aqueous 1% or 25% EtOH and 1% or 25% H2O2</td>
<td>187</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Ac]</td>
<td>5 wt%</td>
<td>100 °C (48 h)</td>
<td>Silk fibroin from Bombix mori (silk fibroin/cellulose fixed at 1/9 weight ratio; 10 wt% total polymer concentration)</td>
<td>Improved thermal stability and elongation at break compared to the individual biopolymers. Hydrogen bonding interactions between the biopolymers.</td>
<td>Water</td>
<td>186</td>
</tr>
<tr>
<td>Microgranular cellulose</td>
<td>[Emim][Cl]</td>
<td>5 wt%</td>
<td>100 °C (24 h)</td>
<td>Wool keratin, 5 wt% dissolved at 100 °C for 10 h. The cellulose and keratin solutions added at 100 °C, stirred for 12 h</td>
<td>Improved thermal stability and elongation at break compared to the individual biopolymers. Hydrogen bonding interactions between the biopolymers.</td>
<td>Water</td>
<td>188</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Emim][Cl]</td>
<td>5 wt%</td>
<td>100 °C (48 h)</td>
<td>Silk fibroin from Bombix mori (silk fibroin/cellulose fixed at 1/9 weight ratio; 10 wt% total polymer concentration)</td>
<td>Improved thermal stability and elongation at break compared to the individual biopolymers. Hydrogen bonding interactions between the biopolymers.</td>
<td>Water</td>
<td>189</td>
</tr>
</tbody>
</table>

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According to their explanation, a regenerated cellulose humidity conditions (at 30% relative humidity (RH)). The addition of xylan made the same woody biomass. They dissolved both biopolymers in extracted from spruce wood, with cellulose obtained from the arabinofuranose and glucuronic acid units) properties. Sundberg et al. 

Fig. 17 (A) Normalised tensile properties of the xyloglucan/cellulose blends. Visual models for composites with (B) continuous cellulose matrix (xyloglucan/cellulose <40%), (C) continuous xyloglucan and cellulose matrix – nanostructured composite (xyloglucan/cellulose ∼40–50%), (D) continuous xyloglucan matrix (xyloglucan/cellulose >50%). Red line represents amorphous xyloglucan domains, black line indicates cellulose semicrystalline domains. (E) AFM phase contrast images of the composites. Reproduced from ref. 169 with permission from Elsevier, copyright 2017.

Several works prepared so called “synthetic wood” composites that contain lignin besides cellulose and hemicellulose, and thus have all the major constituents of lignocellulosic biomass (Table 7). Lignin is the most abundant aromatic bio-

...
4.6.3. Biocomposites with natural proteins: silk fibroin, wool keratin and collagen. Natural proteins have also gained considerable interest for the preparation of binary cellulose/biopolymer composites (Table 8). Silk fibroin, which can be obtained from Bombyx mori cocoons, has been widely studied as a promising additive. This interest has been fuelled by the excellent biocompatibility and biodegradability of this protein, finding various applications in the biomedical field.\(^{176}\) Dissolution of silk fibroin in imidazolium-based ionic liquids was first reported in 2004,\(^{177}\) and regenerated films were also prepared. In this early work, it was already noted that the structure of the regenerated silk fibroin greatly depends on the coagulation solvent and process. Shang et al.\(^{178}\) was the first to study regenerated silk fibroin/cellulose films using [Bmim][Cl] solvent, and methanol coagulation bath. It was recognised that the random coil structure of silk I changes to the β-sheet conformation as a result of the addition of cellulose compared to regenerated silk films, as studied by FTIR spectroscopy. This lead to an increase in the tensile strength of the material, which at a certain composition reached a maximum value (silk fibroin/cellulose 25/75), along with the thermal stability and water resistance. The interesting conformational transition prompted others to further study this binary composite, and find ways to control the developing protein and cellulose structures (most of these works were done by D. Salas-de la Cruz and his co-workers). Stanton et al.\(^{179}\) prepared regenerated silk fibroin/cellulose composite films from [Amin][Cl] solutions of the biopolymers. Their results indicated strong intra- and intermolecular interactions in the blends, which determined the supramolecular assemblies in the matrix as studied by small- and wide-angle X-ray scattering experiments. These features influence the physical and thermal properties of the material. They found that the β-sheet size increases with cellulose content, while increase in silk content results in smaller cellulose microfibril diameter. A more detailed characterisation of the structure and molecular interactions in silk fibroin/cellulose blends (regenerated from [Bmim][Cl] solution) was done by Tian et al.\(^{180}\) through solid-state NMR experiments. Fig. 19 shows the \(^{13}\)C CP/MAS NMR spectra recorded on regenerated silk fibroin, cellulose and cellulose/silk fibroin 3/1 blends as reported in ref. 180. The absence of the peaks at 65 ppm (C6) and 89 ppm (C4), characteristic for crystalline cellulose, indicated the presence of an amorphous cellulose structure. The region between 15–25 ppm is assigned to the Ala C\(_\beta\) (S7) moieties (Fig. 19C), which are sensitive to the secondary protein structure. It can be seen that the amount of well-defined parallel β-sheet increases in the cellulose/silk fibroin blends (see the shoulder around 23 ppm), together with a decrease in the distorted β-turns (peak around 17 ppm). The authors anticipated that the well-defined β-sheet structure could contribute to the enhanced tensile strength and toughness of the binary composite that was widely observed by them and by others in the literature. Furthermore, through \(^1\)H–\(^{13}\)C heteronuclear correlation NMR experiments it was revealed that hydrogen bonding between the –NH group of the protein and the hydroxyl groups connected to the C2 and C3 carbons of cellulose is the most favourable. It was also recognised that some water remains bound to the cellulose structure causing nanoheterogeneity in the system. In a later study by Stanton...
study by the same group, it was revealed that the protein structure can be affected by the type of the anion of the ionic liquid. It appeared that using [Emim][Ac] as solvent leads to the formation of more amorphous protein structure compared to [Emim][Cl].

Wool keratin is another interesting natural protein to consider as additive in cellulose composites. It is an underutilised, low-cost material generated in large quantities as waste by the wool textile industry, and by the food industry through the operation of butcheries. The dissolution of wool keratin in an ionic liquid was first reported by Xie et al. using [Bmim][Cl], and regenerated wool keratin and cellulose/wool keratin blends were also fabricated in this work using methanol as coagulation medium. The properties of the cellulose/wool keratin regenerated films were studied later in detail as a function of the composition by Hameed and Guo. The blends showed higher thermal stability and elongation at break compared to the individual components, these properties reached maximum value at a certain composition (cellulose/wool keratin 60/40). It was also observed through FTIR measurements that hydrogen bonding interactions take place between the biopolymers. In a recent study, the effect of the coagulation bath (1% or 25% EtOH and 1% or 25% H2O2 aqueous solution) on the structure of cellulose and wool keratin was studied using [Emim][Ac] as solvent. It appeared that the amount of β-sheet and α-helical protein structures can be manipulated by the composition, coagulation bath additive and its concentration. The highest amount of α-helices (34.3%) was obtained for 75/25 wool keratin/cellulose composites using 25% H2O2 aqueous solution as coagulation bath, this value is much higher than that of the initial wool keratin sample (8.7%). The highest amount of β-sheets (33.6%) were observed when the coagulation bath was 25% aqueous EtOH solution, this value is close to the initial keratin sample (33.0%). Furthermore, an increase in cellulose crystallinity was observed when higher concentration of H2O2 was used.

Type I collagen is an abundant protein found in vertebrates, it is widely used for biomedical applications, and in the food and cosmetic industry, owing to its biocompatible, biodegradable and edible character. The processing of collagen in an ionic liquid was reported using [Bmim][Cl] for the first time, the dissolution was done at 100 °C (for 6 h). It was recognised through FTIR and XRD analysis that the triple helical structure of collagen is partly destroyed, random coils are formed and possible degradation may also take place. It was also observed that the secondary structure can be significantly influenced by the type of the coagulant (they used water, ethanol, methanol and acetone). Collagen/cellulose blends could also be prepared and shaped into various forms during the coagulation step (films, gels, fibres). Using this processing system ([Bmim][Cl], 100 °C), Wang et al. prepared hydrogel beads by dropping the collagen/cellulose binary solution into water. These beads were used for the adsorption of Cu(n), this process showed a positive correlation with collagen content until a limiting value (a mass ratio of 2/1 collagen/cellulose). Zhang et al. used [Emim][Ac] as solvent to dissolve...
first cellulose at 60 °C (for 4 h), followed by the addition of collagen at room temperature, in order to operate below the denaturation temperature of the protein. They found that the denaturation temperature of the protein increased in the regenerated cellulose/collagen films. Their FTIR results indicated the formation of hydrogen bonds between the polymers. While the addition of relatively small amount of collagen (cellulose/collagen 30/1) increased the thermal stability (maximum decomposition temperature) and mechanical properties (elastic moduli from dynamic mechanical analysis (DMA)), these parameters declined at higher collagen loading (10/1 cellulose/collagen). Cellulose crystallinity also decreased significantly for this higher collagen content. In another study from the same group, it was confirmed that at high collagen loading aggregates exist in the solution (at 10/1 cellulose/collagen; based on dynamic rheology experiments). The lack of homogeneity and phase separation was also observed at high collagen content in the composite films (5/1 cellulose/collagen).

