

ROLE OF IONIC LIQUIDS IN DISSOLUTION AND REGENERATION OF CELLULOSE

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Abstract: Cellulose has found to be one of the renewable, biodegradable and biocompatible resources. The entire prospective of the biopolymers has not been fully exploited due to the obstinate nature of biomass, which allows its solubility only in limited number of common solvents and the inability to easily tailor natural polymer properties. During last few decades, ionic liquids have been suggested as green and sustainable solvents for not only their dissolution but also regeneration of the biomass. A detailed account of different prospects and recent developments in this field has been summarized and presented.

1. INTRODUCTION

Cellulose is the most widely distributed in nature, the most abundant renewable polymer materials. Its annual production is of more than 100 billion tons which is source of green and sustainable energy for the whole mankind. Cellulose has found to be renewable, biodegradable and biocompatible.

Cellulose was discovered in 1838 by A. Payen, who isolated it from plant material and determined its chemical formula [1-3]. Cellulose is the major structural material of plants. Wood is largely cellulose, and cotton is almost pure cellulose.

Cellulose molecule chain contains a large number of -OH groups, Fig. 1. Because of these -OH in cellulose, intramolecular and intermolecular hydrogen bonds have been created. These diverse interactions lead to the formation of higher ordered structures, the semi-crystalline polymers.

The intramolecular hydrogen bonds are highly related to the single-chain conformation and stiffness of cellulose [4,6]. The intermolecular hydrogen bonds are highly related to the crystallinity and

morphology of cellulose. The intermolecular hydrogen bonds between the -OH group in the adjacent C-6 and C-3 positions of cellulose molecules [2], Fig. 2.

Cellulose was used to produce the first successful thermoplastic polymer, celluloid, by Hyatt Manufacturing Company in 1870. Production to rayon ("artificial silk") from cellulose began in the 1890s and cellophane was invented in 1912. Hermann Staudinger determined the polymer structure of cellulose in 1920. The compound was first chemically synthesized (without the use of any biologically derived enzymes) in 1992, by Kobayashi and Shoda [5]. As the oil and mineral resources are depleting and becoming scarce, the world concern for the rational use of resources is increasing in order to make full use of renewable resources.

2. CELLULOSE DISSOLUTION

Lignocellulosic biomass is an eternal and dolefully underspent renewable source comprising of main biopolymers such as cellulose, hemicellulose and

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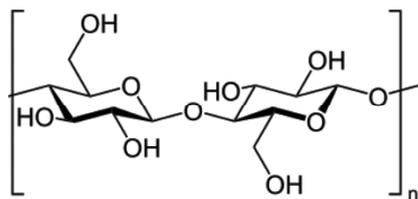


Fig. 1. Structure of cellulose.

lignin. The entire prospective of the biopolymers has not been fully exploited due to the attention of scientists being diverted towards petroleum-based feedstocks from the 1940s [7,8]. Another reason is the obstinate nature of biomass, which allows its solubility only in limited number of common solvents and the inability to easily tailor natural polymer properties.

This has made many of these materials costly and chemically inert [9]. A facilitated way to utilize these natural biopolymers and renewable, biodegradable resources would lead to sustainability and is the current world wide recognized goal. The clean separation of the main components of lignocellulosic biomass, using a practical and environmentally-friendly method without loss of quality of the products, has been clearly renowned by the U.S. Department of Energy as a grand challenge [10]. Various solvents have been proposed for the processing of regenerated cellulose as: copper ammonia solution ($\text{Cu}(\text{NH}_3)_4(\text{OH})_2$), copper ethylene diamine solution ($\text{Cu}(\text{en})(\text{OH})_2$), dimethyl Sulfoxide (DMSO)/paraformaldehyde (PF) chloride, treatment with DMF system and (LiCl/DMAC) system. But main problem arose in the processing of high performance fibers, functional fibers and fibers of renewable resources, most high-performance fibers and fibers of natural resources, such as cellulose, polyacrylonitrile, etc. The origin of the problem was that melting point of certain polymers being higher than their decomposition temperature. Therefore, often solution spinning had been used. Consequently, solution spinning required large amounts of solvents, and most solvents were found to be contaminated or corrosive; requires special equipment, and more power consumption. These factors had been plaguing the entire scientific community and industries, and attracted scientists and researchers all over world to find replacement for the conventional organic solvents.

An ionic liquid as green solvents is an emerging product for the development of green chemistry [11]. Recently, Ionic liquids (ILs) have shown to be green solvents that can dissolve cellulose [12-14] and function as inert and homogeneous reaction media [15-19].

