

The Structure and Physical Properties of Pulpwood Fibers

From Ph.D. thesis by Lorraine C. Vander Wielen

Wood fibers are natural composite structures in which cellulose fibrils are held together by lignin and hemicellulose. The major constituents of wood fibers are lignin, cellulose, hemicellulose, and extractives. Each of these components contributes to fiber properties, which ultimately impact product properties.

Lignin

Lignin is the “glue” that holds the tree together. Although the highest concentration of lignin is found in the middle lamella, the secondary fiber wall contains 70% of the lignin but in lower concentrations. The model for the macromolecular structure of lignin is best described as amorphous and not completely known, but consisting of aromatic rings with three-carbon alkyl side chains as illustrated in Figure 1. One of the main differences between mechanical and chemical pulping is that mechanical pulping does not delignify fibers, while lignin is almost completely removed in chemical pulping and bleaching processes.¹ Although the structure of residual lignin has not been fully elucidated, various lignin isolation and derivatization techniques have been used to determine the structure of lignin functional units, which are considered the building blocks of lignin.¹

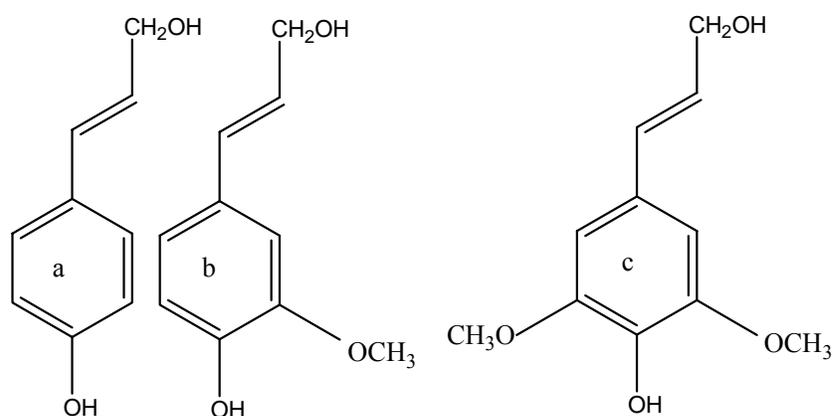


Figure 1. The basic units of lignin; (a) *p*-coumaryl, (b) coniferyl, and (c) sinapyl alcohol.

Softwood lignin, which is of interest in this study, is composed mainly of coniferyl alcohol units (1), while hardwood lignin is composed mainly of coniferyl and sinapyl alcohol units. A small amount of *p*-coumaryl alcohol is also found, usually in compression wood.¹ The majority of linkages between these units are ether bonds. Recently several new lignin linkages have been reported, the most abundant of the new linkages being the dibenzodioxocine linkage.²

The precursors for lignin (Figure) are generated from D-glucose by complex reactions catalyzed by enzymes.³ The two major pathways for this are called the shikimic acid pathway and the cinnamate pathway. In the case of softwoods, the main intermediate precursor is coniferyl alcohol. Enzymes catalyze the reaction of these precursors creating free radical structures which readily combine, resulting in the amorphous polymer known as lignin.³ The main type of linkage found in lignin is the aryl-ether linkage. The proposed structure for softwood lignin, including the dibenzodioxocine linkage, is provided in Figure 2.