4.6.4. Miscellaneous – biocomposites with various other biopolymers. *Gutta percha*, a natural rubber that consists of long chain trans-1,4-polyisoprene molecules, was considered as additive by Xu et al. Interestingly, this long-chain, high molecular weight polymer was not soluble in the ionic liquid [Bmim][Ac] that was used to dissolve cellulose. Therefore, gutta percha was dissolved first in chloroform, and was then added to the cellulose/ionic liquid solution. Hydrophobicity of the films could be conveniently increased by adding the aliphatic long-chain polysoprene molecule to the matrix. The prepared composite exhibited maximum tensile strength (about 73% increase compared to regenerated cellulose) and elongation at break at a certain loading of the natural rubber (10% relative to cellulose). At this composition the material showed minimum oxygen permeability (1.87 cm$^3$ m$^{-2}$ day kPa at 25 °C). These properties make the prepared composite a promising candidate for food packaging applications.

*Heparin*, is a glycosaminoglycan, a negatively charged polysaccharide that can be found in animals, and is an important medication owing to its anticoagulant properties. Murugesan et al. aimed at fabricating blood-compatible dialysis membranes using regenerated cellulose/heparin composites. The imidazolium salt of heparin was first prepared and dissolved in 1-ethyl-3-methylimidazolium benzoate ([Emim][Ba]). Cellulose was separately dissolved in [Bmim][Cl] (10 wt% concentration), and the two solutions were mixed to prepare the binary composite film using ethanol coagulation bath. The successful entrapment of heparin in the matrix was confirmed by leaching test, showing small amount of loss. The excellent blood compatibility of the membrane was demonstrated via Activated Partial Thromboplastin Time (APTT) and Thromboelastography (TEG) tests. The composite exhibited a nanoporous structure; in an equilibrium dialysis test urea could diffuse through the membrane while bovine serum albumin (BSA) was mostly retained. This biocompatible membrane is promising for renal dialysis application while avoiding systemic heparinisation and the complications associated with that process.

Park et al. in a comprehensive work studied agar, agarose, arabic gum, bacterial cellulose, chitosan, collagen, β-cyclodextrin, dextran, gelatine, κ-carrageenan, lignin, silk, starch, tragacanth gum, xanthan gum and xylan biopolymers as additives to cellulose, using [Emim][Ac] solvent (dissolution at 60 °C, stirring with cellulose for 3 h), and ethanol as coagulant (cellulose/biopolymer 4/1). The composites had diverse physicochemical properties. The water contact angle varied between 90.1° (cellulose/chitosan) and 33.0° (cellulose/κ-carrageenan), thus more hydrophobic and hydrophilic films could be obtained, respectively, compared to cellulose (water contact angle of 52.8°). The high light barrier properties of the lignin/cellulose blend were noted below 400 nm, indicating good UV-shielding properties (Fig. 20A). The chitosan/cellulose film exhibited excellent adsorption capacity towards organic dyes (9.1-fold and 7.9-fold higher adsorption capacity, respectively, compared to cellulose film). The biopolymer composite films showed enhanced adsorption for the enzyme lysozyme.
compared to cellulose films, and for the enzyme pepsin some films showed excellent adsorption behaviour exceeding that of cellulose (e.g., for the cellulose/β-cyclodextrin film). Furthermore, outstanding cell viability (TCMK-1 cells) could be observed for some of the films (superior to cellulose), the highest was achieved for the cellulose/gelatine films (Fig. 20B).

### 4.7. Cellulose-based ionogels, hydrogels and aerogels using ionic liquids

#### 4.7.1. Cellulose-based ionogels. Ionogel is a type of gel where ionic liquids are dispersed in a continuous solid matrix. Although they can be found under several names in the literature (such as ionic gel, ionic liquid gel, ion gel, ion-gel, etc.), the term ionogel rose in popularity in recent works. Cellulose-based ionogels have gained significant interest for a wide range of applications including sensor, actuator and energy storage devices.¹⁹³

The first cellulose-based physical ionogel was reported by Kadokawa et al.¹⁹⁶ in 2008. They prepared a concentrated cellulose solution (15 wt%) in [Bmim][Cl] (at 100 °C for 24 h), which was kept between glass slides for 7 days. The obtained gel was washed with ethanol to remove the excluded ionic liquid. Besides the ionic liquid and cellulose, the ionogel contained considerable amount of water as well (in their work water amount was 8.69–16.0 eq. per glucose unit, whereas ionic liquid content was 2.48–4.68 eq. per glucose unit). According to their explanation, the ionogel forms as water slowly diffuses into the ionic liquid/cellulose solution, creating non-crystalline aggregates as physical crosslinking points. Such materials can be classified as physical ionogels, as they are generated through reversible non-covalent interactions, in contrast to chemical ionogels that contain covalent crosslinks between the polymer chains. The physical ionogel obtained this way can be easily reversed to its original fluid form by heating to 150 °C. Please note that a gel material can be easily identified, and its physical/chemical gel character judged most commonly through oscillatory rheometry or dynamic mechanical analysis (DMA) measurements;¹⁹⁷,¹⁹⁸ unfortunately, such characterisation is not always present in the literature. The physical ionogels that were prepared by others through similar strategy to that of the original work of Kadokawa et al.¹⁹⁶ by dissolving cellulose, are summarised in Table 9.

Cellulose-based physical ionogels are promising materials for solid electrolytes in electrochemical applications. The first study towards this direction was done by Yamazaki et al.¹⁹⁹,¹⁰⁰ on hybrid cellulose/chitin ionogels for supercapacitor devices. Cellulose was dissolved in [Bmim][Cl], while chitin was dissolved in [Amim][Br]. The two solutions were mixed (to reach a cellulose/chitin weight ratio of 3/1), and ionogel was obtained after leaving the sample at room temperature for 4 days. Additionally, the obtained gel was immersed in H₂SO₄ solution in order to have an acidic cellulose/chitin ionogel. Symmetric two-electrode device was assembled using the ionogel sandwiched between activated carbon fiber cloths as electrodes.

#### Table 9: Physical ionogels prepared by dissolving cellulose in an ionic liquid

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Cellulose concentration</th>
<th>Dissolution temperature (time)</th>
<th>Properties, observations</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>15 wt%</td>
<td>100 °C (24 h)</td>
<td>Solution kept between glass slides for 7 days. Finally washing with ethanol</td>
<td>—</td>
<td>196</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>5 wt% and 10 wt% chitin solution in [Amim][Br]</td>
<td>100 °C (24 h)</td>
<td>Cellulose/chitin composite ionogel at 3/1 weight ratio (solutions mixed at 100 °C (1 h))</td>
<td>Supercapacitor</td>
<td>199, 200</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>[Bmim][Cl]</td>
<td>13 wt% (DMA as plasticiser and co-solvent)</td>
<td>100 °C (15 min)</td>
<td>Performance superior to common dielectric elastomers</td>
<td>Actuator</td>
<td>201</td>
</tr>
<tr>
<td>Microcellulose (ARBOCEL® MF 40-7, J. Rettenmaier &amp; Sons)</td>
<td>Phosphonate-based ionic liquid with [Emim] cation/ [Emim][NTf₂]</td>
<td>—</td>
<td>—</td>
<td>[NTf₂] anion helps improving ionic mobility, while the phosphonate anion based ionic liquids form gels with cellulose</td>
<td>Flexible paper-based electronics; electrolyte-gated field-effect transistors (FETs)</td>
<td>202</td>
</tr>
<tr>
<td>Cellulose powder (Sigma Aldrich)</td>
<td>1-methyl-3-propylimidazolium iodide ([Mpmim][I])/ [Emim][SCN] 1/1</td>
<td>5 wt%</td>
<td>90 °C (24 h)</td>
<td>A maximum photoconversion efficiency of 3.33%</td>
<td>Gel electrolyte for dye-sensitised solar cells</td>
<td>203</td>
</tr>
<tr>
<td>Cellulose source not defined</td>
<td>[Bmim][Cl]</td>
<td>8 wt%</td>
<td>Not defined</td>
<td>Dynamic ionogel with tunable properties by adjusting the water content</td>
<td>Demonstrated application as electronic skin (sensing). Other possible applications such as flexible electronics, soft robotics, energy storage and other intelligent devices</td>
<td>205</td>
</tr>
</tbody>
</table>
The supercapacitor device exhibited a specific capacitance somewhat higher than the device with H_2SO_4 electrolyte, together with good cycling stability (100,000 cycles, 80% capacitance retention, performed at 5 A g^-1 current density). The device showed good stability for operating at wide temperature window (-10 – 60 °C). Furthermore, Kunchornsup and Sirivat fabricated cellulose/[Bmim][Cl]/DMA ionogels as electro-active paper for actuator applications. According to their results, several electromechanical parameters of the ionogel were superior to other studied dielectric elastomers at room temperature. However, they identified the slow response speed of the ionogel as a limiting parameter, which should be improved in the future. Fig. 21A shows the experimental setup to study the response of the ionogel towards an applied electric field. According to the authors’ explanation, ionic polarisation of the imidazolium cations, together with polarisation of the hydroxyl groups of the cellulose structure cause the movement (Fig. 21B). Images of the bending and swinging responses are shown in Fig. 21C–F.