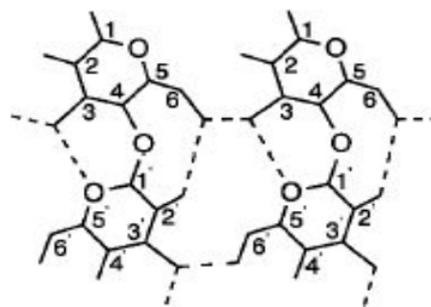


Fig. 2. The intermolecular and intramolecular hydrogen bonds in and between cellulose molecules.

2.1. Cellulose dissolution in ionic liquids

As early as 1934, Graenacher discovered that pyridine-N-oxide chloride salts were able to dissolve cellulose, which is probably the first ionic liquid to dissolve cellulose. Because of its high melting point (118-120 °C), it did not get along in further development in practical applications. Until 2002, Swatoski [12] reported that cellulose can be dissolved directly in 1-butyl-3-methylimidazolium ([BMIM]Cl). The solvation of carbohydrates in [C₄mim]Cl involves the formation of hydrogen bonds between the non-hydrated chloride ions of the IL and the sugar hydroxyl protons in a 1:1 stoichiometry [20]. The IL dissolves cellulose with no prior derivatization in concentrations of up to 300 g·L⁻¹, thus facilitating the development of 'greener' technologies for the production of cellulose-based materials [21]. In the case of cellulose, these interactions disrupt the extensive hydrogen bonding network of the polymer and lead to its dissolution. Additionally, another advantage of the selection of this particular ionic liquid includes minimal sample preparation. Taking its unique properties as a cellulose solvent also into account, the use of this IL in the development of much needed alternative methods for the extraction and processing of polysaccharides from wood and other forms of lignocellulosic biomass had been explored [22]. Moreover it had been found that celluloses which are virtually free of lignin and hemicelluloses can be easily reconstituted from the resulting IL-based wood extracts, and show that the physicochemical properties of the recovered materials are comparable to those of pure cellulose samples subjected to similar processing conditions. However, an interesting aspect found is that although the use of small amounts of DMSO as a co-solvent has no noticeable effect on the solubility of carbohydrates in [C₄mim]Cl, reduces the viscosity of the mixtures, but more importantly, allows for the resulting solu-

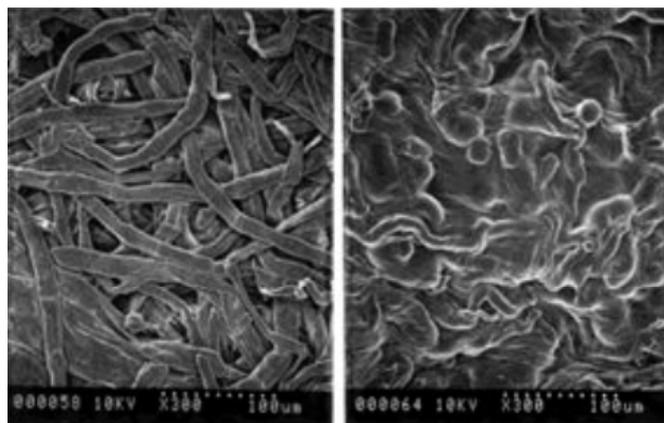


Fig. 3. SEM micrographs of the initial dissolving pulp (left) and after dissolution in [BMIM]Cl and regeneration into water (right), reprinted with permission from R. P. Swatloski, S. K. Holbrey and R. D. Rogers // *J. Am. Chem. Soc.* **124** (2002) 4974, © 2002 American Chemical Society.

bilized materials to be analyzed directly with conventional ^{13}C NMR techniques [23-25].

Afterwards, Ren *et al.* [26, 27] found that ionic liquid 1-allyl-3-methylimidazole chloride ([AMIM]Cl) had good properties for cellulose dissolution. They added cellulose activated with alkali (DP=640) to [AMIM]Cl, placed it on a magnetic stirring plate in oil bath at 80 °C, and obtained 5% solution of cellulose which resisted degradation. The production of paper makes use of cellulose and lignin as a raw material, and almost all cellulose and lignin production comes from raw wood materials, contributing to deforestation and resulting in potential environmental harm. It is therefore beneficial to develop technologies for cellulose and lignin recovery for reuse and sustainability of resources.

