Engineering Materials

Mohd Shabbir *Editor*

Regenerated Cellulose and Composites

Morphology-Property Relationship

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Preface

Exhaustive utilization of petroleum resources and synthetic materials parallelly invested to the climate change and subsequently rise in temperature has been a concern of present time. Products from natural resources are best alternatives of all time, natural polymers play a major role to that. Being the most abundant natural polymer on earth and gateway to large number of applications, cellulose is expected to be explored for higher efficiencies. Challenging part, i.e., dissolution of cellulose, has been explored and several solvents already there. Since morphology of the materials is the key feature and corresponds to associated application to the materials, it is highly needed to assimilate the literature on morphology-property relationship of cellulose materials. This book will try to accumulate all such literature relying on morphology-property relationship of cellulose materials and will give direction to the ongoing research to this relationship. This effort, with the help of eminent authors around the globe with the expertise in related research areas, is expected with a great research outcome in regenerated cellulose chemistry and research.

This book is composed of 12 chapters from various research areas dealing with morphological aspects of regenerated cellulose and characteristic applications of various morphologies. Introduction chapter overviews the dissolution of cellulose and regeneration into various morphologies. Cellulose dissolution and regeneration are explored in detail in the second chapter in view of green chemistry approaches. Further, the regeneration into morphologies such as spherical, sheets, membranes, and films is discussed in the next chapter including recent advances in this area. Surface modifications of regenerated cellulose materials are reviewed in the fourth chapter. Cellulose can be modified via organic and inorganic means that are discussed in detail. The fifth chapter is dedicated to nanocellulose materials and their applications in several fields. Next chapter in continuation discussed spherical morphologies of cellulose, specifically microspheres and beads, their fabrication, and applications. Regenerated cellulose materials modified with functional groups play important role in chromatographic separation of compounds. The seventh chapter is dedicated to the chromatographic separation through cellulose. Next two chapters explored energy applications, textiles, and food applications of regenerated cellulose. From textile fibers to conducting materials are discussed in these chapters. Last group of

chapters reviewed pharmaceutical and biomedical applications. Drug delivery, wound dressing, tissue engineering, dentistry, etc., are discussed through them.

The book *Regenerated Cellulose and Composites—Morphology-Property Relationship* contains informative chapters from the authors of their specialized fields about cellulose and its applications in various sectors. I hope that students, researchers, and academicians of fields such as materials science, chemical engineering, environmental science, textiles, and food industry will find this book of great interest and useful in their curriculum. This book will definitely be helpful for emerging new ideas in cellulose research leading to interdisciplinary research collaborations.

Now it comes to thank those who had been a support to this book in any way. I acknowledge the great efforts of the eminent authors without whom this book was not imaginable, and my family members, colleagues, and students. I appreciate the support of the publisher to show interest and let me compile this referenced book.

Greater Noida, India Mohd Shabbir

Contents

An Introduction to Regenerated Cellulose: Morphologies and Applications

Fehmeeda Khatoon, Mohd Shabbir, and Annu

Abstract Being one of the most abundant materials on earth, cellulose has attracted attention for the practical applications. Since the methods to dissolve and regenerate cellulose have been evolved, the momentum of utilizing the compact nature of cellulose via transformation into various morphologies is accelerated. As the morphology-specific applications are evolved, various methods of transforming regenerated cellulose into various morphologies are developed. From nanocellulose to cellulose beads, hydrogels, fibers, sheets or membranes, microspheres, etc. have been developed and used for several applications such as wastewater treatment, sensing, drug delivery, tissue engineering, wound dressing, separation, catalysis, and energy. This chapter is to introduce the cellulose regeneration and molding into various morphologies for specific applications.

Keywords Cellulose · Nanocellulose · Microspheres · Drug delivery · Wastewater treatment · Energy

1 Introduction

Cellulose is one of the most abundant biopolymers on this planet. Plants and some bacteria synthesize and produce cellulose. It is a homopolymer of glucose, and monomers are linked by β-1,4 linkages (Fig. 1). Cellulose is a tough, fibrous polysaccharide and insoluble in water solvent. Cellulose is responsible for the compact and stable structure of plant cell walls. Cellulose chains are arranged in microfibrils, and

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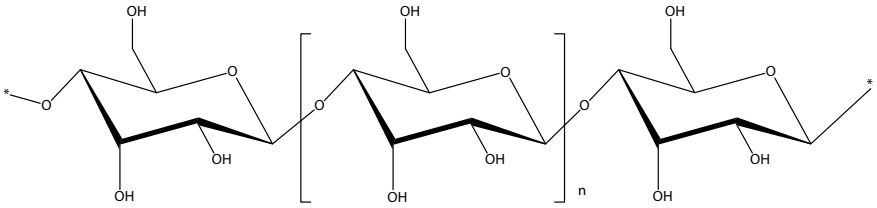

Fig. 1 Cellulose chemical structure

microfibrils arranged in fibrils are bundles of them and ultimately make up the plant cell wall. Polymeric chains are bound to each other via H-bonding in layers. This arrangement provides the strength and superior mechanical properties to cellulose biopolymer. Cellulose is not only synthesized in plants, but also be produced by some bacteria, and it is of high purity and crystallinity unlike it is separated from lignin in case of plants [1].

Cellulose dissolution has been a great challenge to utilize and process for practical applications. Arrangement of polymeric chains and interactions between them, mainly H-bonding, is difficult to weaken and hence the dissolution. Various solvents are used to regenerate cellulose into materials of use. The amine oxides were used to regenerate cellulose into fibers and used in textiles, construction industry. Viscose rayon and lyocell fibers were obtained via dissolution of cellulose into amine oxides such as N-Methylmorpholine N-oxide (NMMO) [2]. Solvents for cellulose dissolution and regeneration methods help in deciding morphology of the regenerated cellulose. Various morphologies of cellulose and their characteristics along with applications are introduced in this chapter.

2 Nanocellulose

Nanocelluloses (NCs) are usually isolated or produced from cellulose fibers of agricultural residues via different methods, and these may include chemical, mechanical, hydrolysis (acid or enzymatic), oxidation, etc., and can also be produced by bacteria from glucose (Fig. 2). NCs can be classified into three categories, that are cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFCs), and bacterial nanocellulose (BNCs) depending on the morphological features, functions, and preparation methods of NCs. CNCs and NFCs are generally obtained via a top-down approach consisting of the disintegration of plant matter, while synthesis of BNCs follows bottom-up approach using cultures of bacteria [3–5].