Thiemann et al. developed cellulose ionogels for flexible electronics application. They fabricated electrolyte gated field-effect transistors (FETs), using multilayer coated flexible paper substrate in one of the devices (Fig. 22A and B). In their work, microcellulose (ARBOCEL® MF 40-7, from J. Rettenmaier & Sons) was casted on a glass slide first, followed by dropping ionic liquid on the film to obtain an ionogel (with cellulose/ionic liquid mass ratio of 3/70). They used ionic liquids that are based on [Emim] cations and methylphosphonate anions or their mixture with [Emim][NTf_2] (Fig. 22C, note that TFSI = [NTf_2]). [Emim] cations with methylphosphonate anions show good ability to dissolve/gelate cellulose, while [Emim][NTf_2] is a non-dissolving ionic liquid that does not interact with cellulose, and its main role in the system is to increase ionic mobility. It was found that the highest specific capacitance (18.4 μF cm^-2 determined via impedance spectroscopy measurement) was obtained for a binary system with [Emim][MeAc(Me)PO_3] (where [MeAc(Me)PO_3] is 2-methoxy-2-oxoethyl methylphosphonate anion)/[Emim][NTf_2] at 9/1 ratio. These ionogels with high ionic mobility performed well for side-gated FET devices. The authors noted that by increasing the bulkiness of the anion (increasing ethylene glycol chain length) of the ionic liquid, the specific capacitance of the ionogel decreases. These ionogels with lower ionic mobility gave rise to higher electron mobility in spray-coated ZnO FETs.

Salvador et al. studied the application of cellulose-based ionogels as electrolytes for dye-sensitised solar cells. They used a mixture of two ionic liquids: 1-methyl-3-propylimidazolium iodide ([Mpim][I]) that can supply ions for the iodide/triiodide...
A redox couple, a mediator in mesoscopic dye-sensitised solar cells,\textsuperscript{204} and [Emim][SCN] which helps decreasing the high viscosity of the [Mpim][I]/cellulose system, thereby increasing ionic mobility. They found that a 50/50 mixture of the two ionic liquids provides the best photovoltaic performance. Increasing cellulose concentration had a positive effect on the photocurrent and photovoltage, reaching a plateau at 5 wt% cellulose loading. Dissolution of cellulose was done in the ionic liquid mixture together with other electrolyte components (LiI and I\textsubscript{2}) at 90 °C (24 h), followed by gelation at room temperature for one day. 4-tert-Butylpyrididine, another important component for the electrolytes of mesoscopic dye-sensitised solar cells, was added after the gelation process due to its volatile nature. A maximum photoconversion efficiency of 3.33% could be achieved with the fabricated dye-sensitised solar cell containing the quasi-solid electrolyte. Interestingly, the authors observed that the photovoltaic performance increases in the beginning of the operation, and reaches a plateau at a later time. According to their explanation, the movement of ions are hindered by the forming hydrogen bonds with the hydroxyl groups of cellulose. During operation, through the energy input, the energy barrier of these interactions can be overcome, releasing free iodide ions that can contribute to the improvement of the photovoltaic performance.

Zhao et al.\textsuperscript{205} developed a dynamic gel based on the [Bmim][Cl]/cellulose type ionogel. They realised that the ionogel exhibits tunable, and reversible dynamic properties based on the water content (Fig. 23A). At low water content (6 wt%), hydrogen bonds are generated between water and the cellulose molecules leading to a loosely packed Turing type topological network. In this system, ions exhibit low mobility, leading to low ionic conductivity. In addition, this ionogel exhibits excellent self-healing properties owing to the reversibility of the hydrogen bonds, and can adhere strongly to various substrates, e.g., glass, plastics and metals (it can lift more than 30 times its weight ones adhered to the metal substrate). At high water content (32 wt%), more hydrogen bonds are formed and a denser Turing microstructure is generated that exhibits robust toughness with excellent strength and formability (e.g., withstanding repeated rolling and folding). This system contains more hydrated ions with enhanced mobility, leading to a high ionic conductivity (a maximum of 40 mS cm\textsuperscript{-1}). Switching between the two topological networks can be reversibly done by adjusting the water content of the ionogel (drying or increasing the relative humidity), with arriving at the original properties as demonstrated by the authors. Such dynamic ionogel can be useful for a range of applications such as soft robotics and flexible electronics. The authors demonstrated the application for electronic skin (e-skin, see Fig. 23B). The e-skin device was fabricated by sandwiching conductors between two ionogels (by taking advantage of the self-healing property of the material). The e-skin device can be applied for sensing various external stimuli such as breathing patterns, air flow and touching.

We would like to note that the ionic diffusion process that determines the conductivity in [Bmim][Cl]/cellulose type ionogels has been studied in detail by NMR spectroscopy.\textsuperscript{206} It was revealed that two cation diffusion processes can be identified in the matrix: (1) a fast translational diffusion in the pores where the ionic liquid behaves similarly to its bulk structure, and (2) a slow ion diffusion close to the surface of cellulose owing to secondary interactions. The authors noted that the small difference between the ionic conductivity of the ionogel and the bulk ionic liquid can be explained by the presence of the fast, unrestricted diffusion process supplying ions through the channels within the matrix.

Besides common unmodified cellulose starting materials, several works used bacterial cellulose,\textsuperscript{207} methylcellulose\textsuperscript{208–210} and nanocellulose\textsuperscript{211} that have already been proven excellent for the preparation of other types of hydrogels (Table 10). The preparation of the physical ionogel is different in these works compared to previous studies discussed above, in that they do not follow the usual dissolution – gelation strategy. Bacterial cellulose is interesting in that it has high water absorption capacity, a hydrogel can have as high as 99 wt% water content. In the work of Smith et al.,\textsuperscript{207} a bacterial cellulose hydrogel was first prepared, followed by a solvent exchange process with...
ethanol to obtain an alcogel. Ionic liquid/ethanol mixture was added to this alcogel, and after evaporating ethanol, an ionogel could form. In a similar fashion, through co-solvent assisted diffusion (using ethanol, which is then evaporated), chemosensory molecules could also be incorporated in the ionogels for NH$_3$ sensing and H$_2$S detection. This bacterial cellulose ionogel was capable of hosting 99 wt% ionic liquid, which is an outstanding performance compared to other ionogels. The authors selected ionic liquids with [NTf$_2$] anion and which is an outstanding performance compared to other ionogels. Ionic liquid incorporation via co-solvent assisted diffusion and then co-solvent evaporation gives the ionogel another reversible sol–gel transformation.212 The same phenomenon occurs when methylcellulose is dissolved in DMF.211 In the work of Mantravadi et al., Bmpy][NTf$_2$] was used as ionic liquid to fabricate ionogels using methylcellulose. Bmpy][NTf$_2$] does not dissolve methylcellulose, the ionic liquid and methylcellulose was first dissolved separately in DMF. After mixing these solutions at certain ratios, gel formation was achieved by a thermal heating–cooling cycle (heating to 90 °C, cooling to room temperature; gelation occurs due to the presence of DMF). After removing DMF, an ionogel could be obtained with high 97 wt% ionic liquid content. This ionogel did not show thermoreversible sol–gel transition anymore, it remains solid until decomposition occurs (at around 300 °C). The authors highlighted that the film is self-standing and flexible with high moduli (>100 MPa) and high ionic conductivity (>10$^{-3}$ S cm$^{-1}$, room temperature). This procedure was later adapted to

**Table 10** Physical ionogels prepared using non-dissolving (cellulose) ionic liquids and cellulose materials that can form gels