Later, three kinds of ionic liquids [C₄MIM]Cl, 3-methyl-1-butyl-*N*-pyridine chloride ([C₄mpy]Cl) and dimethyl benzyl ammonium chloride (BDTAC) were investigated as solvents [28]. The change in the degree of polymerization of cellulose (DP=290–1200) in the process of dissolution had been discussed, and it was found that all three ionic liquids were direct solvents for cellulose. Side reactions forming cellulose derivatives did not occur in the process of dissolution, and the solubility of cellulose lowered with increase degree of polymerization. It has been found that the cellulose with different degrees of polymerization dissolved directly in ionic liquids [BMIM]Cl without other derivative reaction occurring under certain conditions. Afterwards, cellulose which had been dissolved in ionic liquids [BMIM]Cl, was regenerated by treatment with water.

Although the degree of crystallinity and the thermal stability were found to be more decreased than

original cellulose; but these changes did not affect the application value of their materials, and moreover ionic liquids could be recycled. Another imidazolium based ionic liquid had been reported. The new ionic liquid had better capacity to dissolve cellulose. The dissolution of cellulose could also be achieved by derivatization of anions-functionalized ionic liquids [29]. Lignocellulosic materials have been proposed as large renewable resources for chemicals and sugars to reduce society's dependence on nonrenewable petroleum-based feedstocks. And fraction of lignocellulosic materials has become one of most hectic problems in terms of "green environment", because of the presence of the complex structure of lignin and hemicellulose with cellulose. Based on the fact that cellulose could be dissolved in ionic liquids and it could be easily regenerated from the ionic liquids, a facile method of fractionation of lignocellulosic materials had been proposed. However, their main objective was delignification from lignocellulosic materials for pulping process [30]. Lignocellulosic materials, such as wood and straw, are directly dissolved in [BMIM]Cl under microwave irradiation and/or pressure. Then cellulose is precipitated from the [BMIM]Cl solution by the addition of water, and other organic compounds, such as lignin and extractives, still remain in the solution, Fig. 3. Extraction of cellulose from lignocellulosic materials had been carried out on same principle. It had been shown that the presence of extracted cellulose into ethanol had a much higher yield than other refined cellulose, such as from lignocellulosic materials pretreated by steam explosion or chemical pretreatment. Besides the extraction of cellulose from lignocellulosic materials, this method can also be used to extract some natural products. It

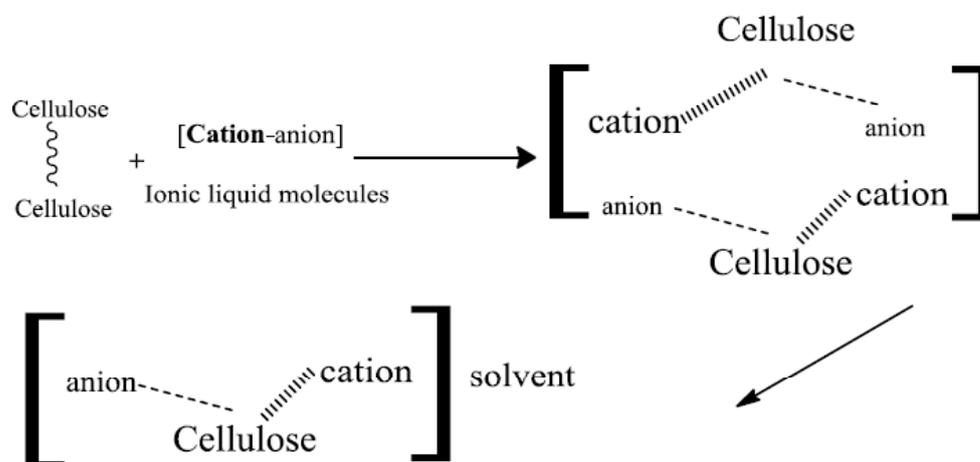


Fig. 4. Dissolution mechanism of cellulose in ionic liquids, according to the pathway suggested in Ref. 43.

had a much higher essential oil yield than such traditional methods as steam distillation and solvent extraction. However, this essential oil had a different composition from that obtained by steam distillation. This is because of the Cl^- concentration and decreased activity, destruction of the ionic liquid and the ability of forming hydrogen bond with the cellulose hydroxyl groups. But even in the microwave heating, cellulose cannot dissolve in ionic liquids with anions BF_4^- , PF_6^- .

