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Evaluation of Ionic Liquids as Direct Solvents for the Manufacturing of Novel Products from Cellulose

Master of Science Thesis in Chemical and Biological Engineering, KBTX05

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Abstract

Cellulose is one of the most abundant biological and renewable materials in the world. The application of cellulose is widely distributed among various industries such as fiber, paper, pharmaceutical, membrane, polymer and paint. However, the utilization of cellulose or cellulosic materials has not been developed entirely because of its poor solubility in common organic solvents. Ionic liquids (ILs) are relatively new family of solvents for dissolution of cellulose. They are organic salts contain only cations and anions with low melting temperature, which make them suitable for the solubilization of cellulose. Moreover, ILs are non-volatile, non-toxic, non-flammable and thermally and chemically stable. Cellulose dissolved in ILs can be regenerated with anti-solvents as water, ethanol and acetone. In this study, both the dissolution and regeneration of hardwood and softwood dissolving pulps with and from two ILs ($[C_4mim^+]CH_3COO^-$ and $[C4mim^+]Cl^-$) were investigated. Furthermore, the impact of treating cellulose with ILs was also evaluated by using different analytical techniques, such as size exclusion chromatography (SEC), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).

Key words: cellulose, dissolving pulp, ionic liquids (ILs)

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1 Background

1.1 Cellulose applications

Cellulose, the most abundant polysaccharide resource in the world, has been used widely in many industrial productions. Wood and cotton are the two basic substances utilized directly as unmodified cellulose-containing raw materials. However, for many other applications such as in paper, pharmaceutical, membrane, polymer, and paint industries, the cellulose has to be isolated and sometimes converted into its derivatives. In principle, the cellulose is firstly extracted from its primal resources (e.g. linocellulosic materials) either chemically or mechanically, and then it can be treated chemically and translated into its derivatives.

Although many previous studies have reported the methods of producing cellulose derivatives and relevant applications, there are four main reasons still block the exploitation of total potential of cellulose: the historical shift to petroleum-based polymers from 1940s onwards, the lack of an environmental-friendly method to extract cellulose from its primitive resources, the difficulty in modifying cellulose properties, and the limited number of common solvents that readily dissolve cellulose.

1.2 Sources of cellulose

The fibers from wood and annual plants such as cotton, grass, algae, hemp, flax, and jute are the major resources of cellulose. Cellulose in plants is the main component of cell walls however its degree of polymerization may vary among species. Moreover, some bacteria can also secrete cellulose to produce biofilms. The amounts of cellulose in different biological origins are shown below in Table 1 [40]:

Table 1 The amount of cellulose in various resources

Resources	Cellulose (%)
Cotton	95-99
Flax	60-65
Wood	40-50
Bacteria	20-25
Bark	20-30
Mosses	25-30

1.3 Wood constituents

Wood is a very old material that has been used for years from prehistoric to present time for the development of mankind. The conversion of wood materials into paper has been one of the most significant applications since about 2200 years ago to establish the foundation of writing based communication. In modern society, the utilization of paper has been developed to include not only communication but also the packaging and hygiene applications. Moreover, besides paper making, the utilization of wood based materials has been deeper developed and expanded in many other aspects, in order to create components that can be further refined, and therefore giving the optimum and balanced production of biomaterials, biochemicals, biofuel and bioenergy. The process is commonly called biorefinery. The main streams of conversion at the present time are shown below in Figure 1 [40]:

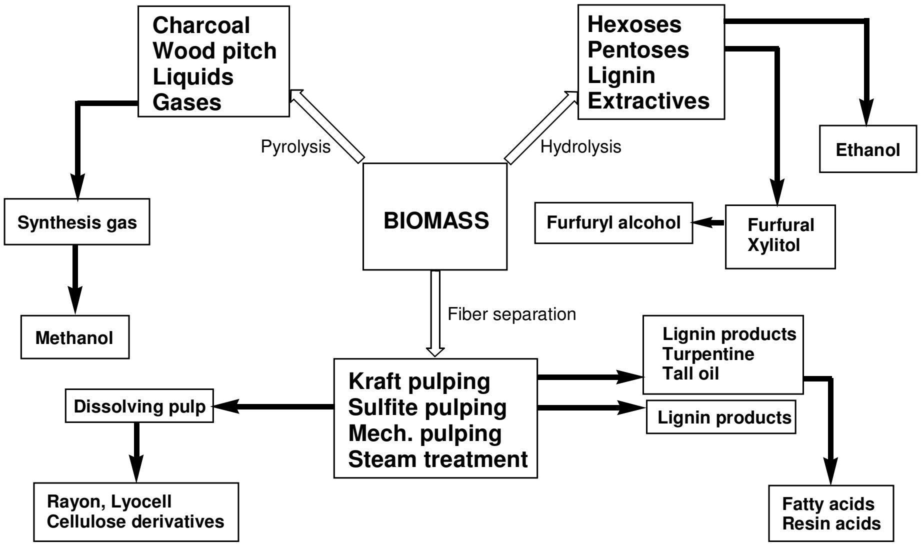

Figure 1 Thermal and chemical techniques for the conversion of wood (or other biomass) into different products

The properties of wood can vary with tree species, growing conditions and age. Wood is mainly composed of approximately 40-45 % cellulose, 25 % hemicelluloses, 20-28 % lignin and small amounts of minerals and organic molecule extractives.

Cellulose, the main biopolymer of wood (about 40-45 % of the dry contents in wood), consists of straight and unbranched polymer chains. Each chain is made up of numerous repeating glucose molecules connected via 1-4-glucosidic ether bridges of β-D-glucose with a high degree of polymerization. The average degree of polymerization (DP) is approximately 10,000 in wood.

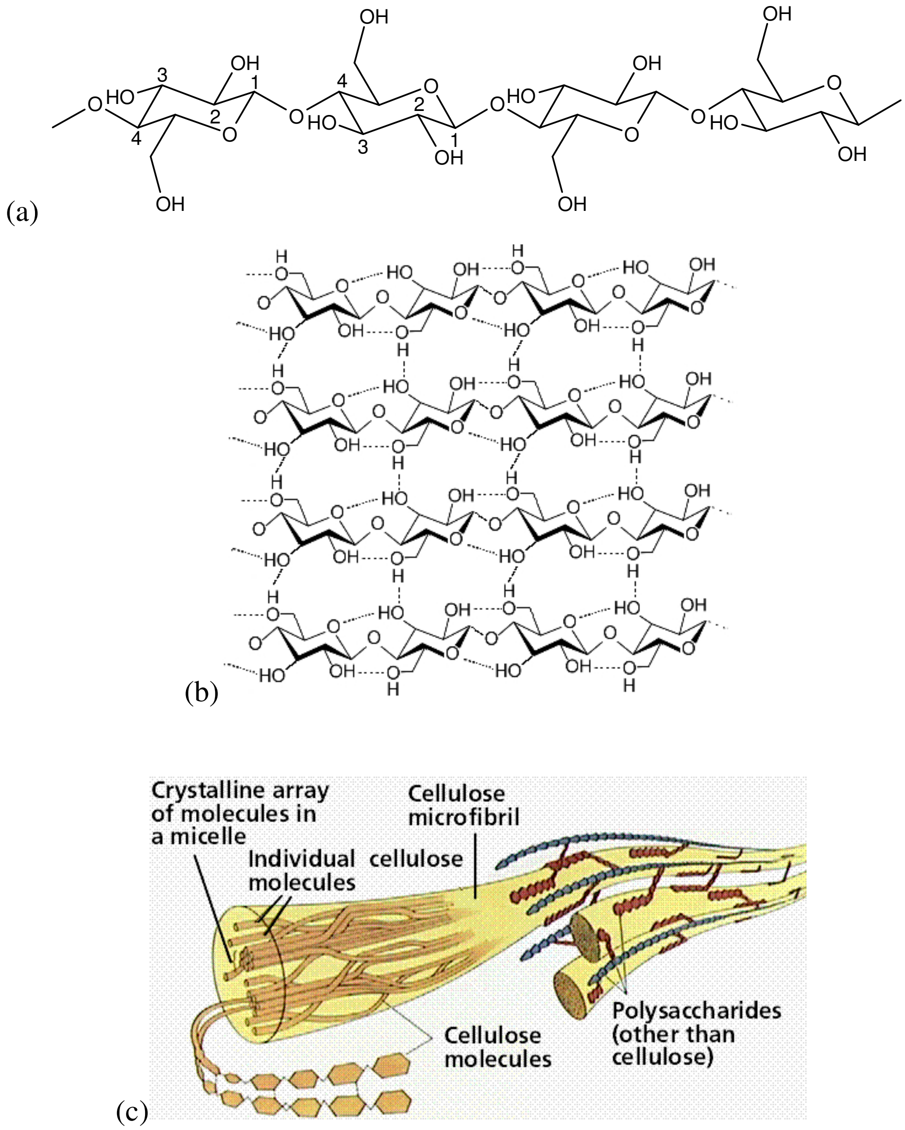

Figure 2 The molecular (a), supramolecular (b) and hierarchical (c) structure (in fiber cell walls) of cellulose

Each glucose unit in cellulose molecule contains three hydroxyl groups, which could be used to form the intra molecular bonds and therefore composing a rigid structure. The inter molecular bonds, on the other hand, are constructed between adjoining cellulose molecules, which gives the cellulose the highly water-insoluble property and stable conformation. Consequently, the aggregated molecules built up through H-bonds are ordered in micro fibrils with crystalline structure [1, 2]. However, in wood, cellulose could form not only lattices with well-organized regions but also slightly disturbed regions with a lower degree of order, which is named as "amorphous cellulose". However, the crystalline and amorphous states are not the only two circumstances of order; there are also other formations such as intermediate or semicrystalline states.

Hemicelluloses are a group of heteropolysaccharides which constitute commonly 20-30 % of the dry content of wood. However, the composition and structure of hemicelluloses are different in softwood and hardwood among stem, branches, roots and bark.

Normally, the hemicelluloses in softwood are galactoglucomannans (about 20 %) and arabinoglucuronoxylan (5-10 %). The galactoglucomannan consists of a chain without or with slender branches formed via 1-4 connected β-D-glucopyranose and β-D-mannopyranose units. The framework is then connected with α-D-galactopyranose via 1-6 bonds. More importantly, the hydroxyl groups at C2 and C3 positions are substituted in each unit by O-acetyl groups. The arabinoglucuronoxylan is formed via 1-4 connected β-D-xylopyranose units and the substitution by 4-O-methyl-α-D-glucuronic acid groups occurs at C2 position. Further, the α-L-arabinofuranose units are also included in the structure.

The common hemicellulose in hardwood is O-acetyl-4-O-methylglucurono-β-D-xylan. The content of xylan differs from 15 % to 30 % with the variation of hardwood species. Additionally, 2-5% of a glucomannan which consists of 1-4 connected β-D-glucopyranose and β-D-mannopyranose units also present in hardwood.