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Ionic liquid</th>
<th>Maximum ionic liquid content</th>
<th>Preparation method</th>
<th>Properties, observations</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacterial cellulose</td>
<td>[Emim][NTf$_2$] or [Bmpy][NTf$<em>2$] or [P$</em>{14,6,6,6}$][NTf$_2$]</td>
<td>99 wt%</td>
<td>First hydrogel, then alcogel after solvent exchange with ethanol. Ionic liquid incorporation via co-solvent assisted diffusion and then co-solvent evaporation gives the ionogel</td>
<td>Ionogels of various shapes and thicknesses can be fabricated by using a template during culturing</td>
<td>Incorporation of chemosensory molecules (via co-solvent assisted diffusion) for ammonia and H$_2$S detection</td>
<td>207</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>[Bmpy][NTf$_2$]</td>
<td>97 wt%</td>
<td>Methylecellulose and [Bmpy][NTf$_2$] dissolved in DMF, then mixed. Gelation occurs after a heating–cooling (up to 90 °C) cycle. DMF removed by vacuum drying</td>
<td>Flexible ionogel with high ionic conductivity (3.3 mS cm$^{-1}$ at 30 °C), wide electrochemical stability window (5.6 V). Thermally stable (no thermoreversible sol–gel transition) until degradation (around 300 °C)</td>
<td>Solid state electrolyte</td>
<td>208</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>[Emim][NTf$_2$]</td>
<td>95 wt%</td>
<td>Same as previous procedure, using DMF as co-solvent</td>
<td>Soft, but mechanically strong (5 MPa storage modulus) gel with good compatibility for the porous carbon nanofiber electrode. High ionic conductivity (5.7 mS cm$^{-1}$ at 25 °C)</td>
<td>Self-standing solid-state supercapacitor</td>
<td>209</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>[G$_4$L][NTf$_2$]</td>
<td>90 wt%</td>
<td>Same as previous procedure, using DMF as co-solvent</td>
<td>High ionic conductivity (0.4 mS cm$^{-1}$ at 30 °C) and storage modulus (60 MPa) at R.T. High thermal (up to 200 °C) and anodic stability (up to 5 V). Li$^+$/iongel/LiFePO$_4$ coin cell with performance comparable to that of the liquid electrolyte</td>
<td>Lithium metal battery</td>
<td>210</td>
</tr>
<tr>
<td>Cellulose nanocrystals (CNC)</td>
<td>Hyperbranched polymeric ionic liquid (PIL) + [Emim][NTf$_2$]</td>
<td>95 wt%</td>
<td>CNC/PIL aqueous suspension first, then solvent exchange with ethanol. [Emim][NTf$_2$]/ethanol diffusion into gel, followed by evaporation of ethanol</td>
<td>High compressive elastic modulus (5.6 MPa) and ionic conductivity (7.8 mS cm$^{-1}$ at 30 °C)</td>
<td>—</td>
<td>211</td>
</tr>
</tbody>
</table>
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prepare [Emim][NTf₂]/methyl cellulose ionogels with 95 wt% ionic liquid content. This ionogel was used as solid electrolyte for symmetric supercapacitors with activated porous carbon nanofiber electrodes. The supercapacitor device exhibited a wide operation window (3.5 V) owing to the ionic liquid, and high gravimetric capacitance (153 F g⁻¹), energy density (around 65 W h kg⁻¹ at 1150 W kg⁻¹ power density) and cycling stability (4% capacitance loss after 20 000 charge–discharge cycles at 1 A g⁻¹ current density) were reported. In the same way of preparation, a solvate (or chelate) ionic liquid/methylcellulose ionogel was also prepared, where the ionic liquid was [G₄Li][NTf₂] (G₄ means tetraglyme here, with 1/1 molar ratio in respect to the Li⁺; 90 wt% ionic liquid content). Glymes can wrap around the Li⁺ ions, resulting in a stable complex; the resulting ionic liquid when combined with [NTf₂] anion has high anodic stability (4.5 V), and exhibits high lithium ion transference number (tₓ⁺ ≈ 0.5; fraction of electric current derived from lithium ions in respect to the total current, it indicates the mobility of lithium ions in the electrolyte). Interestingly, the electrochemical working window of the [G₄Li][NTf₂]/methylcellulose ionogel is about 5 V, somewhat higher than the liquid electrolyte [G₄Li][NTf₂]. The authors attributed this phenomenon to the forming hydrogen bonds between the oxygen groups of glyme and cellulose, thereby protecting them against oxidation. In addition, the ionogel showed high ionic conductivity (4 × 10⁻⁴ S cm⁻¹, 30 °C), storage modulus (60 MPa) and thermal stability (>200 °C). The assembled Li⁺/ionogel/LiFePO₄ coin cell showed comparable performance to that of the cell with the pure [G₄Li][NTf₂] ionic liquid.

Cellulose nanocrystals (CNC) have also been used to prepare ionogels. Lee et al. developed a system that contains a polymeric hyperbranched ionic liquid (PIL; see Fig. 24) and cellulose nanocrystals in order to create a mechanically persistent (high compressive modulus of 5.6 MPa) ionogel that can hold 95 wt% [Emim][NTf₂]. The ionogel exhibited also high ionic conductivity owing to the continuous nanoporous network structure that enables efficient transport of ions throughout the structure. For preparing the ionogel, the authors used similar solvent exchange strategy we discussed above for bacterial cellulose. First, a CNC and PIL binary suspension was prepared in aqueous medium, followed by a solvent exchange process with ethanol. An ionic liquid/ethanol solution was then added, which slowly diffused into the gel. After evaporating the co-solvent ethanol, an ionogel was obtained (4.5 wt% CNC content, 0–2 wt% PIL content).

Chemical ionogels were prepared for example by crosslinking the cellulose solution in ionic liquids using glutaeraldehyde (HCl catalyst) crosslinker (in [Bmim][Cl]) via acrylic acid monomer (AIBN initiator) grafting (Fig. 25A) or cellulose/N,N-diethyl-N-methyl-N-(2-methoxymethyl)ammonium (DEMA)-formate in the presence of water. Furthermore, as another strategy, dual network structure ionogel can also be prepared by polymerising a monomer in the presence of cellulose as it was shown by Rana et al. In their work, cellulose was dissolved in the ionic liquid 1,3-dimethylimidazolium methyl phosphate [DMIM][MeO(H)PO₃] containing small amount of [Bmim][NTf₂] (9/1 weight ratio). During the dissolution process, the hydroxyl groups connected to the C6 carbon atoms get phosphorylated in [DMIM][MeO(H)PO₃] (Fig. 25A). While the role of [DMIM][MeO(H)PO₃] is to dissolve cellulose, [Bmim][NTf₂] increases the conductivity of the ionogel due to the presence of [NTf₂] anion that does not interact with polar groups and exhibits high mobility in the system. The use of [NTf₂] anion is a common strategy seen in the literature to ensure the good ionic conductivity of the ionogels. After the dissolution/modification process, 2-hydroxyethyl methacrylate (HEMA) monomer was polymerised using N,N'-methylenebisacrylamide crosslinker and benzoyl peroxide as initiator (Fig. 25B). The ionogel was used to fabricate flexible symmetric supercapacitors by sandwiching one between two activated carbon electrodes. The flexible supercapacitor device works with high capacitance and other properties.

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Fig. 24 (A) Ionogel containing cellulose nanocrystals, hyperbranched polymeric ionic liquid and [Emim][NTf₂]. (B) Method to prepared the CNC/PIL ionogel containing [Emim][NTf₂]. Note that TFSI = NTf₂. Reproduced from ref. 211 with permission from Wiley, copyright 2021.

Fig. 25 (A) Cellulose dissolution and modification in [DMIM][MeO(H)PO₃] ionic liquid. (B) Polymerisation of HEMA in the presence of phosphorylated cellulose in order to obtain a dual network ionogel. Reproduced from ref. 217 with permission from Elsevier, copyright 2019.
could be operated at 2.5 V within wide temperature range (30–120 °C), exhibiting good performance.

4.7.2. Cellulose-based hydrogels through ionic liquid processing. Hydrogels can be prepared from the corresponding ionogels by simple solvent exchange process with water, when the ionic liquid is water-soluble. In such a way, cellulose physical hydrogels were obtained from [Anim][Cl], [Bmim][Ac]/DMSO, [Emim][Ac], and [Bmim][Cl] solutions. Furthermore, in the work of Kimura et al., 1-ethyl-3-methylimidazolium methylphosphonate ([Emim][MeO][H2PO4]) ionic liquid was used to dissolve cellulose, followed by a coagulation process with methanol, and then solvent exchange with water to obtain the physical hydrogel. Temperature- (e.g., shape is retained in boiling water, no sol–gel transition observed), pH- and solvent-resistant, tough hydrogels could be prepared in this way, even with micrometer-sized patterns by using an appropriate mold. The hydrogel could be post-modified with amino groups, which allowed the immobilisation of negatively charged photoresponsive porphyrin molecules (namely tetrakis(4-sulfonatophenyl)porphyrin) inside the hydrogel via electrostatic interactions.

Cellulose/biopolymer binary hydrogels have also been prepared using polysaccharide additives such as κ-carrageenan, chitosan, guar gum and starch. In the latter work, cellulose sample was extracted from spent tea leaves, and [Anim][Cl] was used as solvent to dissolve cellulose together with the other polysaccharide additives. All of the composites showed cell compatibility without cytotoxicity, and some biopolymer-specific functional properties (such as specific mechanical and physicochemical characteristics) could be also observed. Furthermore, okara-derived (food residue from soybean industry) cellulose hydrogels containing hemicellulose (remained after the extraction process) were prepared by Wu et al. They reported on an improvement in the performance of the hydrogel (e.g., gelling behaviour, mechanical properties) upon TEMPO oxidation of the extracted okara cellulose.