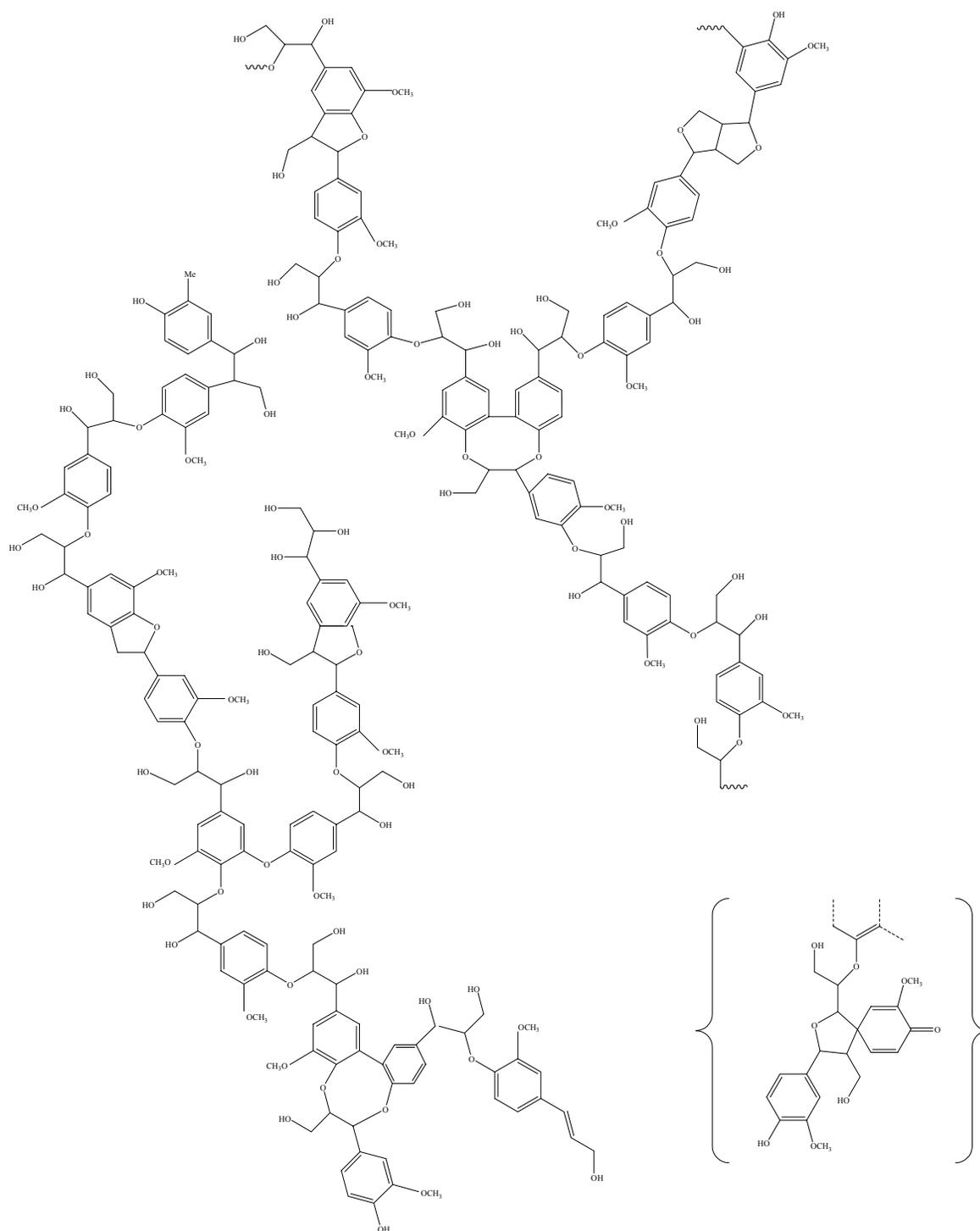


Figure 2. Model for partial structure of softwood lignin.⁴

Cellulose

Cellulose is the most abundant natural polymer on earth.⁵ Cellulose, the major component of papermaking fibers, contributes 40-45% of the wood's dry weight. Located primarily in the secondary cell wall, cellulose polymers are composed of long linear chains of D-glucose linked by β -1,4-glycosidic bonds of glucose in a 4C_1 chair conformation with equatorially oriented substituents as illustrated in Figure 3.¹ The degree of polymerization of these chains ranges from over 10,000 in native wood to as low as 1000 in a bleached kraft pulp. The hydroxyl groups on these linear cellulose chains form strong hydrogen bonding networks within and between fibers.

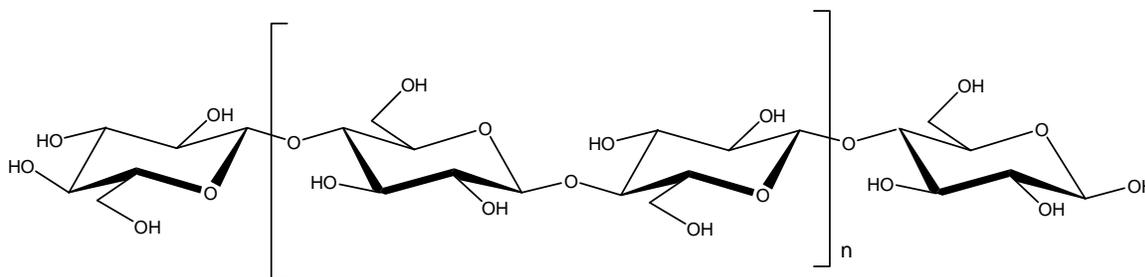


Figure 3. The structure of cellulose (β -1,4-D-glucopyranose).

The structure of the unit cell of crystalline cellulose has been characterized via X-ray crystallography since the 1913 when Nishikawa and Ono reported the first cellulose X-ray diffraction patterns.⁶ A cellulose unit cell is the smallest component of the cellulose crystal that reproduces the whole crystal when repeated.⁷ Cellulose exists in more than one crystalline form, each of which consists of cellobiose disaccharide repeating units, which are shown between the brackets on Figure 3.⁸ Although cellulose has four major crystalline forms or polymorphs (cellulose I, II, III, and IV), only cellulose I and II will be further discussed since they are the most predominant;⁹ cellulose I is the main polymorph found in wood;¹⁰ and cellulose I can be converted to cellulose II by treatment in alkali or regeneration (solubilization followed by recrystallization).

Conflicting reports regarding the crystalline structure of cellulose in terms of various issues including hydrogen bonding patterns and unit cell dimensions can be found in the literature.

The following is not to be considered an exhaustive review of the crystalline structure of cellulose, but a taste of what has long been known complemented by details of recent studies that have shed new light on the structures of cellulose I and II. For the purpose of this discussion, the oxygens of cellulose hydroxyl groups will be numbered with reference to the carbon to which they are bonded, while the ring oxygen will be referred to as O5. This is numbering scheme described on the model for D-glucose seen in Figure 4.

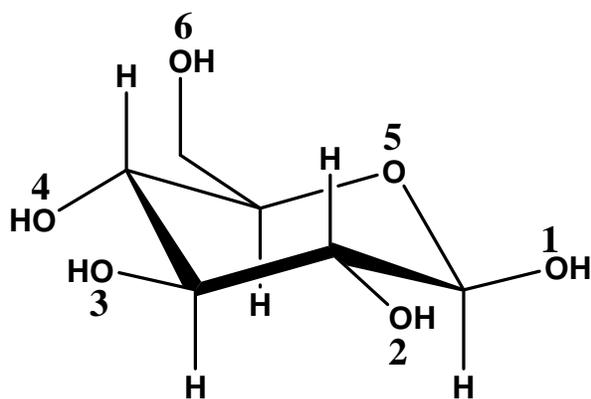


Figure 4. D-glucose carbon numbering scheme.

Cellulose I consists of parallel cellulose chains, meaning its reducing ends are aligned in the same direction, while those of cellulose II are anti-parallel.¹¹ A cellulose I unit cell consists of four D-glucose residues which displaced 180° from their neighbors. The intermolecular hydrogen bonding between chains is responsible for the layered structure of native cellulose, with only weak van der Waals forces holding the layers together.¹² NMR, IR, and X-ray diffraction studies have suggested that two intra-chain hydrogen

bonds exist between O3-H and O5 and between O2-H and O6, along with one inter-chain hydrogen bond between O6-H and O3 and that these hydrogen bonds are responsible for the structure of cellulose I.¹³ Simon *et al.* suggested that cellulose I at the edge of crystalline was different than cellulose I at the center.¹⁴ The existence of more than one polymorph of native cellulose (cellulose I) has been discussed since, known as cellulose I_α and cellulose I_β.⁵ In the past, cellulose II was believed to contain the same intermolecular and intramolecular hydrogen bonds as Cellulose I was believed to have, with cellulose II having additional interchain hydrogen bonds between outer and center chains between O2-H and O2 and between O3-H and O6.⁵

In light of recent studies regarding the structures of cellulose I and cellulose II, the specific information regarding unit cell dimensions and sites of hydrogen bonding reviewed beyond this point will contain the results of recent studies compiled post 1998, which indicate additional hydrogen bonds.

