Chapter 1 General introduction

1.1 Wood as a raw material

Wood serves as the main construction material for trees and allows for the capillary water transport between roots and leafs. It is formed by the vascular cambium and has a cellular structure with an interconnected network of macroscopic intracellular (lumen) and intercellular spaces (Fromm 2013, pp. 2). The cell walls are constructed as a complex biopolymer composite that form a material with high mechanical strength at low weight. Due to the unique properties of wood, it is regarded as one of the most important renewable resources for meeting the growing demand for bioenergy, construction materials and pulp for paper production. Within the UNECE region the consumption of roundwood has increased to 1.26 billion cubic meters in 2014 (UNECE/FAO 2015). The efforts for utilizing renewable raw materials that can be derived from sustainable sources and that can act as carbon sinks are likely to increase the demand for wood products (FAO 2012). In order to prevent shortage of supply and increasing raw material prices, an efficient material utilization is required. Besides recycling and material savings, the extension of the service of wood products is a key aspect.

1.1.1 Wood composition and ultra-structure

On an ultra-structural level, wood can be considered as a biopolymer composite built up of an interconnected network of cellulose, hemicelluloses and lignin with small amounts of extractives and inorganics. Based on its dry weight, wood is mainly composed of polysaccharides (65-75 %) and lignin (18-35%). The polysaccharides consist mainly of cellulose (40-45%) and hemicelluloses (15-25%), as well as of small proportions of starch and pectin (Rowell et al. 2005). The chemical composition differs between the wood species. In general, softwood species contain larger amounts of lignin, but lower amounts of hemicelluloses than hardwood species. Furthermore, the chemical compositions of lignin and hemicelluloses differ in softwoods and hardwoods, while cellulose is a uniform component in all wood species (Fengel and Wegener 1984 pp. 26). The three main polymers of the wood cell wall are briefly described below.

Cellulose is a linear high-molecular weight polymer consisting exclusively of D-glucopyranose units that are linked together by ß-(1→4)-glucosidic bonds. The repeating unit of the cellulose chain is a cellobiose unit, in which one of the two glucose units is turned around its C1-C4 axis of the pyranose ring. The cellulose chain has a reducing (C1-OH) and a non-reducing end (C4-OH) (Fengel and Wegener 1984 pp. 67). The size of the chain is usually specified as degree of polymerization (DP), which is the molecular weight of the cellulose chain related to the molecular weight of one glucose unit. For wood cellulose, an average DP of at least 9,000-10,000 is expected. Within the wood cell wall, cellulose is in a semi-crystalline state. Cellulose molecules have a tendency to form intra- and intermolecular hydrogen bonds and aggregate to microfibrils. These microfibrils contain highly ordered crystalline regions with a high packing density, as well as less ordered non-crystalline regions with a lower packing density. Up to 65 % of the wood cellulose exists as crystalline cellulose (Rowell et al. 2005).

Hemicelluloses are a composition of various sugar units, which may be pentose or hexose sugars. Compared to cellulose, hemicelluloses have much shorter, branched molecular chains and contain acetyl- and methyl-substituted groups (Fengel and Wegener 1984 pp. 106; Rowell et al. 2005). The most common sugar units in hemicelluloses are D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid and D-galactopyranosyuronic acid (Rowell et al. 2005). Softwood species usually have a high proportion of mannose units and more galactose units compared to hardwood species, which have a high proportion of xylose units and contain more acetyl groups (Fengel and Wegener 1984, p. 108).

Lignin is an amorphous, mainly aromatic polymer that consists of phenyl-propane units. These units are linked together to a three-dimensional polymer by C-O-C and C-C linkages. The building units and primary precursors of lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. They have several reactive sides and their formation to a lignin macromolecule occurs through a random coupling to a non-linear polymer, rather than by a regular mechanism that is genetically prescribed (Fengel and Wegener 1984, pp. 132). Guaiacyl lignin, a polymerization product of guaiacyl alcohol, dominates the softwood lignins, while hardwood lignins are mainly syringyl-guaiacyl lignin, which is a copolymer of coniferyl and sinapyl alcohol (Rowell et al. 2005).