Ionic liquids can be also useful for dissolving drugs and cellulose together in order to obtain drug-loaded hydrogels after the gelation and solvent exchange process. The use of ionic liquids can be especially advantageous for drugs with poor solubility profile in other common solvents. As an example, Santra and Sen dissolved cellulose and selenourea in [Emim][Ac]/DMSO solvent (1/2) system, in some cases together with tannic acid or l-methionine, to obtain drug-loaded hydrogels with promising sustained release profile.

Hydrogels obtained via ionic liquid processing can be hosts for catalytic nanoparticles. Su et al. prepared wheat straw cellulose/feather protein physical hydrogel after dropping their [Bmim][Cl] solution into water. Magnetic hydrogel was then obtained by a co-precipitation technique using mixed solution of Fe2+ and Fe3+. Subsequently, the hydrogels were immersed in a solution of copper salt in order to obtain a magnetic hydrogel loaded with Cu nanoparticles after in situ reduction with NaBH4. The magnetic hydrogel showed good catalytic activity for the reduction of 2-nitrobenzoic acid. The hydrophilic functional groups of cellulose and the feather protein

(e.g., –OH, –NH2, –COOH) may have helped the immobilisation of the metal nanoparticles in this case. FTIR results indicated for example the presence of coordination between –COO– groups and Cu2+. In addition, Li et al. dissolved cellulose (cotton pulp) in the 1,1,3,3-tetramethyl guanidine [TMG]/DMSO/CO2 superbase solvent system. Subsequently, cellulose was acylated with cyclic anhydrides (succinic anhydride and pyromellitic dianhydride), in this process 1,1,3,3-tetramethyl guanidine acted as a catalyst and provided the positive counter ion for the forming carboxylate group (Fig. 26). The addition of bicyclic anhydrides was essential to the formation of a chemically crosslinked 3D network leading to a chemical hydrogel. The guanidine moiety is known to exhibit good coordination ability with transition metals. Pd nanoparticles were immobilised in the hydrogel by soaking in the solution of the metal salt (PdCl2), followed by a reduction step (NaBH4). The hydrogel showed good catalytic activity and reusability in the reduction of 4-nitrophenol. The authors attributed the absorption, dispersion, and stabilisation ability of the hydrogel for hosting Pd nanoparticles to the presence of the guanidine moiety.

Conductive chemical hydrogels were fabricated by Liang et al. using [Bmim][Cl]. Cellulose/[Bmim][Cl] solution was crosslinked with N,N-methylene bisacrylamide (benzoyl peroxide initiator), followed by solvent exchange with water to form the chemical hydrogel. Polyppyrrole was in situ polymerised in the hydrogel that was soaked in ferric chloride/sodium p-toluenesulfonate solution (TsONa) first, followed by the addition of the monomer pyrrole. The hydrogel doped with TsONa exhibited good electrical conductivity (∼8 mS cm⁻¹, RT).

Highly tough cellulose/reduced graphene oxide physical hydrogels were prepared by Xu et al. In their work, cellulose was dissolved in [Bmim][Cl], while in a separate experiment graphene oxide was reduced in [Bmim][Cl] using ascorbic acid. The two liquids were mixed and then regenerated in water in
order to obtain the hydrogel by complete solvent exchange (Fig. 27A). At a certain reduced graphene oxide content (0.5 wt%), high compression modulus was observed (~19 MPa) compared to the reference cellulose hydrogel (~5 MPa). After freeze-drying process, mechanically strong cellulose/reduced graphene oxide aerogels could be obtained (Fig. 27B and C).

4.7.3. Cellulose-based aerogels through ionic liquid processing. Cellulose aerogels/foams can be obtained after removing the liquid from the gels. The removal process has been shown to have a critical impact on the developing porous architecture. Tsioptsias et al.230 developed a high-pressure CO2 processing technique for foaming of a cellulose hydrogel regenerated from [Amin][Cl] solution. After the foaming process, the material was subjected to a freeze-drying step at ~2 °C, affording an aerogel with micrometer-size pores. Through another strategy, a methanogel was prepared first, after coagulating the cellulose/[Amin][Cl] solution in methanol, and removing the liquid. Methanol was removed from the gel via supercritical CO2 drying. This process yielded a nanoporous aerogel with pore sizes falling in the micro (<2 nm) and mesopore range (2–50 nm). Furthermore, nanoporous aerogels could be obtained later by Deng et al.231 using a fast cooling process with liquid nitrogen on a regenerated hydrogel (from cellulose/[Bmim][Cl] system), followed by lyophilisation. The obtained aerogel had mainly mesopores (2–50 nm). The authors pointed out that a slow freezing process at 0 °C does not yield nanoporous material due to the formation of larger ice crystals. Oven drying does not yield a porous material either. It was also shown that the mechanical properties of the aerogels are dependent on the starting cellulose material; for example, when cellulose pulp is used with high degree of polymerisation, the aerogel can have significantly higher compression modulus compared to a sample prepared using microcrystalline cellulose.232 In general, freeze drying and supercritical CO2 drying methods are widely used in the literature to prepare aerogels.233

The prepared cellulose aerogels have usually no directional ordering, they possess an isotropic structure. Hierarchically assembled, ordered structures are omnipresent in nature, such features are known to give extraordinary functionality and mechanical properties to these materials, a good example for this is bamboo.234 Design of anisotropic gels and aerogels is of great interest as it could allow the directional control on e.g., cell growth, mechanical properties, and other physical phenomena (e.g., diffusion of molecules, propagation of light, etc.). Efforts towards anisotropic cellulose gels/aerogels regenerated from ionic liquid solution have been made by Plappert et al.235 They dissolved cellulose in the superbase-derived ionic liquid 1,1,3,3-tetramethylguanidinium acetate ([TMGH][Ac]). Cellulose was dissolved in [TMGH][Ac] at 100 °C, and poured into porous molds to allow the homogeneous diffusion of ethanol into the [TMGH][Ac]/cellulose system at 20 °C. Under this condition, the ionic liquid is in a “supercooled” state (melting point of [TMGH][Ac] is ~90–97 °C), exhibiting highly viscous glassy state. Therefore, the diffusion of the antisolvent ethanol is significantly deaccelerated compared to other systems. Furthermore, [TMGH][Ac] has poor miscibility with ethanol, which also contributes to the slow deaccelerated de-mixing of cellulose and the ionic liquid. There is a diffusion zone that slowly progresses as antisolvent induced de-mixing occurs at the interface, where cellulose supramolecular assembly takes place as it slowly coagulates. This process results in onion-like concentrical cellulose layers with higher degree of orientation of the fibrillar network structure from the core towards the skin layer (Fig. 28). The obtained aerogels after the supercritical CO2 drying process have high crystallinity index (~72%; cellulose II polymorph), with a fibrillar strut size of about 2.5 nm. The orientation-dependent compression properties of the obtained aerogels have been also studied.236 When compression test was done parallel to network orientation, the aerogel exhibited more resilience compared to the perpendicular direction.

Addition of a surfactant to the cellulose/ionic liquid solution can help the formation of large μm-sized pores, as reported by...
An et al. In their work, cellulose was dissolved in [Amin][Cl], followed by the addition of sodium dodecyl sulphate (SDS) and vigorous stirring to facilitate foaming. By adjusting the cellulose concentration and the amount of the air phase, a stable biphasic system could be obtained. After the regeneration process with water and freeze-drying, ionic liquid was added to the system again (to a final concentration of 50.1 wt%). The presence of the ionic liquid imparted exceptional superelasticity and ionic conductivity to the system. The authors demonstrated the application of this flexible cellulose/ionic liquid aerogel as a wearable sensing device monitoring motions such as pulse, walking, speaking, etc.

Lignocellulose aerogels have also been fabricated using ionic liquids, these composites contain lignin and hemicellulose fraction in addition to cellulose. Please note that in other works such composition is referred as "synthetic wood". There is a discussion about these composites above in section 4.6 (regenerated cellulose/biopolymer green composites using ionic liquids). The first work in this topic was done by Aaltonen and Jauhiainen. They prepared cellulose, sodalignin, cellulose/sodalignin, cellulose/sodalignin/xylan and spruce wood aerogels using [Bmim][Cl] as solvent, and aqueous ethanol coagulation bath. They pointed out that gels could be obtained at specific biopolymer compositions, and the dissolution time and ethanol concentration in the bath appeared to be also important for the gelation process. The aerogels were then produced after solvent exchange with ethanol, followed by drying with supercritical CO₂. The aerogels had an open pore structure with various morphologies (macropore size depending on the composition), and contained also mesopores. In an interesting work by Li et al., a cyclic freezing-thawing process (from −20 °C to 20 °C) was applied on the wood/[Amin][Cl] solution, followed by coagulation in water bath, and solvent exchange with acetone prior to a supercritical CO₂ drying process. They noted that the freezing-thawing process was important to obtain a gel that can keep its form. According to their explanation, the cyclic freezing-thawing process acts as a physical crosslinker to form a continuous 3D network. Later, an ultralow freezing-thawing process was also developed using liquid nitrogen (from −196 °C to 20 °C), in this way a mesoporous lignocellulose aerogel could be obtained. Th authors argued that the formation of smaller ionic liquid crystals during the fast ultralow freezing process compared to the other freezing process (from −20 °C to 20 °C) facilitates the development of the 3D fibrillar network with mesopores. The fabricated lignocellulose aerogel showed good thermal insulating properties, and exhibited also good performance for noise reduction.