The difference in polymer and solvent molecules size impart different extent of molecular movements. The solvent molecules can move faster and penetrate the polymer chains. On the other hand, diffusion from polymer to the solvent is very slow. Generally, it is believed that the dissolution of the polymer process go through two stages: Firstly, solvent molecules penetrate inside polymer and hence lead to polymer volume expansion, known as the "swell", and secondly, the polymer is dispersed in the solvent to form a completely dissolved molecular dispersion system. For the cellulose dissolved in the ionic liquid, swelling is not obvious. Cuissinat *et al.* [31] and our group [32] also studied the cellulose dissolution and swelling phenomenon in [BMIM]Cl. When the temperature is higher than 80°C , the dissolution of cellulose in [BMIM]Cl is rapid, with the same non-obvious swelling process. Various other studies have been carried out during recent years involving the pretreatment of cellulose and related biomass by means of ionic liquids which would further lead to its fractionation or extraction [33-36]. Certain studies also account for the effect of properties of ionic liquids on different structural aspect of regenerated cellulose [37-39].

2.2. Mechanism involved in cellulose dissolution in ionic liquids

Swatloski *et al.* [12] suggested that the anions and cellulose surface $-\text{OH}$ bonds form new hydrogen bonds, destroying the role of hydrogen bonds between cellulose molecules, resulting in the gradual dissolution of cellulose. Moulthrop *et al.* [40] first use high-resolution ^{13}C -NMR for investigating cellulose and its oligomers in ionic liquid. It was found out that in cellulose/[BMIM]Cl solution, cellulose C1 and C4 chemical characteristics oligomer has shown displacement confirming that cellulose intramolecular and intermolecular hydrogen bonds has been destroyed. Zhang *et al.* [41] suggested that ionic liquid's cation and oxygen in the cellulose hydroxyl groups form hydrogen bonds, thereby destroying the original cellulose and intramolecular-intermolecular hydrogen bonds, leading to complete dissolution of the cellulose. Remsing [42] thought that ionic liquid cations had no interactions with cellulose. However, more and more people believe that only the anions and the surface hydroxyl groups of cellulose form hydrogen bonds. The dissolution mechanism of cellulose in ILs [43], see Fig. 4, involves oxygen and hydrogen atoms of cellulose-OH in the formation of electron donor-electron acceptor complexes which interact with IL. For their interactions, the cellulose atoms act as electron pair donor and hydrogen atoms serve as an electron acceptor. The cations in ionic liquid act as the electron acceptor and anion as electron-donor. Upon interaction of the cellulose-OH and the IL, the oxygen and hydrogen atoms from $-\text{OH}$ groups are separated, causing the opening of hydrogen bonds between molecular

chains of cellulose and, eventually, the cellulose dissolves [44].

3. TERNARY MIXTURES OF POLYMERS

Various aspects of the ternary mixtures of polymers comprising of polymer, solvent and nonsolvent have been studied. Ternary phase diagram provide information related to the thermodynamic properties of polymer solution and polymer/solvent/coagulant ternary system. It had been found to be an effective tool for phase separation. Alena and Smolders [45] studied liquid-liquid phase separation of water/solvent/cellulose acetate ternary system. Barzin [46] studied the PES/solvent/non-solvent mixtures and calculated thermodynamics of phase diagram, membrane morphology evaluation, and discussed the size of the binary interaction parameters of two-terminal position of the impact. In addition, through drip turbidity titration method, Boom [47] proposed ternary polymer cloud point data in a linear relationship between the equation of LCP (Linearized Cloud point Curve Correlation) for ternary systems consisting of polymer, solvent and non-solvent. The cloud drip titration based on the establishment of acrylic acid/sodium thiocyanate/water ternary system phase diagram had also been reported [48].

Various other studies have been carried out the behavioral aspects of different ternary mixtures [49] of polymers such as NMMO/water/cellulose [50]; cellulose acetate/polystyrene blends/THF [51] and water-dimethylformamide-polyacrylonitrile [52]. The liquid-liquid equilibrium of various ternary systems containing an ionic liquid+n-hexane+an organic compound involved in the racemic resolution of *rac*-1-phenylethanol (*rac*-1-phenylethanol, vinyl propionate, 1-phenylethyl propionate or propionic acid) at 298.2K and atmospheric pressure have been measured [53]. More recently, dissolution of cellulose in ionic liquids alongwith co-solvent has been investigated. The studies revealed that rate can be increased by cosolvent addition, and the viscosity can be significantly reduced. The solutions were stable over time at room temperature and could be converted to regenerated textile fibers with good mechanical properties [54].