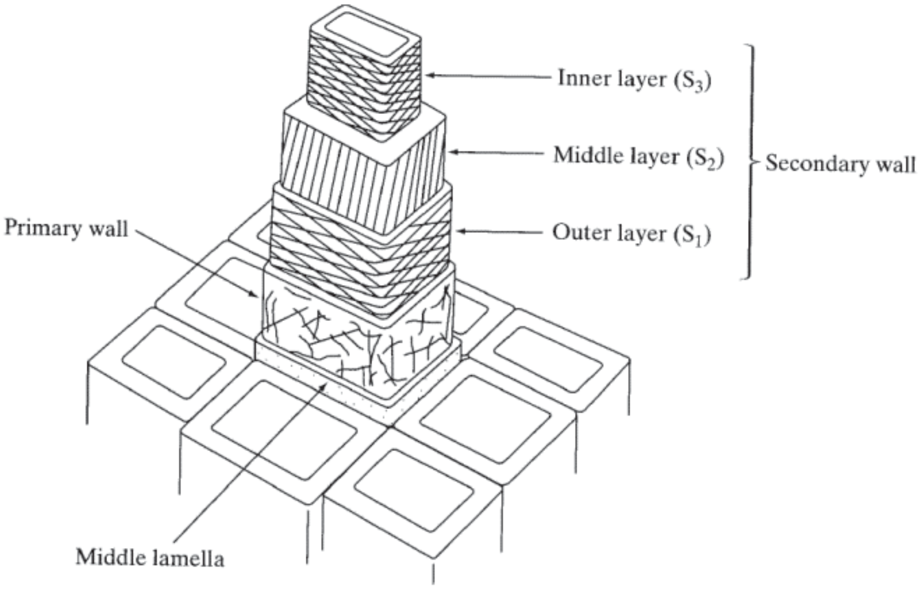

Figure 1: Cell wall structure of wood (derived from Dinwoodie 1989).

The three main polymers are not distributed evenly over the different cell wall layers of wood (**Figure 1**). The middle lamella and primary wall are mainly built up by lignin and contain much lower amounts of hemicelluloses and cellulose. However, the lignin content of the cell wall decreases towards the lumen, from the first layer (S_1 layer) to the second (S_2

layer) and third layer (S_3 layer) of the secondary wall. However, the bulk of all three main cell wall polymers is found in the S_2 layer, since this is the by far thickest layer of the cell wall (Fengel and Wegener 1984 pp. 227; Rowell et al. 2005). It makes up for approximately 80 % of the cell wall by weight and thus has a dominating influence on the wood properties, such as mechanical performance or swelling (Skaar 1988; Salmén and Burgert 2009). More than 50 % of the S_2 layer consists of cellulose (Fengel and Wegener 1984 p. 228; Rowell et al. 2005).

The arrangement of the polymers within the secondary cell wall shows some degree of order (ultra-structure), rather than being a random mixture. The cellulose microfibrils are imbedded in a matrix of amorphous hemicelluloses and lignin. The microfibrils have different inclinations with respect to the cell axis (microfibril angle, MFA) in the different layers. While the MFA is very high in the S_1 and S_3 layers, it is low in the S_2 layer and the microfibrils are almost oriented longitudinally (Rowell et al. 2005). The cellulose microfibrils are approximately 3-4 nm in diameter (Larsson et al. 1997; Wickholm et al. 1998). In the secondary cell wall, they are arranged in an undulating aggregate structure with aggregates reaching up to 30 nm in diameter. The spacing between the aggregates is lens shaped and contains amorphous cell wall polymers, hemicelluloses and lignin (Boyd 1982; Salmén and Burgert 2009; Salmén 2015). Hemicelluloses show a much lower degree of orientation than cellulose (Salmén et al. 2012). Hemicelluloses do not bond to the cellulose fibril surfaces covalently, but mainly by hydrogen bonds, which might be further supported by physical entanglement within the non-crystalline regions (Whistler and Chen 1991; Salmén and Olsson 1998; Salmén and Burgert 2009). In contrast, lignin is not bound to cellulose directly, but there are covalent bonds, i.e. ester, ether and glycosic bonds, between lignin and hemicelluloses that form lignin carbohydrate complexes that are difficult to separate (Whistler and Chen 1991; Koshijima and Watanabe 2003; Du et al. 2013). Hemicelluloses thus play a major role in maintaining the cell wall assembly (Salmén and Burgert 2009).