Cellulose aerogels have found application as adsorbent materials. In order to develop an aerogel with selective adsorption to specific contaminants, the surface of the aerogel can be further modified. As an example, Zhang et al. developed superhydrophobic and superoleophilic aerogel by plasma treatment followed by silanisation of the cellulose hydroxyl groups.

Various nanomaterials can be also incorporated into the cellulose/ionic liquid system to impart additional functions to the aerogels, such as improved thermal insulation by developing cellulose/nanosilica composite aerogels, or incorporating quantum dots to obtain gels/aerogels with photoluminescence properties. In the latter case, the photoluminescence wavelength could be controlled in the visible light spectrum, thus gels/aerogels with colour-tuned photoluminescence could be developed.

It should be noted that the cellulose aerogels can be converted to carbon aerogels through thermal treatment. Carbon aerogels have various applications in energy storage, catalysis, water treatment, gas storage/separation and thermal management.

4.8. Cellulose-based fibres from ionic liquid solutions

Fibres fulfil important functions in living systems, and have been used by humans for creating structural materials since prehistoric times. These high aspect ratio structures possess intriguing properties for materials science, such as a combination of flexibility with strength (exceptional formability), high surface area, network formation possibilities, and small defect size, just to mention a few. Recently, smart textiles comprising of fibres with functional properties came into the forefront, which may change our approach towards personalised healthcare, and the way we communicate with electronic devices in the future.

Textile fibre filament systems for and households have a diameter of about 5–50 μm, although finer fibres with diameters down to about 3 μm have been also achieved with common spinning techniques, they are referred to as microfibres in the literature. Nanostructures sub-micrometer diameters can be produced through electrospinning technique (some common spinning techniques are illustrated in Fig. 29), which usually yields nonwoven fabrics (random web structure with intertwined filaments).

Synthetic and natural cellulose fibres make up a large share of the textile market. The textile industry is continuously growing, and so is the demand for cellulose fibres. Since the production of cotton has several limitations, man-made synthetic cellulose fibres are expected to fill the gap to meet the market demand in the future.

4.8.1. Conventional processing systems to fabricate synthetic cellulose fibres

Synthetic cellulose fibres are generally fabricated by dissolving cellulose in a certain solvent, followed by a spinning method where the solution is pumped through a spinneret into a coagulation bath. Commercial synthetic cellulose fibres for the textile industry are predominantly produced through the viscose process using a wet-spinning technique (Fig. 29). In this process, cellulose is reacted with CS₂ to form cellulose xanthate that can be dissolved in aqueous sodium hydroxide. This solution is spun directly into an acidic coagulation bath containing zinc salts resulting in the decomposition of the metastable intermediate cellulose xanthate and the formation of high-quality pure cellulose fibres. The viscose process generates large amount of hazard.
4.8.2. Ionic liquid/cellulose solution for fibre production.

Early works on fibre spinning using ionic liquid/cellulose systems focused on halide-based first-generation ionic liquids, such as [Bmim][Cl] and [Amin][Cl]. By using a dry-jet wet spinning process (like the Lyocell process), fibres with high tenacity (textile strength) could be obtained compared to Lyocell fibres. Nevertheless, several disadvantages of these systems were recognised: high processing temperatures result in cellulose degradation; and the corrosive nature of the chloride ion poses problems for the spinning apparatus. Later, the use of acetate-based ionic liquids appeared to be a better choice. Kosan et al. studied the dry-jet wet spinning of cellulose using [Bmim][Cl], [Emim][Cl], [Bmim][Ac] and [Emim][Ac] ionic liquids. They noted that the viscosity of the [Bmim][Ac] and [Emim][Ac] solutions are much lower compared to the other systems (Lyocell process, [Bmim][Cl] and [Emim][Cl]), and compensated the difference by increasing the loading of cellulose (to about 20 wt%; e.g., this is 13.5 wt% for the Lyocell process). Although the tenacity of the fibres prepared using [Emim][Ac] and [Bmim][Ac] remained lower compared to [Bmim][Cl]/[Emim][Cl], the values were still somewhat above that of Lyocell fibres. 1-Ethyl-3-methylimidazolium diethyl phosphate ([Emim][DEP]) was also studied as a promising solvent for fibre spinning. When dry-jet wet spinning was used to fabricate the fibres, unlike Lyocell fibres and those produced from [Emim][Ac], the fibres obtained using [Emim][DEP] did not show the typical fibrillation behaviour in the wet state. Dry-jet wet spinning process yields fibres with high crystallinity in contrast to fibres obtained via the wet-spinning process. The interactions between the crystallites are not strong in the lateral direction, which results in the typical fibrillation of such (dry-jet spun) fibres in the wet state. Interestingly, Zhu et al. could prepare mechanically strong fibres via dry-jet wet spinning from microcrystalline cellulose (DP: 200–220) using [Emim][DEP]. Microcrystalline cellulose is mostly used for applications that do not require high mechanical performance, due to the low molecular weight of this type of cellulose. They used high cellulose concentration (>12 wt%) in [Emim][DEP] where the solution showed anisotropic behaviour. Recently, wood pulp cellulose was spun into filaments on laboratory-scale fibre production line (composed of a dissolving and spinning kettle, multihole spinneret, coagulation bath, stretching bath, washing bath, dryer, winder) with the dry-jet wet spinning method using [Emim][DEP]. The authors used relatively low cellulose concentration (8 wt%, 90 °C spinning temperature), and obtained mechanically strong fibres by adjusting the draw ratios (three stretching draws). Furthermore, Zhang et al. compared [Bmim][Cl], [Emim][DEP] and NMMO.H₂O in a dry-jet wet spinning process using dissolving pulp. According to their results, the fibrillation resistance was as follows: [BMIM][Cl] > [Emim][DEP] > NMMO.H₂O. They noted that fibres with denser structure and higher mechanical strength could form from [Bmim][Cl].

Fig. 29 Common spinning techniques for fabricating synthetic cellulose fibres from solutions. Other methods, such as dry-jet spinning uses no coagulation bath, and for melt spinning the polymer melt is extruded through the spinneret (note that this is not possible for cellulose itself).
Thus far, the most successful ionic liquid for the production of synthetic cellulose fibres has been 1,5-diazabicyclo [4.3.0]non-5-eneum acetate ([DBNH][Ac]), a non-imidazolium superbase-derived ionic liquid introduced by researchers from Aalto University and Helsinki University.\textsuperscript{259–261} The process, denoted as Ioncell-F, produces fibres via a dry-jet wet spinning process with properties better or comparable to that of Lyocell fibres. [DBNH][Ac] is excellent solvent of cellulose allowing low processing temperatures to avoid cellulose and solvent degradation. Furthermore, due to the low viscosity of the system, relatively high spinning dope concentrations can be applied (e.g., 10–17 wt\% (ref. 254)). This technique has been studied in detail over the years to optimise the spinning parameters.\textsuperscript{262} The influence of cellulose structure (molecular weight, polydispersity) on the spinnability was also investigated,\textsuperscript{263} and it was demonstrated that even waste papers and cardboards can be upcycled into textiles (Fig. 30).\textsuperscript{264} Recycled newspapers could be also spun into Ioncell-F fibres after drinking and alkaline glyceral pulping processes.\textsuperscript{265} As a notable achievement, even coloured textile waste could be recycled using the Ioncell-F process, the colour of the dyes could be sufficiently retained in the new textile products in most of the cases.\textsuperscript{266} Since recycling of the ionic liquid is crucial for the industrialisation of the technique in order to compete with the Lyocell process (with a closed-loop system, recycling almost 100\% of the solvent), recyclability of the solvent has been studied,\textsuperscript{267} and a spinning bath setup for a closed loop operation has also been suggested.\textsuperscript{268} Ioncell-F fibres were demonstrated to be suitable for the production of printed fabrics. The technology entered the upscaling phase for commercialisation.