4. RHEOLOGICAL BEHAVIOR OF POLYMERIC SOLUTIONS

The understanding of rheological behavior of polymeric solution in ionic liquids is a necessary step

towards realizing the potential of ionic liquids as processing aids (especially in fiber spinning, film casting and spraying), and also in understanding the dynamics and thermodynamics of polymeric chains dispersed in ionic liquids. Specifically, dilute solution viscometry and the resulting intrinsic viscosity measurements provide the simplest method for assessing the pervaded hydrodynamic volume of the dispersed solute and for determining polymer solution properties such as chain flexibility, polymer-solvent interactions and polymer-polymer interactions [55,56]. Further, the characterization of the material response to applied shear deformation, as characterized by flow curves of steady shear viscosity against applied shear rate or applied shear stress, is essential for designing processing strategies. Consequently, the shear rheological characterization of cellulose dissolved in ionic liquids has received a lot of attention in recent years [57-64].

Early studies on the macromolecular nature of cellulose and cellulose derivatives by Staudinger, Mark, Kuhn, Houwink, Ostwald, Flory, and Huggins established many of the fundamental concepts concerning the relationship between solution viscosity, polymer molecular weight and polymer-solvent interactions (solvent quality) [65-70]. In contrast to commonly used synthetic polymers like polyolefins, polyethylene oxide (PEO) or polystyrene (PS), cellulose and cellulose derivatives are characterized by a high intrinsic viscosity, large radius of gyration and large characteristic ratio, (<10 for most polyolefins and PEO, but >10 for many cellulose derivatives) [65]. Cellulose and its derivatives also have a small second virial coefficient, display viscous shear thinning in semi-dilute and concentrated solutions and have a large persistence length, (cellulose in cadoxen=7 nm, hydroxyethyl cellulose in water has=10-30 nm and xanthan in water has=50-210 nm whereas, by contrast, <2 nm for polyethylene oxide and polyolefins). These characteristics are all indications that cellulose chains adopt semi-flexible conformations in solution. Highly concentrated solutions of cellulose and cellulose derivatives can also form lyotropic liquid crystal phases, which can be advantageous in creating fibers, films or composites with a higher degree of inbuilt order and advantageous mechanical properties [71]. Indeed, a number of researchers have used ionic liquid based fiber spinning of cellulose to manufacture pure regenerated cellulose fibers as well as multi-functional cellulose fibers reinforced and functionalized with, for example, carbon nanotubes [72,73], magnetic particles [74] and antibacterial

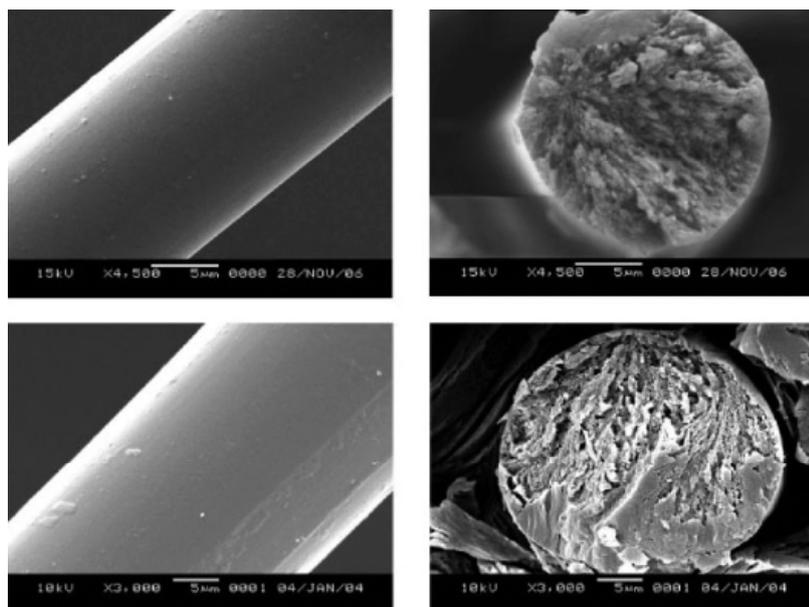


Fig. 5. Scanning electron microscopy photographs of surfaces and cross sections of (a) ionicell fibers and (b) lyocell fibers, reprinted with permission from T. Cai, H. Zhang, Q. Guo, H. Shao and X. Hu // *J. App. Polym. Sci.* **115** (2010) 1047, © 2010 John Wiley & Sons, Inc.

agents [75]. Rheological properties of cellulose dissolved in different ionic liquids with co-solvent are also being studied. The viscosities of ILs are found to be exponentially decreased by the addition of co-solvent [76]. As a processing aid for cellulose, economical and eco-friendly ionic liquids have the potential to drive the latest resurgence in the use of cellulose-based fibers.