Lignin is the second main biopolymer in wood which constitute about 20-30 % of dry substance. In contrast to celluloses and hemicelluloses, lignin is an amorphous and irregular polymer consists of linked aromatic structures. There are three basic phenylpropanoid monomers, trans-p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol that forms lignin via co-polymerization.

The connection of monomers is conducted through rigid covalent bonds and weaker hydrogen bonds.

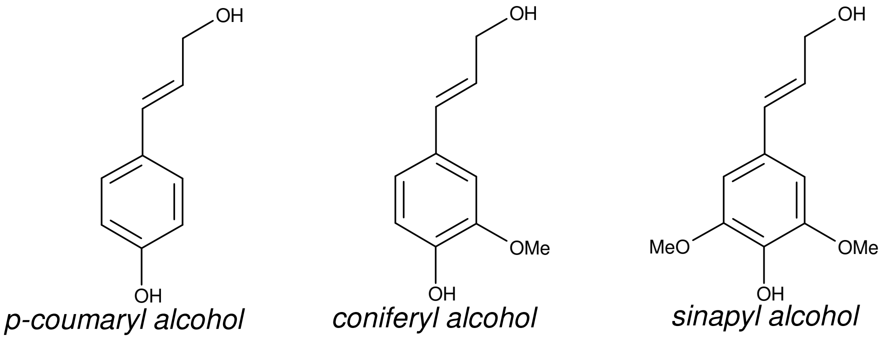

Figure 3 Phenylpropanoid monomers constituting the lignin

Previous study has shown the connection of lignin with arabinoglucuronoxylan, glactoglucomannan, glucomannan and cellulose via covalent bonds [3]. Moreover, the cross-link of lignin with other polysaccharides to form the lignin-carbohydrates network in wood is also issued.

There are also small amount of extractives and inorganic materials present in wood. Moreover, although they are in trace amount, extractives could introduce problems in applications such as papermaking and chemical recovery system.

Table 2 Chemical composition of different wood species (values are shown in % of dry weight of wood)

Main chemical components	Wood species		
	Spruce (*Picea abies*)	Blue gum (*Eucalyptus globulus*)	Birch (*Betula papyrifera*)
Cellulose	41.7	51.3	39.4
Glucomannan	16.3	1.4	1.4
Xylan	8.6	19.9	29.7
Other carbohydrates	3.4	3.9	3.4
Lignin	27.4	21.9	21.4
Extractives	1.7	1.3	2.6

1.4 Separation methods of fibers

Pulping is the common process for the separation of fibers from wood or other lingo-cellulosic materials. The pulping process can be executed through mechanical, thermal and chemical ways, or their combinations. The mechanical pulping is to treat woods with steam or aqueous sulphite solution before the abrasive refining or grinding for fiber separation. Chemical pulping is conducted with chemical reactants and heating. The main purpose of chemical pulping is to remove lignins. Moreover, the choice of specified method depends on the application of final products.

Kraft pulping is the dominant global process of producing chemical pulp. The principle of Kraft pulping is to impregnate chips with cooking liquor, contains mainly NaOH and Na_2S, and then the digester is normally heated up to 150~170 °C for reaction. The treatment is so vigorous that ether bonds are cleaved and therefore lignin is depolymerized. However, because of low selectivity, the carbohydrates such as hemicelluloses and cellulose can also be dissolved through Kraft pulping partly. Therefore the process should be stopped in time after 90% of lignin is removed. The principle is shown as follows:

$$S^{2-} + H_2O \Leftrightarrow HS^- + H_2O$$

$$HS^- + H_2O \Leftrightarrow H_2S + HO^-$$

$$E.A.(\%) = \frac{\eta_{EA} \cdot M_{NaOH}}{m_{wood}} \times 100 = \frac{\eta_{EA} \cdot 40}{m_{wood}} \times 100$$

$$Sulphidity(\%) = \frac{2\eta_{Na_2S}}{2\eta_{Na_2S} + \eta_{NaOH}} \times 100 = \frac{2\eta_{Na_2S}}{\eta_{Na_2S} + \eta_{EA}} \times 100$$

There are three stages during Kraft cooking, a rapid initial lignin removal stage, a first order bulk delignification stage and the residual delignification stage. Previous studies [4-8] have shown that, cooking liquor with high ionic strength could influence delignification and reduce the length of cellulose chain.

The preparation of sulphite pulping is conducted with aqueous sulphur dioxide (SO_2) and base, such as calcium, sodium, magnesium and ammonium. Nowadays, the sulphite pulping by using magnesium and sodium as base are two main methods since they can be recovered after the pulping. The principle of preparation is shown as follows:

$$H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O$$

$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O$$

$$MgCO_3 + 2H_2CO_3 \rightarrow Mg(HSO_3)_2 + CO_2 + H_2O$$

$$Mg(HSO_3)_2 + MgCO_3 \rightarrow 2MgSO_3 + CO_2 + H_2O$$

Then the pulping is carried out with cooking liquor at the pH from 1.5 to 5. The time range of pulping reaction is normally between 4 and 14 hours at the temperature from 130 to 160 ˚C. The variation of time and temperature depend on the chemical used for pulping.

$$ROR' + H^+ \rightarrow R^+ + R'OH$$

The degradation of lignin is carried out through protonation of carbon double bonds, or breaking the ether bonds, which connect numerous components of lignin, under acidic condition. Then the intermediates with electrophilicity can react with bisulfite ions (HSO_3^-) and finally produce sulfonates.

Compared to kraft pulping, the sulphite pulping is less used and it is more applied in certain purpose of paper making. Moreover, the sulphite pulping is a flexible method and can be utilized to produce different types and grades of pulps. However, the sulphite pulping does have disadvantages. For instance, the pulps produced through this way have lower strength than kraft pulps in paper making industries, though the poor strength maybe useful for specific reasons sometimes.

1.5 Dissolving grade pulps

Dissolving grade pulps (sometimes referred as linters) are nowadays used as the raw materials for the production of regenerated cellulose. Because of its high cellulose content (90-99 %), low hemicelluloses content (2-4 %), only traces of lignin, high brightness and uniform molecular weight distribution, dissolving pulp is suitable for the production of different cellulose derivatives and rayon.

Commonly, there are two different methods for producing dissolving grade pulps. The sulphite process is conducted through the treatment of wood chips with chemicals (e.g. $Mg(HSO_3)_2$) at a high temperature. It can give the outcome with a cellulose content up to 92 % or more [48], which is mostly used for the fabrication of viscose rayon. On the other hand, the kraft process, which produce the sulphate pulp with a higher cellulose content up to 96 %, is carried out through the impregnation of chips with cooking liquor contains mainly NaOH and Na_2S, followed by heating the digester to 150~170 °C for further reaction [41, 42]. The products are mainly used to make rayon yearn. Recently, the exploration about upgrading paper grade pulp into dissolving grade pulp materials has gained increased interests. Since the conversion is more cost effective than conventional techniques, it might be later applied in the production of dissolving pulps [44].

1.6 The solvents of cellulose

The sufficient development and utilization of cellulose materials are still challenging tasks because of their poor solubility of cellulose. The strong fibrillar structures of cellulose caused by inter and intra molecular hydrogen bonds, dipole and Van der Waals interactions which lead to the binding of the cellulose molecules to form intensive framework are the main reasons. As a result, only the less ordered (amorphous) regions in the cellulose molecule located on and between the surfaces of the fibrils or in shorter segments within the fibrils are accessible to chemicals [13].

The traditional methods of cellulose dissolution such as cuprammonium and xanthate processes are normally either cumbersome or expensive. Moreover, the requirement of unusual solvents, typically those with high ionic strength, and the need of relatively harsh conditions for processing [10-12] are the main disadvantages of these methods. In addition, since the solvents can hardly be recycled after the dissolution, those conventional methods may result in serious environmental problems, which could become a huge obstacle for them to be used as preferable solvents.

Generally, the cellulose solvents used nowadays can be divided into three types, which are the derivatizing solvents and non derivatizing solvents including aqueous and non aqueous medias. The derivatizing solvents contain commonly CF_3COOH, HCOOH, CS_2, N, Ndimethylformamide/N_2O_4. During the dissolution, the derivatizing solvents can lead to the occurrence of side reactions and the production of undefined structures, so that the dissolved material can be reproduced hardly. However, some of them are useful for the synthesis cellulose derivatives. As to the non derivatizing solvents, the aqueous media, which are widely used for cellulose regeneration, can be subdivided into aqueous inorganic complexes such as cuprammonium hydroxide (Cuam, $[Cu(NH_3)_4\ ](OH)_2$) and cupriethylenediamine hydroxide (Cuen, $[Cu(H_2N\text{-}(CH_2)_2\text{-}NH_2)_2\ ](OH)_2$); aqueous bases such as NaOH; mineral acids and melts of inorganic salt hydrates. The structure of Cuam and Cuen are shown below in Figure 4:

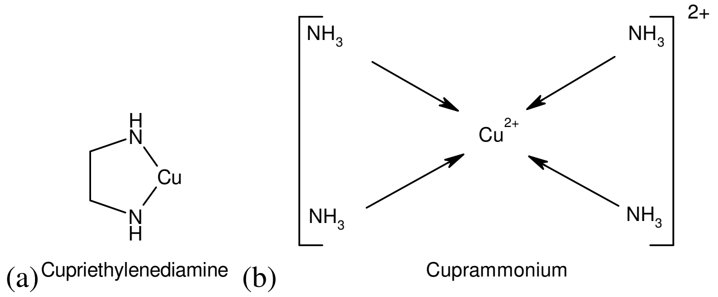

Figure 4   The molecular structure of Cuen (a) and Cuam (b)

On the other hand, the non aqueous media can be classified by organic liquid/inorganic salt such as N, N-dimethylacetamide (DMAc)/LiCl, organic liquid/amine/SO_2 such as dimethylsulfoxide/triethylamine/SO_2, ammonia/ammonium salt such as NH and NH_4SCN, oxides of tertiary amines such as N-methylmorpholine-N-oxide (NMMO, which can be used as a suitable medium for producing textile cellulose fibers and many alkylation reactions), and a relatively new solvent family-ionic liquids. The sum of commonly used solvents for cellulose is shown below in Figure 5 [43]:

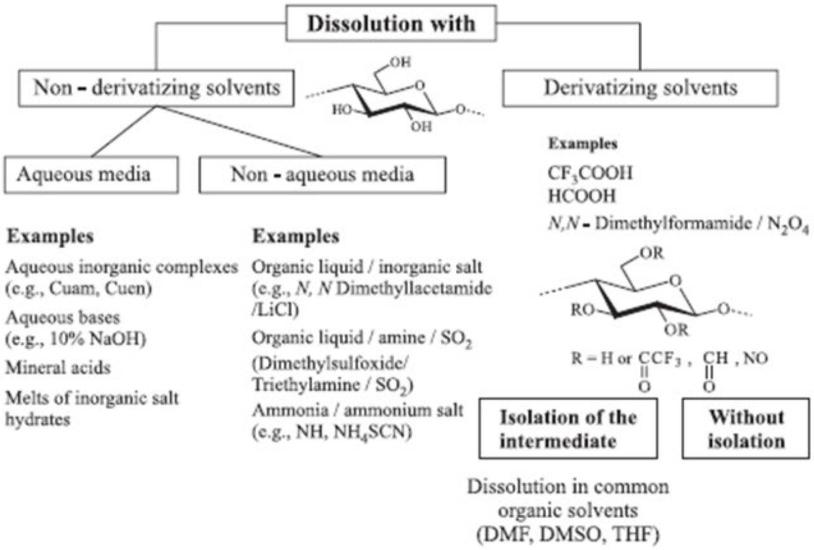

Figure 5 The solvents for cellulose

1.7 Ionic Liquids – new type of cellulose solvents

Ionic Liquids (ILs), containing cations as well as anions, are a class of non-volatile solvents with unique solvating properties. Because of their inert attributes, IL's are attractive new alternative solvents for the dissolution of cellulose to produce various cellulose derivatizations.

