博士論文 (要約)

Application of aqueous alkali/urea cellulose solvent system to wood pulps

(アルカリ-尿素水系セルロース溶剤の木材パルプへの適用)

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Doctoral dissertation

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Chapter 1

General Introduction

1.1 Chemical compositions of plant cell wall

In recent decades, the increasing petrochemical-based energy crisis and environmental pollution have led to more attention to development of efficient and convenient technologies for converting biomass to valuable biomaterials, biofuels and chemicals.[1] The biomass are mainly composed of a wide variety of renewable agricultural and forestry feed stocks, including wood, grasses, crops, and so on.[2]

Wood is the most important biomass for material and energy, which is mainly composed of cellulose (40%−50%), hemicelluloses (20%−30%) and lignin (15%−25%).[3] The three components constitute the supporting frame of wood, where the cellulose microfibrils constitute the skeleton network of the cell wall and the lignin and hemicelluloses are present among the cellulose microfibrils as "bonding agents" and "fillers". The wood cell wall consists of several layers, *i.e.* middle lamella (mL), the primary wall (P), and the outer (S1), middle (S2), and inner (S3) layers of the secondary wall, as shown in Figure 1.1.[4] These layers have different structures. The contents and distributions of cellulose microfibrils, hemicelluloses and lignin in the different cell wall layers are different. Moreover, even within the secondary wall of the wood cell wall, its outer (S1), middle (S2), and inner (S3) layers are also different from each other in terms of the different orientations of cellulose microfibrils (Figure 1.1).
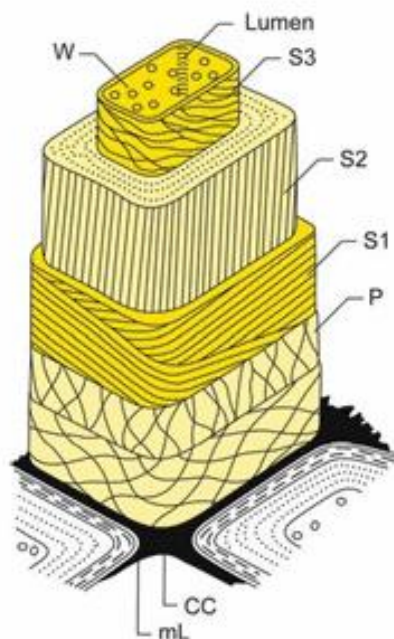
Figure 1.1. Configuration of wood cell wall: middle lamella (mL), cell corner middle lamella (CC), the primary wall (P), the outer (S1), middle (S2), and inner (S3) layers of the secondary wall, and the thin warty layer in cell lumen (W).[4] Reproduction from ref. 4 with permission from Springer (© Springer 2006).

1.1.1 Cellulose

Cellulose is the predominant component in plant cell wall. Compared with the other two main components (hemicelluloses and lignin) in plant cell wall, cellulose is well-characterized and described as a linear polymer consisting of repeated cellobiose units through a β-(1-4)-glycosidic bonding.[5] The structure of cellulose is shown in Figure 1.2. A large number of hydroxyl groups are present in cellulose, thus forming extensive inter- and intra-molecular hydrogen bonds between cellulose molecules, which make cellulose microfibrils highly crystalline with a width of 3–4 nm for wood.[6] The chain length of isolated cellulose expressed in the number of constituent anhydroglucose units (AGUs) (degree of polymerization, DP) varies with the origin and treatment of the raw material. The molecular weight of cellulose is equal to $162 \times DP$.
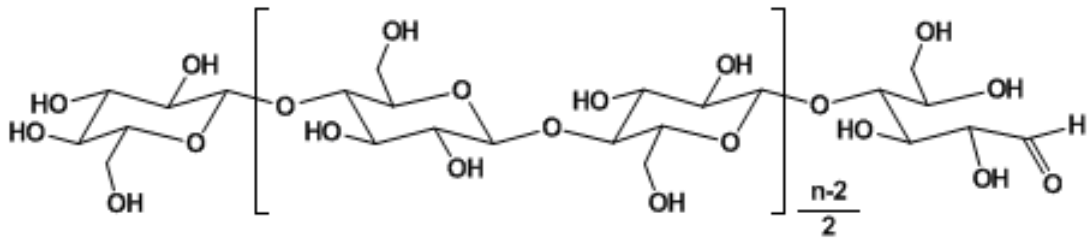
Figure 1.2. Molecular structure of cellulose (n = DP, degree of polymerization).

Diffraction angle 2θ (degree)
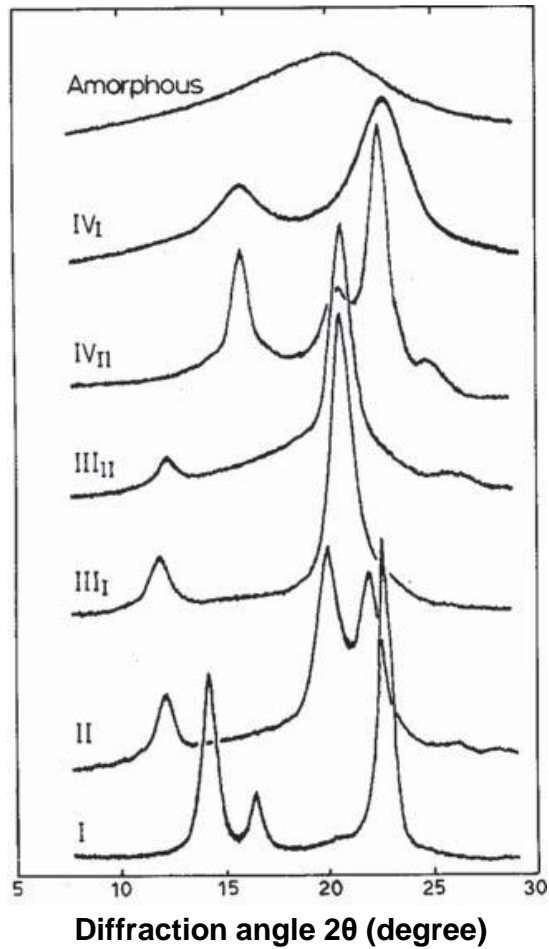
Figure 1.3. X-ray diffraction patterns of the cellulose polymorphs.[9]
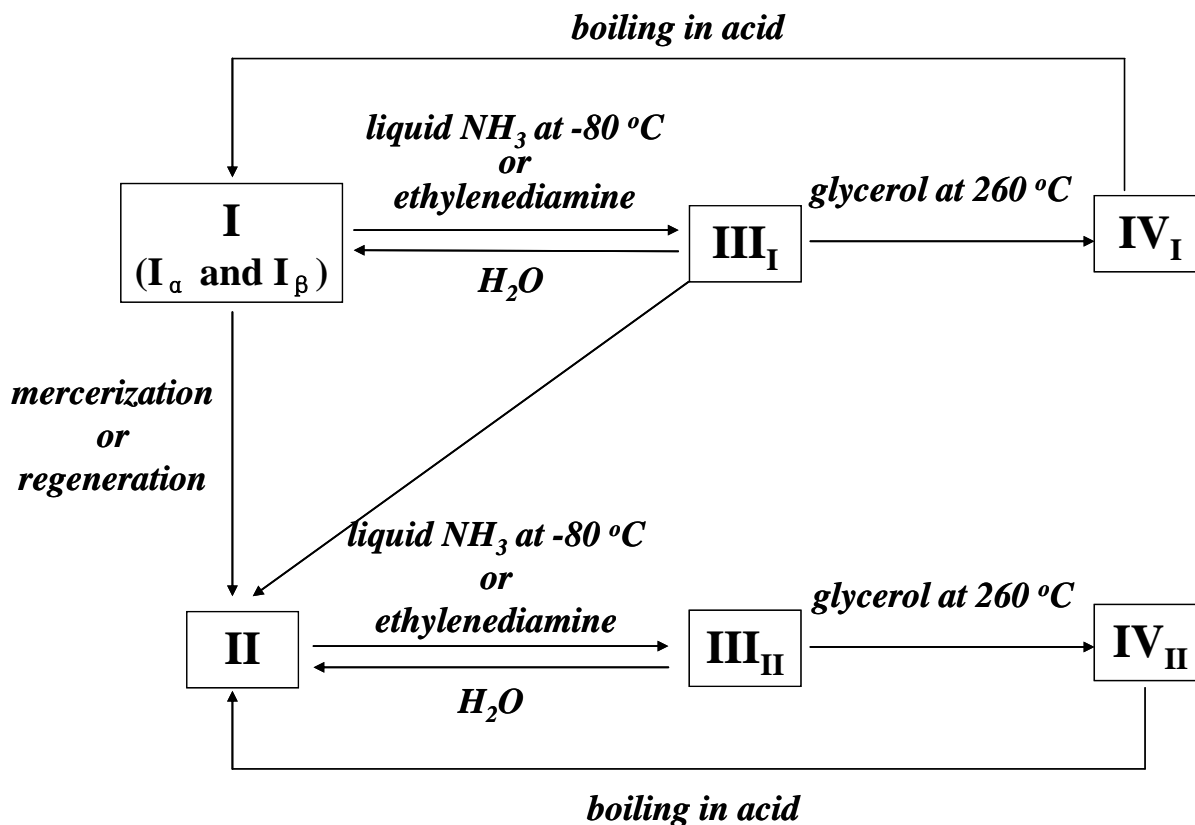
Figure 1.4. Transformation between different cellulose polymorphs.[10]

Cellulose has several crystalline polymorphs with the different packing arrangements.[7] Six kinds of cellulose polymorphs have been found so far, namely cellulose I, II, III_I, III_{II}, IV_I and IV_{II}.[8,9] The X-ray diffraction patterns of the different cellulose polymorphs are shown in Figure 1.3.[9] Cellulose I is the native cellulose and the others are "artificial" cellulose polymorphs produced by manual processing. As shown in Figure 1.4, according to a certain chemical and thermal treatments, the native cellulose could be converted to a relevant cellulose polymorph.[10] Among the polymorphs of cellulose, cellulose I and cellulose II are most widely used. The native cellulose in plant cell wall is present as cellulose I and cellulose II is obtained from cellulose I by a regeneration or mercerization process. Treatments of cellulose I or II with pure liquid ammonia or ethylenediamine lead to formation of cellulose

III. When the starting material is cellulose I, the converted cellulose is cellulose III_I and cellulose III_I also be converted back to cellulose I. On the other hand, cellulose II be converted to cellulose III_{II}, and cellulose III_{II} also be converted back to cellulose II. Furthermore, heating treatment of cellulose III_I or cellulose III_{II} in glycerol led to the formation of cellulose IV_I or cellulose IV_{II}, respectively. Cellulose IV_I or cellulose IV_{II} also be converted back to original celluloses I or II by boiling in acid, respectively.
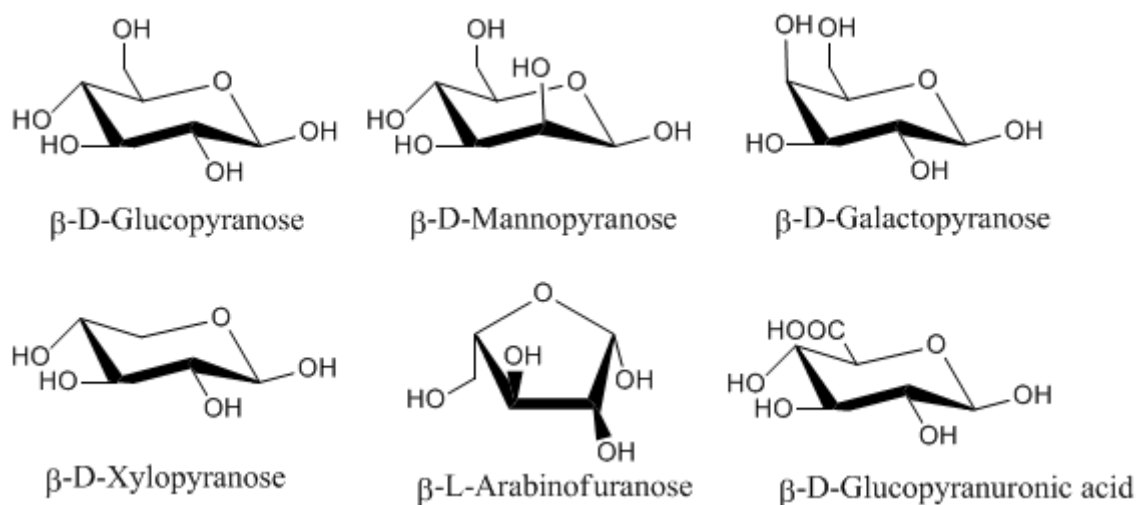
Figure 1.5. Monomer components of wood hemicelluloses.