The removal of amorphous regions by hydrolysis (acidic or enzymatic) from cellulose fibers usually give CNCs. They are of high purity rod-like or whisker shape cellulose crystals having diameters and lengths in nanoscale sizes. Flexibility is reduced relatively in these types of NCs due to the removal of amorphous regions in the structure [7–9]. Aggregation of long thread-like bundles of cellulose chain

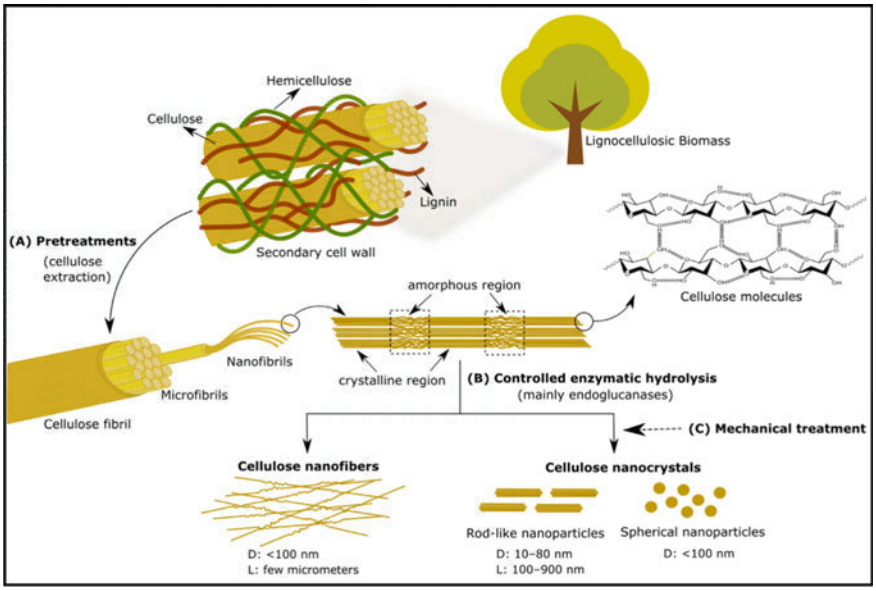

Fig. 2 Production of nanocellulose, pretreatments, and enzymatic hydrolysis [6]

molecules with flexible, long, and entangled cellulose nanofibers (CNFs) forms NFCs. They are equipped with less than 100 nm diameter and several micrometers length and also called as nanofibrils, nanofibrillar, and nanofibers made of cellulose. NFCs are usually generated/extracted through the mechanical disintegration processes, by using electrospinning technique. NFCs have a high aspect ratio and, unlike CNCs, contain both crystalline and amorphous regions and exhibit a web-like structure [10, 11]. Third category, i.e., bacterial nanocelluloses (BNCs) or bacterial cellulose (BC) is composed of continuous 3D network of CNFs, usually produced as hydrogels or nanofilms via "bottom-up" synthetic routes by synthesizing cellulose from carbon sources such as glucose in the aqueous culture media of specific bacteria such as *Gluconacetobacter xylinus*. These nanocelluloses demonstrate better purity, crystallinity, and mechanical stability compared to the CNCs and NFCs [12, 13]. Nanocelluloses find its applications in various fields including biomedical, food packaging, reinforcements, bioplastics, optics, adhesives, coatings, and engineering (Fig. 3).

3 Cellulose Beads and Microspheres

Spherical morphology of regenerated cellulose is studied into two categories depending on the size range. If the size range of materials is in micrometers (up to 500 μm), then they are included in category microspheres, and if this size range

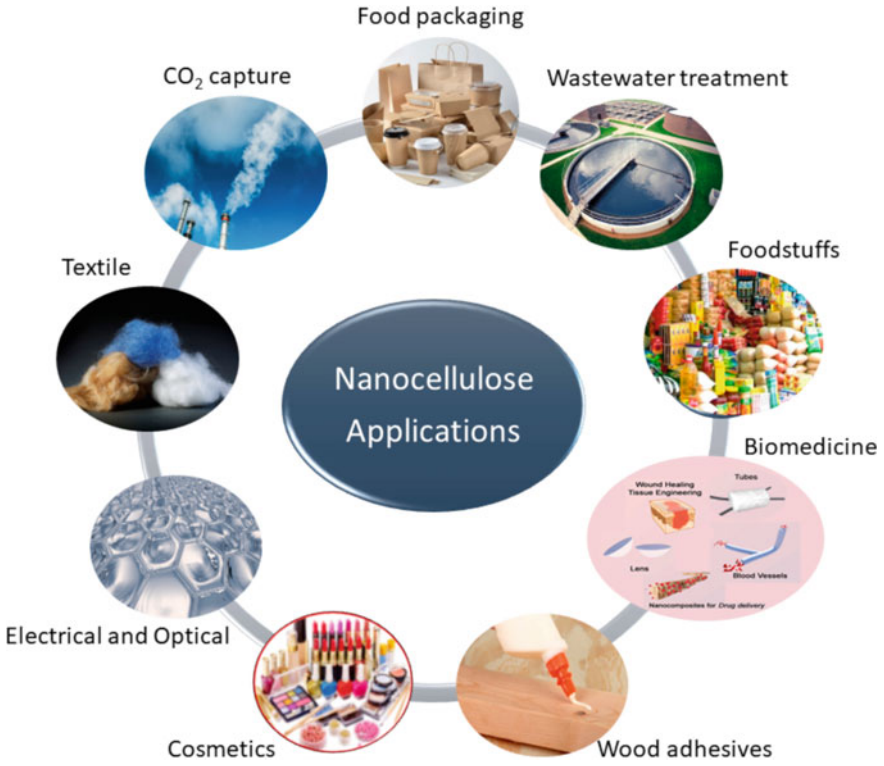

Fig. 3 Various application areas of nanocellulose [14]

extends further, materials are categorized as beads. Regenerated cellulose microspheres or beads are designed usually porous to enhance the active surface area. Dispersion method is generally opted for microspheres formation, in which cellulose is dissolved in solvent first, and then, emulsion is made. Dispersed phase particles' size can be controlled by the speed of mixing the emulsion. Once the optimum size achieved the dispersed phase, solidification of dispersed phase via solvents of different polarities is carried out. While cellulose beads are of size greater than 500 μm and are designed by dropping and solidifying them in their sizes, depending on the pore size of syringe, size of the cellulose beads can be regulated [15, 16].