Cellulose I_α and cellulose I_β were studied using synchrotron X-ray to determine positions of carbon and oxygen, while neutron diffraction was used to evaluate the positions of deuterium and hydrogen in deuterated and hydrogenated samples.^{15,16} These were the first reports in which the positions for carbon, oxygen, and hydrogen in the unit cell of cellulose were experimentally determined. The cellulose I_α unit cell dimensions are 6.717Å by 5.962Å by 10.400Å, while those of I_β are 7.784Å by 8.201Å by 10.38Å.^{15,16}

In both forms of cellulose I, the hydrogen bonds on H-O3 are well defined, while those on H-O6 and H-O2 are split between more than one location.^{15,16} The hydrogen bond between O2-H and O6 was shorter in cellulose I_α, while the hydrogen bond between O6-H and O3 was shorter in I_β. Furthermore, one O6-H intra-chain hydrogen bond per unit cell was found in cellulose I_α and two were found in cellulose I_β; while cellulose I_α had two inter-chain hydrogen bonds between O2-H and O6 per unit cell and cellulose I_β had only one.^{15,16} In addition, the hydrogen bonds between O3-H and O5 have different geometries in cellulose I_α and cellulose I_β. The main difference is the relative

displacement of the chains in cellulose I_{β} which suggest that cellulose I_{β} occurs when the chains of cellulose I_{α} slip by one another¹⁶ as was previously predicted by computer simulation.¹⁷

In cellulose I_{β} , the outer and center chains of the crystal also show differences in hydrogen bonding.¹⁶ Although both have intra-chain hydrogen bonds between O2-H and O6, the outer chain can also form simultaneous intra-chain hydrogen bonds between O2-H and O1 providing a three centered intra-chain hydrogen bonding arrangement. Among center chains, an inter-chain hydrogen bond can form between neighboring chains between O6-H and O2 and between O6-H and O3, resulting in a three centered inter-chain hydrogen bonding arrangement; while the outer chains contain inter-chain hydrogen bonds between O6-H and O3. In outer chains the O2-H and O6 form an intra-chain, rather than inter-chain hydrogen bond.^{15,16}

These studies show how cellulose I_{β} differs from cellulose I_{α} and previous cellulose I models, as cellulose I_{β} contains two unique sheets with distinct chains having different hydrogen bonding.⁸⁻¹⁶ Thus, the structure of cellulose I_{β} is more complicated than had previously been proposed.¹⁶

Conversion of cellulose I to cellulose II is an irreversible process. The dimensions of cellulose II determined by X-ray diffraction are 8.01Å by 9.04Å by 10.36Å.¹⁸ In the past it was believed that cellulose II had hydrogen bonds between outer and center chains located between O2-H and O2 and between O3-H and O6 which provided the thermodynamically favored structure. This structure of crystal structure of cellulose II was recently revised based on neutron diffraction studies of hydrogenated and deuterated cellulose II.¹⁹ This study provided the first coordinates of all the atoms in cellulose II. In light of this research, the proposed structure for cellulose II is as follows. Outer chains contain intermolecular hydrogen bonding between O2-H and O6 and intramolecular hydrogen bonding between O3-H and both O5 and O6. Center chains contain intermolecular hydrogen bonding between O6-H and O2 and, like outer chains, intramolecular hydrogen

bonding between O3-H and both O5 and O6. Between outer and center chains, intermolecular hydrogen bonding occurs between O2-H and O2 and between O6-H and O6. In addition, a small amount of intermolecular hydrogen bonding occurs between outer and center chains between O6H and O3, and between O6-H and O5.

Cellulose crystallization is favorable as cellulose chains are linear, hydroxyl groups tend to form hydrogen bonds, and the geometric arrangement of atoms in the cellulose chain allows for a close packed structure. However, cellulose is said to exist in the cell wall in both crystalline and amorphous forms. IUPAC definitions describe crystalline materials as having “three-dimensional order on the level of atomic dimensions” and describes amorphous materials as being “poorly ordered regions of a polymer specimen”. Since regions of amorphous cellulose are not completely formless and indicate some degree of order, amorphous cellulose should not be considered truly amorphous material.⁸

Bundles of cellulose molecules known as microfibrils contain both crystalline (50-70%) and amorphous regions. Microfibrils in the secondary cell wall give wood fibers their strength and rigidity. Microfibrils are described differently throughout the literature. According to Hon (2000), cellulose in wood exists as microfibrils which are approximately 2 to 5 nm wide and encased in a matrix of hemicellulose and lignin.²⁰ Sjöström (1993) describes a microfibril as 10 to 20 nm wide. According to Frey-Wyssling, these fibrillar structures, which consist of smaller fibrillar structures, can be classified as macrofibrils (4000 by 4000 Å), microfibrils (250 by 250 Å), and elementary fibrils (30 by 100 Å).²¹ A microfibril, is proposed to be a threadlike “bundle of parallel cellulose molecules which are theoretically held together by hydrogen bonds.” Microfibrils are combined to form layers of fibrils called lamellae.²⁰