1.1.2 Natural properties of wood

The properties of wood are a result of a broad number of factors. On a macroscopic and microscopic level, factors such as the grain angle, the fiber length, the distribution of early- and latewood and various growth characteristics influence the mechanical properties of wood strongly (Winandy and Rowell 2005). There are also many factors that explain the differences in the properties of the various wood species. Nevertheless, the most fundamental aspects of wood properties can be explained by the general chemical composition and ultra-structure of the wood cell wall, mostly irrespective of the individual wood species.

Mechanical properties

Clear wood (free of knots, defects or irregular growth characteristics) has a high specific strength when compared to other building materials (Askeland et al. 2010, pp. 702), which can be linked to its unique structure and composition. When an external load is applied, the cell wall constituents contribute in different degrees to the strength of wood. The cellulose microfibrils function as tensile reinforcement of the cell wall. The tensile strength of cellulose is strongly dependent on its DP, with a decrease in DP leading to a reduction in strength (Ifju 1964). They exhibit an extremely high modulus of elasticity (MOE) under tension and thus contribute greatly to the stiffness of wood (Eichhorn and Young 2001). In compression, however, cellulose microfibrils buckle easily in contrast to their high strength and stiffness in tension (Gindl et al. 2004b). This low resistance against compressive loads of cellulose microfibrils is compensated by the rigid lignin matrix in which the microfibrils are imbedded. Lignin also limits the access of water to the cell wall and thereby contributes to the ability of wood to retain its strength and stiffness when exposed to moisture (Lagergren et al. 1957; Klüppel and Mai 2012). Since there are no direct bonds between cellulose and lignin, the hemicelluloses act as coupling agent between the cellulose microfibrils and the lignin matrix, thereby enabling the transfer of stresses between the individual cell wall polymers (Sweet and Winandy 1999; Winandy and Lebow 2001; Winandy and Rowell 2005).

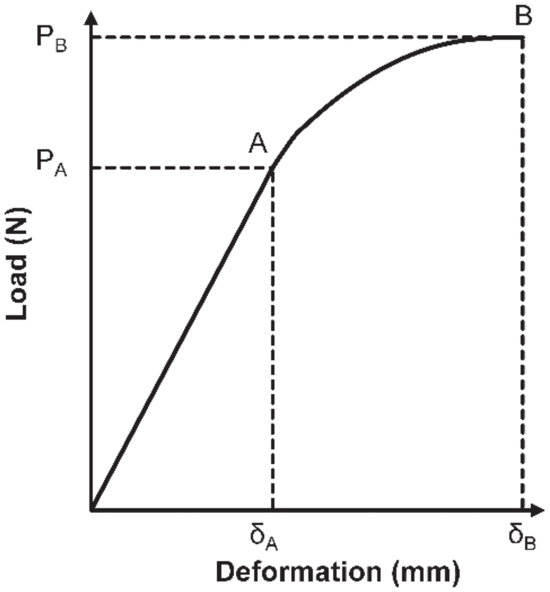

Figure 2: Schematic load-deformation curve showing the proportional limit (A) with its corresponding deformation (P_A) and load (δ_A) as well as the ultimate strength (B) with its corresponding load (P_B) and deformation (δ_B).

When load and deformation are plotted against each other, the result for wood materials is a load-deformation curve as shown in **Figure 2**. The test methods that can be used differ considerably in the way the external load is applied, leading to different types of stress within the specimen. The three primary types of stress are tensile, compressive and shear stress. When not considering creep and focusing on the immediate deformation, the behavior of wood under external load is characterized by a linear, elastic behavior below the proportional limit, and a non-linear, inelastic behavior above the proportional limit (see **Figure 2**). Below the proportional limit, all deformations are recoverable. The elastic deformation that occurs is caused by the breakage of hydrogen bonds between and within individual polymer chains, sliding of polymers by one another and subsequently the reformation of hydrogen bonds. Additionally, covalent bonds are distorting within the ring structures of polysaccharide chains. When exceeding the proportional limit, the stresses can no longer be distributed in a linear elastic manner and become great enough to cause covalent bond scission, which results in a permanent deformation. This non-linearity is associated with stress-induced plastic flow, during which the material is undergoing a rearrangement of its internal molecular and microscopic structure. In approaching the ultimate strength (see **Figure 2**), the elastic behavior becomes less notable, while failure and disorientation of microfibrils, the separation of the various cell wall layers, and the distortion of wood cells in relation to one another and finally failure of the wood cells by either scission of the cell, or cell-to-cell withdrawal occur (Winandy and Rowell 2005).