Owing to the spherical morphology (Fig. 4) of these materials, they are highly used for adsorptive removal of pollutants from wastewater, drug delivery systems, catalysis, and chromatographic separation applications [18, 19]. Various surface modifications are carried out for higher efficiencies of regenerated cellulose and act as a carrier for particular compounds. High surface area of spherical morphology leads to higher adsorption, and porous nature of these materials also enhances that surface area and ultimately the efficiency of adsorptive removal of pollutants from wastewater. Sometimes, to adsorb specific ions or molecules, surface modifications are carried out accordingly. Photocatalytic materials can also be embedded into regenerated

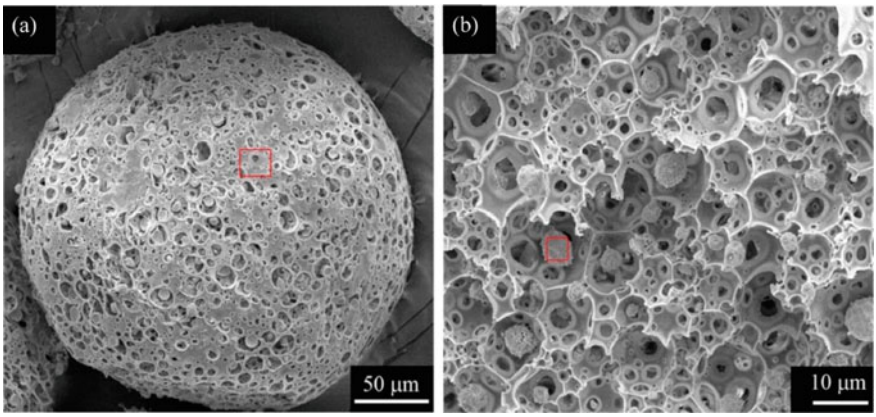

Fig. 4 Cellulose-based microspheres and their porous structure [17]

cellulose microspheres for catalytic degradation of organic pollutants such as dyes or pharmaceuticals [20, 21].

4 Cellulose Fibers

Cellulose fibers have been used in our daily lives for long. They are widely used for clothing purposes. Common regenerated cellulose fibers used for clothing are rayon and fabricated by viscose process; cellulose is converted into the cellulose xanthogenate and spun into fibers. Rayons are usually of three types that are regular rayon, high wet modulus rayon, and high tenacity rayon, and regular rayon (Viscose® rayon) has the largest market share among them. Viscose solution is prepared by reacting cellulose with NaOH and then with CS2 to get cellulose xanthogenate, and then, it is forcefully passed through a spinneret into acidic coagulating solution to generate regenerated cellulose filaments [22]. Cuprammonium rayon is another commercial regenerated cellulose fiber fabricated by cellulose dissolved in cuprammonium solution. Copper and ammonia are removed by treating with coagulating solution. By varying the solvents, several chemical modifications, and methods of manufacturing, regenerated cellulose fibers of varying characteristics have been obtained with different names [23, 24].

5 Cellulose Membranes and Sheets

Cellulose is also developed into membranes and sheets commonly by casting method. Cellulose is dissolved into solvents first and then casted on flat surface such as glass, and thickness of the membranes can be maintained in this step. Casted cellulose is regenerated by treating it with coagulating solution, generally acidic solutions

such as H_2SO_4. The concentration of the cellulose solution and the coagulation temperature control the porosity and pore size of the membranes [25]. Vacuum filtration, solution regeneration, electrospinning, phase inversion, etc. are other methods for the preparation of cellulose membranes. Regenerated cellulose membranes are used for various applications in food packaging, water treatment, cosmetics, medicals/pharmaceuticals packaging, and sensing. Several organic and inorganic components (metal nanoparticles, fluorophores, organic dyes, and antigen-antibodies) are introduced into cellulose to design for specific use of membranes [22, 26].

6 Cellulose Hydrogels and Scaffolds

Hydrogels are three-dimensional network structures formed of polymeric chains held via physical and chemical cross-linking. Hydrogels have tendency to absorb and retain large amounts of water in their interstitial structures, maintained by the interactions responsible for the unique 3D structure. Physical and chemical interactions of polymeric chains also help in preventing the dissolution in solvents and swelling during water absorption while maintaining structure. Water absorbing tendency is due to the presence of hydrophilic groups such as—OH, –COOH in their 3D structure. Cellulose-based hydrogels are fabricated from pure cellulose solution by physical cross-linking of the chains owing to the hydroxyl groups in cellulose structure. Hydrogen bonding is the primary force to hold polymers into network structures [27]. These hydroxyl groups can also attract various interactions toward other moieties or derivatization of cellulose and resulting into cellulose composite hydrogels. Cellulose hydrogels are well-known structures for their swelling and mechanical properties. Owing to these characteristics, hydrogels find their application area in biomedical fields (drug delivery, wound healing, tissue engineering), textiles, agricultural fields, etc. These promising aspects of cellulose hydrogels make their studies important for researchers and scientists [22, 28].

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Green Chemistry Approaches to Cellulose Dissolution and Regeneration

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Abstract The dissolution of cellulose is a critical step for the efficient conversion of the cellulose into a high added value product. Yet, so far, attention had been paid mostly to the conventional solvents such as *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl). Therefore, initiatives to develop highly efficient and green cellulose solvents can broaden the cellulose regeneration for various applications. Dissolution of cellulose in green solvents allows the comprehensive utilization of cellulose by combining the green chemistry principles involving the usage of environmentally preferable solvents. Green solvents including ionic liquids (ILs) and deep eutectic solvents (DESs) have played unique roles in the cellulose dissolution. ILs are novel green and attractive solvents due to their favorable properties. ILs with high thermal stability, nearly non-volatility, and structural diversity consequently show an outstanding capability for dissolving cellulose. In addition, deep eutectic solvents (DESs) with unique physicochemical properties, has emerged as green alternative to ILs, have shown considerable potential as versatile solvents for cellulose dissolution. Herein, this chapter underlines a more appropriate dissolution mechanism and provides an insight into the effectiveness of cellulose dissolution in the ILs and DESs.

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1 Introduction to Green Solvents

Solvents are used in many important chemical processes, especially fine chemical manufacturing. The toxicity and flammability of the conventional solvents used in wide range of industrial and domestic applications provide a great challenge to green chemistry. Since the introduction of "the 12 Principles of Green Chemistry" in 1998, as one of it explicitly claims the use of "safer solvents and auxiliaries", there has been a persistent attempt to replace conventional solvents with more environmentally friendly alternatives [1].

Green solvents are one of the most important ways to express the goal of minimizing environmental effect in a variety of industrial applications for long-term development. A chemical production process's sustainability can be significantly improved by selecting the right solvent for the operation. Figure 1 shows the general characteristics of green solvents.