Layered Structure

The dimensions of pulpwood fibers vary among species, geographical locations, and within individual trees. Softwoods consist of tracheid and ray cells. Tracheids make up 90-95% of softwood fibers. Softwood tracheid fibers are approximately 2.5 to 5.9 mm long and 25-50 μm wide.^{29,22} Ray cells are smaller than tracheid cells, with lengths of approximately 10-160 μm . Further, earlywood and latewood in a given loblolly pine tree differ in that the earlywood has thinner (1.67-2.12 μm) and latewood coarser (4.01-6.15 μm) cell walls.²³ A model for the layered structure of a typical softwood tracheid is described in Figure 5. The middle lamella and primary cell wall of these fibers are often referred to as the compound middle lamella. The middle lamella contains a high proportion of amorphous material which holds neighboring fibers together. The primary cell wall is approximately 0.03-1.0 μm thick, and also contains a high percentage of lignin. The secondary cell wall consists of three layers, labeled S1 through S3 from the outer to the inner layer. The S1 and S3 layers are thin, at 0.1-0.3 μm , while the middle layer (S2) is thick at 1-5 μm , and is said to be most responsible for the strength properties of individual fibers. The fibrils of secondary cell wall layers are wound helically around the fiber axis, while those of the primary wall are randomly oriented.²⁴ The distribution of fiber constituents throughout the fiber is further described in section 0 of this dissertation.

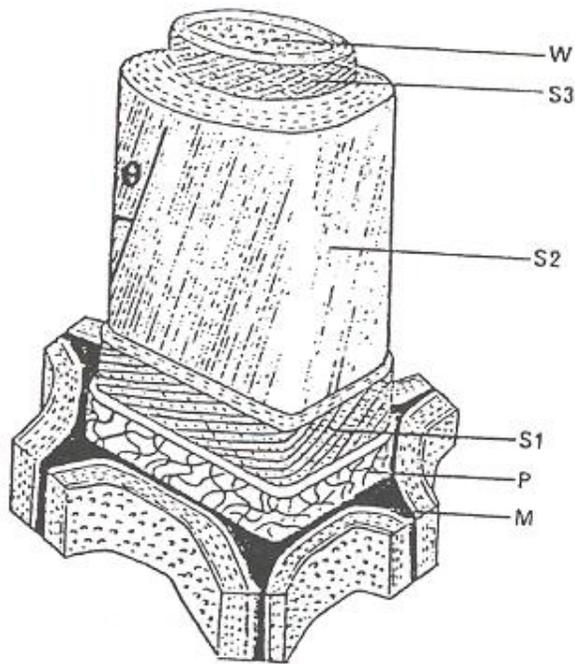


Figure 5. Model for a pulpwood fiber.

The middle lamella (ML), primary wall (P), outer (S1), middle (S2), and inner (S3) layers of the secondary wall, and the warty layer (W) are labeled accordingly.

Surface studies employing atomic force microscopy (AFM) and scanning probe microscopy provide clues regarding the layered surface structure of the fiber wall. Deposits of materials on the surface of spruce, pine, and birch kraft pulp fibers have been examined by AFM and scanning probe microscopy, and reported to be 40 – 300 nm granules.²⁵⁻²⁷ These granular deposits are believed to consist of amorphous lignin, hemicellulose and extractives. AFM work shows microfibrils of spruce kraft pulps with diameters of approximately 20 nm and loose, random orientations among the primary cell wall layer.²⁵ Microfibrils from the secondary cell wall layer show diameters of 10 – 40 nm and are found in a tightly parallel arrangement.²⁵

Hemicellulose

Hemicelluloses, which lend support to cell walls, make up 20-30% of the dry weight of wood. Unlike cellulose, these amorphous polymers have monosaccharides as side chains and degrees of polymerization of approximately 100-200, which makes them susceptible to chemical attack. Although hemicelluloses are more susceptible to degradation during chemical pulping, hemicelluloses can adsorb back onto pulp fibers towards the end of the kraft cook.²⁸ In comparison, mechanical pulps contain a greater proportion of hemicellulose than chemical pulps.²⁹

Hemicelluloses are white, solid, noncrystalline materials known to increase the tensile strength, burst strength, and fold strength of paper. Depending upon their plant source, hemicelluloses can be comprised of 4-O-methylglucuronic acids and five sugars: glucose, mannose, galactose, xylose, and arabinose.⁹ The main types of hemicellulose in most softwoods are arabinoglucoronxylans (5-10% by weight) and galactoglucomannans (approximately 20% of wood by weight), with the exception of larch trees, which contain a significant amount arabinogalactin.

Galactoglucomannans are chains of β -1,4-D-glucopyranose and β -1,4-D-mannopyranose units. They are of two types, with low and high relative galactan contents. Proportions of galactose:glucose:mannose are either 0.1:1:4 or 1:1:3, with the 1:1:3 configuration sometimes called, simply, glucomannan. In a galactoglucomannan, an α -D-galactopyranose unit is linked to the main chain by a 1,6 glycosidic linkage. In addition, the hydroxyl groups at carbons 2 and 3 can be substituted by an O-acetyl group. The principle structure of galactoglucomannan is described in Figure 6.

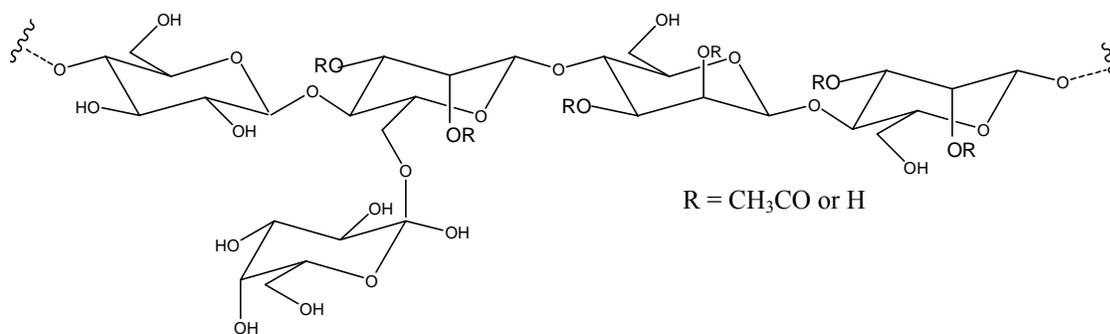


Figure 6. Principle structure of galactoglucomannans.