1.1.2 Hemicellulose

Hemicellulose is a branched polymer consisting of various 5- and 6-carbon sugar units (*e.g.* glucose, xylose, mannose, galactose, arabinose, glucuronic acid and so on) with a shorter molecular chain than cellulose.[11] The structures of monomer components of wood hemicelluloses are shown in Figure 1.5. Cellulose in the wood cell wall is crystalline, strong, and resistant to dilute acid hydrolysis. Hemicelluloses are not easily hydrolyzed with an aqueous dilute acid but fairly dissolve in it without degradation.[12–14] Hemicelluloses in different wood species are both qualitatively and quantitatively different. In hardwoods, the

major component of hemicelluloses is *O*-acetyl-4-*O*-methylglucuronoxylan, sometimes simply denoted as xylans. However, in softwoods, galactoglucomannan is the major component of hemicelluloses.[4] The hemicelluloses together with cellulose and lignin build up the plant cell wall in a fashion that ensures mechanical strength and water resistance of cell wall.[15,16]
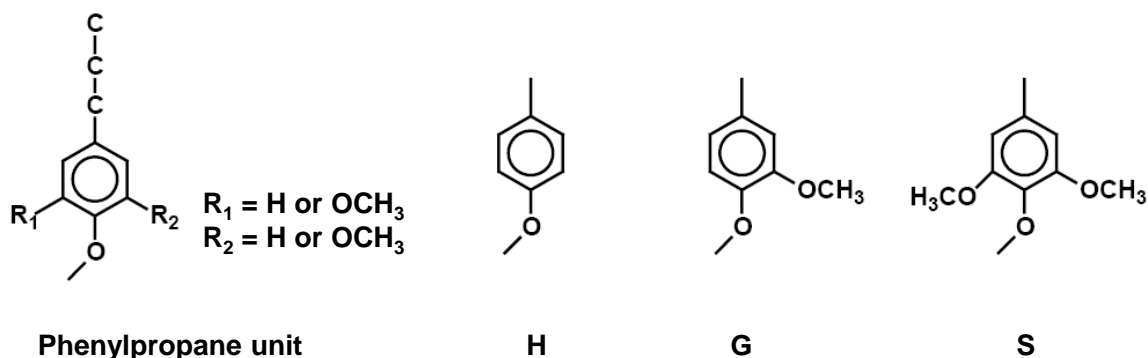
Figure 1.6. Phenylpropane (C9) unit, p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) types of aromatic nuclei.[17]

1.1.3 Lignin

Lignin, an amorphous, racemic polymer, consists of three phenylpropanoid units: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) (Figure 1.6).[17] Lignin in softwood is mainly composed of guaiacyl units and a small amount of p-hydroxyphenyl units. However, lignin in hardwood is mainly composed of guaiacyl and syringyl units, and a small amount of p-hydroxyphenyl units.[18] These monomeric units are linked in lignin macromolecule by different type of ether linkages and carbon-carbon bonds.[19] It is known that the most typical bonds in lignin are the so called arylglycerol-β-aryl ether (β-O-4) linkages, which are the targets of various depolymerization procedures. Besides the main linkage, there are also some other linkages, such as phenylcoumaran (β-5), diarylpropane (β-1), resinol (β-β), biphenyl (5-5), diaryl ether (4-O-5), and dibenzodioxocins (5-5/β-O-4, α-O-4).[20,21] The lignin in middle

lamella of wood cell wall serves the purpose of cementing the fibers together. The remaining part occurs throughout the secondary wall of wood cell wall, where it interpenetrates and encrusts the cellulose microfibrils and the hemicelluloses.[14] Most of the lignin is generally present in the secondary wall, especially in middle layer (S2), even though the concentration of lignin in secondary wall is rather lower than that in middle lamella.

1.1.4 Lignin-carbohydrate network in plant cell wall

The interactions among cellulose, hemicellulose and lignin in plant cell wall have attracted more and more attention in the fields of wood and pulping chemistry. Actually the difficulties in complete delignification of lignocelluloses and dissolution of them have been in part attributed to the chemical bonds (*i.e.* covalent bonds) between lignin and carbohydrates (LC bonds).[22–25] LC bonds have been proposed to exist in wood[26] and chemical pulp[27–30] to form the lignin-carbohydrate complexes (LCCs) although types, frequencies, and quantity are ambiguous.[22] Generally four main types of native LC bonds are suggested, namely benzyl esters, benzyl ethers, β-O-4 bridge type and phenyl glycosides.[31] However, it has not been clarified whether these interactions are due to chemical interaction or physical interaction, although many indirect observations have been reported.[24] Therefore, it is important to clarify whether chemical bonds exist between these polymers in the native wood and the corresponding pulps. One important method was application of the solvent to lignocellulose to study the dissolution limitation of lignocellulose in the solvent. On the other hand, dissolution of lignocellulose itself is also important for the practical application of wood, although lignocellulose is difficult to dissolve in normal solvents.[32]

1.2 Pretreatment of lignocellulose

Lignocellulose is the most abundant natural biomass resource and the traditional utilizations of lignocellulose are performed by the pulp and paper industries.[33] Besides these applications, development of solvent system to dissolve lignocellulose and conversion of cellulose to biofuel and chemicals are also important and necessary for practical application

of lignocellulose.[34–36] Moreover, if the present cellulose solvents could be successfully applied to dissolve lignocellulose, their application will also be widely expanded. However, cellulose molecules contain very strong hydrogen bonding which makes it difficult to dissolve in normal solvents. Moreover, the complicated structure of lignocellulose makes it more difficult to dissolve lignocellulose than cellulose. Therefore, pretreatment is an important tool for practical lignocellulose dissolution and conversion processes. Pretreatment is required to alter the structure of lignocellulose to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars or more accessible to the solvents that make lignocellulose dissolving as represented in the schematic diagram of Figure 1.7.[37] The aims of pretreatments are to break the lignin seal and disrupt the crystalline structure of cellulose, change the aggregation state of cellulose, decrease the molecular weight (or degree of polymerization), reduce the degree of crystallinity and crystallite size, break the hydrogen bonding network, and so on. In general, the pretreatments include chemical methods, physical methods and biological methods.
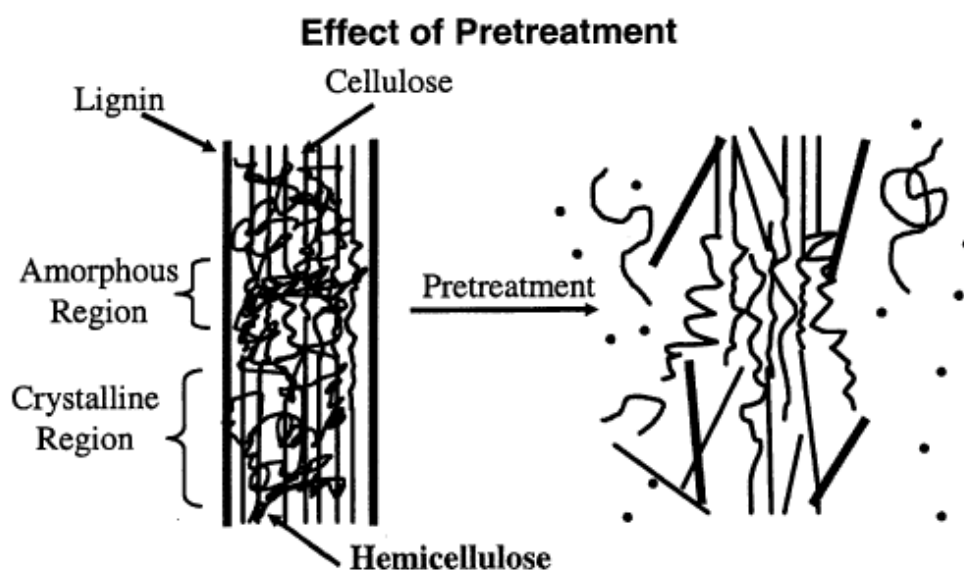
Figure 1.7. Schematic goal of pretreatment on lignocellulosic material.[37] Reproduction from ref. 37 with permission from Elsevier Publishing Group (© Elsevier Publishing Group 2005).

1.2.1 Ethylenediamine pretreatment

Ethylenediamine (EDA) is a strong chemical agent for cellulose treatment. When cellulose I and cellulose II are swollen in EDA, the structures of cellulose I and II change to cellulose III after washing with methanol. The structures of cellulose III are stable under laboratory conditions, but they be reconverted to their previous structures by washing in water.[38] Wang *et al.*[24] reported that after pretreatment with EDA, the wood pulp with high lignin content (up to ca. 10.5%) and high molecular weight completely dissolves in a lithium chloride/dimethyl sulfoxide (LiCl/DMSO) solvent.

1.2.2 Acid pretreatment

After the two oil crises in the 20th century, the idea to develop cost efficient replacement for fossil fuels by acid-catalyzed hydrolysis of cellulose into fermentable sugars has attracted more and more attentions.[39] It has been proposed that the acid-catalyzed hydrolysis of cellulose could follow three steps. The reaction starts with a proton from acid interacting rapidly with the glycosidic endocyclic oxygen. The cleavage of the C-O bond to the cyclic carbonium ion then takes place. After the addition of water, free sugar (or low molecular weight cellulose) and a proton are liberated.[39] According to several investigations of the heterogeneous hydrolysis of cellulose, the degree of polymerization of cellulose decreases rapidly until it reaches the so-called "levelling-off" or "limiting" degree of polymerization (LODP).[40–43] Acid hydrolysis has been applied as a pretreatment to reduce the degree of polymerization of cellulose and make cellulose more accessible for chemicals or complete hydrolysis to produce glucose, which is beneficial to produce biofuels.[44–47] Traditional acid hydrolysis for preparing fermentable sugars has been carried out at high acid concentration and low temperature or vice versa.[48] Mild conditions of acid hydrolysis were not strong enough to hydrolyze cellulose into mono-/di-/oligo-saccharides, but may disrupt the more accessible amorphous regions and cut the linear chains, resulting in changes in molecular parameters and physicochemical properties, thus promoting the dissolution of cellulose.[49]

1.2.3 Ball milling

Cellulose is a highly crystalline polymer which can effectively absorb mechanical energy

during milling process to change the fine structure and morphology, including the degree of polymerization, the degree of crystallinity, and the morphology of cell wall, thus improving the solubility of cellulose in solvents. As early as 1946, the ball milling method has been used to obtain amorphous cellulose.[50] Wang *et al.* reported that the wood meal could be successfully dissolved in LiCl/DMSO solvent after ball milling for 2 h under their milling conditions.[23]

1.2.4 Steam explosion

Steam explosion treatment is a low-cost, non-polluting technology and has been rapidly developed in recent decades. It was originally used in pulping process for efficient separation of plant fibers. Steam explosion utilizes high temperature (183–252 ℃) and high pressure (1.0–4.9 MPa) steam to treat cellulose feedstocks. Some properties of the raw material were changed this process, such as the separation of the raw material component, the structural changes, the reduction of molecular weight, breaking of hydrogen bonding, and so on. Kamide *et al.* used steam explosion technology to treat pulp to break the inter and intra hydrogen bonds of cellulose, leading to the dissolution of cellulose in NaOH aqueous solution.[51-53]