Water is the best solvent of all green solvents since it is abundant in nature. It is non-toxic to human health and the environment, easily available, and has a high specific heat capacity. Ionic liquids (ILs) and deep eutectic solvents (DESs) have emerged as promising green solvents because of their low vapor pressure *and* high chemical and thermal stability, which offers advantages such as ease of containment, product recovery, and recycling ability [2]. Meanwhile, liquid polymers have been established as solvents for catalytic reductions to avoid the inactivation of air-sensitive catalysts [3]. Biosolvents derived from renewable feedstocks are used as an alternative to hazardous petroleum solvents like hexane in extraction of oils [2]. Among supercritical fluid, carbon dioxide is the most commonly utilized because it is harmless, incombustible, widely available, and inexpensive. Its properties can be controlled by altering the temperature and pressure, and it can be easily removed from the extract by relaxing the conditions to room temperature and pressure [4]. Different types of green solvents are shown in Fig. 1b. It should be noted that each of the green solvents has benefits and drawbacks that must be considered before selecting one for a specific application.

Green solvents are utilized for a variety of functions and are used in wide range of applications. It can be used as a solvent in biocatalytic processes, extraction and purification of bioactive compounds [5]. Fundamental and industrial applications of green solvents have been applied in reaction synthesis including lipase-catalyzed reactions, organic synthesis and esterification reactions, oil extraction, sensors and biosensors, lignocellulosic biomass utilization, and bio-based chemicals. In petroleum industry, green solvents are used in extractive desulfurization (EDS) process to reduce SO2 emissions [6]. There are an increasing number of publications dealing with the use of green solvents to dissolve and increase the processability of renewable natural biopolymers in the biomedical area. The usage of green solvents in several areas is depicted in Fig. 1c.

This chapter covers the use of ionic liquids (ILs) and deep eutectic solvents (DESs) as two types of designable green solvents [7] that are used in cellulose dissolution application. Ionic liquid is a liquid molten salt made up of organic cations and organic

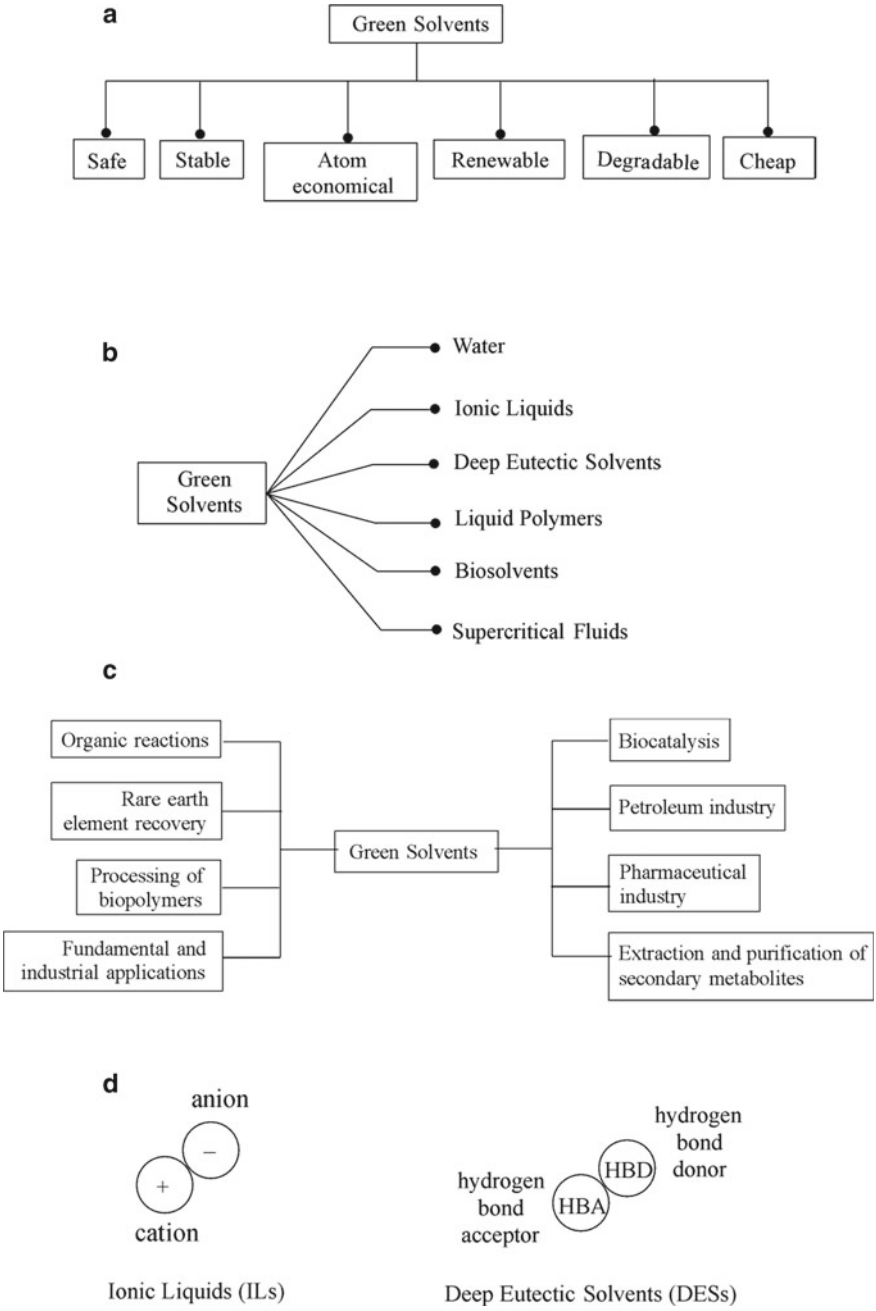


Fig. 1 **a** Characteristics of green solvents. **b** Different types of green solvents. **c** Applications of green solvents. **d** Green solvents from ionic liquids and deep eutectic solvents

or inorganic anions that melt below 100°C. DESs, a subclass of ILs, are made by mixing solid compounds to generate an eutectic mixture with a melting point lower than either of the individual components. This is due to the formation of intermolecular hydrogen bonds between the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) (Fig. 1d).

2 Cellulose Dissolution and Mechanism

Cellulose is the most ubiquitous natural biopolymer, accounting for half to one-third of all plant tissues [8]. Further, cellulose is a homopolysaccharide made up of long chains of D-glucose units connected by β-1, 4-glycosidic bonds [9]. Moreover, the presence of hydrophobic carboxyl groups and a plentiful hydrophilic hydroxyl group in the backbone of cellulose illustrates the amphiphilic nature of cellulose [10]. Cellulose has gained prominent assurance for a wide range of applications due to its unique properties. However, cellulose is a long polymer that is insoluble in most organic solvents due to its tightly packed crystalline structure [11]. Therefore, good dissolution is required to transform the cellulosic into high-value products.