Arabinoglucuronoxylans have a main chain consisting of β -1,4-xylopyranose units which may or may not contain 4-O-methyl- α -glucuronic acids at C2. It also consists of approximately 1.3 α -arabinofuranose units for every 10 xylose units. The principle structures of this hemicellulose is featured in Figure 6.

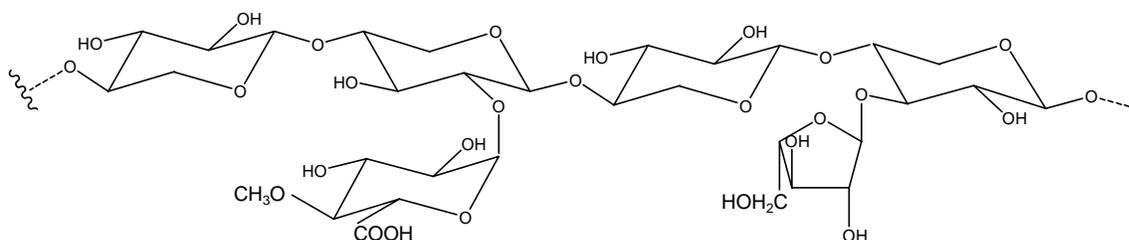


Figure 1. Principle structure of arabinoglucuronoxylan.

Carboxylic acid groups found among softwood xylans contribute to the ionic properties of papermaking fibers and can greatly impact their performance. Fibers have ionic properties due to the presence of the polysaccharide hydroxyl groups, carboxylic acid groups mainly among hemicellulose, and lignin's phenolic groups. However, at typical papermaking conditions, it is the carboxylic acid groups that are responsible for the fiber charge.³⁰ The

published acid group contents of various pulps are listed in Table 1; however, the wood species included in the generation of the data were not indicated by the authors.

Table 1. Acidic group content of various pulps.

Pulp	Sulfonic Acid Groups ($\mu\text{eq/g}$)^{31,32,33}	Total Acidic Groups ($\mu\text{eq/g}$)^{31,32,33}
Unbleached TMP		80-110
Bleached TMP (Peroxide)		150-250
Unbleached CTMP	40-70	120-180
Peroxide Bleached CTMP	40-70	190-320
Unbleached Sulfite (K<32)	<100-120	<150-180
Unbleached Pine Kraft (K=25.9)		85
Unbleached Kraft (K<32)		<60-80
ECF Bleached Softwood Kraft (ODEDED)		32
ECF Bleached Hardwood Kraft (DEOPDD)		55
TCF Bleached Softwood Kraft (OOQPO)		70
TCF Bleached Hardwood Bleached Kraft		120

Ionic groups, specifically carboxylic acids, have long been associated with fiber swelling.³⁴ According to classic studies, the behavior of fibers containing sufficient numbers of charged groups in water is that of a polyelectrolytic gel, in which the fixed acid groups must have counter ions.^{35,36} Thus, a concentration gradient due to cations associated with acid groups in the fiber is believed to create osmotic pressure, causing the fiber to swell. This increased fiber swelling is associated with increased paper strength. The location of acid groups across the fiber wall is also key to fiber performance. The impact of certain oxidative bleaching regimes upon the surface of mechanical pulp fibers

has been known for nearly two decades. Ampulski's (1985) study of the impact of the surface charge and bulk charge of CTMP fibers on tensile strength, showing that tensile strength is directly proportional to ionic content and suggesting that surface charge provides the greater contribution to strength improvements. Engstrand *et al.* (1991) oxidized spruce wood-meal and TMP with peroxide and oxygen, resulting in increased tensile strength, swelling and sheet density.³⁷

Barzyk *et al.* (1997) demonstrated that when carboxylic groups are placed on kraft fiber surfaces, as opposed to bulk carboxylation or no carboxylation, the specific bond strength increases. When the surface carboxylic acid concentration is increased by 50%, sheet tensile shows a 45% increase and Scott-Bond strength is increased by 50%. When Fors (2000), carboxymethylated kraft fibers, tensile strength increased, as in the case of Barzyk *et al.* (1997), with no web densification.³³

Extractives

A diverse array of relatively low molecular weight compounds which often give wood color and can protect wood from decay are known as extractives. Extractives may be hydrophobic or hydrophilic; that is, they may be soluble in organic solvents or water. The extractives content of trees is typically less than 10%, and the distribution of extractives varies by species, as well as location within an individual tree. The functions of extractives are diverse. For example, they may provide energy, or protect trees from microbiological or insect attack. Extractives include (1) terpenes, which are found in relatively high amounts in the resin ducts of pines, and can be used to make turpentine; (2) resin acids, which can be used to make rosin size; (3) triglycerides and fatty acids, which can be used for soaps; and (4) phenolic compounds.

The Distribution of Fiber Constituents

The major constituents of wood are not evenly distributed among species or across individual cell walls. The typical composition of North American hardwoods and woods is described in Table 2. The distribution of cellulose, hemicellulose, and lignin across a softwood fiber is uneven across the cell wall. For example, lignin is at its highest concentration in the middle lamella and primary cell wall. However, the greatest net amount of lignin is found in the secondary cell wall.

Table 2. Percent chemical composition of typical North American hardwood and softwood species.

	Hardwoods	Softwoods
Cellulose	40-50	45-50
Hemicelluloses:		
(Galacto) glucomannans	2-5	20-25
Xylans	15-30	5-10
Lignin	18-25	25-35
Extractives	1-5	3-8
Ash	0.4-0.8	0.2-0.5

Kraft pulps contain a good portion of the cellulose found in native wood fibers, while a major portion of the hemicellulose, lignin, and extractives have been removed (

Table 3). Bleaching removes further lignin and extractives. In this study, the fully bleached kraft market pulp long fibers consisted of approximately 0.85% Klason lignin, 0.037% acetone extractable extractives, 0.07% ash, with the balance made up of carbohydrates.