Due to the low melting temperature (below 100 ˚C) of salts, Ionic Liquids are often liquid state at room temperature. Moreover, IL's have the reputation of "environmentally friendly" solvents that could fulfill the requirements of sustainable development and "green chemistry", since they are noninflammable, thermally and chemically stable, and have fairly low vapor pressure. Based on these advantages, recently, the development and generalization of ILs applications in many scientific and technological areas have gained increased interests, in order to achieve the enhancements of process biocompatibility and economy.

Previous studies by Prof. Rogers and et al., The University of Alabama, USA, on utilization and regeneration of ILs for dissolution of cellulose have given comprehensive evidence of ILs advantages [12, 16]. Further, Prof. Rogers has become a winner of the 2005 US Presidential Green Chemistry Challenge Awards for demonstrating a new way to dissolve and use cellulose in producing environmentally friendly materials based on his contribution. The extensive research were conducted by Zhang and his colleagues from The Institute of Chemistry, Chinese Academy of Science, Beijing, China and group of Thomas Heinze from The Center of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Germany [17, 18]. The investigation about application of ILs for biorefinery - dissolution of wood material as whole for thorough characterization, for separation of wood biopolymers and for the development of wood thermoplastic composites, was explored by Prof. Dimitris Argyropoulos and his group [19].

The patents of Prof. Rogers and his colleagues concerning the dissolution, regeneration and treating cellulose through using ionic liquids were purchased by the chemical company BASF in March, 2006. BASF now is the leader in both manufacture and utilization of ionic liquids, and its products of ionic liquids are distributed in several specifications and quantities.

Previous studies reported that, both the refined and natural cellulose can be dissolved in IL which contains imidazolium cations. Under the condition of heating with microwave, the ILs incorporating anions play an important role of being strong hydrogen bond acceptors. In fact, the IL containing chloride was reported to be more effective. It was hypothesized that, the cellulose was solubilized through hydrogen-bonding between hydroxyl functions and anions of IL.

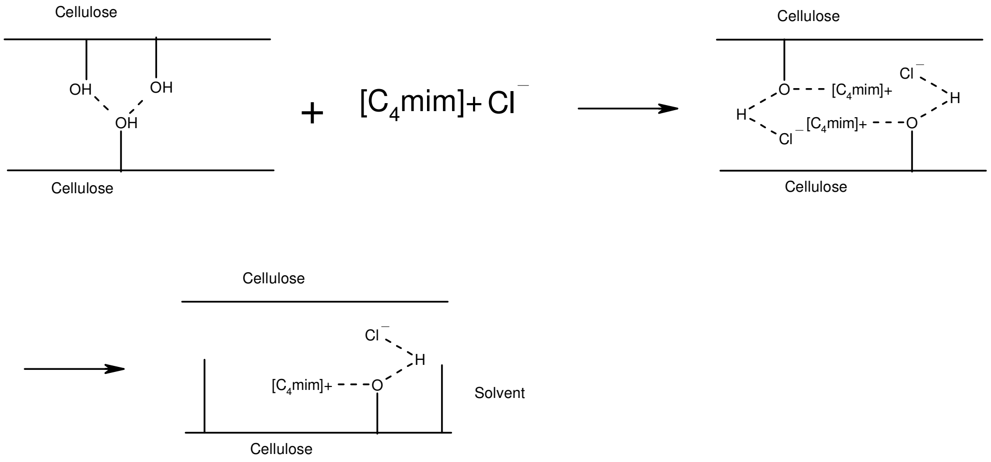

Figure 6 Proposed dissolution mechanism in ionic liquids

The cellulose was found to be disorganized in the solution and the reaction was proofed by ^{13}C NMR studies at atomic level [20]. Moreover, because of reduced concentration of chloride, the longer-chain substituted IL becomes less effective for dissolution of cellulosic materials. 1-Butyl-3-methylimidazolium chloride ($[C_4mim^+]Cl^-$) and 1-Allyl-3-methylimidazolium chloride are two commonly used IL's for the dissolution of cellulosic materials.

Furthermore, it has been reported that, water can decrease the solubility of cellulose in IL's significantly. The inhibited solubiliztion caused by competitive hydrogen-bonding between water and cellulose microfibrils might be one of the possible explanations.

The cellulose dissolved in IL can be regenerated with water, ethanol or acetone. After the precipitation, the degree of polymerization and polydispersity of cellulose were reported to be the same as before except the morphology. The structural forms of regenerated cellulose, such as powder, tube, beads, fiber and film, can also be varied with the different processes of precipitation. In fact, the microstructures of cellulose are influenced by the way of regeneration. Firstly, the condition of regeneration was proofed to have impact on the degree of crystallinity of cellulose. It could manipulate and enable the changing of amorphous to crystalline. Secondly, previous studies has also showed the evidence that, the microstructure of cellulose could be affected by the time of storage of cellulose-ionic-liquid solution [12].

By means of evaporation, ionic exchange, pervaporation, reverse osmosis and salting out, the ILs can be recycled after the regeneration of cellulose [21].

1-Butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium chloride, which were commercially available ILs produced by BASF, were chosen for the present study since they have been proved to be the most effective reagents for the dissolution of cellulosic materials.

1.8 Aim of the project

To investigate the solubility of various wood pulps, softwood and hardwood, in the commercially available Ionic Liquids, such as 1-Butyl-3-methylimidazolium acetate ($[C_4mim^+]CH_3COO^-$) and 1-Butyl-3-methylimidazolium chloride ($[C_4mim^+]Cl^-$) (BASF, 95%) with a focus on the determination of solubilization and regeneration conditions and their impact on the molecular weight, thermal properties and morphology of cellulose. The 8%

LiCl/DMAc system, which is very powerful and is often used for molecular weight determination for cellulose, was chosen as a reference solvent system.

2 Materials and methods

2.1 Materials

Total chlorine free (TCF) bleached and dried hardwood (Eucalyptus Globulus) dissolving pulp, and softwood (spruce 60%, pine 40%) were provided by Sniace, Spain and Domsjö, Sweden respectively. The viscosity was 17.7 and 18 mPa.s (Tappi T-206) and the content of Alpha cellulose was 92.3 and 93% (Tappi T-203) respectively.

1-Butyl-3-methyl-imidazolium acetate ($[C_4mim^+]CH_3COO^-$, Mp -20 °C, ≥95%) and 1-Buthyl-3-methyl-imdazolium chloride ($[C_4mim^+]Cl^-$, Mp 70 °C, ≥95%) were commercially available (Sigma-Aldrich), and chosen as Ionic Liquids, with the viscosity of 22.4 mPa.s and 146.8 mPa.s at 80 °C respectively.

Other chemicals such as lithium chloride (LiCl) (Sigma-Aldrich, ≥99.0%) and dimethylacetamide (DMAc) (Fisher Scientific, 99.8%) were commercially available and used directly without further purification.

2.2 Dissolution of dissolving pulps

2.2.1 Dissolution of dissolving pulps with $[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$

Ten cellulose samples were dissolved during this step. The samples marked with odd numbers (1, 3, 5, 7, 9) were for hardwood dissolving pulps (HW), and the softwood dissolving pulps (SW) were marked with even numbers (2, 4, 6, 8, 10).

Both hardwood and softwood dissolving pulps were dried in oven at 105 °C for more than 4 hr before the dissolution. The dried samples 1-6 were added into six 16 ml vials (71×21 mm, column) respectively. The rest samples 7-10 were added into four 250 ml round flasks. For sample 1, 2 and 7-10, the dissolving pulps were mixed with $[C_4mim^+]CH_3COO^-$, and the rest samples 3-6 were mixed with $[C_4mim^+]Cl^-$, respectively. The concentration of all the samples was set up at 4.76 % (wt %) except sample 2, which was 5.46 %. Samples 1-8 were then heated up to 80 °C with oil bath and maintained at this condition with magnetic stirring until the sample was dissolved totally. The rest samples 9 and 10 were heated up to 105 °C with reflux and treated by following the same steps as other samples. The phenomenon and time of dissolution were recorded as the reaction was processing.

Table 3   Materials and methods for the dissolution of pulp samples with ionic liquid

Sample No.	Sample	Solvent	Method No.	Method in details (weight of sample (g), solvent (g), concentration (wt %), heating temperature (°C) and container for reaction)
1	HW	$[C_4mim^+]CH_3COO^-$	1	0.5; 10 (8.66 for sample 2); 4.76 (5.46 for sample 2); 80; 71 × 21 mm 16 ml vial
2	SW			
3	HW	$[C_4mim^+]Cl^-$		
4	SW			
5	HW			
6	SW			
7	HW	$[C_4mim^+]CH_3COO^-$	2	1; 20; 4.76; 80; 250 ml round flask
8	SW			
9	HW		3	1; 20; 4.76; 105 (with reflux); 250 ml round flask
10	SW			