Theoretically, cellulose dissolution is a process of hydrogen bond breaking, especially in the crystalline regions. Several definitions of cellulose dissolution have been proposed, while [12] defined it as the solvent's capability to break the inter- and intramolecular hydrogen bonds between the molecules of the biopolymer. The derivatizing solvents chemically react with hydroxyl groups and reduce the hydrogen bond network; the non-derivatizing solvents destroy inter- and intra-molecular hydrogen bonds either by hydrogen bond formation between one or more components of the solvent systems and the hydroxyl groups of the cellulose or by coordination bond formation between the metal ion present in the medium and the hydroxyl group of cellulose molecules [13, 14]. In general, the solvent's capacity is important in breaking the hydrogen bond network during cellulose dissolution. Nonetheless, hydrophobic interactions between solvent and cellulose have been suggested to play a substantial role in its dissolution due to the amphiphilic nature of cellulose [15–17].

Xu and Zhang [18] show that during the dissolution process, the crystalline structure of cellulose is destroyed. According to [12], completed dissolution is achieved when the supramolecular structure is completely destroyed, resulting in a solution in which the polymer is molecularly dispersed. On the other hand, crystallinity and associated constrained accessibility are the only inhibiting factors in cellulose dissolution [19]. It has been proposed that dissolution process may disrupt the unknown long-range ordering or interaction, thereby limiting cellulose dissolution. Studies on the dissolving of cotton fibers under stress reveal that there is not sufficient for cellulose chains to be non-crystalline but, rather, cellulose chains must exhibit local conformational motions that lead to chain disentanglement [20–22]. The research found that interactions that effect disentanglement may be distinct. As a result, the processes of decrystallization and chain disentanglement are intertwined in the breakdown of

semicrystalline cellulose. And thus, the total kinetics of dissolution is determined by their balance [23].

The dissolution of cellulose includes several stages consisting of solvent diffusion, swelling, cellulose decrystallization, chain disentanglement, and diffusion of disentangled chains towards the bulk solution, as shown in Fig. 2a. During the dissolution, the solvent diffuses into the structure of the cellulose to affect both the amorphous and crystalline regions. Succeeding the solvent diffusion into the solid cellulose [24] proposed that the solvent-cellulose interactions are capable of overcoming the strong molecular forces between cellulose chains. Meanwhile, this could enhance the probability of conformational chain motion as the crystalline network of cellulose is gradually broken down. Hence, it resulted in the transformation of cellulose into a gel-like medium as well as the swelling of the cellulosic particles [25, 26]. Swelling is the process where the solvents penetrate the cellulose structure by interacting with the polymer to a certain extent, leaving the physical properties and volume of the biopolymer significantly changed while the solid or semi-solid state remains practically unchanged [27]. However, the swelling process cannot dissolve the cellulose.

Due to the difference between chemical and stereochemical design, cellulose will experience different inter-chain forces that are responsible for maintaining the chain in the solid state [27]. The crystallinity and polar groups that may take part in the hydrogen bonding thus play a major role in the solubility and reactivity of cellulose. Therefore, cellulose decrystallization and chain disentanglement are both involved in the dissolution of semicrystalline cellulose [24]. High diffusivity and effective solvent disrupt the crystalline network of the cellulose molecules and disentangle the cellulose chains from each other in the amorphous regions [23]. In a consecutive manner, the cellulose chains are gradually disentangled and move out of the network into the bulk solution [15].

The dissolution of cellulose in a solvent is governed by free energy mixing thermodynamically [28]. All negative free energy variation indicates that the mixing process will occur spontaneously. Conversely, the mixing process may result in phase separation. Hence, the molecular weight of a polymer is an important factor in dissolution. This is due to the fact that the higher the molecular weight, the lower the entropic driving force contribution to dissolve [29]. Under these conditions, the enthalpy term is critical in establishing the sign of the Gibbs free energy change. It is indeed mentioned that polymer dissolution is frequently governed by kinetics rather than thermodynamics. A desired solvent for cellulose breakdown must be able to overcome the poor entropy gain through advantageous solvent and polymer interactions from a thermodynamic perspective [12]. Therefore, the development of new solvents should focus not only on eliminating hydrogen bonding but also on reducing the hydrophobic interactions among cellulose chains.

A good solvent is a solvent that coordinates well and is strong with the polymer [27]. The intramolecular hydrogen bonding network was broken and disrupted by the solvent, which had a significant effect on the dissolution of cellulose [30]. The ability of solvents to form hydrogen bonds is crucial for the dissolution of cellulose [31]. A good solvent for cellulose dissolution is able to overcome the low entropy gain