1.3 Solvents of cellulose

Cellulose is an almost inexhaustible source on earth. However, cellulose is difficult to dissolve in normal solvents mainly due to the presence of very strong inter- and intra-molecular hydrogen bonds. To develop an efficient, environment-friendly solvent and understand the relevant dissolution mechanism is still long-standing goal in the cellulose field until now.[54,55] An approximate classification of cellulose solvents is given in Figure 1.8. There are two types of systems, namely non-derivatizing and derivatizing systems.[56] Examples of the non-derivatizing solvents of cellulose are aqueous inorganic complexes (cuoxam, cadoxen, and cuen), 8-10 wt% NaOH aqueous solution, NH_3/NH_4SCN aqueous solution, $Ca(SCN)_2$ and NaSCN aqueous solution, $ZnCl_2$ aqueous solution, N,N-

dimethylacetamide (DMAc)/LiCl, dimethyl sulfoxide (DMSO)/LiCl, 1,3-dimethyl-2-imidazolinone (DMI)/LiCl, N-methylmorpholine-N-oxide (NMMO), ionic liquids, and alkali/urea or thiourea (NaOH/urea, NaOH/thiourea and LiOH/urea) aqueous systems. Examples of the derivatizing solvents mainly are N,N-dimethlylformamide (DMF)/N_2O_4, DMSO/paraformaldehyde and NaOH/CS_2 (viscose route). The traditional viscose route still dominates production methods. However, it inevitably generates hazardous byproducts (*e.g.* H_2S) during manufacture and in post-treatment processes, resulting in serious pollution.[57] Among the new cellulose solvents, NMMO, LiCl/DMAc, ionic liquids, and alkali/urea solutions are the most promising alternative cellulose solvent systems.
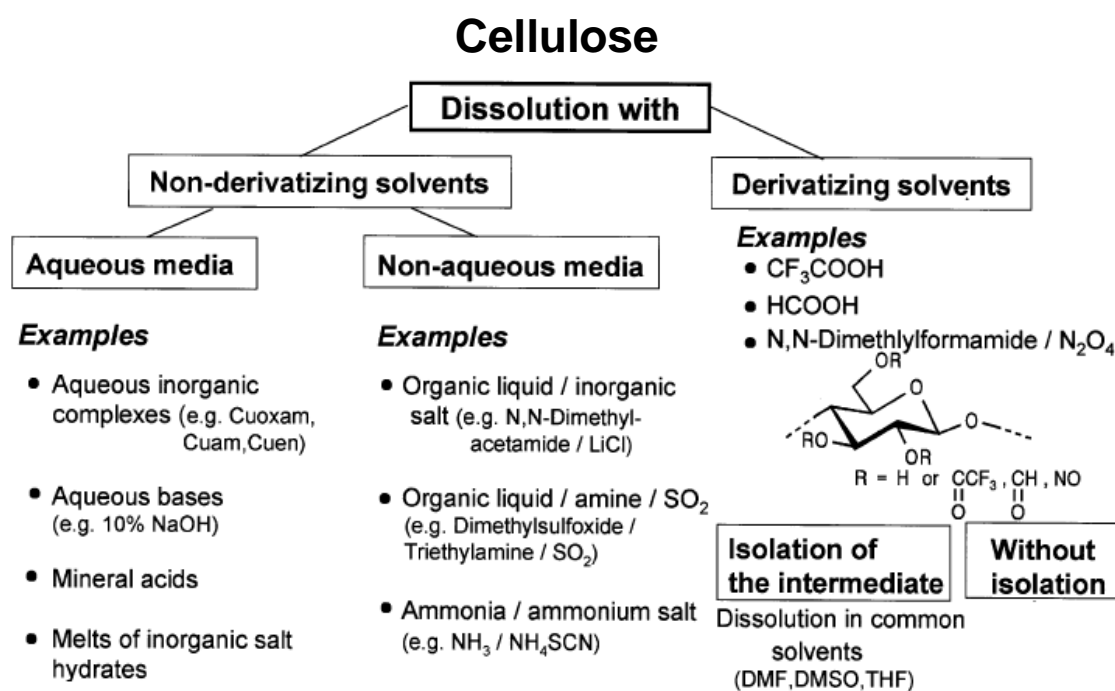
Figure 1.8. Classification of cellulose solvents.[56]

1.3.1 N-methylmorpholine-N-oxide hydrate (NMMO)

In 1969 Johnson described a cellulose solvent system using cyclic amine oxides,

particularly N-methylmorpholine-N-oxide (NMMO), which is nowadays used in the industrial Lyocell process.[58,59] The solvent does not produce toxic waste pollutants, and can be recycled with over 98% recovery.[60] The melting point of pure NMMO is 170 ℃. Hydration with one water molecule per NMMO molecule leads to the NMMO monohydrate with 13.3 wt% water content and it has a melting point of about 74 ℃ and improved dissolution ability for cellulose owing to its strong N-O dipole.[61] McCorsley and Varga developed a method to produce highly concentrated cellulose solutions of up to 23% by treating cellulose with NMMO and water and subsequently removing water with an applied vacuum until the dissolution of the cellulose was achieved.[62] Even though the NMMO/water system has been applied in large scale and some commercial textile fibers were produced, two problems are still present in the NMMO process, namely the instability of the solvent and the tendency of the Lyocell fiber towards fibrillation.[63] The instability of NMMO may cause a safety risk due to its possible spontaneous decomposition[64] and side reactions may cause consumption of the expensive solvent and can lead to undesired staining of the cellulose regenerated.[65] Furthermore, the unique, highly crystalline structure of Lyocell, and weaker lateral links between the crystallites make the fibers undergo localized separation of fibrous elements at the surface, namely fibrillation, mainly under conditions of wet abrasion, which restricts the applications of Lyocell.[66]

1.3.2 LiCl/N, N-dimethylacetamide (LiCl/DMAc)

The system N,N-dimethylacetamide (DMAc)/LiCl shows a large potential for the dissolution and analysis of cellulose and for the preparation of a wide variety of derivatives.[56] Its application in analysis is due to the fact that this solvent is colorless and successful dissolution of cellulose can be attained with negligible degradation even in case of high molecular weight cellulose, *e.g.* bacterial cellulose. The cellulose/LiCl/DMAc solution is fairly stable, and little or no degradation of the samples has been observed.[67] However, several problems were reported when this solvent system was applied to pulp dissolution. One is the limited solubility of softwood kraft pulps in this solvent, probably caused by the gelation of the glucomannan fraction.[68] When the softwood semi-bleached kraft pulp with kappa number of 18 was applied to this system, the dissolution was incomplete.[68] Another

drawback is the high salt concentration, which both increases the viscosity of the solution and complicates preparative SEC. Berthold *et al.* reported that the unbleached softwood kraft pulp with kappa number around 50 which was derivatized with ethyl isocyanate could be dissolved in 8% LiCl/DMAc.[69]

1.3.3 Ionic liquids

Ionic liquids are a group of new organic salts that exist as liquids at a relatively low temperature (< 100 ℃). They have many attractive properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure. As early as 1934, the work using N-alkylpyridinium salts as ionic liquids (ILs) to dissolve cellulose was reported by Charles Graenacher, which was the first application of ILs to cellulose dissolution.[70] However, until Rogers's group carried out comprehensive studies on cellulose dissolution in ionic liquids and its regeneration, the value of cellulose dissolution in ionic liquids has not been evaluated.[71,72] The solubility of cellulose and properties of solution could be controlled by selection of the ionic liquid constitutes.[54] At the high temperature, more cellulose could be dissolved in ionic liquid.[73] Microwave heating could significantly accelerate the dissolution. Solution containing up to 25 wt% cellulose was prepared in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) under microwave heating.[54] In recent years, some researches on direct dissolution of wood or lignocellulose using ionic liquid have been reported.[74-76] The dissolution efficiency was largely affected by the water content and the particle size of the wood chips. The dependence of dissolution efficiency on the wood particle size were reported as follows: ball-milled wood powder > sawdust ≥ thermo-mechanical pulp (TMP) fibers ≫ wood chips.[74] Zavrel et *al.*[75] carried out high-trough put screening of ionic liquids for dissolution of wood with the particle size range of 1–2 mm. The effect of particle size of wood chip on the dissolution power of 1-ethyl-3-methylimidazole acetate ([EMIM]OAc) and [BMIM]Cl was systematically investigated by Sun *et al.*[76] The presence of water significantly hampered the dissolution efficiency of ionic liquids.[73] Although the dissolution efficiency of ionic liquids are very strong, the applicability of ILs to the industrial production is still debatable because of their water sensitivity and difficulty in purification.[77]

1.3.4 NaOH aqueous solution

Treatment of cellulose with NaOH aqueous solution is one of the most important technical processes for cellulose activation and dissolution, which has been intensively investigated for a long time.[63] Researches of the ternary system cellulose/NaOH/water led to a variety of dissolution procedures and the established phase diagram suggests that there is a dissolution zone of cellulose in aqueous NaOH below 268 K at a NaOH concentration of 7–10 wt%.[78] Dissolution of cellulose in aqueous NaOH solution could be achieved depending on molecular weight, crystalline form and the degree of crystallinity. Rheology of the cellulose/NaOH/water system was studied in detail.[79] Kamide *et al.*[80] reported that non-crystalline celluloses with low molecular weights could dissolve in NaOH aqueous solution with an 8–10 wt% concentration at about 4 ℃. The applicable cellulose should be the steam-exploded wood pulp with DP lower than 250, rather than the cotton linters pulp with medium molecular weight. In technical papers, they claimed that a spining of 5 wt% solution of steam-exploded dissolving pulp in 9.1 wt% NaOH at 4 ℃ in 20 wt% H_2SO_4 at 5 ℃ yielded fiber of poor quality.[63] Isogai *et al.* described a procedure for a complete dissolution of microcrystalline cellulose in 8–9 wt% NaOH aqueous solution by a freezing-thaw-dilution process.[32] A 5 wt% or lower concentration cellulose solution could be obtained when NaOH concentration was in the range from 7.9 to 14.9 wt%.[81] However, the restriction of low-molecular weight cellulose and the easy gelation of the cellulose solution from $NaOH/H_2O$ system suggest that this system is unable for the industrial manufacture.[82]

1.4 Alkali/urea aqueous solvent system and application

In recent years, a new cellulose solvent system, *i.e.* alkali/urea system including NaOH/urea and LiOH/urea aqueous solutions pre-cooled to −12 °C, have been developed by Zhang's group.[83–87] Celluloses with molecular weights below 1.2×10^5 could be dissolved well in the NaOH/urea aqueous solution without significant degradation. Compared with the other cellulose solvent systems such as $NaOH/CS_2$, LiCl/DMAc, NMMO and ionic liquids, this solvent system is environmentally less harmful, cheap and rather simple in handling.