Moisture sorption and swelling of wood

Wood responds to variations in temperature and relative humidity with changes in moisture content. When temperature and relative humidity remain constant, wood will eventually reach a stable equilibrium moisture content. Wood reaches the fiber saturation point (FSP) at equilibrium conditions close to 100% relative humidity (RH), which corresponds to about 40% moisture content (Hoffmeyer et al. 2011). Above FSP, free water can be found in the cell lumen, whereas only bound water within the cell wall is present during water vapor sorption below the FSP (Zelinka et al. 2012; Engelund et al. 2013). Hydroxyl (OH) groups of the wood polymers are the main sorption sites for bound water. Water-accessible OH groups are mainly found in the hemicelluloses of the wood cell wall. In contrast, lignin has generally less OH groups compared to cell wall polysaccharides and cellulosic OH groups are only water-accessible on the surface of the microfibrils (Runkel 1954; Runkel and Lüthgens 1956).

When plotting the EMC against the relative humidity at a constant temperature (<75 °C), the result is a sorption isotherm with a hysteresis between adsorption (uptake) and desorption (release of water molecules) (Seborg and Stamm 1931; Stamm and Woodruff 1941), as shown in **Figure 3**. Typically, sorption isotherms of wood have a sigmoidal shape with a convex course at low relative humidity and a concave course at high relative humidity. To explain this shape of sorption isotherms, various theories have been developed over the past decades (Skaar 1988 pp. 86). Recent studies consider matrix polymer relaxation to explain the sorption behavior of wood (Vrentas and Vrentas 1991; Hill et al. 2012a; 2012b; Popescu and Hill 2013). Following their explanations, the adsorption of water by wood causes a swelling pressure that leads to an expansion of the cell wall nanopores and thereby creates additional sorption sites within the wood matrix. This creation of additional sorption sites is hindered by the limited free volume in the cell wall matrix that restricts the expansion of the nanopores and requires the rearrangement of the matrix polymers. During desorption, the nanopores that are opened by adsorbed water are closed, which requires the relaxation of the surrounding matrix polymers. In this theory, the upward bend in the sorption isotherm of wood at around 60-70 % RH and room temperature is related to the softening of amorphous polymers. Below the glass transition at low relative humidity, the reduced polymer mobility hinders the response of the cell wall matrix to adsorption or desorption of water and delays the opening or closure of the nanopores. Therefore, adsorption and desorption occur in a material that is in different states. When exceeding glass transition by increasing the relative humidity and/or the temperature, the mobility of the cell wall matrix polymers is enhanced. This results in a decrease in hysteresis and in an increase in the additional sorption sites formed upon the expansion of the cell wall nanopores, along with the upward bend in the sorption isotherm. The latter has previously been attributed to sorption of free water in capillaries (Barkas 1937; Kollmann 1962), which was later considered insignificant in wood cell walls below 99.5% relative humidity (Engelund et al. 2010; Thygesen et al. 2010).

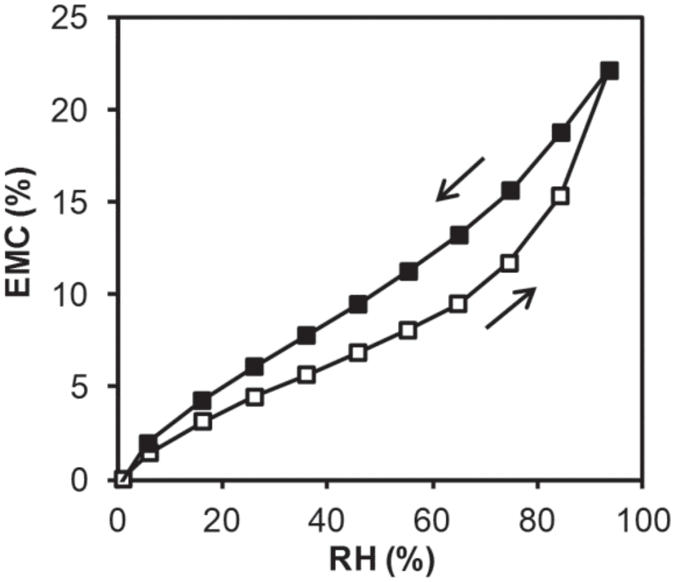

Figure 3: Adsorption (open symbols) and desorption (closed symbols) isotherms of Scots pine sapwood (*Pinus sylvestris* L.) measured at 25°C within the RH range between 0 and 95%.