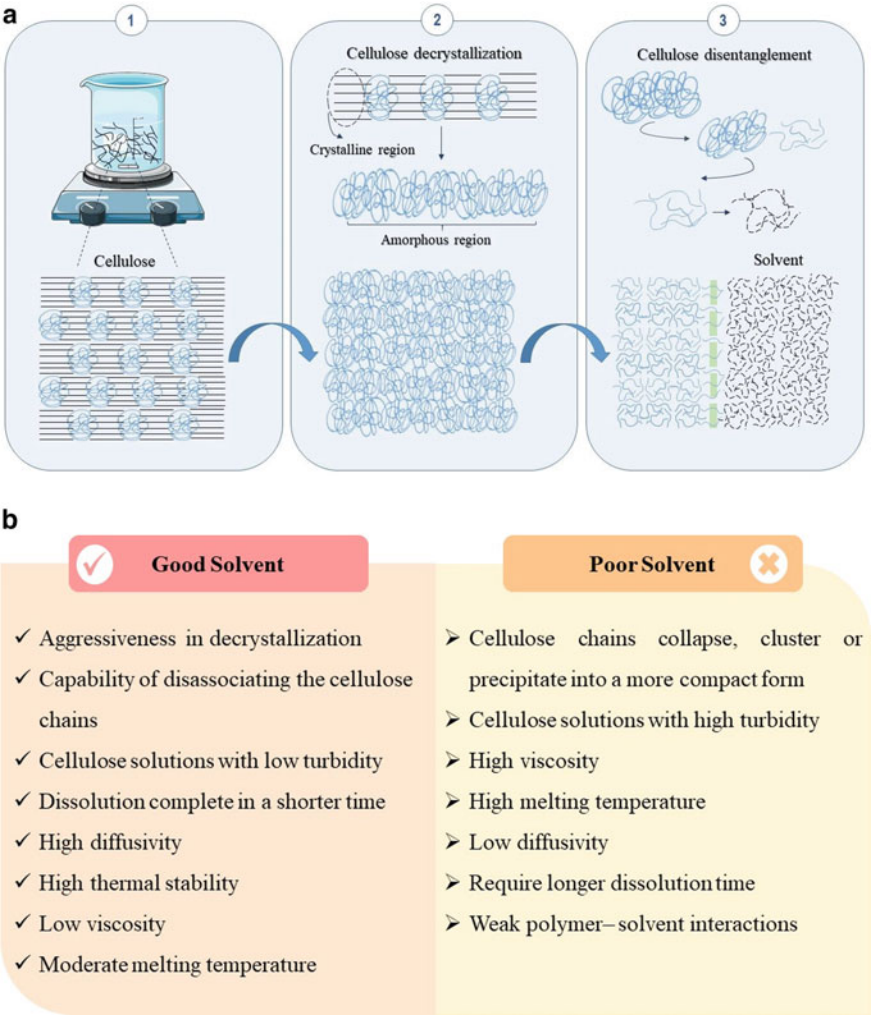


Fig. 2 **a** Schematic representation of cellulose dissolution involving the process of cellulose decrystallization and cellulose disentanglement. Stage 1: The solvent diffuses into cellulose chains, and crystalline regions are gradually break down. Stage 2: Cellulose chains disentangle from each other in the amorphous regions and move out of the network into the bulk solution, where equilibrium state is achieved. The figure (stirrer and magnetic stirrer) was partly generated using Servier Medical Art, provided by Servier, licensed under a Creative Commons Attribution 3.0 unported license". **b** Properties of the good solvent and poor solvent

by favorable solvent/polymer interactions, and better dissolution results are obtained using amphiphilic solvents that are not only able to eliminate hydrogen bonding but also eliminate hydrophobic interactions [32]. Furthermore, cellulose dissolution benefited by the solvent with lower viscosity such as deep eutectic solvent and ionic liquids [33, 34]. Low viscosity enhanced cellulose's solubility by facilitating the accessibility of the solvent to the hydrogen bonds [35, 34, 31, 32] Also, good solvents showed high solubility with the properties of high transparency and low viscosity after the cellulose dissolution and regeneration process. The increase in transparency of the cellulose solutions due to good cellulose solubility was caused by the reduction of the crystalline area.

Meanwhile, in the majority of the poor solvents, cellulose is not dissolved down to a molecular level, and the cellulose chains collapse, precipitating and clustering into a more impact form [32]. In addition, a poor solvent only has weak or almost no coordination with the polymer [27]. Poor solvent with high viscosity leads to the reduction of the intermolecular collisions as high viscosity is not conducive to the mass transfer between the cellulose and the solvent [37]. This can reduce the solubility and thus increase the turbidity of the cellulose solutions. Hence, a desirable cellulose solvent should meet the term such as high diffusivity, low viscosity, and capability to maximize the solvent-polymer interactions, high thermal stability, and moderate melting temperature as well. The characteristics of the good solvent and the poor solvent are shown in Fig. 2b.

3 Ionic Liquids and Their Physicochemical Properties

Ionic liquid (IL) chemicals the so-called 'designer chemical' can be categorized as organic-based or inorganic-based IL. Generally, IL as a form of a green solvent which comprises of anion (negative ion) and cation (positive ion). Some ionic liquids (ILs) are categorized as room temperature ionic liquid (RTIL)-based which is defined as IL being present below/under room temperature. This organic-based IL, RTIL [38], is usually more favorable in the industrial applications due to its milder technical and environmental-friendly handling characteristics [38]. They are usually composed of organic cation and combined with an inorganic or organic anion [39]. Examples of cation skeletons are observed which include imidazolium, pyridinium, pyrrolidinium, piperidinium, quaternary ammonium, sulfonium, and phosphonium-based [40] IL. It was shown by the work of [39] that there is no covalent bond between anion and cation of the IL and the weak hydrogen bonds are present.

In general, there are many kinds of IL examples for various application, for instance, phenyltrifluoborate-based $[PhBF3]^-$ anion based [40], dicationic [41] (i.e., high-temperature lubricant), carbon functionalized liquids [42], hydrophilic immidazolium based IL [43], lithium ionic liquid LiTFA [44], organoindate ionic liquid [45], tetrabutylphosphonium carboxylate [46], phosphorodithioate-functionalized ionic liquid [47], protic ionic liquid [48], imidazolium ionic liquid [49], and trialkylphosphonium-based protic IL [50]. These 'designer chemicals' of IL can

function according to the many kinds of intended tasks, for instance, for electrochemical industrial applications [40], membrane separation, or even for the pretreatment of certain lignocellulosic biomass (LCB) with the tailored anion and cation [51]. Table 1 shows some of the examples of cation and anion skeletons from the most common cation skeletons mentioned earlier with the pretreatment of LCB for cellulosic dissolution.

Table 1 indicates the lists of ionic liquid for imidazolium, pyridinium, pyrrolidinium, piperidinium, including piperazinium and quaternary ammonium based from reported cellulosic dissolution investigations as tabulated. The investigations covered wood or microcrystalline cellulose or Avicel particles for cellulose dissolution results. In overall, the acetate anions are seen to be very effective in increasing the dissolution of these IL. Besides being proven by Zavrel et al. [52] the effectiveness of [EMIM]Ac (acetate as anion), even to the hardest dissolution using pyrrolidinium, piperidinium including piperazinium and quaternary ammoniu, can now with the help of newly formulated mixture with dimethyl sulfoxide (DMSO) co-solvent, dissolution is already partially possible.

The physicochemical properties of the IL are crucial for the technical understanding of the applicability of the anion or cation roles in any industrial applications, specifically with the optimized alkyl-chain length design [38]. Most common physicochemical properties are molecular weight, melting point temperature (i.e., for solid IL), density, thermal stability, viscosity, thermal stability, and hydrophilicity/hydrophobicity. The anion effect on the melting point and viscosity relationship is significant, and it is known that the viscosity of IL is higher than the viscosity of water [51].

The determination of these physicochemical properties can be carried out using density functional theory (DFT) theoretically or by using the program of Cosmotherm [39] to correlate the viscosity and Van der Waals energy of the ionic liquid, via chromatography method [38], nuclear magnetic resonance (NMR) spectroscopy [57] (gas solubility), thermogravimetric analysis (TGA) [41, 50] (thermal decomposition temperature/thermal stability), UV-Vis spectroscopy, thermogravimetric mass spectrometric analysis (TG-MS), differential scanning calorimeter (DSC) [41, 50] (melting points), viscometer [41, 50] (viscosity), ac impedance measurement [50] (conductivity), electrospray ionization mass spectrometry (ESI-MS) [41] (molecular weight), specific gravity pycnometer [41] (density), etc. It was reported that gas chromatography method is the most favorable as compared to the conventional method determination due to few advantages besides being fast during determination and having an excellent accuracy, the sample needed to measure in gas chromatography is also very minimal [38].