Zhang *et al.* demonstrated that NaOH "hydrates" could be easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperatures.[88] The urea hydrates could not associate directly with cellulose, but could be self-assemble at the surface of the NaOH hydrogen-bonded cellulose to form a worm-like inclusion complex (IC). The cellulose IC surrounded with urea reduces greatly the self-association of the cellulose molecules, leading to the increased solubility and stability of the cellulose solution. The cellulose solution is relatively unstable and can be very sensitive to temperature, molecular weight, polymer concentration and storage time. Therefore, this cellulose dissolution at low temperature arises as a result of a fast dynamic self-assembly process among small solvent molecules (NaOH, urea and water) and the cellulose macromolecules.[82] According to the dynamic self-assembly definition, if fluctuation or energy exchange can be avoided, the cellulose solution may be highly stable for a long period of time.[89,90] The dissolubility of cellulose in LiOH/urea aqueous solution is stronger than that of cellulose in NaOH/urea aqueous solution, in terms of dissolution of celluloses with higher molecular weights and preparation of cellulose solutions with higher cellulose concentrations. The dissolution mechanism and solution properties of cellulose in LiOH/urea aqueous system are similar to that in NaOH/urea aqueous system. In LiOH/urea system, a channel IC hosted by urea encages the cellulose macromolecule bonded with LiOH hydrated. The solvent containing Li^+ has relatively small ionic radius and high charge density, and thus, more easily penetrates into cellulose than Na^+ ions to be imbibed on the cellulose chain, leading to the relatively stable IC and higher dissolubility of cellulose.[91]

Actually, cellulose molecules are difficult to be truly dispersed in most solvents at the molecular level. The cellulose chains in NaOH/urea solution formed aggregates with a radius of gyration (R_g) of about 232 nm and an apparent hydrodynamic radius (R_h) of about 172 nm[92] which was similar to the value of about 200 nm for the cellulose molecules in NMMO using the same technique.[93] The cellulose solution easily aggregated and either a heating or a cooling treatment could induce the gelation processing.[84] The energy of the hydrogen bonds is higher at low temperature, leading to the strong tendency of aggregation of the cellulose molecules. Therefore, the cellulose solution prepared at low temperature formed gels by reducing temperature to below 0 ℃. However, it could be stored at 0 to 5 ℃ for a long time

and still remained in its stable liquid state.[84] Navard *et al.*[94] studied the binary phase diagram of urea/water, the ternary urea/NaOH/water phase diagram and the influence of the addition of microcrystalline cellulose in urea/NaOH/water solutions by differential scanning calorimeter (DSC). Urea/water solutions had a simple eutectic behavior with a eutectic compound formed by pure urea and ice (one urea per eight water moles), melting at −12.5 ℃. In the presence of microcrystalline cellulose, the interactions between cellulose and NaOH/water were exactly the same as without urea, and urea was not interacting with cellulose. A tentative explanation of the role of urea was to bind water, making cellulose-NaOH links more stable.
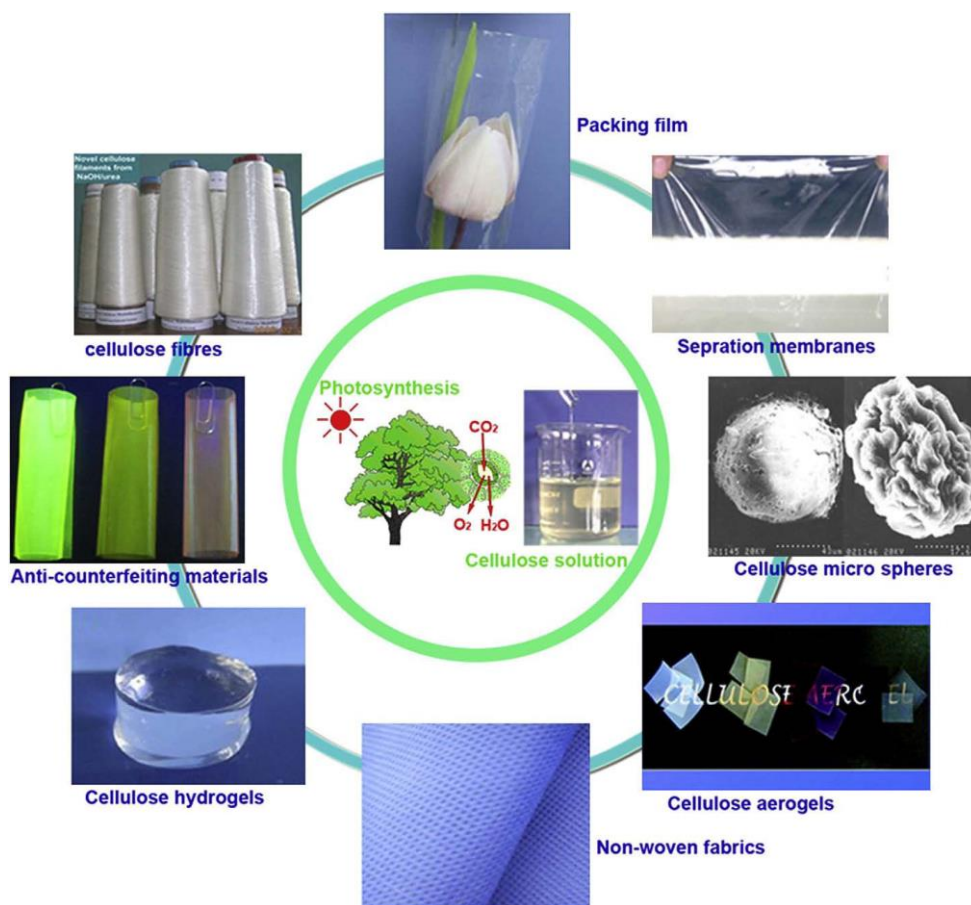
Figure 1.9. Schematic illustration of novel cellulose materials from cellulose/alkali/urea solution.[95] Reproduction from ref. 95 with permission from Elsevier Publishing Group (© Elsevier Publishing Group 2013).

From the cellulose/alkali/urea solution, all kinds of high-performance cellulose materials have been prepared, such as fibers, films, microspheres, hydrogels, aerogels, and their relevant composite materials. The schematic illustration of these novel cellulose materials is shown in Figure 1.9.[95] They are promising in the fields of textile, packaging, separation technology, biomedicine, and so on.

1.5 Objective of this work

Lignocellulose is the most abundant biomass on the earth. Dissolution of lignocellulose is not only important for utilization of the lignocellulose resource but also useful for understanding the interactions among the main components of the plant cell wall (cellulose, hemicelluloses and lignin). Compared with the other developed cellulose solvents such as LiCl/DMAc, ionic liquids, and NMMO, the NaOH/urea aqueous system is a simple, low-cost, and does not produce any toxic byproduct. Although cotton linters pulp could dissolve well in NaOH/urea solvent system and the obtained cellulose/NaOH/urea solution has been used to produce all kinds of cellulose materials, dissolution of lignocellulose in this system has never been examined in detail until now. It is meaningful to expand potential applications of alkali/urea systems and to deepen related fundamental studies. If NaOH/urea solvent could be successfully applied to lignocellulose, its application will be widely expanded and utilization of lignocellulose as a new source of materials will also be facilitated. Therefore, the objective of this work is to do fundamental studies on dissolution of lignocellulose in aqueous NaOH/urea system and analysis of the interactions among the plant cell wall components. The effects of lignin content, hemicellulose content, crystallinity, crystal form, and molecular weight of lignocellulose on its dissolution will be evaluated and different pretreatment methods (dilute acid treatment and ball milling treatment) will also be used to improve the dissolution. It is a new route of an advance environment-friendly technology to prepare lignocellulose solution and materials. The research and application of the new lignocellulose solution will benefit for creating a sustainable society.

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Chapter 2

Effects of lignin and hemicellulose contents on dissolution of wood pulp in aqueous NaOH/urea solution

2.1 Introduction

The development of renewable and biodegradable bio-based materials is indispensable for the building of a sustainable society.[1] Cellulose is the most abundant natural polymer on the earth, and has attracted more and more attention as a renewable resource for applications in the fields of material and energy. Cellulose is not a thermo-plastic material and must be dissolved in a solvent and regenerated from the cellulose solution for it to form fibers, films, spheres, hydrogels, aerogels or other regenerated cellulose materials.[2] However, the presence of highly regulated and numerous inter- and intra-molecular hydrogen bonds makes native cellulose difficult to dissolve in common solvents, which restricts its potential applications in forming processes. Several solvent systems have been developed to dissolve cellulose, such as NaOH/CS$_2$,[3] lithium chloride/N,N-dimethylacetamide (LiCl/DMAc),[4] N-methylmorpholine-N-oxide (NMMO)[5] and ionic liquid[6]. Among the sources of cellulose, wood is one of the most important; it is mainly composed of microfibrils of cellulose (40%–50%) and hemicellulose (20%–30%) impregnated with lignin (15%–25%).[7] However, the preparation of dissolving pulp from wood for the dissolution of cellulose requires the removal of almost all the hemicellulose and lignin, which greatly increases the cost. Therefore, direct dissolution of wood pulp is important and necessary for the practical application of wood cellulose.[8,9]

In recent years, some cellulose solvents have been applied to dissolve wood pulps with cellulose, hemicellulose and lignin.[10–12] However, most of them could not completely dissolve

wood pulps.[10,13] Recently, Wang et al.[14] succeeded in dissolving wood pulp with as high as 10% lignin content; even in this case, ethylenediamine pretreatment was necessary, like in other cases such as steam explosion[15] and ball milling treatments[16]. Moreover, several problems were reported when these solvent systems were applied to dissolve cellulose and wood pulps. They are expensive, toxic and require harsh dissolution conditions. Recently, a new cellulose solvent was developed by Zhang's group, namely, a NaOH/urea solvent system at low temperature.[17–20] This solvent is cheap, environmentally less harmful and rather simple to handle. Although cotton linter cellulose dissolves very well in this solvent system, dissolution of wood pulps with cellulose, hemicellulose and lignin has never been examined in detail until now. If NaOH/urea solvent could be successfully applied to wood pulps, its application would be widely expanded and the utilization of wood pulps as a new source of material would also be facilitated.

In this chapter[21], four species of original woodchips, softwood thermo mechanical pulp and unbleached kraft pulp were firstly pretreated to obtain wood pulps with different cellulose, hemicellulose and lignin contents. Then, these wood pulps were dissolved in NaOH/urea solvent to study their dissolved proportion. The effects of hemicellulose and lignin on the dissolution of glucan and woodpulps themselves were carefully studied and we discussed the reason why wood pulps were difficult to dissolve in NaOH/urea solvent.

2.2 Experimental Section

2.2.1 Materials

Four kinds of hardwood woodchip (*Acacia mangium*, *Acacia mearnsii*, *Eucalyptus globulus* and *Eucalyptus camaldulensis*), softwood thermomechanical pulp (TMP) and softwood unbleached kraft pulp (UKP) were provided by Oji Paper Co., Ltd., Tokyo, Japan. $NaClO_2$ was purchased from Sigma-Aldrich Inc. All the other reagents and solvents were of laboratory grade and used as received from Wako Pure Chemicals, Tokyo, Japan.

2.2.2 Preparation of woodchips with low lignin content

The original woodchips (size of a woodchip: about 20 mm × 10 mm × 3 mm) with a weight of 30 g were delignified for 9 days using a mixture of 20 g of NaClO$_2$, 4 ml of acetic acid and 180 g of water at room temperature. This procedure was further repeated twice. The mixture was occasionally shaken by hand. After 27 days, the woodchips were washed with water and dispersed by a juice mixer. Woodchips with low lignin content were finally obtained after filtration and defined as Chlorite-Woodchips. In order to exclude the influence of high temperature and drying conditions on the dissolution of Chlorite-Woodchips, the delignification of woodchips was carried out at room temperature and all the Chlorite-Woodchips were never dried, unless specifically mentioned.

2.2.3 Preparation of woodchips with low hemicellulose content

About 2 g of Chlorite-Woodchips were added to 30 g of 4 wt% or 18 wt% aqueous NaOH solution and stirred at room temperature for 43 min. Then, 30 g of water was added to the obtained mixture followed by stirring for 2 min. Finally, the woodchips were washed with a half concentration of original NaOH solution (*i.e.* 2 wt% or 9 wt% NaOH solution, respectively), further washed with water, filtrated and then defined as 4% NaOH-Chlorite-Woodchips or 18% NaOH-Chlorite-Woodchips, respectively.