5. CELLULOSE SOLIDIFICATION PROCESS DURING FIBER FORMING PROCESS

The coagulation bath is undoubtedly the most critical factor for the solidification of the fiber. The polymer solution was extruded through a spinneret air section or directly into a coagulating bath. The solvent present a concentration gradient between the solvent and non-solvent and as a result double diffusion occurs immediately. The yarn inside the solvent and non-solvent components is changed leading to the final solidification shape. Biganska *et al.* [77] used crystalline cellulose/NMMO solution of the cellulose gel samples in order to elaborate solidification kinetics of solvent. Gavillon *et al.* [78] studied cellulose/NaOH aqueous solution and investigated cellulose gel regeneration process and diffusion kinetics. On comparison with cellulose/NMMO solution, it was found out that when cellulose concentration is 5-7%, NaOH, and NMMO, diffusion coefficient is almost the same. The results showed that, as expected, the diffusion coefficient

increases as the viscosity of the coagulation bath decreases. During the spinning process of forming lyocell yarn, Liu *et al.* [79] detected that the NMMO concentration in the solidification process has two diffusion regions: Rapid diffusion region (which is formed mainly because of NMMO and water to form a hydrogen bond), and slow diffusion region. Compared with conventional solvents, ionic liquids act as a special surface structure and the cellulose hydroxyl groups resulted in the formation of a new bond dissolving cellulose [12]. On the other hand, the cellulose/ionic liquid have a large molecular size and a higher viscosity [80]. Thus, ionic liquids and cellulose macromolecules show specific interactions between the solidification processes will cause the cellulose/ionic liquid diffusion kinetics and other solvents vary. However, so far on the ionic liquid in cellulose fibers diffusion kinetics studies have not been reported.

5.1. Ionic liquid as a solvent for regenerated cellulose fibers

Following the production of NMMO cellulose fiber as a successful industry, ionic liquids acting as solvents may also be directly applied to form the cellulose fibers and have been successfully processed [81]. Many ionic liquids as a solvent for spinning cellulose fibers has been reported by Laus *et al.* [82] The cellulose pulp was dissolved in [BMIM]Cl and [AMIM]Cl with dissolution temperature of 100~105 °C (30 mBar). The nozzle diameter is of

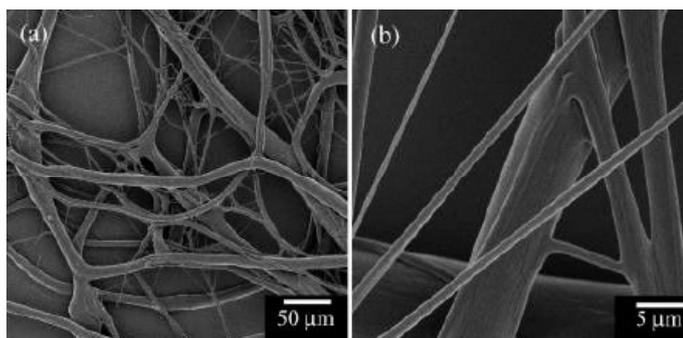


Fig. 6. Field emission scanning electron microscope images of cellulose only fibers (a, b) 10% (w/w), reprinted with permission from G. Viswanathan, S. Murugesan, V. Pushparaj, O. Nalamasu, P. Ajayan and R. Linhardt // *Biomacromolecules* **7** (2006) 415, © 2002 American Chemical Society.

0.1 mm, in order to make coagulation bath of pure water was prepared by a dry jet wet strength 3.79 cN/dtex, breaking elongation of 11.3%, of the cellulose fibers. By comparison of the two different solvents, regenerated cellulose fiber was obtained by [BMIM] Cl solution is not only of good stability, and exhibit more excellent mechanical properties of the fiber.

Hermanutz *et al.* [83] prepared regenerated cellulose fibers by wet spinning by using 1 - ethyl-3-methylimidazolium acetate ([EMIM] Ac) as solvent. Tensile strength can be achieved up to 3.0-3.5 cN/dtex, and Lyocell fiber performance improves considerably. And the ratio of ionic liquid as a solvent in comparison to NMMO showed higher productivity, while the production process is easy to control, and can adjust the process to obtain different properties of regenerated cellulose fibers.