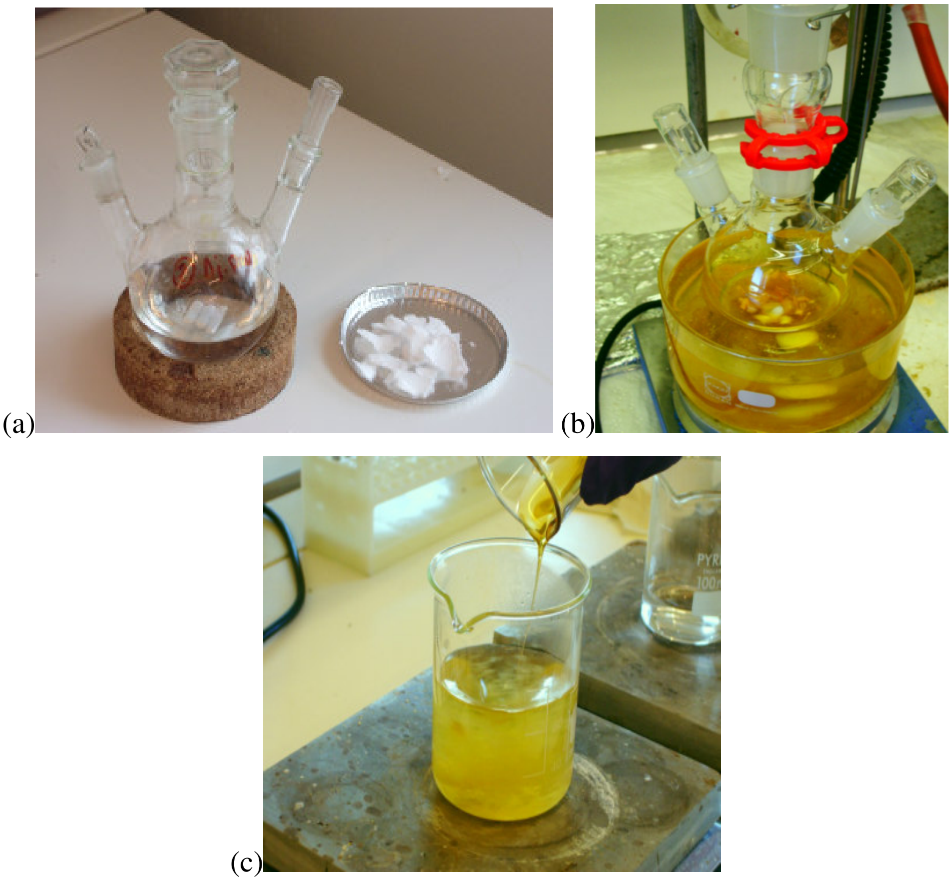

Figure 7   The dissolution (a, method 4) (b, method 2 and 3) and regeneration (c, method 5 and 6) of pulp samples

2.2.2 Dissolution of dissolving pulps with 8 % LiCl/DMAc solution

For both hardwood and softwood dissolving pulp (sample 11 and 12), 1g of each was added into the round flask together with 50 ml DMAc respectively. Each mixture was then heated up to 120 °C through oil bath and the temperature was maintained for 2 hr under magnetic stir and reflux. The mixture was cooled down to 100 °C and 4 g of dried LiCl was added step-by-step in small portions afterwards. The newly prepared mixture was kept under stirring for 15 min and cooled down to room temperature for storage over night. The method is numbered as 4.

2.3 Regeneration of cellulose samples

2.3.1 Regeneration of cellulose samples with deionized water

Prior to the regeneration, each solution (sample 4, 5, 7-12) was heated at 105 °C with magnetic stirring for 1 to 2 hr. The hot solution was then poured gently into the beaker with 80 °C deionized water (the volume was about ten times as that of the solution). The residue was washed with little 80 °C deionized water to ensure that the solution was transferred totally. After the heating at 80 °C with magnetic stir for 30 min, the mixture was filtrated by vacuum. Each regenerated sample was washed with 80 °C deionized water sufficiently until no yellow color could be observed (except sample 9 and 10). The volume was about 100 times as that of sample solution used for regeneration. The colorless sample was transferred into the 250 ml round flask to be freeze dried for 16 hr afterwards. Finally, the dried sample was weighed and stored in the desiccators for later use. The method is numbered as 5.

Table 4 The pulp samples regenerated with deionized water

Sample No.	Solvent	Method (for dissolution) No.	Concentration (wt %)	Regenerated solution (g)
4 (SW)	$[C_4mim^+]Cl^-$	1	4.76%	10.5
5 (HW)				
7 (HW)	$[C_4mim^+]CH_3COO^-$	2		21
8 (SW)				
9 (HW)		3		7
10 (SW)				
11 (HW)	8% (wt %) LiCl/DMAc	4	1%	20
12 (SW)				

2.3.2 Regeneration of cellulose samples with ethanol and deionized water

Prior to regeneration, each sample (1, 2, 3, 6) was heated at 105 °C with magnetic stirring for 1 to 2 hr. The hot solution was then poured gently into the beaker with 96% ethanol 100 ml first. The residue was washed with little 96% ethanol to ensure the solution was transferred totally. After stirring at room temperature for 30 min, the mixture was filtrated by vacuum. The regained sample was added into 80 °C deionized water (the volume was about ten times as that of sample solution) for further regeneration and the mixture was heated at 80 °C with magnetic stir for 2 hr (except sample 1). After the filtration with vacuum again, the solid sample was washed with the 80 °C deionized water sufficiently (the volume was about 100 times as that of sample solution used for regeneration) until it was colorless and transferred into a 250 ml round flask to be freeze dried for 16 hrs afterwards. Finally, the dried sample was weighed and stored in the desiccators for later use. The method is numbered as 6.

Table 5 The pulp samples regenerated with ethanol and deionized water

Sample No.	Solvent	Method (for dissolution) No.	Concentration (wt %)	Regenerated solution (g)
1 (HW)	$[C_4mim^+]CH_3COO^-$	1	4.76 % (except sample 2 which is 5.46 %)	10.5 (except sample 2 which is 9.16)
2 (SW)				
3 (HW)	$[C_4mim^+]Cl^-$			
6 (SW)				

2.4 Size exclusion chromatography (SEC)

30 mg of each regenerated pulp sample was activated sufficiently for 2 to 3 hr in 30 ml deionized water at 4 °C with magnetic stir. The exceeding water was removed by vacuum filtration and the pulp samples were subjected to the solvent exchange three times with both 30 ml of methanol and DMAc with 30 min for intermediate equilibration. The exceeding solvent was removed by vacuum filtration respectively. Each batch of the samples was added into 3.8 ml of 8 % LiCl/DMAc. The mixture was stirred gently and left at 4 °C for 5 days. The formed solutions were diluted to the concentration of 0.5 % (wt %) with 57 ml of DMAc afterwards. Ultimately, prior to chromatographic characterization, the solutions of cellulose samples were filtered through a 0.45-μm poly (tetrafluorethylene) filter and stored in vials.

The SEC system was consisted of a DGU-20A$_3$ degasser (Shimadzu), a LC-20AD liquid chromatography (Shimadzu), a Rheodyne 7725i fixedloop (100 μl) and a RID-10A refractive index detector (Shimadzu). The injection volume was 100 μl. The separation system consisted of a mixed-A 20 µm guard column (7.5 × 50 mm, Polymer Laboratories) and four mixed-A 20 µm columns (7.5 × 300 mm, Polymer Laboratories) connected in series. The flow rate was set at 0.5 ml/min. The columns were thermostated at 80 °C and the mobile phase was 0.5% LiCl/DMAc. The Pullulan standards with nominal masses of 800 KDa, 400 KDa, 200 KDa, 110 KDa, 50 KDa, 22 KDa, 12 KDa, 6 KDa, 1.3 KDa, and 320 Da (Fluka) were used for the calibration. The linear coefficient of determination (r^2) was 0.996 for the curve of pullulan molecular weight versus the elution time. The system and data were controlled and evaluated with LC Solution software (Shimadzu).

2.5 Thermogravimetric analysis (TGA)

TGA was performed on a Mettler Toledo TGA/SDTA 851^e (Greifensee, Switzerland) in nitrogen atmosphere. STAR^e software was used for data evaluation. The samples were heated from 25 °C to 600 °C at a rate of 10 °C/min in a 70 µL aluminum pan with a gas flow of 50 ml/min.

2.6 Scanning electron microscopy (SEM)

The morphology of the samples was examined by means of a Hitachi S-4800 FE-SEM (Tokyo, Japan). The regenerated samples were chosen randomly. The samples were mounted on metal studs and sputter coated with a 3 nm gold/platinum layer using a Cressington 208HR high resolution sputter coater (Watford, UK) equipped with a Cressington thickness monitor controller.

3 Results and discussion

3.1 Dissolution of cellulose samples

3.1.1 Dissolution of cellulose samples with 8% LiCl/DMAc solution

Table 6 listed down shows the results obtained by using 8% LiCl/DMAc solution to solubilize hardwood (HW) and softwood (SW) dissolving pulp. Since the dried samples could not be dissolved by the solution directly, they were firstly suspended in DMAc for 2 hrs at 120 °C with magnetic stir for swelling. Then the LiCl was added slightly step by step to prevent the aggregation.

One commonly accepted mechanism behind the dissolution of cellulose with LiCl/DMAc is that, the lithium ions can bind tightly with the carbonyl groups of DMAc, therefore the chloride ions can facilitate the cleavage of the inter and intra hydrogen bonds of cellulose freely through nucleophilic attack [22].

The concentration reached 2% wt in 2 hrs easily. It could actually be higher as 3% mentioned in previous studies in a homogenous solution [23]. The chloride ions, which connected with macro cation $[\text{Li DMAc}]^+$, formed hydrogen bonds with anhydroglucose units and this led to the repulsion among groups with the same charge, so that the intermolecular bonds between the cellulose chains were disrupted, and therefore the solvent could further penetrate into the polymer frame. The bonding enabled the dissolution process rapidly [45]. Moreover, the utilization of LiCl/DMAc system can enable the derivatization of cellulose for further application [24]. Besides, previous studies have shown that cellulose dissolved in LiCl/DMAc solution was suitable for electrospin. In addition, for the size exclusion chromatography, LiCl/DMAc can be used as mobile phase and therefore the sampling could be simplified [22].

However, the LiCl/DMAc solvent system actually has some disadvantages, as LiCl is well known for its corrosive property.

Table 6 The time for dissolution of dissolving pulps with 8% LiCl/DMAc

Sample No.	Sample	Method No.	Time for dissolution (h)
11	HW	4	App. 2
12	SW		

3.1.2 Dissolution of cellulose samples with $[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$

Two ILs ($[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$) were chosen as the solvents. It has been reported in the literature that, the ILs with imidazolium cation were suitable solvents for cellulose [12]. Table 7 shown down summarizes the time for dissolution of cellulose samples by using ILs. The pretreatment of samples in oven (105 ˚C) for drying is crucial for the dissolution process. It has been reported that, the presence of water in ILs could affect the solubility of cellulose negatively. According to former study, the possible bonding effect between water and cellulose fibrils could compete with the hydrogen bond acceptation of anions in ILs and therefore became the obstacle for solubilization of cellulose [16].

The dried samples were then added directly into ILs for dissolution. As mentioned above, the incorporating anions of IL are strong hydrogen bond acceptors and play the key role of cleaving the links among hydroxyl function groups of cellulose. Simultaneously, the solubilization of cellulose could be realized through the new bonding reaction between its hydroxyl groups and IL's anion.