Below FSP, swelling and shrinkage of wood occurs in response to the uptake and release of water molecules. Swelling and shrinkage of wood is not only depending on the expansion of nanopores within the cell wall matrix, but also on the orientation of the microfibrils within the different cell wall layers. Due to the low MFA in the large S_2 layer, the stiff cellulose microfibrils prevent longitudinal swelling. In a similar way, swelling circumferential to the cell wall is reduced by the high MFA in the S_1 and S_3 layers. Therefore, swelling and shrinkage occur mainly perpendicular to the cell wall (Skaar 1988 pp. 127; Schulgasser and Witztum 2015).

Deterioration of wood by decay fungi

A deterioration of wood can be caused by various organisms, i.e. insects, bacteria and fungi. Fungal decay is very critical, because it can cause a rapid failure of wood products. There is a vast variety of decay fungi that can colonize and degrade wood, including brown rot, white rot and soft rot fungi. The mechanisms involved in the degradation of wood by decay fungi are complex and depend on many factors. In general, decay fungi depolymerize and/or modify cell wall constituents to provide themselves with energy and metabolites for synthesis via metabolism. Major growth requirements for most wood-inhabiting fungi are:

- free water on the surfaces of the cell lumina,
- presence of atmospheric oxygen within the wood,
- a favorable temperature and pH range,
- a digestible substrate that provides energy and metabolites
- chemical growth factors, such as nitrogen compounds, vitamins and essential elements, and
- the absence of toxic extractives (Zabel and Morrell 1992 pp. 90).

In practice, prevention of fungal decay can be achieved by making sure that these requirements are not fulfilled. Fungal decay of wood involves the action of various chemicals, including enzymes. Although the chemicals involved differ considerably between the fungal species, it is a common principle that the wood degrading chemical has to diffuse into the cell wall in order to cause the depolymerization of wood polymers. However, even if a sufficient amount of water as diffusion medium is present, the enzymes involved in fungal degradation are too large to enter the cell wall (Srebotnik et al. 1988; Daniel et al. 1989). Therefore, the fungi must employ smaller diffusible agents to initiate decay, such as reactive oxygen or chelators (Goodell et al. 1997; Hammel et al. 2002).

1.1.3 The need for wood modification

The low dimensional stability and the low biological durability limit the service-life of most European wood species greatly, when applied in exterior conditions in which the requirements for fungal growth are fulfilled. The most common treatment to increase the service-life is the impregnation of these wood species with chemicals that are toxic to microorganisms and/or insects. Inorganic biocides (e.g. based on chromated copper), organic biocides (e.g. quaternary ammonium compounds), or oilborne preservatives (e.g. creosotes) have been used successfully to increase the durability of native wood species for decades (Stirling and Temiz 2014). However, problems arise from some of these chemical treatments such as serious health risks (Willeitner 1973; Jermer and Edlund 1990), leaching of chemicals from treated wood in service (Hingston et al. 2001; Townsend et al. 2005), or difficulties with the disposal of treated wood after service (Voß and Willeitner 1993; Voß and Willeitner 1995). Consequently, there is a tendency of legislation to abandon the use of chemicals that are toxic to humans or the environment, which necessitates the search for alternative treatments.

As an alternative, wood modification provides decay resistance and dimensional stability through non-biocidal modes of action. In contrast to preservative-treated wood, the modified wood should remain non-toxic and no release of toxic components is supposed to take place, neither during service, nor during disposal or recycling (Hill 2006 pp. 20). Wood modification aims at changing the basic chemistry of the wood cell wall polymers to overcome undesired properties of wood, i.e. its low dimensional stability and biological durability (Militz et al. 1997). Treatments with non-toxic chemicals that are deposited in the lumens, but do not diffuse into the cell wall are not in accordance with this definition for