As we have discussed earlier, several other biopolymers can be dissolved in ionic liquids (polysaccharides, proteins, etc.), which enables the preparation of cellulose composite fibres by properly choosing the ionic liquid system (see section 4.6). Sun et al.\textsuperscript{269} directly dissolved lignocellulosic biomass (southern yellow pine and bagasse) in [Emim][Ac] and prepared all-wood composite fibres via a dry-jet wet spinning process. The authors highlighted the importance of high temperature and short dissolution time (175 °C, 30 min) as a prerequisite for the preparation of continuous filaments from dissolved wood. Furthermore, Nypelö et al.\textsuperscript{270} prepared cellulose/lignin, cellulose/xylan and cellulose/lignin/xylan all-wood composite fibres based on the Ioncell-F method. Chitosan/cellulose fibres could be also prepared via the Ioncell-F process.\textsuperscript{271} Chitin/cellulose fibres were obtained via a wet and dry-jet wet spinning method using [Emim][OPr] ([OPr] – propionate) as solvent.\textsuperscript{272} Cellulose/lignin composite fibres have also gained interest, they have been fabricated using the Ioncell-F process,\textsuperscript{273} or using [Emim][Ac] as solvent.\textsuperscript{274}

Cellulose/lignin fibres gained interest as precursors for the preparation of carbon fibres, in order to improve the carbon yield which is generally low for carbon fibres prepared using only cellulose as precursor.\textsuperscript{275} Cellulose/lignin filaments from the Ioncell-F process,\textsuperscript{276–281} and from a process that uses [Emim][Ac],\textsuperscript{282–286} were studied in detail for this purpose. Interestingly, cellulose/chitosan fibres also gave higher carbon yield compared to pure cellulose precursors due to the intimate connection of the two biopolymers.\textsuperscript{271,287}

Various organic and inorganic additives can be included in the cellulose/ionic liquid system to prepare functional fibres. By loading magnetite into cellulose/[Emim][Ac] solution magnetic fibres were produced via a dry-jet wet spinning process.\textsuperscript{288} In a similar manner, cellulose/TiO\textsubscript{2} composite fibres could also be fabricated from [Emim][Cl] solution.\textsuperscript{289} Fibres with improved tensile properties could be prepared via dry-jet wet spinning using nano-SiO\textsubscript{2} additive included in the cellulose/[Amin][Cl] solution.\textsuperscript{290} Cellulose/multiwalled carbon nanotube composite fibres fabricated through a dry-jet wet spinning process from [Amin][Cl] showed also better mechanical and thermal properties compared to pure synthetic cellulose fibres.\textsuperscript{291} Similar results were reported by Rahatekar et al.\textsuperscript{292} using [Emim][Ac]. The Ioncell-F process was also used to fabricate functional fibres. Silver and gold nanoparticles could be incorporated into the [DBNH][Ac] solution to obtain fibres with promising UV-shielding properties.\textsuperscript{293} Furthermore, by adding the nature-derived plant-based water repellents betulin and betulinic acid to the spinning dope, hydrophobic fabrics could be obtained.
Electrospinning technology has also been applied to prepare cellulose nanofibers using ionic liquids. This topic has been comprehensively reviewed in recent works. The use of pure ionic liquid/cellulose solutions is rather difficult for this process on account of the low volatility of the solvent (usually the solvent evaporates during electrospinning), together with its high ionic strength. Xu et al. for example used the co-solvent DMSO for [Amin][Cl] to decrease surface tension and viscosity, and employed a high humidity chamber for electrospinning in order to solidify the fibres. The electrospun fibres were washed with ethanol to remove the residual solvent. Furthermore, a wet electrospinning process was also introduced by Quan et al., in this case fibres were directly electrospun from [Bmim][Cl] solution at 100 °C into a water bath as “collector”.

5. Critical outlook on the future of cellulose processing in ionic liquids for material fabrication

Ionic liquids are considered green solvents based on their non-volatile character, with chemical and thermal stability. They gained popularity as designer solvents – their physico-chemical properties can be tuned with the cation–anion combination. These features have nevertheless sparked significant interest into their environmental fate, biodegradability and toxicity profile, with several comprehensive reviews published to date. As a result of continuing efforts, several ways to produce non-toxic and biodegradable ionic liquids have been introduced. It became apparent that not only the ionic liquid itself but the preparation method also needs to be placed under scrutiny for a more holistic picture (cradle-to-gate assessment), if they are to be considered green solvents.

We expect to see more research on using non-toxic, biodegradable ionic liquids for cellulose processing and material fabrication in the future. We would like to highlight here that machine learning approaches could provide time- and cost-effective ways to navigate within the large chemical space of ionic liquids, in order to design optimal processing media for material fabrication. We believe that designing ionic liquids that can tolerate high water content (present typically in biomass) while dissolving cellulose is an important direction for practical applications.

Furthermore, for the economic viability of the technology, the cost of the ionic liquid and its recyclability need to be considered. In particular, the ionic liquid needs to be recovered and recycled with favourable energy consumption that will not compromise the economics of the technology. For the recyclability, possible side reactions with cellulose (which has been seen for e.g., [Emim][Ac] need to be avoided. In cellulose processing with ionic liquids, some efforts have been made to recycle the solvent, for example during the production of Ioncel-F fibres using the distillable non-derivatising ionic liquid [DBNH][Ac]. We hope to see more development in this field. Furthermore, to understand the real cost of ionic liquids, it is important to perform life cycle assessment (LCA). LCA considers the cradle, production, uses, disposal, and environmental impact of the chemicals. IL have been seen as expensive chemicals partly owing to the lack of comprehensive LCA data. The LCA data of IL can help understand the process improvement when these solvents are used. There are only few LCA reports on IL, based on these works, IL can be very competitive with common organic solvents. Baqaeq et al. for example applied monetisation method which combines LCA and process simulation on protic ionic liquids used for lignocellulose pretreatment (delignification, cellulose non-dissolving ionic liquids). They found that triethylammonium hydrogen sulfate ([TEA][HSO₄]) had the lowest cost among the studied systems (four systems were taken into consideration: [TEA][HSO₄], 1-methylimidazolium hydrogen sulfate ([Hmim][HSO₄]), acetone, and glycerol for cost comparison) for pretreatment of lignocellulose. In a previous report, technical assessment indicated that the cost of these ionic liquids could be below that of common organic solvents (about 1.24 $ per kg, compared to the price of acetone/ethyl acetate being around 1.3–1.4 $ per kg). It was also found that in biomass pretreatment, imidazole-based IL ([Emim][Ac]) for example have higher cost mainly due to their multistep synthesis process. However, on bulk scale the regeneration and recycling process of IL can eventually make them cost effective, thus emphasising the importance of this issue for the economic viability of the technique. At last, we should mention that although ionic liquids are sometimes denoted as expensive solvents of cellulose, when we consider alternative petroleum-derived materials with large carbon footprint – in light of the carbon pricing, advocating the “high” cost of ionic liquids for cellulose processing may be misguiding. When comparing different technologies and materials, a more holistic assessment is necessary, as we pointed out on using LCA.

In addition, the energetics of cellulose dissolution should not be neglected either – it must be minimised. Ionic liquids with low melting point and viscosity may be preferred, to perform the mixing with low energy input at low temperatures. Alternative heating methods, such as microwave-heating and ultrasonication may facilitate the dissolution process (decrease dissolution time), and lower the energy requirements. Cellulose degradation under such conditions must be avoided. There may be other ways to decrease the energy consumption of the dissolution step, this issue needs to be addressed more in detail in the future. Recently, reactive extrusion (REX) has proven to be a fast and efficient technology for cellulose dissolution and modification using ionic liquids. Cellulose chemical modification in ionic liquids via REX can outpace the conventional heterogeneous batch process due to the continuous flow, scalability and higher cellulose concentration. Moreover, the combination of homogeneous dissolution of cellulose in ionic liquids with efficient
mixing in an extruder can yield a desired product within minutes of reaction time.\textsuperscript{216,317}