However, the ILs could not be effective without heating. It has been described that, the solubility of cellulose samples could be increased significantly under higher temperature for dissolution (but not excessively high, since cellulose are sensitive to temperature) [16]. In this study, the time needed for dissolution of both hardwood and softwood pulps to reach the same concentration decreased obviously (sample 7 and 9 for hardwood pulps, from 119 hrs to 38 hrs; sample 8 and 10 for softwood pulps, from 50 to 28 hrs) when the temperature enhanced from 80 °C to 105 °C. It is possible that, since the ILs are normally in liquid states with fairly high viscosity or in solid state under room temperature, the solubilization process under higher temperature could help to lower the viscosity of ILs and therefore facilitate the ions to penetrate in and interact with cellulose fibrils.

Table 7 The time for dissolution of cellulose samples with ionic liquids

Sample No.	Sample	Solvent	Method No.	Time of dissolution (h)
1	HW	$[C_4mim^+]CH_3COO^-$	1	48
2	SW			48
3	HW	$[C_4mim^+]Cl^-$		330
4	SW			264
5	HW			330
6	SW			264
7	HW	$[C_4mim^+]CH_3COO^-$	2	119
8	SW			50
9	HW		3	38
10	SW			28

The constituent of IL can also influence the solubilization of cellulose. It has been reported that, ILs with chloride ions were thought to be the most effective solvents compared to other ILs which had the same cation groups, as high chloride concentration is crucial for breaking hydrogen bonds effectively [12]. However, in this study, the dissolution time of both hardwood and softwood dissolving pulps to have the same concentration of cellulose prolonged dramatically when $[C_4mim^+]Cl^-$ was used as the replacement of $[C_4mim^+]CH_3COO^-$ (from 48 hrs to 330 hrs for hardwood pulps, sample 1 and 3/5; from 48 hrs to 264 hrs for softwood pulps, sample 2 and 4/6). The phenomena introduce another factor which might be important for the dissolution process-the mixing between cellulose samples and ILs.

Indeed, the $[C_4mim^+]Cl^-$ used in this study present a solid state at room temperature (the liquification temperature of $[C_4mim^+]Cl^-$ is 41 °C at 1 atm [12]). It could be liquefied at the temperature of 80 °C which was chosen for the dissolution process as mentioned in the table above. However, even in the liquid state it could still hardly be mixed with cellulose samples homogeneously because of the extremely high viscosity, even a strong magnetic stirring was used, let alone the effective dissolution.

Moreover, the container used for the dissolution could also be a factor that apparently could influence the process in this study. The identical reactions between cellulose samples and IL at the same temperature and with the same magnetic stirring but in different containers (sample 1 and 9 for hardwood samples; sample 2 and 10 for softwood samples; both of whose dissolution time were prolonged not less than 10 hr) resulted in different time for the complete solubilization of cellulose. Clearly, the process of mixing was limited in vials since the space for magnetic stir and contact between cellulose sample and IL was insufficient compared to the reactions occurred in larger flasks.

The factors, such as the origin and amount of dissolving pulps might also affect the dissolution time. In this study, the softwood samples needed less time to be dissolved totally than the hardwood samples did. Possibly, the softwood pulps which had normally longer fibers swelled better in the ILs led to better solubility.

3.2 Regeneration of cellulose samples

3.2.1 Regeneration of cellulose samples with deionized water

Table 8 The yield of regeneration with deionized water

Sample No.	Solvent	Method (for dissolution) No.	Concentration (wt %)	Regenerated solution (g)	Yield
4 (SW)	$[C_4mim^+]Cl^-$	1	4.76%	10.5	99 %
5 (HW)					98 %
7 (HW)	$[C_4mim^+]CH_3COO^-$	2		21	99 %
8 (SW)					90 %
9 (HW)		3		7	76 %
10 (SW)					79 %
11 (HW)	8 % (wt %) LiCl/DMAc	4	1%	20	95 %
12 (SW)					90 %

Table 8 given above shows the regeneration of cellulose samples by using method 5. As it has been reported in previous studies, the dissolved cellulose samples in both $[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$ could be easily precipitated by adding the cellulose solution into anti-solvents such as water, ethanol or acetone [16]. The mechanism may be according to the competitive hydrogen bonding with cellulose between IL and anti-solvents, since the existence of water or other anti-solvents could hamper the anions of IL to bind with cellulose molecules [16]. Moreover, since ILs are commonly water soluble, they can be mixed with water readily and therefore removed through sufficient washing.

However, it is not a straightforward issue to define “sufficient washing”. In current study, sample 9 and 10 were first selected to be regenerated after the dissolution with $[C_4mim^+]CH_3COO^-$. For both hardwood dissolving pulp and softwood dissolving pulp, the solution was poured gently into a beaker filled with 80 °C deionized water, and simultaneously, the precipitate of fibrils was formed. Then the mixture was kept under stirring for 30 min and the produced flocs were collected through vacuum filtration without further washing with deionized water. Then, the gained flocs were freeze dried for 16 hr and a mixture of white and yellow granules was given as the final product. However, the yellow granules which were actually the aggregation of unregenerated cellulose together with dried

IL had to be removed before the calculation of yield. Moreover, since cellulose enclosed in the wasted yellow granules could not be isolated and recycled. As a result, the yield of regeneration was lower for sample 9 (76 %) and sample 10 (79 %).

Another parameter that might be important for the regeneration process is the temperature of anti-solvents. As mentioned above, the dissolution of cellulose samples should be conducted with heating, and the lowest temperature for the solubilization of samples listed above was 80 °C (method 1 and 2). Therefore, in order to avoid the potential effects on cellulose by using overhigh temperature, the deionized water used in this step was also heated to 80 °C prior to the regeneration. The purpose of using hot water was to keep the IL away from clot as much as possible to form aggregation with regenerated cellulose if the temperature became lower than 80 °C. Moreover, the heating of mixture (water and flocs) should also be kept through the entire regeneration process and the flocs should be washed with 80 °C deionized water to remove the IL as much as possible before the collection. The water used for washing was about 100 times of the weight of cellulose solution. As a result, a homogeneous, powder-shaped and pure white product was obtained. The yields of obtained products were all above 90%.

3.2.2 Regeneration of cellulose samples with ethanol and deionized water

Table 9 The yield of regeneration with ethanol and deionized water

Sample No.	Solvent	Method (for dissolution) No.	Concentration (wt %)	Regenerated solution (g)	Yield
1 (HW)	$[C_4mim^+]CH_3COO^-$	1	4.76 % (except sample 2 which is 5.46 %)	10.5 (except sample 2 which is 9.16)	82 %
2 (SW)					96 %
3 (HW)	$[C_4mim^+]Cl^-$				92 %
6 (SW)					99 %

According to the mechanisms discussed above in 3.2.1, the regeneration could also be implemented by using ethanol. Moreover, ethanol used for regeneration could be removed easily through evaporation which was helpful for the recycling of ILs [25]. Practically, in this study, sample 1 was firstly chosen to be regenerated with only ethanol (96 %). The cellulose solution was poured gently into 100 ml ethanol with magnetic stir. However, gel fibers were produced instantly, and they assembled together to form the gel aggregation after the vacuum filtration. The obtained conglomerations after drying were heterogenous as partially yellow "fibers" were included, which might be the mixture of regenerated cellulose and solid $[C_4mim^+]CH_3COO^-$. Ultimately, a low yield of 82 % was obtained for the pure cellulose

(Table 9). In fact, unlike the regeneration with water, ethanol used in this section could not be heated up to 80 °C. Therefore it was easy to form gel aggregates when the cellulose solution was poured into cold ethanol. Moreover, the precipitated cellulose clotted together so that part of the IL was possibly encapsulated inside the aggregates and hardly to be replaced by ethanol.

To obtain an acceptable yield, the procedure of regeneration should be further ameliorated. As it was described in earlier study [26], the mixture of regenerated cellulose conglomerations with ethanol and IL could be poured into hot water for further solvent-exchanging with magnetic agitation. Therefore, sample 2, 3 and 6 were regenerated by using method 6 and correspondingly homogeneous and pure white outcomes (still fiber-shaped however) were received. The yields of received products were all above 90%.

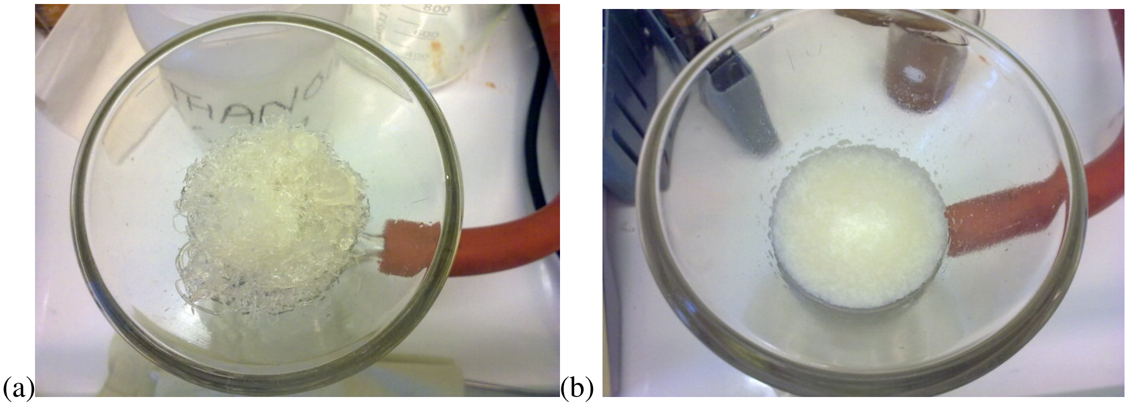

Figure 8 The comparison of outcome's form between samples regenerated with method 6 (a, fiber-shaped) and method 5 (b, powder-shaped)

3.3 Size exclusion chromatography (SEC)

3.3.1 Hardwood dissolving pulp

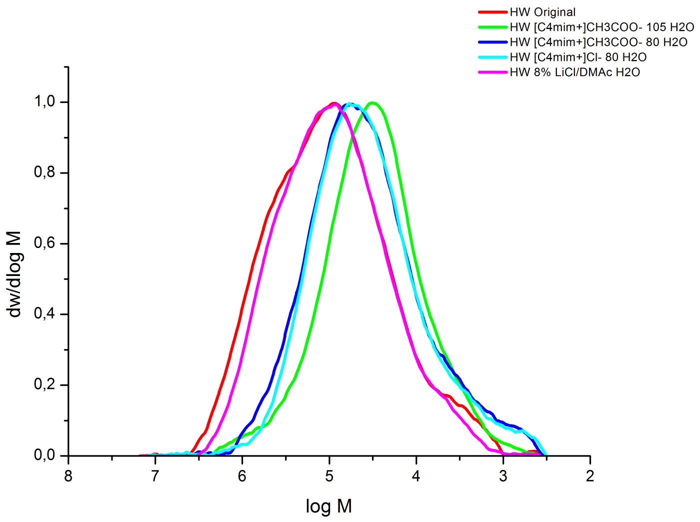

Figure 9 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for the original hardwood dissolving pulp, pulp dissolved in 105 °C [C_4mim$^+$]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim$^+$]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim$^+$]Cl^- and regenerated with H_2O, pulp dissolved in 8 % LiCl/DMAc and regenerated with H_2O

