Introduction

Definition of Wood Polymer Composites

The term Wood Polymer Composites refers to any material that contains wood (of any form) or natural fibers and thermoplastics. On today's market there are several definitions and descriptions of the terms Wood Polymer Composites.

In the Anglo-American area 'Wood(-fiber) Plastic Composites' often is used for the description of this material class. In the European area mostly the term 'Wood Polymer Composite' is used nowadays. Several descriptions of the term WPC can be found in the literature:

Wolcott and Smith (Smith 2005)

> *„These composite materials are produced by combining thermoplastic polymers with natural fibers derived from wood and agricultural crops"*

Kirsch and Daniel (Kirsch 2004)

> *„Wood-Plastic Composites (WPC) are a composite material of the natural polymer „wood" with the synthetic polymer „plastic" and belong to the group of reinforced plastics"*

Vogt (Vogt 2005)

> *'Wood-Plastic-Composites (WPC) are composites with a thermoplastic behavior in the production process. The variation of different ratios of wood, plastic and additives is processed under thermoplastic processes e.g. extrusion, injection molding and pressing techniques"*

Stadlbauer (cited by (Vogt 2005)

> *„With wood fiber filled or reinforced plastic, with the processing behavior of plastic materials, for process in extrusion and injection molding processes"*

Labat (Labat 2006)

> *"Definition of Wood-Plastic Composite: product being the result of the combination of cellulose based fiber material with one or several polymer(s) and being processed through plastic processing techniques"*

Klyosov (Klyosov 2007) describes the term as follows:

> *'Wood-Plastic Composite (WPC) are extruded or molded products of a specific shape and, definition, represents plastic filled with cellulose fiber and other ingredients. In this context "wood" is a proxy for fibrous materials of plant origin"*

Oskman-Niska & Sain (Oksman-Niska 2008) describes the term also for duromeric systems as follows:

> *'Wood-polymer composites (WPC) are materials in which wood is impregnated with monomers that are then polymerized in the wood to tailor the material for special applications"*

A definition of Wood Polymer Composites can be described as follows after prCEN/TS15534-1:2006 (E):

> *"The denomination "wood-plastic composites", WPC, is usually used to designate materials or products made of one or more natural fibers or flours and a polymer or a mixture of polymers. Natural fibers and flours come from different vegetable sources (e.g. wood, hemp, sisal, jute, kenaf, rice) and all kind of polymers (virgin or recycled) can be used but the most current ones are poly(vinyl chloride) PVC, polypropylene PP, and polyethylene PE."*

In this work the terms Wood Polymer Composites and abbreviated WPC are used; even if the origin literature uses the term Wood Plastic Composites or related definitions.

Wood-Polymer Composites (WPC) represent a relatively new class of hybrid materials that have been gaining rapid market share (Wolcott 1999; Clemons 2002a; Schirp 2005). A fiber composite is a made-to-measure combination of two or more materials designed to improve the properties of the individual components (Richter 2004).

Wood and natural fiber filled polymer composites in particular, have received a lot of attention particularly on the types of fiber, filler or reinforcement characteristics, types of coupling agents and processing technologies (Arnold 1992; Flemming 1995; Youngquist 1995; Bledzki 1998a; Bledzki 1998b; Nabi Saheb 1999; Sperber 1999; Wolcott 1999; Damery 2001; Shi 2001; Shook 2001; Smith 2001; Merl 2003; Wolcott 2003; Teischinger 2003a; Teischinger 2003b; Fulmer 2004; Maine 2004; Vogt 2005; Wolcott 2005; Radovanovic 2006; Tichy 2006; Gahle 2007; Gardner 2007; Klyosov 2007; Markarian 2007; Radovanovic 2007; Rowell 2007; Oksman-Niska 2008; Schirp 2009; Sercer 2009).

The content of wood ranges between 50…80% (Oksman 1996; Stark 1997b; Bledzki 1998a; Bledzki 1998b; Sperber 1999; Wolcott 1999; Clemons 2000; Damery 2001; Clemons 2002a; Teischinger 2003b; Kirsch 2004; Vogt 2005; Klyosov 2007; Rowell 2007) depending on the application and the performance of the product.