2.2.4 Preparation of fully delignified woodchips

In order to obtain fully delignified woodchips, the desired amount of Chlorite-Woodchips was further delignified in a mixture of 80 ml of water, 10 ml of 2 mol/L sulfuric acid and 10 ml of 0.02 mol/L potassium permanganate at 25 °C in a water bath for 10 min with stirring. After termination of the reaction by the addition of potassium iodide, the generated iodine was titrated using 0.05 mol/L Na$_2$S$_2$O$_3$ solution. Then, the fully delignified woodchips were washed, filtrated and defined as OPP-Chlorite-Woodchips.

2.2.5 Preparation of kraft pulps with different lignin contents

Softwood thermomechanical pulp (TMP, 5 g) or unbleached kraft pulp (UKP, 5 g) was placed in a 250 ml Erlenmeyer flask with 160 g of water, 0.3 ml of acetic acid and 1 g of sodium chlorite. Then, the obtained mixture was kept at 75 °C in a water bath. The pulps with different lignin contents were prepared by controlling the times of reagent addition and the

reaction time.

2.2.6 Dissolution of woodchips and kraft pulps

Pretreated woodchips (Chlorite-Woodchips, NaOH-Chlorite-Woodchips and OPP-Chlorite-Woodchips) and pulps (delignified TMP and UKP) were dispersed in the 7 wt% NaOH/12 wt% urea/81 wt% H_2O solutions at room temperature (20 °C). The concentration of the woodchips or pulps was 1 wt%. The dispersion was frozen at −20 °C and thawed at room temperature 2 times. The resulting mixture was centrifuged at 10,000 rpm for 10 min at 5 °C and then filtrated. The remaining undissolved fractions were washed with 7 wt% NaOH/12 wt% urea/81 wt% H_2O 3 times and further washed with water until they were neutral. Then, they were dried in a vacuum oven with P_2O_5 at 40 °C for 48 h, weighed and named In-Chlorite-Woodchips, In-NaOH-Chlorite-Woodchips, In-OPP-Chlorite-Woodchips, In-TMP and In-UKP, depending on the original material. The dissolved proportions of woodchips and pulps were calculated according to the following equation:

$$\text{Dissolved proportion} = \frac{m_{ow} - m_{res}}{m_{ow}} \times 100\% , \tag{1}$$

where m_{ow} is the dry mass of the woodchips or pulps before dissolution and m_{res} is the dry mass of the residual undissolved fractions of woodchips or pulps. The dissolved proportion measurements were repeated more than three times and the average was obtained.

2.2.7 Characterizations

Degrees of polymerization measurement: The viscosity-average degrees of polymerization (DP_v) of Chlorite-*A. mangium*, Chlorite-*A. mearnsii*, Chlorite-*E. globulus* and Chlorite-*E. camaldulensis* were determined for their solutions in 0.5 M copper ethylenediamine (CED) using a Cannon−Fenske capillary viscometer and calculated using the Mark−Houwink−Sakurada equation[22] to be 1180, 1160, 1160 and 1110, respectively.

Lignin determination: The Kappa number method and Klason method were used to determine the lignin content of the samples.[23]

Sugar analysis: The carbohydrate compositions of the samples were determined by the alditol-acetate method.[24] Sulfuric acid (72 wt%, 1 ml) was added to 100 mg samples and kept at room temperature for 4 h, and then diluted with water to adjust the concentration of sulfuric acid to 4 wt%. Hydrolysis of the samples in 4 wt% sulfuric acid was performed in an

autoclave at 120 °C for 1 h. After cooling to room temperature, the hydrolyzed solution was filtrated with a glass filter, and the filtrate was adjusted to 100 ml with water. As an internal standard, 1.00 ml of myo-inositol aqueous solution (1.00 mg/ml) was added into 5.00 ml of cooled solution obtained above. The solution was neutralized using aqueous barium hydroxide solution to pH 5.5. After removal of the precipitate, about 20 mg of NaBH$_4$ was added to the filtrate and the reaction mixture was kept at room temperature for 24 h. Excess NaBH$_4$ was degraded with acetic acid. After the mixture was evaporated to dryness, a small amount of methanol was added and dried, which was repeated several times; then, the mixture was heated in an oven at 105 °C for 15 min to ensure complete removal of the water. The dry residue was acetylated using 1 ml of acetic anhydride at 120 °C for 3 h, and then analyzed with a gas chromatograph GC-14b with FID (Shimadzu Co., Kyoto, Japan) using a column TC-17 (fused-silica capillary column, 30 m, 0.25 mm i.d., GL Science Inc., Tokyo, Japan) with a temperature program of 20 min at 220 °C, injection temperature of 220 °C and detector temperature of 230 °C.

From the carbohydrate composition, the contents of each sugar (glucan, mannan, xylan, *etc.*) in the original sample and insoluble fraction of the sample were obtained and the dissolved proportions of sugar were calculated according to the following equation:

$$\text{Dissolved proportion of sugar} = \frac{m_{so} - m_{\sin}}{m_{so}} \times 100\% , \tag{2}$$

where m_{so} is the sugar content of the original sample and m_{sin} is the sugar content of the insoluble fraction of the sample.

X-ray diffraction (XRD): The samples were dried in a vacuum oven with P$_2$O$_5$ at 40 °C for 48 h. Then, XRD patterns of the samples were acquired in reflection mode using a RINT 2000 diffractometer (Rigaku, Tokyo, Japan) with monochromator-filtered Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. Scans were obtained from 4 to 40° 2θ at a speed of 1° per min.

2.3 Results and Discussion

2.3.1 Characteristics of Chlorite-Woodchips

Tables 2.1 and 2.2 show the yields, lignin contents, carbohydrate compositions and dissolved proportions of Chlorite-Woodchips prepared from the four different wood species.

The yields of Chlorite-Woodchips based on the original woodchips ranged from 64.8% to 78.8%, depending on the wood species. The lignin content of the Chlorite-Woodchips was about 1.0%, indicating that most of the lignin had been removed by the sodium chlorite delignification. The dissolved proportion of the Chlorite-Woodchips in NaOH/urea solvent ranged from 36.2% to 46.4%. The different wood species had different dissolved proportions, even though they have similar degrees of polymerization (DP) ranging from 1180 to 1110. In order to clarify which components of the Chlorite-Woodchips dissolved in the NaOH/urea solvent, the carbohydrate compositions of the Chlorite-Woodchips and their insoluble fractions in NaOH/urea solvent were studied. The dissolved proportions of different sugars in Chlorite-Woodchips are also shown in Tables 2.1 and 2.2. All the results show that the dissolved proportions of glucan of Chlorite-Woodchips in NaOH/urea solvent were very low, and significantly different from each other (1.1%–11.5%). In particular, the two acacia species exhibited extremely low values (1.1% and 3.6%, Table 2.1) compared with the eucalyptus species (10.4% and 11.5%, Table 2.2). It seems that not only the composition and the amount of cell wall components but also their arrangement in the cell wall affect the solubilization. Contrary to the glucan dissolution, most of the xylan and mannan were dissolved, and the dissolved proportion of xylan was more than 90%. This indicated that most of the hemicellulose was dissolved in the NaOH/urea solvent.

Table 2.1. Characteristics of Chlorite-*A. mangium* and Chlorite-*A. mearnsii.*

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Lignin (%)	Yield* (%)
Chlorite-*A. mangium*	100	56.9	12.4	2.4	1.0	73.9
In-Chlorite-*A. mangium*	63.8	54.9	1.0	0.8	-	-
Dissolved proportion	36.2	3.6	92.1	64.8	-	-
Chlorite-*A. mearnsii*	100	51.4	19.2	1.6	0.9	78.8
In-Chlorite-*A. mearnsii*	60.7	50.9	0.7	0.7	-	-
Dissolved proportion	39.3	1.1	96.3	55.2	-	-

*Yield of chlorite treatment, based on the original *A. mangium* or *A. mearnsii*

Table 2.2. Characteristics of Chlorite-*E. globulus* and Chlorite-*E. camaldulensis*.

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Lignin (%)	Yield* (%)
Chlorite-*E. globulus*	100	52.4	16.9	1.5	1.1	71.4
In-Chlorite-*E. globulus*	55.1	46.9	0.5	0.3	-	-
Dissolved proportion	44.9	10.4	97.3	80.8	-	-
Chlorite-*E. camaldulensis*	100	48.9	13.4	0.8	1.5	64.8
In-Chlorite-*E. camaldulensis*	53.6	43.3	0.5	0.4	-	-
Dissolved proportion	46.4	11.5	96.1	52.6	-	-

*Yield of chlorite treatment, based on the original *E. globulus* or *E. camaldulensis*

The Chlorite-Woodchips were also treated with NaOH/urea solvent at room temperature (20 °C) for comparison with those treated by the general dissolution method at low temperature (–20 °C) shown in the experimental part. Figure 2.1 shows the XRD patterns of the untreated Chlorite-*E. globulus*, the insoluble fraction of Chlorite-*E. globulus* after treatment with 7% NaOH/12% urea/81% H_2O at room temperature (20 °C) or at low temperature (–20 °C). Three 2θ peaks at 15.1°, 16.3° and 22.6° found in the untreated Chlorite-*E. globulus* were assigned to (1-10), (110) and (200) crystal planes of cellulose I.[25,26] However, the insoluble fraction of Chlorite-*E. globulus* after treatment with 7% NaOH/12% urea/81% H_2O at low temperature showed three 2θ peaks at 12.6°, 20.9° and 21.7°, which could be assigned to the (1-10), (110) and (020) crystal planes of cellulose II.[25,26] This indicated that, although the cellulose molecules present in the insoluble fraction could not dissolve in NaOH/urea solvent at low temperature, their efficient swelling in NaOH/urea solvent at low temperature resulted in some molecular mobility, leading to the crystal transforming from cellulose I to cellulose II, which is similar to the mercerization process of cellulose in NaOH solution. On the other hand, the pattern of the insoluble fraction of Chlorite-*E. globulus* after treatment with NaOH/urea solvent at room temperature showed a

mixture of cellulose I and II, although most of crystal in it was present as cellulose I. This indicated the importance of low-temperature treatment in the NaOH/urea solvent system.
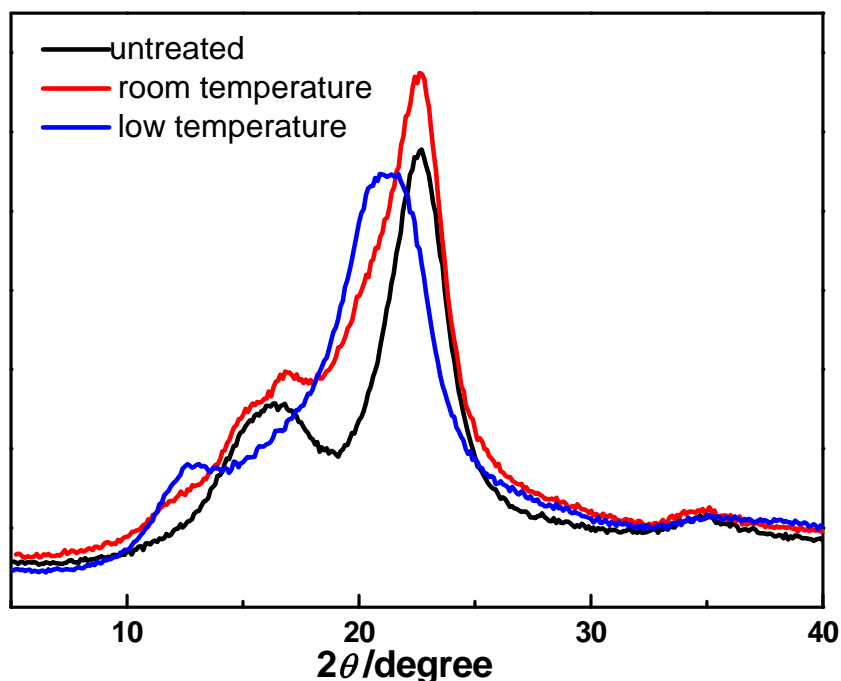
Figure 2.1. XRD patterns of the untreated Chlorite-*E. globulus* and the insoluble fraction of Chlorite-*E. globulus* after treatment with 7% NaOH/12% urea/81% H_2O at room temperature (20 °C) or at low temperature (–20 °C). Reproduction from ref. 21 with permission from Springer (© Springer 2014).