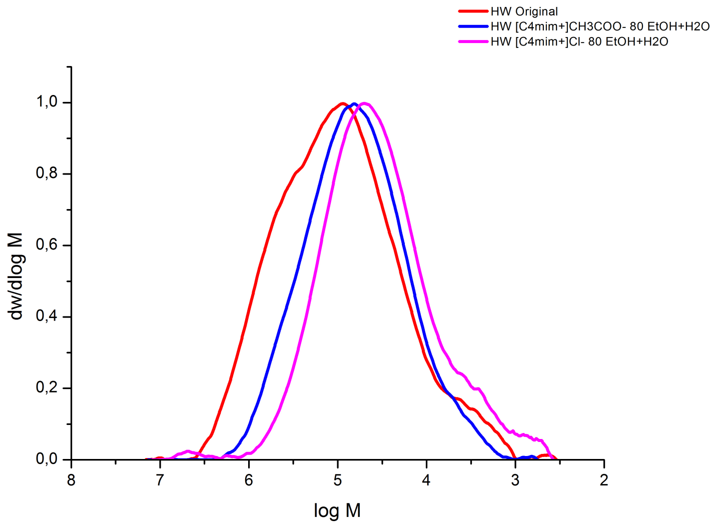

Figure 10 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for the original hardwood dissolving pulp, pulp dissolved in 80 °C [C_4mim$^+$]CH_3COO^- and regenerated with EtOH and H_2O, pulp dissolved in 80 °C [C_4mim$^+$]Cl^- and regenerated with EtOH and H_2O

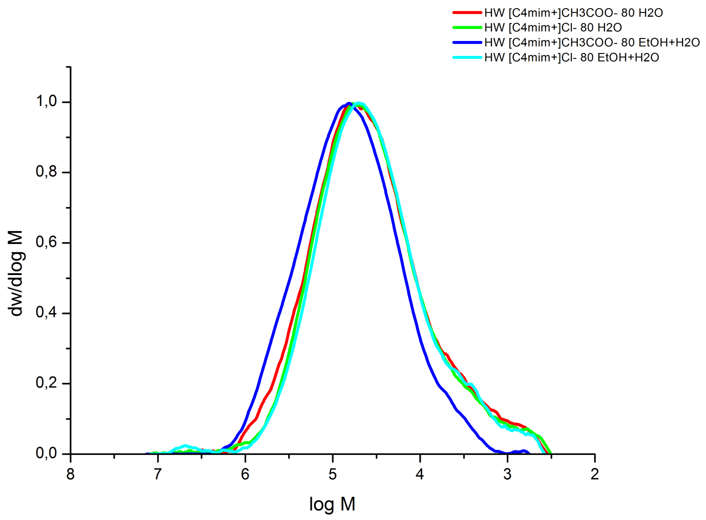

Figure 11 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for pulp dissolved in 80 °C [C_4mim^+]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim^+]Cl^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim^+]CH_3COO^- and regenerated with EtOH and H_2O, pulp dissolved in 80 °C [C_4mim^+]Cl^- and regenerated with EtOH and H_2O

Table 10 Numerical evaluation of the molecular weight distribution of HW relative to pullulan, where DPw stands for the weight average degree of polymerization, DPn stands for the number average degree of polymerization, and PDI stands for the polydispersity index (DPw/DPn)

Sample no.	DPw	DPn	PDI
HW original	2265	271	8.4
11	2160	287	7.5
9	816	133	6.1

Figure 9-11 and Table 10 shown above illustrate the information of molecular weight distribution before and after the treatment of hardwood dissolving pulp with ILs and 8 % LiCl/DMAc. Theoretically, for biopolymer studies, SEC could be used to isolate fractions containing cellulose and hemicellulose molecules effectively based on their differences in hydrodynamic molecular size. Larger molecules with higher molecular weight (Mw) (e.g. cellulose) could be eluted prior to smaller molecules with lower Mw (e.g. hemicelluloses) from columns filled with porous gel materials, so that the molecular weight distribution (MWD) could be detected [27, 28]. Practically, the aim of using SEC in current study was to evaluate the impact of ILs' treatment on the molecular weight properties of dissolving pulp samples.

Based on the information given by Figure 9 and Table 10, the polydispersity index (PDI), which is an important parameter reflecting the width of MWD, of hardwood dissolving pulp regenerated from both 8 % LiCl/DMAc and ILs was not changed significantly, as the shape of curve was almost the same as that of the original (untreated) sample. The phenomena were consistent with the result reported in previous study [16]. However, a clear shift of MWD towards lower Mw was observed. Moreover, HW dissolved with $[C_4mim^+]CH_3COO^-$ at 105 °C and regenerated with deionized water had the most obvious shift. According to former research, the change in Mw might be caused by the degradation of polymer during the dissolution [29, 30]. ILs purchased were of 95 % purity, therefore the impurities (5 %) in ILs probably catalyzed the hydrolysis of cellulose at high temperature. Furthermore, as for samples treated with ILs at a relatively lower temperature (80 °C), the shift of MWD was not as obvious as that of pulp treated at a higher temperature (Figure 9 and Figure 10). But still, either the dissolution in IL or the method of regeneration gave a slight decrease of Mw averagely. As a result of the rapid regeneration [32], the remaining IL (even pinpoint) might bond chemically with the reducing ends of cellulose [26, 31], which could at least influence the structure and Mw (the mechanism in details is not known). Another possible explanation is that, some of the polysaccharides were deploymerized. The deduction could be indirectly supported by the increased cellulase adsorption after the treatment with ILs reported in previous study [26], since the cleavage of long chains to shorter chains or oligosaccharides could improve the cellulose accessibility [33]. Or, since the reaction was kept being exposed to atmosphere oxygen, the continuous dissolution of cellulose samples for days at a lower temperature of 80 °C might result in the degradation [46].

For the sample treated with 8 % LiCl/DMAc, there is a slight shift and alteration of the Mw (Figure 9 and Table 10). As described in previous study, the dissolution of cellulose in LiCl/DMAc system could introduce the disintegration to cellulose chains. The N,N-dimethylketeniminium ions, which came to exist when the temperature of solvent was above 80 °C, was fairly electrophilic and could cut the glycosidic bridges directly [47].

The selection of anti-solvents for displacement during the regeneration process was not related directly to the shift of MWD, as no huge difference in MWD of cellulose precipitated with deionized water and ethanol followed by deionized water was given by the last figure (Figure 11). The phenomenon proved again that, ILs could be one of the main reasons for the decrease of Mw. Moreover, both $[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$ seemed to have the same effect on MWD (Figure 11), which implies [C_4mim$^+$] is possibly the factor that is relevant to the change of cellulose structure.

3.3.2 Softwood dissolving pulp

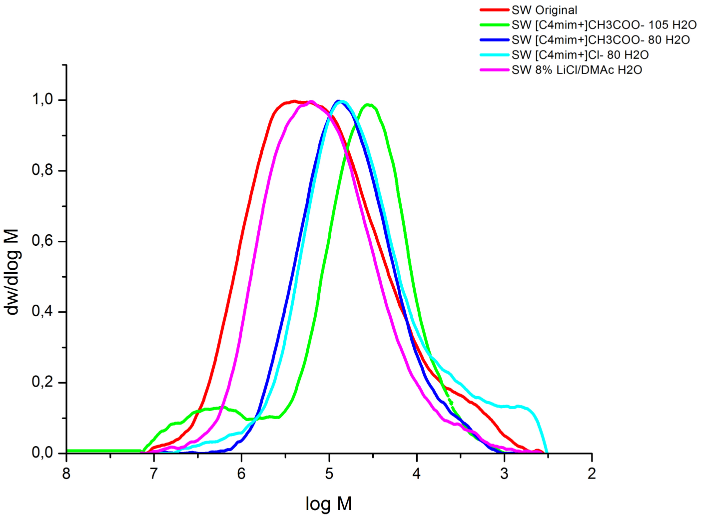

Figure 12 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for the original softwood dissolving pulp, pulp dissolved in 105 °C [C_4mim$^+$]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim$^+$]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim$^+$]Cl^- and regenerated with H_2O, pulp dissolved in 8 % LiCl/DMAc and regenerated with H_2O

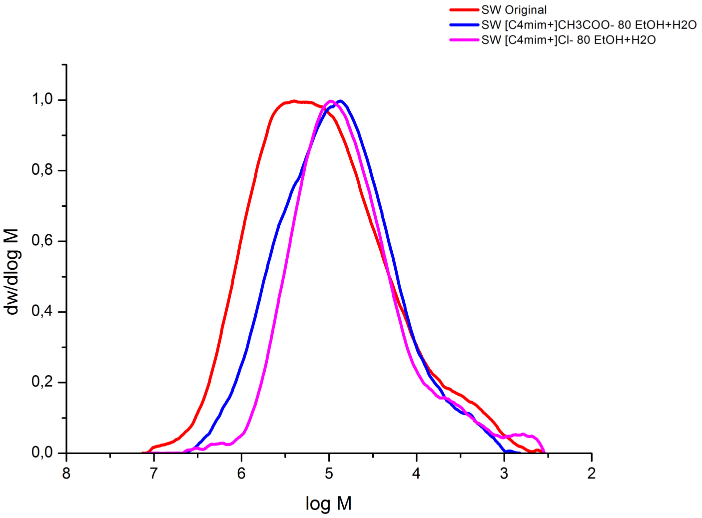

Figure 13 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for the original softwood dissolving pulp, pulp dissolved in 80 °C [C_4mim$^+$]CH_3COO^- and regenerated with EtOH and H_2O, pulp dissolved in 80 °C [C_4mim$^+$]Cl^- and regenerated with EtOH and H_2O

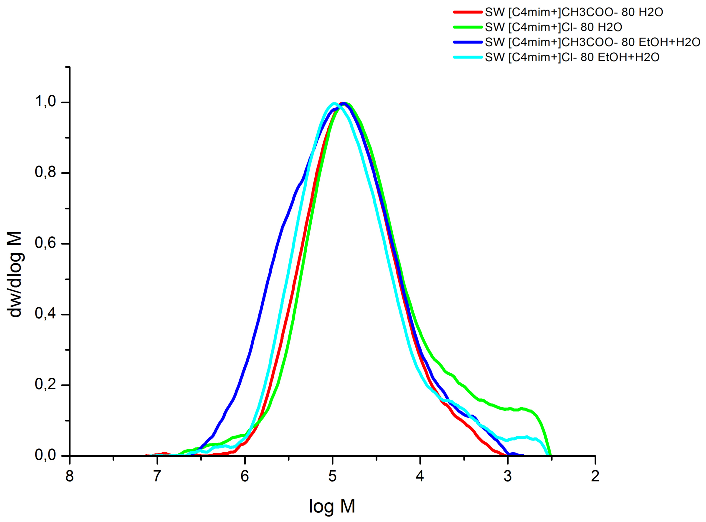

Figure 14 Molecular weight distribution (MWD) curves (by SEC in 0.5 % LiCl/DMAc) for pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with EtOH and H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with EtOH and H_2O

Table 11 Numerical evaluation of the molecular weight distribution of SW relative to pullulan, where DPw stands for the weight average degree of polymerization, DPn stands for the number average degree of polymerization, and PDI stands for the polydispersity index (DPw/DPn)

Sample no.	DPw	DPn	PDI
SW original	3922	224	17.5
12	2963	341	8.7
10	2235	189	11.8

Figure 12-14 and Table 11 shown above give the information about MWD of softwood dissolving pulp before and after the treatment with ILs.