The physicochemical properties change with different combinations of certain cations to variety of anions. Poole and Atapattu [38] reported the solubility parameters via gas chromatography for various ionic liquid. The solubility parameters are used to estimate the solubility of solutes of ionic liquid. When the anion was changed for instance from bromide to chloride with the same cation, the solubility parameter increased slightly, for instance, for 1- Allyl-3-methylimidazolium-based IL from 26.24 to slightly above the earlier solubility parameter, respectively. As

Table 1 Most common cation and anion skeletons for ionic liquid imidazolium, pyridinium, pyrrolidinium, piperidinium, quaternary ammonium, sulfonium, and phosphonium based from reported cellulosic dissolution investigations

Name	Abbreviation	Cation	Anion	Dissolution potential, C[a]	Dissolution potential, C[a]	References
Imidazolium-based						
1-Allyl = 3-methylimidazolium-chloride	[AMIM] Cl	[AMIM]	Cl	//, Wood	//, Avicel	[52]
1-Butyl-3-methylimidazolium-bromide	[BMIM] Br	[BMIM]	Br	–	/, Avicel	
1-Butyl-3-methylimidazolium-chloride	[BMIM] Cl	[BMIM]	Cl	/, Wood	//, Avicel	
1-Butyl-3-methylimidazolium-hexafluorophosphate	[BMIM]PF_6	[BMIM]	PF_6	–	X	
1-Butyl-3-methylimidazolium-iodide	[BMIM] I	[BMIM]	I	–	/, Avicel	
1-Butyl-3-methylimidazolium-methanesulfonate	[BMIM] CH_3SO_3	[BMIM]	CH_3SO_3	–	X	
1-Butyl-3-methylimidazolium-tetrafluoroborate	[BMIM]BF_4	[BMIM]	BF_4	–	X	
1-(2-Hydroxylethyl)-3-methylimidazolium-tetrafluoroborate	[HEMIM]BF_4	[HEMIM]	BF_4	–	X	
1-Ethyl-3-methylimidazolium-acetate	[EMIM]Ac	[EMIM]	Ac	//, Wood	//, Avicel	
1-Ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide	[EMIM]BTI	[EMIM]	BTI	–	X	
1-Ethyl-3-methylimidazolium-chloride	[EMIM]Cl	[EMIM]	Cl	/, Wood	//, Avicel	
1-Ethyl-3-methylimidazolium-ethylsulfate	[EMIM] $C_2H_5OSO_3$	[EMIM]	$C_2H_5OSO_3$	–	X	
1-Ethyl-3-methylimidazolium-tetrafluoroborate	[EMIM]BF_4	[EMIM]	BF_4	–	X	
1-Hexyl-3-methylimidazolium-chloride	[HMIM] Cl	[HMIM]	Cl	–	/, Avicel	
1-Hexyl-3-methylimidazolium-tetrafluoroborate	[HMIM]BF_4	[HMIM]	BF_4	–	X	
1-Methyl-3-octylimidazolium-chloride	[OMIM] Cl	[OMIM]	Cl	–	X	
1,3-Dimethylimidazolium-dimethylphosphate	ECOENG	[ECOENG]	Dimethylphosphate	/, Wood	//, Avicel	

(continued)

Table 1 (continued)

Name	Abbreviation	Cation	Anion	Dissolution potential, C[a]	Dissolution potential, C[a]	References
Pyridinium-based						
1-Butyl-3-methylpyridinium-chloride	[BMPY]Cl	[BMPY]	Cl	–	/, Avicel	[52]
Pyrrolidinium-based						
N-Butyl-*N*-methylpyrrolidinium	[C4mpyr][OH]	[C4mpyr]	[OH]	–	/, Avicel	[53]
N-ethyl-*N*-methylpyrrolidinium acetate	([EMPyrr][Ac])/DMSO	([EMPyrr] with DMSO solvent)	[Ac]	–	/, MCC	[54]
Piperidinium-based or piperazinium-based						
Poly(ethylene glycol) PEG-functionalized piperidinium-based	[Me(OCH_2CH_2)3-Et-Pip][OAc]	[Me(OCH_2CH_2)3-Et-Pip]	[OAc]	–	/, Avicel	[55]
N,*N*'-Dimethyl-*N*-ethylpiperazinium acetate	[DMEPpz][Ac]/DMSO)	[DMEPpz][with DMSO solvent	[Ac]	–	/, MCC	[54]
Quaternary ammonium-based						
Tetra(n-butyl)ammonium acetate	NBu_4AcO	NBu_4	AcO	–	/, Avicel	[56]
Diallyl-benzyl-methylammonium (AlAllyl)	NAl2BzMe AcO	NAl2BzMe	AcO	–	/, Avicel	

C = type of cellulosic matter investigated

[a] Defined as at 40–50 °C operating temperature high throughput screening; / = partial dissolution; // complete dissolution; X = no dissolution; MCC = microcrystalline cellulose

for 1-Butyl-3-methylimidazolium as IL cation, when the anion changed from like hydrogen sulfate, perchlorate, methyl sulfate, thiocyanate, and octyl sulfate, causing the solubility parameter to change/differ to be in the range of between 23 and 27. Another example of the change of the solubility parameter happens on 1-Ethyl-3-methylimidazolium as IL cation, changed from 23.2 to 25.56 for the use of anion of acetate and trifluoroacetate, respectively.

Table 2 below shows the exemplary physicochemical properties of various ionic liquids as previously reported able to dissolve cellulose completely by Zavrel etal. [52]. The exemplaries were taken from Sigma Aldrich Safety Data Sheet (SDS) indicating molecular weight, melting point, density, flash point, melting point, and pH. The melting point temperature of lower or close to the ambient temperature or pressure, resulting in the IL to be in the liquid form. Vice versa, if the melting point is higher than the ambient, either crystal solid or solid particles are formed like 1-Allyl-3-methylimidazolium chloride [AMIM]Cl and 1-Butyl-4-methylpyridium chloride [BMPY]CL (refer to Table 2).

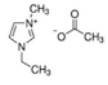
3.1 Role of Ionic Liquid in Cellulose Dissolution

In this case, the cellulose and hemicellulose matters are partly comprised in the lignocellulosic biomass (LCB), the biopolymer source [58]. The biopolymer itself which contains polysaccharides, is regarded as mainly containing the cellulosic matter in majority percentage of the LCB besides the noncellulosic matter which is lignin. The cellulosic matter (cellulose or hemicellulose) dissolution is one of the methods used to separate the cellulose compounds from the LCB, knowing the fact that the biopolymer which contains the cellulose, hemicellulose, and lignin, is being strongly bonded by the carbon-hydrogen structures or by the strong intermolecular interactions within the biopolymer.