2.3.2 Characteristics of NaOH-Chlorite-Woodchips

Although the above result demonstrated that most of the hemicellulose could dissolve in the NaOH/urea solvent, in order to clarify further whether or not hemicellulose affects the dissolution of cellulose in NaOH/urea solvent, hemicellulose of the Chlorite-Woodchips was removed using NaOH solution before their dissolution in NaOH/urea solvent. Tables 2.3 and 2.4 show that the NaOH-Chlorite-Woodchip yields after NaOH solution treatment of

Chlorite-Woodchips ranged from 62.4% to 69.8%. The low NaOH-Chlorite-Woodchip yields were caused by the removal of most of the hemicellulose and part of the glucan during the NaOH treatment. Furthermore, the dissolved proportions of the NaOH-Chlorite-Woodchips in NaOH/urea solvent were lower than those of the Chlorite-Woodchips because the Chlorite-Woodchips contained more soluble hemicellulose than the NaOH-Chlorite-Woodchips. However, the dissolved proportion of glucan of the NaOH-Chlorite-Woodchips was higher than that of the Chlorite-Woodchips. For example, the dissolved proportion of glucan of 18% NaOH-Chlorite-A. mearnsii was 21.1% and that of Chlorite-A. mearnsii was only 1.1%. Furthermore, it is interesting that the dissolved proportion of 18% NaOH-Chlorite-Woodchips was higher than that of the 4% NaOH-Chlorite-Woodchips, although the 4% NaOH-Chlorite-Woodchips had higher soluble hemicellulose content than the 18% NaOH-Chlorite-Woodchips. This result indicates the higher dissolved proportion of cellulose in 18% NaOH-Chlorite-Woodchips than those of cellulose in 4% NaOH-Chlorite-Woodchips. It is conjectured that the hemicellulose still remaining in 4% NaOH-Chlorite-Woodchips impeded the dissolution of cellulose. Navard et al. also found that the presence of a small amount of hemicellulose may prevent or decrease the solubility of cellulose in aqueous NaOH solution.[27] Another reason may be that the 18% NaOH solution treatment could change the cellulose crystal structure (shown in Figure 2.3), leading to higher dissolved proportion of cellulose.

Tables 2.3 and 2.4 also show that most of the hemicellulose was removed after the NaOH solution treatment, and the residual hemicellulose could further dissolve in NaOH/urea solvent. For easy comparison of the dissolved proportions of NaOH-Chlorite-Woodchips and corresponding glucan in NaOH/urea solvent, the relevant values are shown in Figure 2.2. It shows that the dissolved proportion of NaOH-Chlorite-Woodchips decreased compared with that of the Chlorite-Woodchips; however, the dissolved proportion of the corresponding glucan increased. The dissolved proportions of glucan of Chlorite-*A. mearnsii* and Chlorite-*E. globulus* increased from 1.1% and 10.4% to 21.1% and 28.1%, respectively, after pretreatment with 18% NaOH. These results further confirmed that removing the hemicellulose could promote the dissolution of glucan in NaOH/urea solvent. Moreover, the increased dissolved proportion of glucan should be responsible for the higher dissolved proportion of the 18% NaOH-Chlorite-Woodchips than the 4% NaOH-Chlorite-Woodchips.

**Table 2.3.** Characteristics of NaOH-Chlorite-*A. mearnsii*.

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Yield* (%)
4% NaOH-Chlorite-*A. mearnsii*	100	78.5	6.6	2.1	69.8
In-4% NaOH-Chlorite-*A. mearnsii*	81.9	68.8	0.8	0.8	-
Dissolved proportion	18.1	12.5	87.7	63.2	-
18% NaOH-Chlorite-*A. mearnsii*	100	78.3	5.8	1.1	69.4
In-18% NaOH-Chlorite-*A. mearnsii*	76.0	61.8	0.6	0.6	-
Dissolved proportion	24.0	21.1	89.0	43.6	-

*Yield of NaOH treatment, based on the Chlorite-*A. mearnsii*

Table 2.4. Characteristics of NaOH-Chlorite-*E. globulus*.

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Yield* (%)
4% NaOH-Chlorite-*E. globulus*	100	75.0	5.1	2.1	69.3
In-4% NaOH-Chlorite-*E. globulus*	84.6	66.2	0.6	0.7	-
Dissolved proportion	15.4	11.8	88.0	66.8	-
18% NaOH-Chlorite-*E. globulus*	100	78.5	2.8	0.8	62.4
In-18% NaOH-Chlorite-*E. globulus*	70.9	56.5	0.8	0.5	-
Dissolved proportion	29.1	28.1	71.7	56.9	-

* Yield of NaOH treatment, based on the Chlorite-*E. globulus*
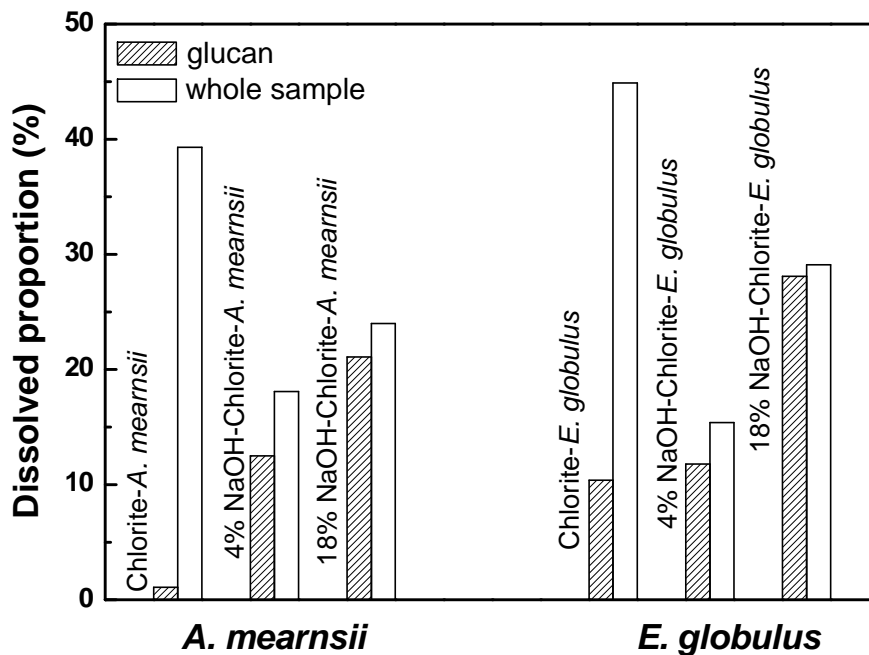
Figure 2.2. The dissolved proportions of Chlorite-Woodchips, NaOH-Chlorite-Woodchips and their corresponding glucan based on the samples before dissolution in NaOH/urea solvent. Reproduction from ref. 21 with permission from Springer (© Springer 2014).

Figure 2.3 shows the XRD patterns of Chlorite-*E. globulus* and Chlorite-*E. globulus* pretreated with NaOH solution at different concentrations. Three obvious crystal peaks at 2θ =15.1°, 16.3° and 22.6° were shown for Chlorite-*E. globulus* and 4% NaOH-Chlorite-*E. globulus*, assigned to (1-10), (110) and (200) crystal planes of cellulose I,[25,26] respectively. On the other hand, after 18% NaOH pretreatment, the crystal peaks of 2θ of Chlorite-*E. globulus* moved to 12.5°, 20.6° and 21.8°, assigned to the (1-10), (110) and (020) crystal planes of cellulose II,[25,26] respectively. This indicated that the crystal structure of Chlorite-*E. globulus* changed from cellulose I to cellulose II after the 18% NaOH pretreatment. Maybe this is also a reason for the higher dissolved proportion of 18% NaOH-Chlorite-*E. globulus* than of 4% NaOH-Chlorite-*E. globulus*.
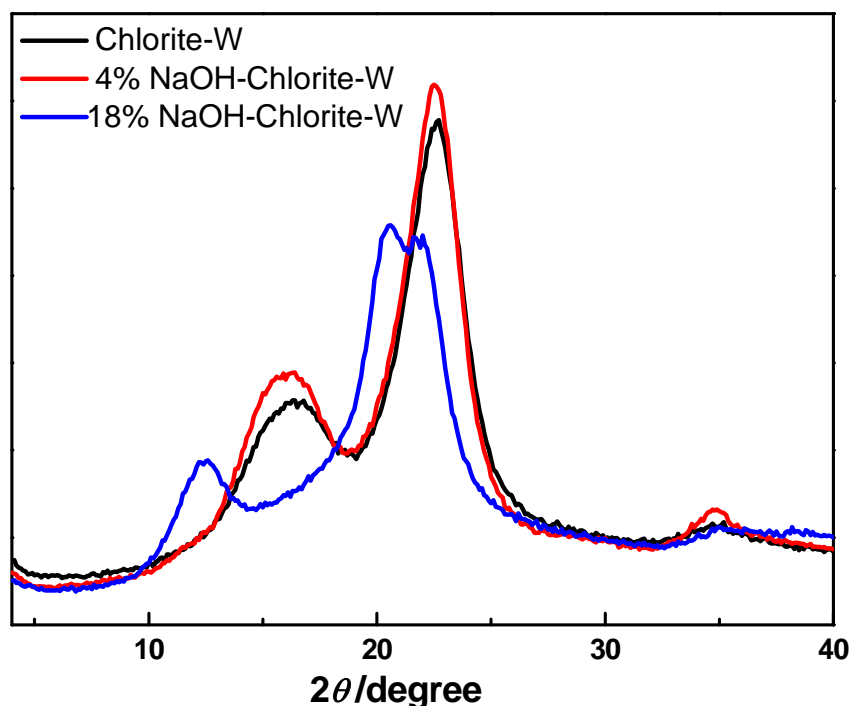
Figure 2.3. XRD patterns of Chlorite-W (W: *E. globulus*), 4% NaOH-Chlorite-W and 18% NaOH-Chlorite-W. Reproduction from ref. 21 with permission from Springer (© Springer 2014).

2.3.3 Characteristics of OPP-Chlorite-Woodchips

Chlorite-woodchips still contain a small amount of lignin. In order to remove lignin completely, permanganate treatment was performed (OPP-Chlorite-Woodchips). Tables 2.5 and 2.6 show the yields, carbohydrate compositions and dissolved proportions of OPP-Chlorite-Woodchips. Their dissolved proportions ranged from 45.6% to 52.5%, which were higher than those of the corresponding Chlorite-Woodchips (ranging from 36.2% to 46.4%, as shown in Tables 2.1 and 2.2), probably due to the complete removal of the residual lignin after delignification. The results show that hemicelluloses (xylan and mannan) were still present in OPP-Chlorite-Woodchips after the treatment with potassium permanganate. Compared with the Chlorite-Woodchips, the dissolved proportions of glucans of OPP-Chlorite-Woodchips increased, and the highest dissolved proportion of glucan reached 28.7%.

It is also shown that xylan and mannan contents in the insoluble fraction of OPP-Chlorite-Woodchips were nearly 0, indicating that almost all the hemicellulose of OPP-Chlorite-Woodchips dissolved in NaOH/urea solvent.

Table 2.5. Characteristics of OPP-Chlorite-*A. mangium* and OPP-Chlorite-*A. mearnsii*.