Subsequently, Hermanutz *et al.* use [BMIM] Cl as solvent for preparation of cellulose fibers, and discovered that wet spinning and dry-jet wet spinning are feasible. However, since [BMIM]Cl has higher melting point, which is about 68 °C the spinning solution viscosity need high requirements for equipment for the smooth spinning. The melting point of the [EMIM]Ac solvent is quite lower (melting point <-20 °C). For preparation of cellulose fibers, it was found that cellulose spun by [EMIM]Ac has good solubility (concentrations of up to 20 wt.%), and also spun at higher temperatures (80~90 °C) processing still has good stability. Further, by adjusting the temperature or the cellulose concentration in a wide range (50 ~ 3000 Pa s) could adjust the viscosity of the spinning solution, which formed cellulose fibers at a high flexibility spinning. Properties of cellulose fibers prepared by the conventional viscose fiber similar to the prepared fiber strength, toughness remains substantially constant.

Kosan *et al.* [84] comparatively studied four different ionic liquids ([BMIM]Cl, [EMIM]Cl, [BMIM]Ac and [EMIM]Ac) as solvent for regenerated cellulose fibers. The results show that the ionic liquid has a strong dissolving power, and in the concentration range with good spinnability, obtained by dry jet wet, mechanical properties of the regenerated cellulose fibers are more than Lyocell fiber. The toughness of regenerated cellulose fibers, ring crush strength and elongation are more preferable, respectively 53.4 cN/tex, 33.1 cN/tex, 13.1%.

Cai Tao *et al.* [85], see Fig. 5, used [BMIM] Cl as solvent for wet spinning of regenerated cellulose fibers by orthogonal experimental design and system and have studied the gap length, nozzle stretch ratio, coagulation bath concentration, coagulation bath temperature and other process parameters on regenerated cellulose fiber. Cai *et al.* [86] studied structure and mechanical properties of cellulose fibers and Lyocell fibers by using [BMIM]Cl as a solvent. Lyocell cellulose fibers have found to have similar smooth surfaces and dense section.

Cai Tao also discussed [BMIM]Cl as spinning solvent for cellulose fiber preparation process and investigated the concentration of fibers in the coagulation bath, crystal structure and mechanical properties. The results showed that the coagulation bath concentration, fiber crystallinity and amorphous orientation factor increases first and then decreases. When the crystal orientation is same, coagulation bath concentration, fiber grain size decreases, and crystallinity increases. Fiber tensile strength and modulus first increases and then decreases, while the elongation at break is quite opposite.

Meanwhile, our group [87] gave a comparison of conventional viscose fibers (Viscose), high wet modulus of cellulose fibers (Newdal), to NMMO solvent regenerated cellulose fibers (Lyocell), and in [BMIM]Cl regenerated cellulose fibers as the sol-

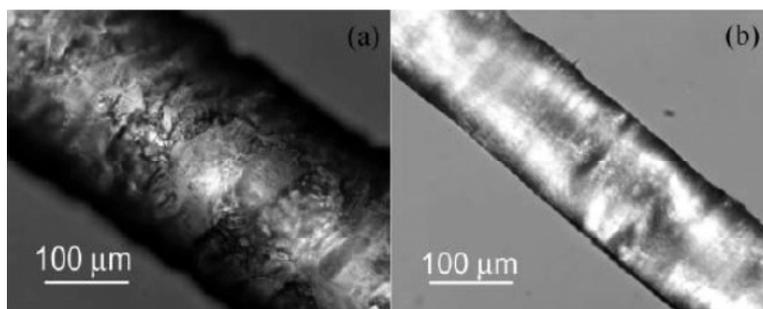


Fig. 7. Polarized optical microscopy images of silk fibers coagulated in methanol (a) as spun and (b) with a 2× draw ratio, reprinted with permission from H. Xie, S. Li and S. Zhang // *Green Chem.* **7** (2005) 606, © 2005 Royal Society of Chemistry.

vent. The results show that, because of Lyocell fibers and IL-cell (obtained by the direct method and the dry-jet wet dissolution) and regenerated cellulose fiber, showed a smooth surface, uniform cross-section, dense submicroscopic morphology and high crystallinity, grain zone orientation, and mechanical properties.

The above studies show that with ionic liquid as solvent, regenerated cellulose fibers and Lyocell fiber not only has similar mechanical properties, surface morphology, crystal structure and dyeing properties, but also controlling the spinning process is simple. However, in relation to the ionic liquid as solvent spinning cellulose fiber, structure and properties of reported are rare, especially in some key technologies such as spinning speed, and post-treatment process.

Viswanathan *et al.* [88] used ionic liquid as a solvent, ethanol as coagulant and cellulose fibers were first prepared by electrostatic spinning cellulose-heparin mixed fibers, Fig. 6. Pure cellulose fibers have a smooth surface; the regenerated cellulose-fiber blend heparin was rough. Xu *et al.* [89] also used the [AMIM]Cl/DMSO solution as the solvent mixture and prepared regenerated cellulose fibers by the electrostatic spinning. And pointed out that through technological improvements, massive ultrafine cellulose fibers can be produced by electrostatic spinning.