Based on the information given by Figure 12 and Table 11, the PDI of softwood dissolving pulp regenerated from ILs changed significantly, which is contradictory to the result of previous study [16]. As it has been discussed above in 3.3.1, the dissolution of SW in ILs at a higher temperature of 105 °C and a lower temperature of 80 °C but for a fairly long span of time with exposure to oxygen resulted in the degradation of cellulose molecules [46]. Possibly, the polysaccharide chains became shorter but more homogeneous, which caused the decrease of PDI and therefore gave a more homogeneous MWD. Moreover, as shown in Figure 12, the MWD of sample 10 after the treatment divided into two sections. Most of the molecules degraded led to the shift of Mw to lower values. However, it is clear that, there is a small portion of molecules had larger Mw (Figure 12), which might result from the reconnection among degraded cellulose molecules. The bimodal MWD gave sample 10 a higher PDI compared to sample 12's.

On the other hand, a clear shift of MWD towards lower Mw was also displayed in Figure 12, which implies again that, the Mw of cellulose treated with both $[C_4mim^+]CH_3COO^-$ and $[C_4mim^+]Cl^-$ was decreased averagely, regardless of which anti-solvent was used (Figure 13). According to the former discussion, the decrement of Mw was possibly caused by the degradation of polysaccharides, which rooted in either the dissolution at a higher temperature of 105 °C [29, 30] or the continuous process at a lower temperature with exposure to oxygen. Further, it is clear that, the Mw of samples treated at higher temperature decreased stronger than that of samples processed at lower temperature, which implies the high temperature may play the main role in the catalysis of cellulose molecules' degradation.

Besides, unlike HW, there is a noticeable shift and variation of the signal for the sample treated by 8 % LiCl/DMAc for SW (Figure 12 and Table 11). Moreover, the result was contradictory with the one from earlier study that, the using of LiCl/DMAc system would not change the sample's Mw and structure significantly [34]. Indeed, referring to the numerical evaluation (Table 11), the DP and PDI of sample 12 changed significantly after the treatment. It seems the MWD became more homogeneous which might possibly result from the degradation of cellulose chains with dissolution of shorter chains in the anti-solvent. As discussed above in 3.3.1, the dissolution of cellulose in LiCl/DMAc system could introduce the disintegration to cellulose chains by N,N-dimethylketeniminium ions [47].

Finally, as no huge difference was shown in Figure 14, it is hard to say the selection of anti-solvents for displacement during the regeneration process could influence the structure and Mw of cellulose for softwood dissolving pulp, which additionally implies that, $[C_4mim]^+$ might take the responsibility of the change of cellulose structure, as illustrated above.

3.4 Thermalgravimetric analysis (TGA)

3.4.1 Hardwood dissolving pulp

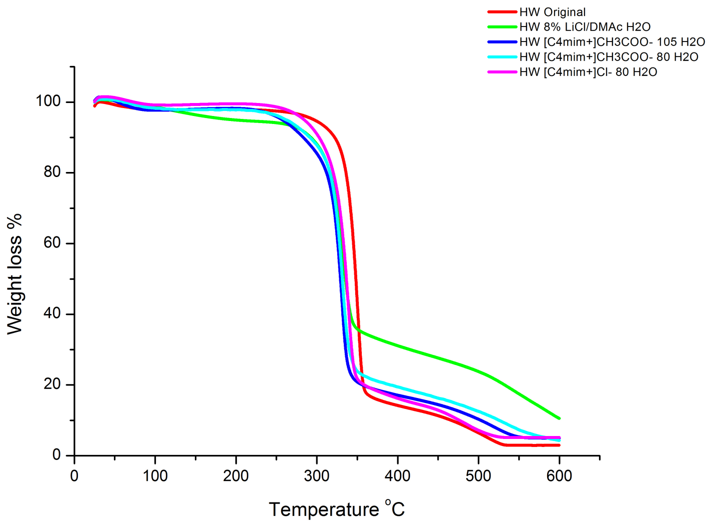

Figure 15 Thermal decomposition curves of original hardwood dissolving pulp, pulp dissolved in 8 % LiCl/DMAc and regenerated with H_2O, pulp dissolved in 105 °C $[C_4mim^+]CH_3COO^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with H_2O

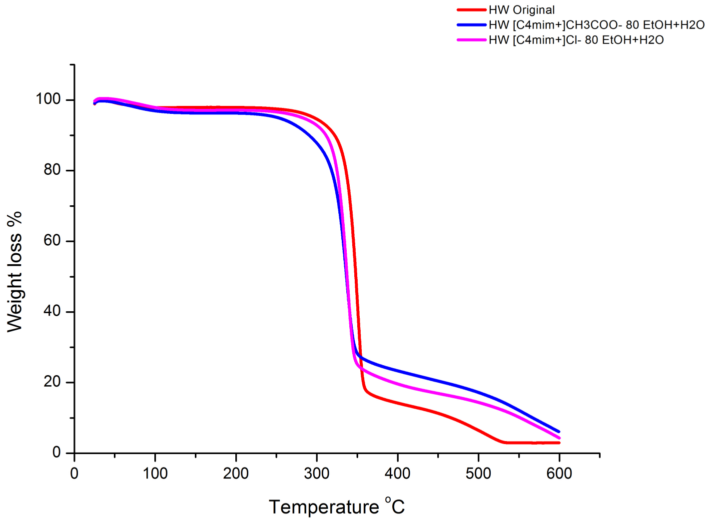

Figure 16 Thermal decomposition curves of original hardwood dissolving pulp, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with EtOH followed by H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with EtOH followed by H_2O

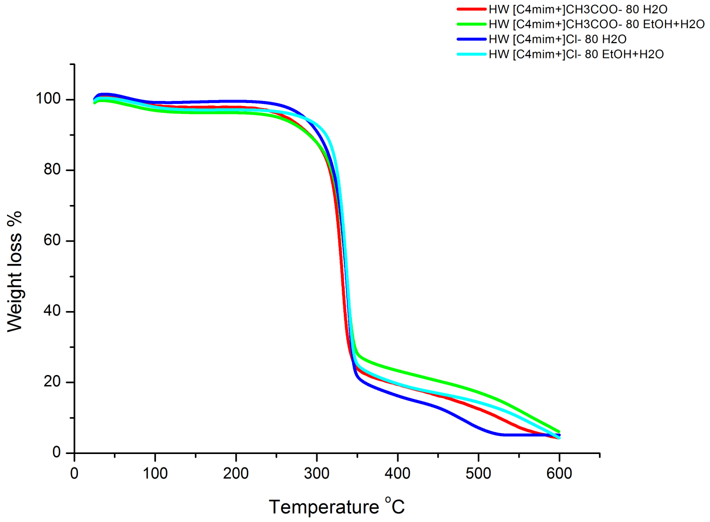

Figure 17 Thermal decomposition curves of original hardwood dissolving pulp, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ *and regenerated with* H_2O*, pulp dissolved in 80 °C* $[C_4mim^+]CH_3COO^-$ *and regenerated with EtOH followed by* H_2O*, pulp dissolved in 80 °C* $[C_4mim^+]Cl^-$ *and regenerated with* H_2O*, pulp dissolved in 80 °C* $[C_4mim^+]Cl^-$ *and regenerated with EtOH followed by* H_2O

The thermalgravimetric analysis (TGA) is used to detect the connection between the materials' composition and thermal stability. TGA analysis uses heat to force the reactions and physical changes in materials. It provides quantitative measurements of mass changes in materials in associate with transition and thermal degradation through recording the changes in mass from dehydration, decomposition, and oxidation of sample with time and temperature. The thermogravimetric curves of materials shows the weight loss on heating, due to the unique sequences from physic-chemical reactions occurring over specific temperature rages and heating rates. These characteristics are related to the molecular structure of sample. TGA used in current study aimed to determine the effect of treatment with both 8 % LiCl/DMAc and ILs on the molecular properties of dissolving pulp samples. All of the samples were heated in aluminum containers with a nitrogen atmosphere at 10 °C/min.

Figure 15 shows TGA's curves for samples regenerated from 8 % LiCl/DMAc and ILs with deionized water. The regenerated cellulose clearly gave a lower temperature of decomposition compared to the original sample (350 to 360 °C). For cellulose treated by ILs, the degradation of longer cellulose chains, caused by either the high temperature or long time for dissolution, or even caused by the possible reaction between cellulose and ILs as discussed above in 3.3.1, could create shorter chains and therefore lower the materials' thermal stability.

For cellulose treated by 8 % LiCl/DMAc, its thermal stability also decreased, which might be explained with the degradation of cellulose during the dissolution in LiCl/DMAc solvent system, as it has been reported in former studies [47]. The degradation of cellulose molecules could lead to the decline of their thermal stability.

Moreover, the curve of sample treated by LiCl/DMAc solvent system gives higher char yield (in associate with non-volatile carbonaceous material or inorganic materials), which might result from incomplete removing of LiCl during the regeneration.

Figure 16 together with Figure 17 show that, the char yields of cellulose treated with ILs but regenerated with deionized water were lower and more similar to the original sample than those of cellulose regenerated with ethanol followed by deionized water (slightly higher char yield was displayed in the figure). Therefore, based on the discussion above, it seems the combination of ethanol and deionized water was not as effective as using only deionized water for the removal of ILs during the regeneration.