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Yield* (%)
OPP-Chlorite-*A. mangium*	100	62.6	13.6	1.7	96.3
In-OPP-Chlorite-*A. mangium*	52.3	44.7	0.2	0.5	-
Dissolved proportion	47.7	28.6	98.3	74.1	-
OPP-Chlorite-*A. mearnsii*	100	56.9	20.0	1.5	97.1
In-OPP-Chlorite-*A. mearnsii*	54.4	48.5	1.5	0.5	-
Dissolved proportion	45.6	14.7	92.5	67.3	-

*Yield of permanganate treatment, based on the Chlorite-A. mangium or Chlorite-A. mearnsii

Table 2.6. Characteristics of OPP-Chlorite-*E. globulus* and OPP-Chlorite-*E. camaldulensis*.

	Whole (%)	Glucan (%)	Xylan (%)	Mannan (%)	Yield* (%)
OPP-Chlorite-*E. globulus*	100	58.7	18.2	1.7	98.5
In-OPP-Chlorite-*E. globulus*	48.5	41.9	0.4	0.4	-
Dissolved proportion	51.5	28.7	98.0	76.7	-
OPP-Chlorite-*E. camaldulensis*	100	56.0	14.6	0.9	90.9
In-OPP-Chlorite-*E. camaldulensis*	47.5	40.6	0.4	0.4	-
Dissolved proportion	52.5	27.6	97.5	58.5	-

*Yield of permanganate treatment, based on the Chlorite-*E. globulus* or Chlorite-*E. camaldulensis*

For the sake of easy comparison, the dissolved proportions of glucan of Chlorite-Woodchips and OPP-Chlorite-Woodchips are illustrated in Figure 2.4. Compared with those of Chlorite-Woodchips, the lignin contents of the corresponding OPP-Chlorite-Woodchips were extremely low (close to 0); their dissolved proportions of glucan increased. The dissolved proportions of glucan of Chlorite-*A. mangium*, Chlorite-*A. mearnsii*, Chlorite-*E. globulus* and Chlorite-*E. camaldulensis* increased from 3.6%, 1.1%, 10.4% and 11.5% to 28.6%, 14.7%, 28.7% and 27.6%, respectively, after their complete delignification by permanganate. This indicated that removal of the residual lignin of the woodchips may also promote the dissolution of glucan. Furthermore, the molecular weight of cellulose probably decreased after permanganate delignification, which may also have led to the increase in the dissolved proportion of glucan of OPP-Chlorite-Woodchips. The effect of molecular weight on the dissolution of wood pulp will be discussed in detail in future work.
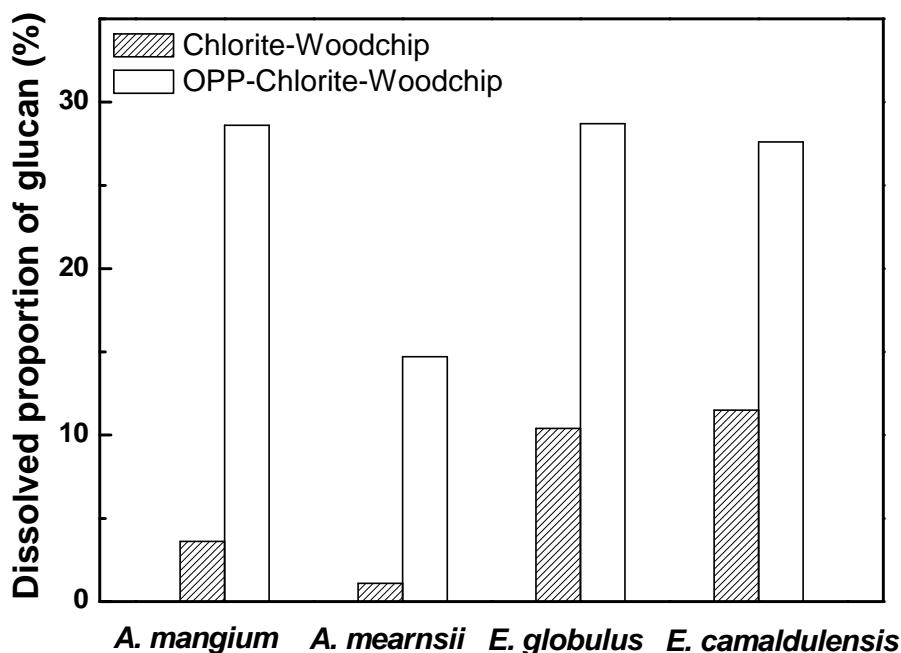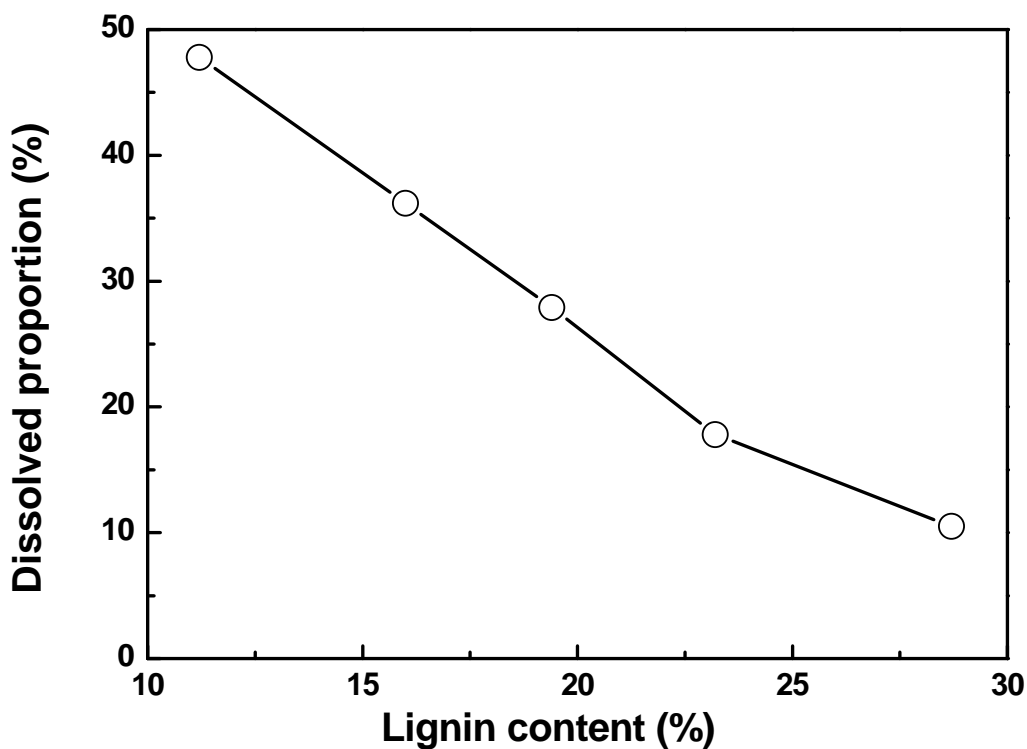

Figure 2.4. The dissolved proportions of glucan of Chlorite-Woodchips and OPP-Chlorite-Woodchips based on the samples before dissolution in NaOH/urea solvent. Reproduction from ref. 21 with permission from Springer (© Springer 2014).
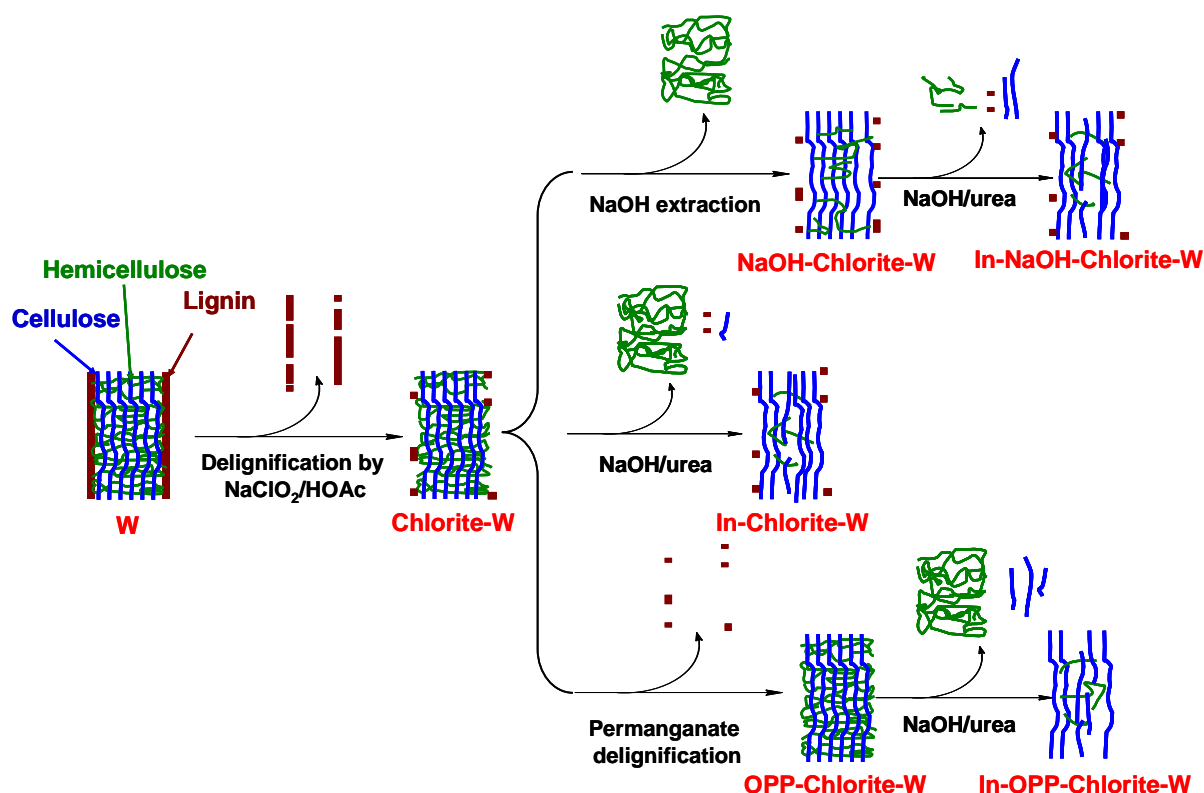
Figure 2.5. Schematic diagram of preparation of Chlorite-Woodchips, NaOH-Chlorite-Woodchips and OPP-Chlorite-Woodchips from original woodchips (W) and their dissolution in NaOH/urea solvent. Reproduction from ref. 21 with permission from Springer (© Springer 2014).

Figure 2.5 shows a schematic diagram of the preparation of Chlorite-Woodchips, NaOH-Chlorite-Woodchips and OPP-Chlorite-Woodchips from original woodchips (W) and their dissolution in NaOH/urea solvent. Original woodchips consisting of cellulose, hemicellulose and lignin were first delignified using NaClO$_2$/HOAc to obtain the Chlorite-Woodchips with a small amount of lignin (about 1%). The Chlorite-Woodchips could be partially dissolved in NaOH/urea solution. Moreover, most of the hemicellulose in the Chlorite-Woodchips was dissolved in NaOH/urea solution. Furthermore, some Chlorite-Woodchips were treated with NaOH solution to remove the hemicellulose to obtain the NaOH-Chlorite-Woodchips. Others

were completely delignified using potassium permanganate to obtain OPP-Chlorite-Woodchips. The dissolved proportions of glucan of both NaOH-Chlorite-Woodchips and OPP-Chlorite-Woodchips were higher than that of Chlorite-Woodchips, indicating that a small amount of hemicellulose and lignin restricted the dissolution of glucan. As we know, most of lignins in wood are bonded to hemicellulose components which are also bonded to cellulose like a cementing agent, resulting in a complex and inaccessible structure of wood.[28] Actually the difficulties in completely delignification of wood pulps and dissolution of them have been in part attributed to the bonds between lignin and carbohydrates (LC bonds) [14,16,27,29] although ambiguous in the types, frequencies, and quantity exist.[28] Thus, removing most of the hemicellulose and all of the lignin may promote the dissolution of glucan, although it was still limited.