The pretreatment of the LCB is the most crucial step particularly to support the sustainability green energy-efficient method and the overall cost incurred due to the pretreatment of the LCB. Cellulose is not easily dissolved in water due to the highly organized cellulose chain structure (highly crystalline) [58]. The known internal bonds present in LCB which are ®-(1,4)-glycosidic bond, ®-(1,3)-glycosidic bond, hydrogen bond, aryl-ether bond, and C–C bond, contribute to the recalcitrance of dissolution of LCB [58]. These bonds can be broken with various methods, for instance, with strong acidic or alkaline solution at certain temperature and pressure as the so-called chemical or physicochemical methods, for instance, besides the ionic liquid pretreatment method.

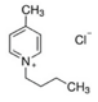
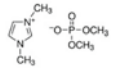
Ionic liquid assisted dissolution method is already known to be one of the pretreatment methods used, using ionic liquid with certain characteristics of the anions and cations and able to dissolve cellulosic matter either from wood chip or fibrous plant, as indicated by Fig. 3a. In order to obtain the cellulosic biomass from liquid to solid, after the pretreatment step, certain anti-solvents are mixed (as quenching) to the pretreated solution (containing dissolved cellulose) at ambient temperature for

Table 2 Exemplary physicochemical properties of various ionic liquids as reported able to dissolve cellulose completely[a]

Name	Form	Empirical formula	Structure	Molecular weight [g/mol]	Density [g/cm^3] at 25 °C	Flash point [^{o}C]	Viscosity	Color	Melting point [^{o}C]	pH	HB/HF	Brand/References
Aprotic room temperature ionic liquid RTIL												
1-Ethyl-3-methylimidazolium acetate 96.5% (HPLC)	Liquid	$C_8H_{14}N_2O_2$ [EMIM]Ac		170.21	1.027	164	NDA	NDA	>30	5.4 at 100 g/L	HP	Sigma Aldrich
Thermostable and task-specific ionic liquid (TSIL)												
1-Allyl-3-methylimidazolium-chloride ε 97.0% (HPLC)	Crystal	$C_7H_{11}ClN_2$ [AMIM]Cl		158.63	NDA	NA	NDA	Light orange	NDA, 35 °C	NDA	HP	Sigma Aldrich
Organoaluminate molten salt												
1-Butyl-3-methylimidazolium chloride ε 98.0% (HPLC)	Solid	$C_8H_{15}ClN_2$ [BMIM]Cl		174.67	1.086 (at 20 °C)	192	NDA	Light yellow	70	7.9 at 100 g/L	HB	Sigma Aldrich
Organic salt and RTIL, organic reaction solvent, small vapor pressure, high thermal stabilities, ionic conductivity												
1-Ethyl-3-methylimidazoliu chloride ε 98.0%	Solid	$C_6H_{11}ClN_2$ [EMIM]Cl		146.62	1.189 (at 20 °C)	188	NDA	Beige	77–79	NDA	HP	Sigma Aldrich

(continued)

Table 2 (continued)

Name	Form	Empirical formula	Structure	Molecular weight [g/mol]	Density [g/cm^3] at 25 °C	Flash point [^{o}C]	Viscosity	Color	Melting point [^{o}C]	pH	HB/HF	Brand/References
Other												
1-Butyl-4-methylpyridinium-chloride ε 97.0%	Crystal	$C_{10}H_{16}ClN$ [BMPY]Cl		185.69	NDA	NDA	NDA	Light brown	158–160	NDA	HB	Sigma Aldrich
1,3-Dimethylimidazoliu m dimethyl phosphate ε 98.0%	Liquid	$C_7H_{15}N_2O_4P$ ECOENG		222.18	1.277 (at 20 °C)	NDA	NDA	Yellow	NDA	2.4 at 20 °C	–	Sigma Aldrich

[a] NA = non applicable, NDA = No data available, HB = hydrophobic, HP = hydrophilic

instance by using water, ethanol, or acetone. This is called as regeneration of dissolved cellulosic matter after pretreatment step. In a recent study, ethanol was applied as non- solvent to regenerate rice straw cellulose-based hydrogel via phase inversion method [57]. Highly disordered structures as observed via X-ray diffraction analysis (for the 2 readings versus intensity) indicate lower crystalline with higher amorphous regions [60]. These anti-solvents which are considered as non-toxicity chemicals, not as much as some other organic co-solvent like dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or dimethylacetamide (DMAc). In some reports, it was reported that the ionic liquid-cosolvent combinations are becoming also effective with the recent report (see below).

The ionic liquid's role is mainly to disrupt the crystalline structure of cellulose, thus reducing the crystallinity of the cellulosic matter mainly the cellulosic matter [61]. Cellulose itself is bonded to oxygen-hydrogen atoms (OH) and during the dissolution, the strong bond of hydrogen to others is the key to dissolution. The interactions between oxygen and hydrogen atoms of the cellulose-OH together with the anions and cations from ionic liquid break the intended bond holding the cellulose and hemicellulose within lignin in LCB within the molecular chains of cellulose in LCB. It was reported that cations (positive ions) interacted with hydroxyl oxygen atom present in the cellulosic bond of the cellulosic matter.

Figure 3b shows the effect of the cation and anion examples from 1-Ethyl-3-methylimidazolium acetate [EMIM]Ac on the OH bonds in cellulose and hemicellulose. The green and red boxes refer to cation and anion from [EMIM]Ac, respectively, which then influence the attack on respective OH bonds in cellulose and hemicellulose (as shown by the color coding boxes), in addition to the influence of the physicochemical parameters of the operating steps, for instance, temperature, power input via shaking frequency (for mixing/agitation mode), particle size (surface area), and solid loading (solid to liquid ratio) during the pretreatment. For some other ILs other than [EMIM]Ac, the possibility of bond breakage in lignin by cation and anion is also possible (not shown here).

Ionic liquid which was earlier mentioned to be capable to dissolve the cellulosic matter, the 1-ethyl-3-methylimidazolium acetate [EMIM]Ac was concluded by the major comprehensive investigations. Verma et al. [51] and Zavrel et al. [52] have already started the investigations, for instance, via the high-throughput screening of the possible ionic liquids, in ensuring the green solvent method application by Verma et al. [51] and Zavrel et al. [52], since 2009, comprising of imidazolium, pyridinium, and butyl phosphonium chloride of two different states of solid and liquid. The study found out that EMIMAc from the imidazolium based was the most effective IL during the dissolution of cellulosic matter. Figure 3a below shows the dissolution of lignocellulosic matter in ionic liquid overview from lignocellulosic biomass feedstock being introduced to various ionic liquid types which are capable to dissolve the cellulosic content producing liquid sample containing dissolve cellulose prior to the regeneration of cellulose using antisolvent solution. It indicates the solid LCB was in total dissolution with pure ionic liquid.

As mentioned in the earlier section, the physicochemical properties of the ionic liquid are crucial in this case for the designed role of the cation and anion, in the sense