Regarding the \textit{choice and structure of the ionic liquid}, the most popular ones for material fabrication are first generation ionic liquids based on dialkylimidazolium cations, such as [Emim][Ac], [Amim][Cl] and [Bmim][Cl]. While in many cases an ionic liquid with good dissolution power proved sufficient to fulfill the target purpose (e.g., for thin film and coating applications), there are cases where the \textit{structure of ionic liquid could substantially influence the performance for the application}. We showed that the choice of the ionic liquid can have a substantial impact on the mechanical properties of regenerated cellulose films (section 4.1), by influencing the crystallinity index and degree of polymerisation of the final material. Some studies suggested that [Amim][Cl] is superior compared to other ionic liquids (e.g., [Emim][Ac], [Bmim][Cl]).\textsuperscript{80,97} More studies are needed involving other types of ionic liquids as well, to have a clear picture on the influence of ionic liquid structure on the mechanical properties. The dissolution conditions (temperature and time) also need to be considered to avoid cellulose degradation. Furthermore, we think that by tuning the structure of the ionic liquid, the structure of the obtained membrane (section 4.2), such as its porosity, could be tailored during the phase inversion process.\textsuperscript{116} It is needless to say that the porosity of the membrane is crucial for filtration performance. We expect to see more progress in this field. Furthermore, it is also important to consider the structure of ionic liquid when adding enzymes to the system (section 4.3): in order to maintain the activity of the enzyme the interactions between the ionic liquid and the protein must be considered. It was shown for example that the addition of a hydrophobic ionic liquid (\texttt{[Bmim][NTf2]}) to \texttt{[Bmim][Cl]/cellulose system} can have a beneficial effect on enzyme activity, by providing a better environment to accommodate the protein.\textsuperscript{120} More understanding is needed to tailor enzyme/ionic liquid/cellulose ternary systems. When cellulose composites are prepared with other biopolymers (section 4.4), the solubility of the other biopolymer in the ionic liquid needs to be considered, and binary ionic liquid systems might be necessary, as we could see with cellulose/chitin composites.\textsuperscript{161} We would like to highlight here the nice work done on cellulose/natural protein composites, with valuable studies focusing on how the structure of the ionic liquid can be used to tailor the nanostructure of the material.\textsuperscript{181} Ionogels gained substantial interest as solid state electrolytes (section 4.7). It was shown that addition of ionic liquid, which does not interact with cellulose (\texttt{[Bmim][NTf2]}), can improve ionic mobility within the ionogel, beneficial for various electronic applications. Thiemann \textit{et al.}\textsuperscript{202} showed that increasing bulkiness of the anion can lead to a decrease in ionic mobility, and pointed out the superiority of \texttt{[NTf2]} to improve this property. We think that more research could be done to tailor the ionic mobility in these materials. For fiber fabrication (section 4.8), the viscosity of the system and processing temperature are crucial parameters with a focus on avoiding cellulose and solvent degradation, and thereby enabling solvent recycling with advantageous energetics. In this field, the superbase ionic liquid [DBNH][Ac] came to the forefront. It is clear that more research is needed to understand the influence of ionic liquid structure on the properties of the fabricated materials for the target applications. Studies should go beyond the use of common first generation dialkylimidazolium cation based ionic liquids, and should more eagerly involve the large chemical space of ionic liquids. Computational methods may be involved here to replace time and resource consuming screening processes, as discussed in a recent comprehensive review by Koutsoukos \textit{et al.}\textsuperscript{306} Machine learning can be a very helpful tool in various aspects. It could be used to develop ionic liquids with good ability to dissolve cellulose, and together with life cycle assessment, aid the realisation of cost-effective systems. Furthermore, it could also help designing ionic liquids for achieving specific material properties, an approach sometimes referred to as \textit{machine learning-assisted materials design}. Recent advancement can be taken as example from ongoing efforts on tailoring organic molecule and polymer properties via machine learning algorithms.\textsuperscript{318}

As of similarities in selecting an ionic liquid for material fabrication, when mechanical properties are important, ionic liquids that can process cellulose without appreciable degradation at low temperature with acceptable viscosities are preferred. Furthermore, the recyclability of the system necessitates the use of non-derivatising ionic liquids that can be recycled with favourable energetics. The latter is especially important when studies go beyond laboratory experiments, and industrial scale realisation is the target. This issue came to the fore especially for fiber formation processes. So far, the dialkylimidazolium cation based ionic liquid [Amim][Cl], and the superbase derived ionic liquid [DBNH][Ac] are the most promising choices. We need to emphasise here that more studies are needed since our knowledge on other types of ionic liquids is very limited. As of differences between ionic liquid systems, we would like to draw attention to physical ionogels as promising materials for solid state electrolytes. In this specific case, the use of non-dissolving ionic liquids, with anions that would interact with cellulose the least (\texttt{[Bmim][NTf2]}), are preferred. This is due to the high ionic mobility required within the gelous network for achieving high ionic conductivity. This is in contrast to the requirements when cellulose solvents are considered.

The \textit{purity of the final regenerated cellulose material} is not examined in most of the studies, although the purity of the ionic liquid itself has been the focus of more intense investigation among works that study solvent recyclability. It can be expected that remaining ionic liquid in the final product could have a considerable impact on mechanical as well as other properties (e.g., ionic liquids have been reported as plasticiser additives,\textsuperscript{319,320} and other functions have also been revealed when added to various polymer matrices\textsuperscript{321}) important for the target application. Therefore, we highly recommend future studies to address this issue. It is clear that even small amount of impurities from the ionic liquid could have a devastating effect on the recycling step on an industrial
scale, compromising the economics of the whole process. Therefore, it is crucial to optimise the regeneration step. We have to note here that purity assessment solely based on \(^1\)H-NMR analysis may not be sufficient enough in some cases, and more sensitive analysis (e.g., more sensitive HPLC techniques) may be required to claim the purity of the final material, especially when the target application is e.g., food packaging, biomedical sensing (i.e., artificial skin), etc.

Another issue is related to the prudent choice of the technical cellulose. Many studies focus on the commercially available microcrystalline cellulose. From a technological point of view, however, the use of industrially relevant technical cellulosics such as dissolving pulp would be preferred (e.g., if we think about packaging application). This should be considered in the first place, and the use of a certain grade of technical cellulose should be justified (to be necessary for the material to fulfill its function/property). Dissolving pulp has high degree of polymerisation and therefore, a viscous solution may be obtained in some cases that can be more difficult to process. Handling of microcrystalline cellulose is although easier, it has higher cost that may jeopardise the economics of the technology, and its conversion from the raw cellulose will certainly increase the ecological footprint of the process.

We would also like to raise attention to the source of cellulose, in particular to the importance of upcycling agri-food losses and wastes into value-added materials for a circular economy. This topic has been comprehensively addressed in a recent review.\(^{322}\) These resources can represent sustainable alternatives, as they can be readily available. A good example is banana stem – banana can grow fast, and once yielding fruits, the stalk is cut back and the stem is disposed, representing an untapped source of agri-food residue derived cellulose.\(^{323,324}\)

There are many more examples of agri-food wastes produced annually at millions of tons of quantities,\(^{322}\) such as the sugar beet pulp, which contains about 22–30% cellulose (on a dry weight basis). Furthermore, sugar beet pulp has a comparatively low lignin content (about 3 wt%) with respect to other lignocellulosic materials (e.g., wheat straw has about 15 wt% lignin), making it an exciting biomass to study for cellulose valorisation. Sugarcane bagasse is considered the most abundant biomass waste on Earth and it consists of 40–50 wt% cellulose – making it a material with a huge potential for obtaining cellulosic pulp for industrial applications. Recently, brewer’s spent grain from the brewing industry (cellulose content around 16–25 wt%) has also emerged as a new source of cellulose. Upcycling agri-food waste could also make local communities and industries more prosperous and resilient. We believe that technological innovations in the near future will provide farmers and related businesses with both economic and social incentives to fully take advantage of the chemical diversity present in the biomass they grow.

Finally, as a goal of a tutorial review, we would really like to encourage those who have not necessarily worked with ionic liquids before, to explore this promising area of green chemistry. Although we do not really see any problems in preparing these materials, for starting practitioners, there may be some difficulties in the dissolution step of cellulose, due to the high viscosity of the solution in some cases. Handling of such solution may need some practice, and proper machinery. Furthermore, we need to note that most of the ionic liquid systems available at present do not tolerate water impurities present in raw cellulose materials or in the ionic liquid itself, so the starting materials must be dried before any processing. As we have noted above, development of ionic liquid systems that can tolerate high water content is underway. We hope to see many more interesting cellulose-based functional materials created via ionic liquid processing systems in the near future.

Conflicts of interest

The authors declare no conflict of interest.

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References

7. K. Heise, G. Delepiere, A. W. T. King, M. A. Kostiainen, J. Zoppe, C. Weder and E. Kontturi, Chemical modifi-
9 P. Zugenmeier, Order in celluloses: a historical review of crystal structure research on cellulose, Carbohydr. Polym., 2021, 254, 117417.
31 Y. Fukaya, A. Sugimoto and H. Ohno, Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates, Biomacromolecules, 2006, 7, 3295–3297.
Green Chemistry Tutorial Review


98 X. Liu, J. Pang, X. Zhang, Y. Wu and R. C. Sun, Regenerated cellulose film with enhanced tensile strength prepared with ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc), Cellulose, 2013, 20, 1391–1399.


modified glass microfiber separator for flexible lithium-ion batteries, *EcoMat*, 2021, 3, e12126.


Tutorial Review

Green Chemistry


191 M. Zhang, C. Ding, L. Huang, L. Chen and H. Yang, Interactions of collagen and cellulose in their blends with 1-ethyl-3-methylimidazolium acetate as solvent, *Cellulose*, 2014, 21, 3311–3322.


Green Chemistry


231 M. Deng, Q. Zhou, A. Du, J. van Kasteren and Y. Wang, Preparation of nanoporous cellulose foams from cell-


259 A. Michud, A. King, A. Parviainen, H. Sixta, L. Hauru, M. Hummel and I. Kilpeläinen, Process for the pro-


280 N.-D. Le, M. Trogen, Y. Ma, R. J. Varley, M. Hummel and N. Byrne, Understanding the influence of key parameters on the stabilisation of cellulose-lignin composite fibres, Cellulose, 2021, 28, 911–919.


298 S. Xu, J. Zhang, A. He, J. Li, H. Zhang and C. C. Han, Electrospinning of native cellulose from nonvolatile solvent system, *Polymer*, 2008, **49**, 2911–2917.