Cellulose can easily be dissolved in the ionic liquid in most, but the lignin is difficult to be dissolved in the ionic liquid. Generally, ionic liquids in the imidazole ring is connected to, methyl, ethyl, butyl, allyl and benzyl group, and the anion is Cl⁻, Br⁻, acetate, and fluoroborate [90-92]. It has been reported that hemicelluloses can be dissolved in the ionic liquids, [93,94] while trees, [95-97] bagasse [98,99] and corn stalks and other biological polymers can be partially or completely dissolved in the ionic liquid. Ionic liquids cannot only dissolve silk

fibroin, [100] the solution also has a certain spinnability [101], Fig. 7.

In addition to the silk fibroin, the scientists also found that wool keratin, [102] corn starch and protein, [103] feather protein, the collagen fibers, chitin and chitosan [101] can also be dissolved directly in ionic liquids. Wang *et al.* [104] explored mechanism of polyacrylonitrile dissolved in ionic liquids and process of polyacrylonitrile/dilute solution properties of ionic liquids, as well as polyacrylonitrile/ionic liquid rheological behavior of concentrated solution has been started [105,106]. Subsequently, Wan [103] first reported that polyacrylonitrile fibers in [BMIM]Cl as a solvent obtained by dry jet-wet method exhibit high strength, a high degree of orientation and surface smoothness.

In addition, poly-phthalimido-phenylenediamine (PMIA) can be dissolved in [BMIM]Cl and DMAc/LiCl [107] in a mixed solvent. However, polyarylsulfone (PASU), [108] polyaniline polybenzoxazole imidazole (PBI) can also be dissolved in the ionic liquid [109,110], see Fig. 8.

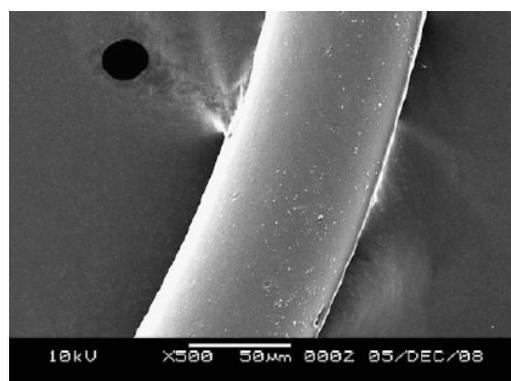


Fig. 8. SEM image of regenerated PBI fibers with [BMIM]Cl as solvent, reprinted with permission from B. Wang, Y. Tang, Z. Wen and H. Wang // *Eur. Poly. J.* **45** (2009) 2962.

5.2. Aggregated structure of cellulose fibers

Cellulose fiber containing a number of molecules is a semi-crystalline. Forming the machining process, the cellulosic fibrous structure will inevitably affect the performance, especially aggregation structure, including the crystal structure (crystalline and amorphous regions, cell size, and form, the molecular chain in the form of a pile inside the cell, crystallite size), the orientation structure (orientation of the molecular chains and crystallites), fibril structure and the pore structure [112]. The cellulose fibers are generally semi-crystalline cellulose, a long chain with multiple folded stacked together to form folded chain lamellae, and many fibrils arranged together to form a fiber. Fibrils are distributed between the amorphous areas and holes. After stretching the fibers, usually stretched holes, these holes affect morphology and distribution of the mechanical properties of the fiber.

While using the wet spinning or dry jet-wet method in order to obtain regenerated cellulose, the resultant fiber has usually a certain amount of pores. Pore size has a certain influence on the mechanical properties of the fibers, but a certain number of pores can enhance fiber thermal capacity.

6. CONCLUSION AND FUTURE PROSPECTS

The continuous utilization and depletion of petroleum resources has made it increasingly important to explore ways for the dissolution of lignocelluloses biomass. Ionic liquids have proven to be the best way for their dissolution and regeneration. These solvents are not only green but also recoverable. Their full exploitation is still inhibited by their higher viscosities. In order to overcome this problem, recently concept of addition of co-solvent along with ionic liquids for dissolution of cellulose has been under consideration by the researchers. However, still more research is needed to understand the kinetics, and interactions of ternary polymeric solutions. Moreover, the role of co-solvent in the regeneration of cellulose by ionic liquid and the properties of resultant fibers or films still needed to be studied in detail.

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