3.4.2 Softwood dissolving pulp

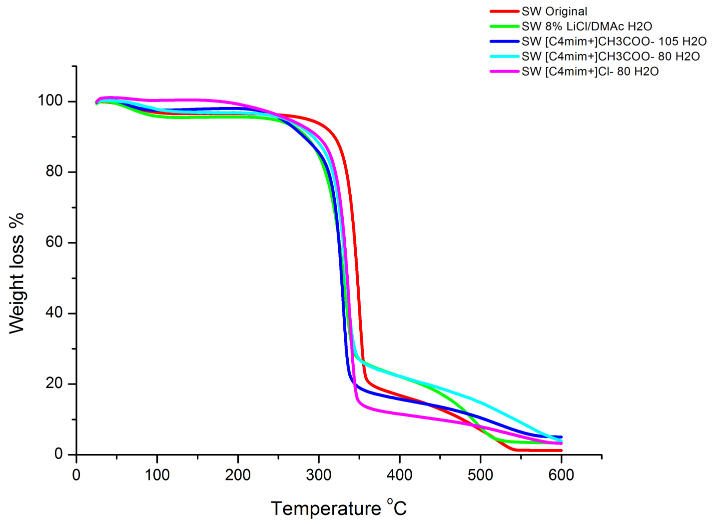

Figure 18 Thermal decomposition curves of original softwood dissolving pulp, pulp dissolved in 8 % LiCl/DMAc and regenerated with H_2O, pulp dissolved in 105 °C $[C_4mim^+]CH_3COO^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with H_2O

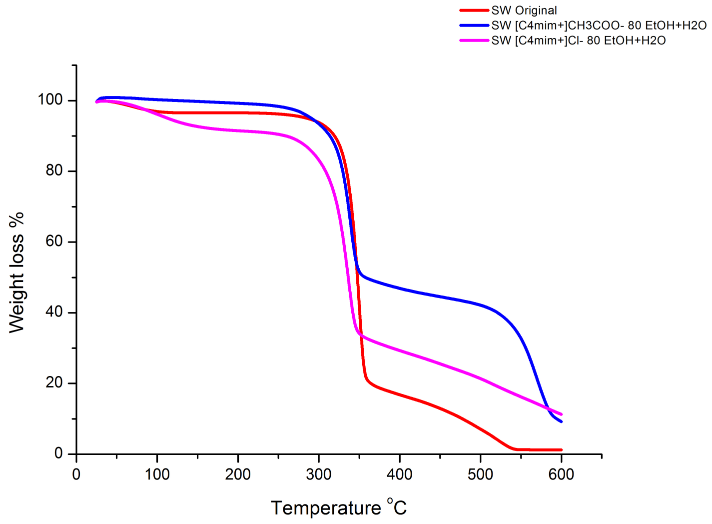

Figure 19 Thermal decomposition curves of original softwood dissolving pulp, pulp dissolved in 80 °C $[C_4mim^+]CH_3COO^-$ and regenerated with EtOH followed by H_2O, pulp dissolved in 80 °C $[C_4mim^+]Cl^-$ and regenerated with EtOH followed by H_2O

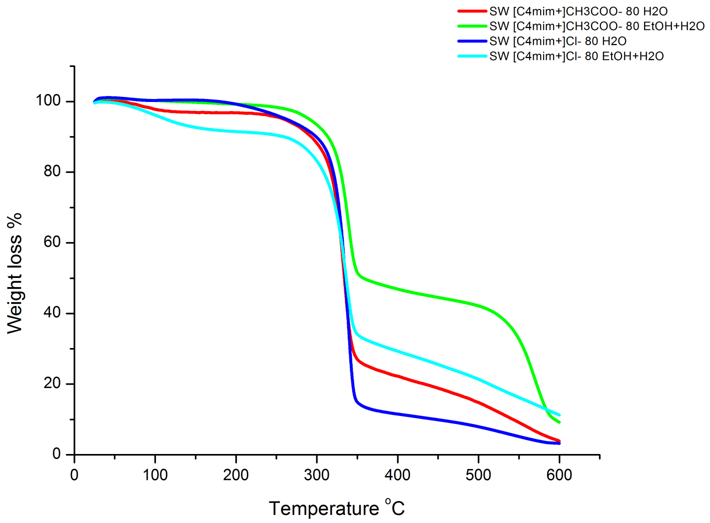

Figure 20 Thermal decomposition curves of original softwood dissolving pulp, pulp dissolved in 80 °C [C_4mim^+]CH_3COO^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim^+]CH_3COO^- and regenerated with EtOH followed by H_2O, pulp dissolved in 80 °C [C_4mim^+]Cl^- and regenerated with H_2O, pulp dissolved in 80 °C [C_4mim^+]Cl^- and regenerated with EtOH followed by H_2O

Figure 18 shows TGA's curves for softwood dissolving pulps regenerated from 8 % LiCl/DMAc and ILs with deionized water. Similar to the results mentioned above for HW in 3.4.1, the regenerated cellulose presented a lower thermal stability than the original sample (350 to 360 °C) for SW as well. Identically, the decomposition of SW treated with ILs could be explained with the possible decrease in the degree of polymerization of cellulose molecules during the treatment, as discussed above in 3.3.2.

On the other hand, the LiCl/DMAc solvent system treated pulps had a clear decrement of thermal stability also, and the degradation of cellulose during the treatment could be one possible interpretation as it is discussed in 3.4.1 about hardwood pulp samples [47].

In addition, again, it seems the removal of substance used as solvent during the regeneration was not sufficient enough, since a slightly higher char yield of the sample treated with LiCl/DMAc solvent system was observed as well as the sample treated with [C_4mim^+]CH_3COO^- at 80 °C.

Figure 19 and Figure 20 show that, the char yields of pulps dissolved with ILs and regenerated with ethanol followed by deionized water were obviously higher than those of pulps regenerated with only deionized water, which implies again that, the washing with ethanol followed by deionized water was not an effective method for the purpose of removing solvents and inorganical substance during the regeneration.

3.5 Scanning electron microscopy (SEM)

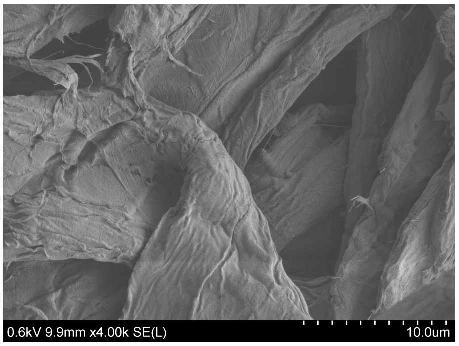

Figure 21 Scanning electron microscopy (SEM) micrograph of the original hardwood dissolving pulp

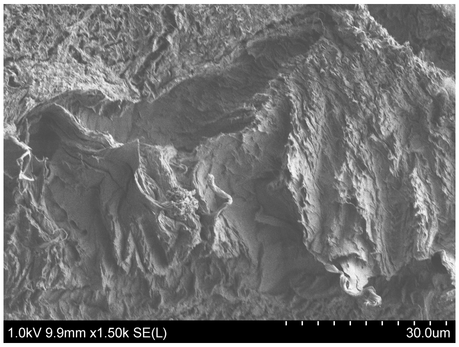

Figure 22 Scanning electron microscopy (SEM) micrograph of the treated hardwood dissolving pulp by 8 % LiCl/DMAc

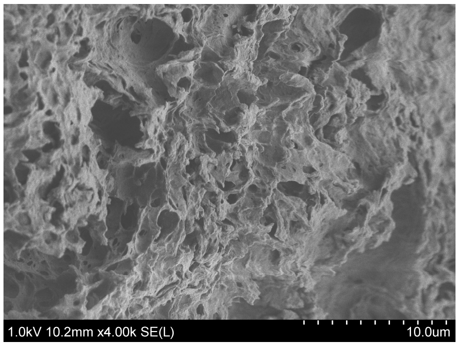

Figure 23 Scanning electron microscopy (SEM) micrograph of the treated hardwood dissolving pulp by $[C_4mim^+]CH_3COO^-$ at 105 °C

The scanning electron microscopy (SEM) used in this study aimed to detect the change of morphology of dissolving pulp after the treatment with 8 % LiCl/DMAc and $[C_4mim^+]CH_3COO^-$.

Figure 23 clearly shows that, the IL treated cellulose lost its fibrous structure, compared to the original one (Figure 21). It has been reported in previous studies [16, 32], the phenomenon might result from the formation of more amorphous structure. The newly formed structure enables the regenerated cellulose to react with chemical or biological reagents more easily, due to the increased accessibility and reactivity after the treatment with IL [26, 36].

Moreover, Figure 22 shows the morphology of hardwood dissolving pulp treated with 8 % LiCl/DMAc was also changed significantly. As described in previous study, the dissolution of cellulose in LiCl/DMAc system introduced the penetration of solvent, and the disintegration to cellulose chains by LiCl [37, 38, 47]. In this study, the production of more amorphous regions on cellulose sample might be caused by the penetration and swelling effect of LiCl/DMAc solvent system [38]. Another reason might be that, the rapid regeneration led to the crack of smooth surface, and therefore fractured the defined region to be more amorphous, as described in previous study about microcrystalline cellulose (MCC) [39].

3.6 Optimized approach of dissolution with Ionic Liquids

It has been discussed above in 3.1.2 that, the dissolution of dissolving grade pulps with ILs under magnetic stir was not so effective and actually took a fairly long time, even at higher temperature of 105 °C. Moreover, either the overhigh temperature or the overlong time for the dissolution of pulp samples in current study was suspected to give a negative influence on the structure of original cellulose based on the discussion in 3.3 and 3.4. Therefore, a new approach of dissolution was created to decrease the time or temperature effect. Practically, the mixture of 20 g IL and 1g cellulose sample was placed in a beaker in the 80 °C oil bath based on method 2, however the mechanical stir with motor and screw propeller were used instead.

The result came out that, the time was shortened significantly from more than 50 hr to 18 hr for the sufficient dissolution of both HW and SW. However, due to the time limit, further investigation on structure changing of the regenerated pulp according to this dissolution approach is needed.

4 Conclusions

In this study, as both hardwood dissolving pulp and softwood dissolving pulp could be solubilized completely, the ionic liquids seem to be suitable as the solvents of cellulose. However, the method of dissolution is very important because it may influence the efficiency a lot. Moreover, cellulose dissolved in ILs could be regenerated by adding anti-solvents such as water and ethanol. The regeneration with deionized water could give homogeneous powder type cellulose almost free of IL and the regeneration with ethanol could produce fiber shaped outcome. However, the ILs could not be sufficiently removed, even the regenerated cellulose was further treated with deionized water.

The degree of polymerization of treated cellulose was decreased clearly as it was shown by the SEC. Either the high temperature or the overlong heating time for the dissolution, or even the possible reaction between cellulose and ILs gave an undesired change on cellulose structure, and therefore the molecular weight declined. This assumption could be further supported by TGA's result. Besides, the higher char yield (non-volatile carbonaceous material or inorganic materials) of TGA's curve also implied that, the ILs could not be isolated from cellulose adequately with the combination of ethanol and deionized water during the regeneration.

The result of SEM indicates that, the ILs' treatment on dissolving pulp could change the morphology of cellulose. The treated material seems to be more amorphous, and therefore might be easier for the enzymatic attack, as the enhancement on accessibility and reactivity of IL treated cellulose was reported in previous studies.

Generally, ILs, as the environmentally friendly solvents, have the strong potential to be used for cellulose dissolution and derivatization. The efficiency of dissolution could be further improved by using ILs with suitable mixing approaches such as mechanical stir. However, further investigation by using X-ray and solid state NMR to evaluate the impact of ILs' treatment on the crystallinity of cellulose are needed.

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