Table 3. Yields of wood constituents of Scots Pine (*Pinus sylvestris*) after kraft pulping.

Pulp Constituents	Scots Pine Kraft Pulp Yield and (Original Wood Composition)
Cellulose	35 (39)
Glucomannan	4 (17)
Xylan	5 (8)
Lignin	3 (27)
Extractives	0.5 (4)

Fiber Surface Chemistry: TMP and Kraft Pulps

Advances in instrumental techniques are allowing researchers to gain new insights into the nature of fiber surfaces. Pere *et al.* (2001) applied ESCA to the analysis of the coverage of unbleached and peroxide bleached TMP fibers. ESCA analysis showed that approximately 50% of the surface area of these fibers is covered in lignin and extractives as described in Table 4.³⁸ The results indicated that the amount of surface lignin decreases with peroxide bleaching, but that the surface extractives content remains the same.

Kleen *et al.* (2001) also explored the application of time-of-flight secondary ion mass spectrometry (ToF-SIMS) to the analysis of surface lignin and extractives on unbleached spruce TMP fibers. ToF-SIMS results were compared to those gathered via ESCA. Both methods showed that there is more lignin on the surface of primary and secondary fines than on long fibers Table 4.⁴⁰ When Luukko *et al.* (1999) applied ESCA analysis to the characterization of the surfaces of mechanical pulp fines the bulk content of lignin and extractives was 37%; however, the surface content of lignin and extractives of the TMP fines was as high as 74%. Exposed polysaccharides accounted for only 26% of the fiber surface.³⁹

Table 4. Surface coverage of unbleached and peroxide bleached thermomechanical pulp (TMP) fibers by extractives, lignin, and carbohydrates.

Pulp	Treatment	% Surface Coverage by Extractives	% Surface Coverage by Lignin
TMP ³⁸	Unbleached	16	37
TMP ³⁸	Bleached	15	32
TMP ⁴⁰	Unbleached Fines	13-19	56-59
TMP ⁴⁰	Unbleached Fibers	10	57-58
Kraft ⁴¹	Unbleached	8.3	16.2
Kraft ⁴¹	Bleached with OZEP	1.4	5.5
Kraft ⁴¹	Bleached with OPZ	1.0	5.6
Kraft ⁴¹	Bleached with OPZE	8.9	3.8
Kraft ⁴¹	Bleached with OPZEP	5.1	3.4
Kraft ⁴¹	Bleached with ODEDED	2.8	1.2
Kraft ⁴¹	Bleached with DEDED	6.8	3.9
Kraft ³²	Unbleached, Kappa 27.6		27.7
Kraft ³²	Unbleached, Kappa 26.0		27.7
Kraft ³²	Unbleached, Kappa 24.2		25.5
Kraft ³²	Unbleached, Kappa 21.0		29.8
Kraft ³²	Unbleached, Kappa 17.4		23.4
Kraft ⁴²	Unbleached, Kappa 17.7, Effective Alkali 20	11	12.2
Kraft ⁴²	Unbleached, Kappa 19.0, Effective Alkali 26	14	13.9
Kraft ⁴²	Unbleached, Kappa 34.7, Effective Alkali 20	13	21.1
Kraft ⁴²	Unbleached, Kappa 56.6, Effective Alkali 20	12	31.3
Kraft ⁴²	Unbleached, Kappa 56.7, Effective Alkali 20	17	31.7

Bleached and unbleached kraft fibers have also been analyzed (Table 4). Laine *et al.* (1994) used ESCA to study the surface properties of kraft pulps. Unbleached kraft pulps showed decreased surface lignin with decreased kappa number.^{32,42} This study showed

that kraft pulps with kappa numbers between 20 and 60 contained 10% to 20% extractives on the fiber surface. The pulps containing 3% to 6% total lignin contained 10% to 20% of their surfaces covered with lignin. Furthermore, the pulps containing 9% total lignin (60 kappa) had 30% to 40% surface coverage of lignin.⁴³

When bleaching kraft pulps, Laine *et al.*(1995, 1996) found that oxygen delignification decreases surface lignin by 15% or less.^{41,43} Bleaching sequences containing an O stage result in greater removal of surface extractives, although an O stage alone does not contribute a major decrease in surface lignin. Ozone in an OZ sequence reduces surface lignin and extractives by approximately 77% and 45% respectively, but is not as effective when followed by a peroxide bleaching stage. Chlorine dioxide, or D stages, result in incremental removal of surface lignin with each D stage, and the D stage is more effective when preceded by an O stage.⁴¹ Peroxide bleaching has only a small impact on surface lignin, but reduces extractives except when followed by an alkaline extraction, or E stage.^{41,43}

These surface studies suggest that TMP and kraft fibers have greater concentrations of lignin and extractives on their surfaces relative to the total fiber concentration by weight, and that the fines fraction of TMP contains more extractives than the long fiber fraction. Further more, kraft pulps showed a decrease in coverage of surface extractives and lignin with decreased kappa number, and increased bleaching. However, indications of reprecipitation of lignin onto the fiber, especially in alkali extraction stages of bleaching exist, and chlorine dioxide more effectively removes surface lignin and extractives when preceded by an oxygen delignification stage. In these studies the range for surface coverage of lignin and extractives is wide. The common factor is that in all studies, the surface coverage greatly exceeds the fiber contents of lignin and extractives by weight.

Fiber-to-Fiber Bonding

Theories for the promotion of adhesion bring together approaches from varied fields. The most well-know theories include mechanical interlocking, electrostatic, weak boundary layer, adsorption, diffusion, and chemical bonding theories.⁴⁴ Since these models do not negate one another, it is possible to apply a combination of each of these theories to bonding between papermaking fibers.