Figure 2.6. Effect of lignin contents on the dissolved proportions of thermo mechanical pulps.

2.3.4 Characteristics of thermomechanical pulp (TMP) and unbleached kraft pulp (UKP)

In order to further study how the lignin content affects the dissolution of wood pulps in detail, the thermomechanical pulps and unbleached kraft pulps were treated by chlorite delignification to obtain pulps with different lignin contents. Figure 2.6 shows that with the increase in delignification times, the Klason lignin content of TMP decreased from 28.7% to 11.2%, and the relevant dissolved proportion of them increased from 10.5% to 47.8%. The dissolved proportions show a linear relationship with the lignin contents.
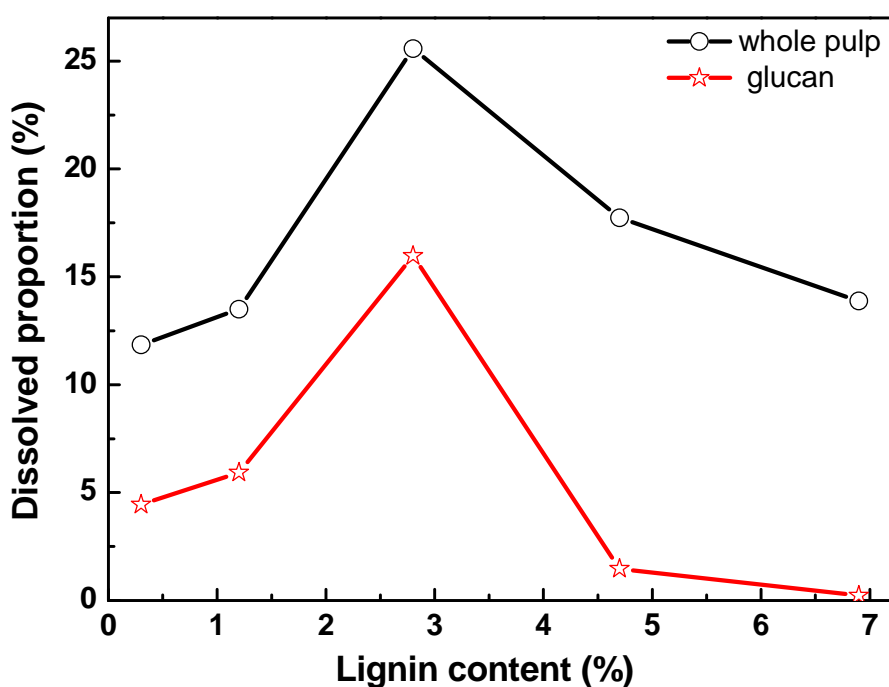
Figure 2.7. Effect of lignin contents on the dissolved proportions of unbleached kraft pulps and corresponding glucan in NaOH/urea solvent. (☆: dissolved glucan based on glucan originally present in pulp) Reproduction from ref. 21 with permission from Springer (© Springer 2014).
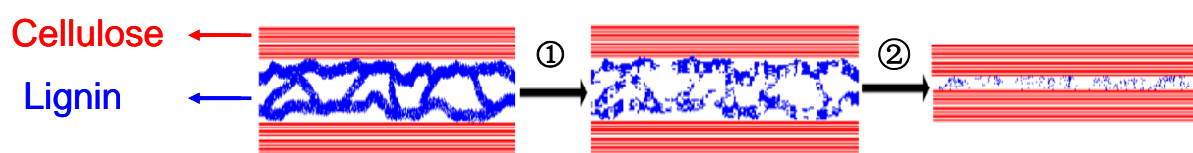
①: Initial delignification

②: Further delignification

Figure 2.8. Schematic view of the fiber cell wall segment during chlorite delignification. Reproduction from ref. 21 with permission from Springer (© Springer 2014).

Figure 2.7 shows the effect of lignin contents on the dissolved proportions of unbleached kraft pulps and corresponding glucan in NaOH/urea solvent. The results indicated that the dissolved proportions of the pulps and corresponding glucan did not show a linear relationship with the lignin content. The dissolved proportions of the pulp and glucan first increased from 13.9% and 0.2% to 25.6% and 16.0%, respectively, with a decrease in lignin content from 6.9% to 2.8%. It is interesting to note that further reduction of the lignin content from 2.8% to 0.3% led to decreases of the dissolved proportions of the pulp and glucan from 25.6% and 16.0% to 11.8% and 4.5%, respectively. Maybe this is because, after the initial removal of lignin, the residual lignin could still support the cell wall framework and the removal of lignin promoted the interaction between solvent (NaOH/urea) and cellulose molecules, leading to the improved dissolution of cellulose and pulp. Therefore, the dissolved proportions of pulp and glucan first increased after the lignin content decreased. However, when most of the lignin had been removed by further delignification of the pulp and the residual lignin could not support the cell wall framework anymore, collapse of the cell wall framework took place and strong interaction between cellulose microfibrils was created, resulting in the interference of interaction between solvent and cellulose and restriction of the

dissolution of cellulose and pulp. Therefore, the dissolved proportions of pulp and glucan finally decreased after the lignin content further decreased from 2.8% to 0.3%. The relevant schematic view of the fiber cell wall segment during chlorite delignification is shown in Figure 2.8. On the other hand, after further permanganate treatment of the pulp with 0.3% lignin content to completely remove lignin, the dissolved proportions of the pulp increased from 11.8% to 39.9%, further indicating that even very small amount of lignin content (0.3%) probably restricts the dissolution of the pulp. It should be noted that even after the complete removal of lignin, the dissolved proportion was still about 40% and much lower than that of cotton linter pulp (close to 100%). There should be some factors other than lignin content which cause this difference between cotton linter cellulose and wood cellulose.

2.4 Conclusions

Dissolution of woodchips and wood pulps in NaOH/urea solvent was studied. After chlorite delignification to about 1% lignin content, most of the hemicellulose in woodchips became soluble in this solvent, but the dissolution of glucan was very limited at 1.1% to 11.5%. The different woodchips had different dissolved proportions, maybe due to their different compositions, amounts and arrangements of components in the cell wall. The Chlorite-Woodchips were further treated with NaOH solution to remove most of the hemicellulose or treated with potassium permanganate to remove lignin completely. After these treatments, their dissolved proportions of glucan increased (*e.g.* dissolved proportions of glucan of Chlorite-A. mearnsii, 18% NaOH-Chlorite-A. mearnsii and OPP-Chlorite-A. mearnsii were 1.1%, 21.1% and 14.7%, respectively), probably because removal of lignin and hemicellulose could promote the dissolution of glucan. The effects of lignin contents on the dissolution of wood pulps were further studied. For the thermomechanical pulp with higher lignin content, removing the lignin could promote the dissolution of the pulp. However for the unbleached kraft pulp (UKP) with not so high lignin content, the dissolved proportions were not a liner relationship with the lignin contents. The dissolved proportions of UKP and glucan first increased from 13.9% and 0.2% to 25.6% and 16.0%, respectively, with a decrease in

lignin content from 6.9% to 2.8%. However, further reduction of the lignin content from 2.8% to 0.3% led to decreases of the dissolved proportions of the pulp and glucan from 25.6% and 16.0% to 11.8% and 4.5%, respectively. Initial removal of lignin could probably promote the dissolution of cellulose and pulp, but further delignification may have led to collapse of the cell wall framework and strong interaction among cellulose microfibrils was formed, resulting in interference of the interaction between solvent and cellulose and restriction of the dissolution of cellulose and pulp. Lignin content in woodchips or pulps does not seem to be a decisive factor preventing the dissolution of wood cellulose in this solvent.

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Chapter 3

This part could not be open to the public because it will be submitted to scientific journals and be published within three years.

Chapter 4

This part could not be open to the public because it will be submitted to scientific journals and be published within three years.

Chapter 5

This part could not be open to the public because it will be submitted to scientific journals and be published within three years.

Research Achievement

Journal Articles

1. <u>Zhuqun Shi</u>, Quanling Yang, Jie Cai, Shigenori Kuga, Yuji Matsumoto, Effects of lignin and hemicellulose contents on dissolution of wood pulp in aqueous NaOH/urea solutions, *Cellulose*, **2014**, 21, 1205-1215.

2. <u>Zhuqun Shi,</u> Huichang Gao, Jiao Feng, Beibei Ding, Xiaodong Cao, Shigenori Kuga, Yingjun Wang, Lina Zhang, Jie Cai, In-situ synthesis of robust conductive cellulose/polypyrrole composite aerogels and their potential application in nerve regeneration, *Angewandte Chemie International Edition*, **2014**, 53, 5380-5384.

3. <u>Zhuqun Shi</u>, Quanling Yang, Shigenori Kuga, Yuji Matsumoto, Dissolution of lignocellulose in aqueous NaOH/urea solution via dilute sulfuric acid pretreatment, *Journal of Agricultural and Food Chemistry*, **2014**, submitted.

4. <u>Zhuqun Shi,</u> Beibei Ding, Qiang Fu, Jie Cai, Lina Zhang, Shigenori Kuga, Transparent, flexible, and solvent-resistant polymer nanocomposites using three-dimensionally nanoporous cellulose gels with reinforced mechanical properties and low coefficient of thermal expansion, **2014**, submitted.

5. <u>Zhuqun Shi</u>, Quanling Yang, Shigenori Kuga, Yuji Matsumoto, Dissolution of lignocellulose in NaOH/urea solution by ball milling pretreatment, to be submitted.

6. Zhuqun Shi, Beibei Ding, Jie Cai, Lina Zhang, Mechanical performance tailoring of tough cellulose aerogels, to be submitted.

Conference

International conference

1. Jie Cai, <u>Zhuqun Shi</u>, Polymer nanocomposites from cellulose-based materials, The 241th ACS National & Exposition, Anaheim, California, USA, Mar. **2011**. [Oral]

2. <u>Zhuqun Shi</u>, Jie Cai, Shigenori Kuga, Yuji Matsumoto, Effects of cellulose, hemicellulose and lignin on dissolution of softwood pulp in aqueous alkali/urea solutions, 4th International Conference on Pulping, Papermaking and Biotechnology, Nanjing, China, Nov. **2012**. [Poster]

3. <u>Zhuqun Shi</u>, Jie Cai, Shigenori Kuga, Yuji Matsumoto, Dissolution of lignocellulose in NaOH/urea solvent, The 247th American Chemical Society National Meeting, Dallas, Texas, USA, Mar. **2014**. [Oral]

Conferences in Japan

1. <u>Zhuqun Shi</u>, Jie Cai, Shigenori Kuga, Yuji Matsumoto, Dissolution of wood cellulose in NaOH/urea solution -- Trial with woodchips delignified by NaClO2/HOAc at room temperature --, The 63rd Annual Meeting of the Japan Wood Research Society, Morioka, Japan, Mar. **2013**. [Oral]

2. <u>Zhuqun Shi</u>, Jie Cai, Shigenori Kuga, Yuji Matsumoto, The effect of lignin content on the solubilization of wood pulp in NaOH/urea solvent system, The 80th Pulp and Paper Research Conference of Japan, Tokyo, Japan, Jun. **2013**. [Poster]

3. <u>Zhuqun Shi</u>, Quanling Yang, Shigenori Kuga, Yuji Matsumoto, Dissolution of wood pulp in alkali/urea system: Effects of lignin and hemicellulose contents and molecular weight, The 81th Pulp and Paper Research Conference of Japan, Tokyo, Japan, Jun. **2014**. [Oral]

Patents (Granted)

1. Jie Cai, <u>Zhuqun Shi</u>, Lina Zhang, Prepare of optically transparent cellulose/acrylic composites by in situ chemical polymerization, China Patent, **2012**, ZL201010239586.9.

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