The bonding of papermaking fibers is commonly evaluated by measuring tensile properties. Tensile strength, often reported as breaking length or tensile index, is a measure of the load a sample can hold. The stretch, or percent elongation, and tensile energy absorption (TEA), which describe the work required to break a sample, are also important tensile properties. The Page equation, Equation 1, describes the tensile strength of paper made from chemical pulps, and considers the importance of the contributions of both fiber strength ($9/8Z$) and bonding ($12A\rho g/bPL(R.B.A.)$) to the strength of paper.⁴⁵

Equation 1. $[1/T = 9/8Z + 12A\rho g/bPL(R.B.A.)]^{45}$

Where:

T = Finite span tensile

Z = Zero-span tensile

A = Mean fiber cross-sectional area

ρ = Density of fibrous material

g = Acceleration due to gravity

b = Shear strength per unit area of inter-fiber bonds

P = Perimeter of fiber cross-section

L = Mean fiber length

R.B.A. = Fraction of bonded fiber surface

Throughout the literature, cellulose-to-cellulose hydrogen bonds are referred to as the primary theoretical fiber-to-fiber bonding mechanism. Hydrogen bonding between fibers can occur when the fibers become closer than 2.5 Å.⁴⁶ According to Campbell (1959), fiber surface area, fiber-to-fiber contact, and hydrogen bonding must be maximized to provide optimal fiber-to-fiber bonding. Fiber surfaces available for bonding may be developed during the beating of chemical pulps due to internal and external fibrillation. When manufacturing TMP, fibers are developed in the secondary refining stage so as to provide increased surfaces by peeling and creating delaminated surfaces and fines.⁴⁷ The greater the surface area available, the greater the extent of bonding. Increased relative bonded area (R.B.A.) among kraft pulps provides increased tensile strength.⁴⁵

Fiber-to-fiber contact occurs when water is vacuum removed, during wet pressing, and due to evaporation during the drying process. The diffusion theory of adhesion and the Campbell effect may be used to explain how fibers may be brought into close contact. McKenzie (1984) applied the diffusion theory of adhesion to papermaking. According to this theory, cellulose fibers in the presence of water can adhere via intermingling of molecular segments. When changes such as cooling and water removal occur,

intermolecular bonds (in this case hydrogen bonds) can form.⁴⁸ The Campbell effect, which describes the impact of surface tension on papermaking fibers, explains how fibers may be brought into close contact.⁴⁹ The model for this effect describes water at the interface between two very thin rods which creates a strong force pulling the rods closer to one another. According to this model, meniscus forces cause fibers and microfibrils to become aligned and pull closer together as water removal occurs.⁵⁰

Hydrogen bonds are molecular interactions due to strong attractive forces. For hydrogen bonding to occur, a group consisting of a hydrogen atom covalently bonded to an electronegative atom on a polar structure, and a group consisting of a region of high electron density, such as a lone pair of electrons, is required. The polar groups on fibers are loosely hydrogen bonded to water, but are eventually directly hydrogen bonded as the drying process proceeds.⁵¹

Of the mechanisms named, hydrogen bonding between hydroxyl (OH) groups is considered the primary mechanism for fiber-to-fiber bonding.²⁹ Although hydrogen bonds are fairly weak (Table 5), the abundance of hydrogen bonding sites on wood fibers allows for many interactions, resulting in an additive effect providing strong bonding.²⁹

Table 5. Strength of various bonds.

	Bond Energy (kJ/mole)²⁹
Covalent Bonds	150-500
Hydrogen Bonds	8-32
Van der Waals Forces	2-8

Due to differences between pulps, each provides various degrees of bonding in the sheet. Table 6 summarizes physical and chemical differences between kraft and

thermomechanical pulps, which contribute to the differences in the ability of these fibers to bond.

Table 6. Comparison of kraft and thermomechanical pulp (TMP) fibers.

Kraft Pulp	TMP
Low Yield (45-50%).	High Yield (97-98).
More Long Fibers (up to 90%). ²⁹	Fewer Long Fibers (approx. 40%). ²⁹
Fewer Fines (<10%). ²⁹	More Fines (20-40%). ²⁹
Easily Collapsed, Flexible Fibers(apparent density 564 kg/m ³). ⁵²	Less Collapsed, Less Flexible Fibers (apparent density 314-364 kg/m ³). ⁵²
Fiber Surface Composition, Approx. 3.4-16.2% lignin, 1.4-8.3% extractives. ⁴¹	Fiber Surface Composition, Approx. 35% lignin, 15% extractives. ⁴¹
Bulk Lignin Content, <5%. ²⁹	Bulk Lignin Content, Approx. 28%. ²⁹
Greater Fiber Shrinking and Swelling, Less Lignin. ⁵³	Less Shrinking and Swelling, More Lignin. ⁵³
Stretch (3.0 %) ⁵²	Stretch (1.84-2.28 %) ⁵²
Greater Burst, Breaking Length, Tear (4.52 KPam ² /g, 6130 m, 8-8.6 mNm ² /g) ⁵²	Lower Burst, Breaking Length, Tear (1.6-2.1 kPam ² /g, 3200-4150 m, 8.0-8.6 mNm ² /g) ⁵²
R 14 Bauer McNett Fraction (Very long) 54.1% ⁵²	R 14 Bauer McNett Fraction (Very long) 2.8-6.9% ⁵²
P14/R48 (Long) 35.7% ⁵²	P14/R48 (Long) 46.6-50.2% ⁵²
P48/R100 (Middle)4.9% ⁵²	P48/R100 (Middle) 11.0-15.4% ⁵²
P100 (Fines) 5.3% ⁵²	P100 (Fines) 30.7-35.5% ⁵²

Wet tensile reflects the load paper can bear in the wet state, when water can interfere with hydrogen bonding in the sheet. Taylor⁵⁶ found that during wet tensile failure bonds, rather than individual fibers, fail when no wet strength additives are used. The extent of fiber flexibility, collapsibility, fibrillation and fines content in the sheet have been associated with improved wet tensile strength and wet stretch, and curl and microcompressions have been associated with increased wet stretch.⁵⁴

In his review of the mechanism by which additives improve wet strength, Espy (1995) discussed two mechanisms, (1) a protective mechanism by which water is prevented from interrupting hydrogen bonding and (2) a covalent cross-linking mechanism. In the past, wet strength agents, such as urea-formaldehyde (UF) (Figure 8) and melamine-formaldehyde (MF) (Figure 9) systems, which function by forming an insoluble network, were used.⁵⁵

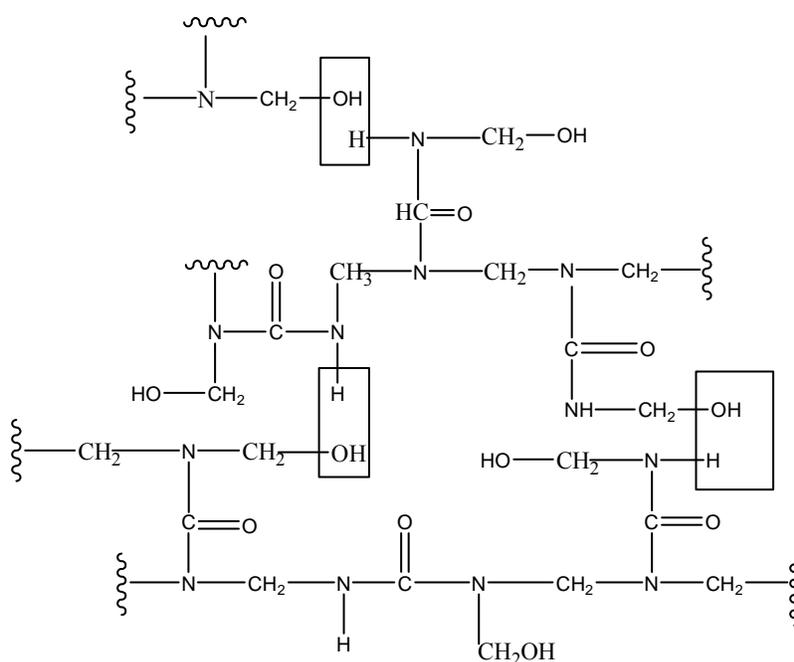


Figure 8. Cross-linking of the formaldehyde-urea insoluble network.

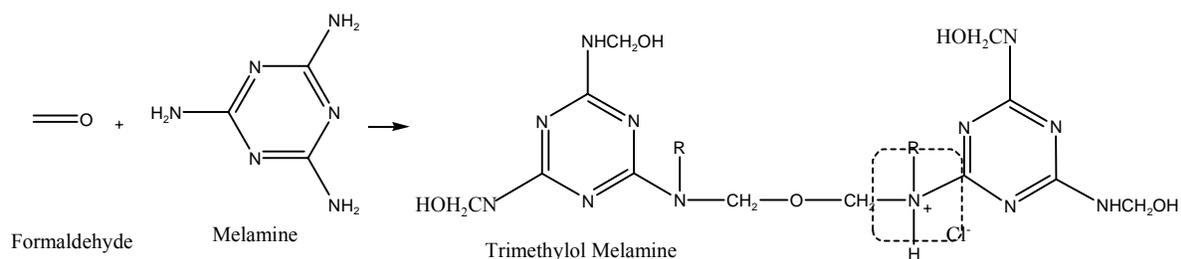


Figure 9. The formation of the formaldehyde-melamine insoluble network.

Wet strength increases due to the use of the wet strength resin melamine-formaldehyde are associated with decreased swelling of the fiber.⁵⁶ Typical wet strength additives, such as poly(amide epichlorohydrin) resins (commonly known as PAE-resins) function by cross-linking with themselves as well as fibers Figure 2.⁵⁷ PAE resins can provide dramatic increases in wet strength and small increased in dry strength Table 7.⁵⁷ The cross-linking of compounds containing carboxylic acid groups to form ester bonds with cellulose (Figure 3) also hold much promise for the development of wet strength.^{58,59}

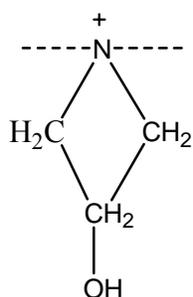


Figure 2. The reactive, cationic portion of the poly(amide-epichlorohydrin) wet strength resin.

Table 7. The impact of PAE resins on the wet and dry strength of bleached kraft sheets.

Sample	Dry breaking length (km) ⁵⁷	Wet breaking length (km) ⁵⁷
No PAE resin	4.35+/-0.26	0.13+/-0.028
0.5% PAE resin	5.55+/-0.36	1.13+/-1.10
2.0% PAE resin	5.63+/-0.38	1.34+/-0.13

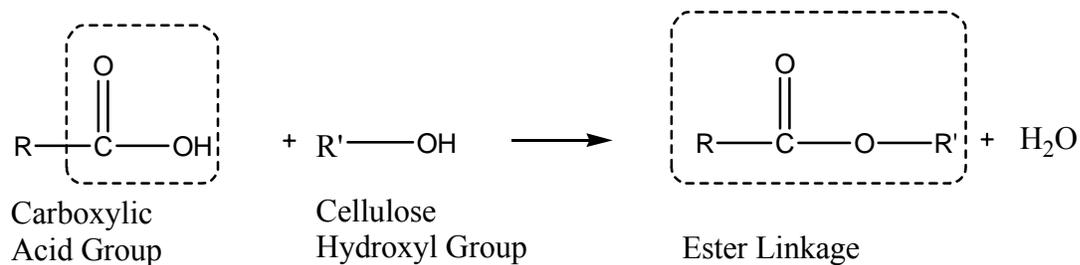


Figure 3. Model for the reaction of a carboxylic acid with cellulose to form an ester linkage.

Wet strength additives can function on a temporary or permanent basis. Chemically, the temporary additives typically contain aldehyde groups which cross-link to form acetals or hemiacetals with the cellulose, while the permanent additives are able to form covalent bonds with themselves and/or the fiber that do not easily hydrolyze in water.^{57,60}

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