Market situation

Wood Polymer Composites are used for several decades on the North American market; in Europe these materials gained attraction a few years ago. The biggest market share for Wood Polymer Composite products is in the area of building products. Wood Polymer Composites are mainly used as decking materials and primarily seen as substitute for wood decking (Shook 2001; Smith 2001; Merl 2003; Schirp 2005; Wolcott 2005; Tichy 2006). Other applications for Wood Polymer Composites including automotive parts, window frames, roof singles, pallets, daily use items, and many other applications with minor market share (Shook 2001; Smith 2001; Merl 2003; Wolcott 2005). However, the largest and fastest growing markets for Wood Polymer Composites are extruded residential decking, railing and siding applications on a global scale (Wolcott 2001; Clemons 2002a; Vogt 2005; Wolcott 2005; Klyosov 2007; Radovanovic 2007; Schmitz 2007).

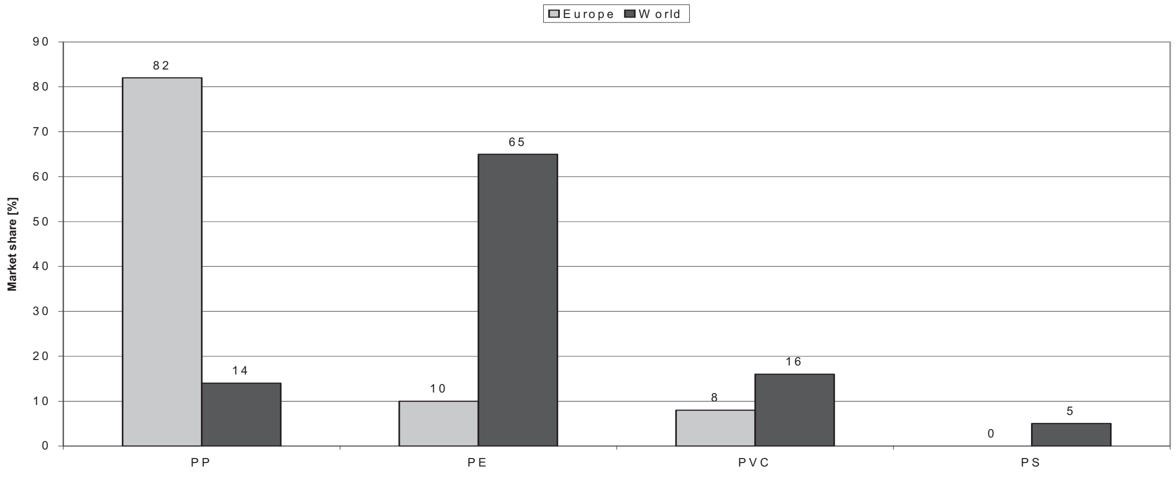

Figure 1: Use of Polymers in Wood Polymer Composites - Europe vs. World [mod. Vogt et al. 2005]

In Europe mainly polypropylene PP is used for the production of Wood Polymer Composites, followed by polyvinyl chloride PVC, and polyethylene PE. In the global situation mainly PE is used, followed by PVC and PP. Small fractions of other thermoplastic polymers are used as well (Figure 1)(Wolcott 1999; Clemons 2000; Wolcott 2001; Clemons 2002a; Vogt 2005; Gardner 2007; Klyosov 2007; Euwid 2009).

Polymers

Table 1 gives an overview on the used polymers within several research projects for the use as matrix for fiber reinforced composites:

Table 1: Overview on the used polymer in research

Polymer	Used by
Polypropylene (PP)	(Klason 1984; Woodhams 1984; Gatenholm 1991; Sain 1993; Mieck 1995a; Mieck 1995b; Avella 1997; Stark 1997a; Stark 1997b; Clemons 1998; Rana 1998; Bledzki 1998b; Van de Velde 1999; Kazayawoko 1999a; Kayazawoko 1999b; Falk 2000; Rowell 2000; Mahlberg 2001; Stark 2001; Van de Velde 2001; Clemons 2002a; Bledzki 2003; Hristov 2003; Ahmad 2004; Biagotti 2004; Gehrmann 2004; Gregorova 2004; Hristov 2004; Le Digabel 2004; Lucka 2004; Mohanty 2004; Raukol 2004; Seldèn 2004; Simonsen 2004; La Mantia 2005; Wang 2005; Borysiak 2006; Danyadi 2006; Fink 2006; Gramlich 2006; Guo 2006; Khalil 2006; Kiguchi 2006; Panthapulakkal 2006; Steckel 2006; Westin 2006; Gardner 2007; Najafi 2007; Oporto 2007; Panaitenescu 2007; Shi-fa 2007; Bouza 2008; Fabiyi 2008; Kim 2008; Wolkenhauer 2008; Ares 2009; Ashori 2009; Bledzki 2009; Schirp 2009)
Polyethylene	(Raj 1989c; Oksman 1996; Park 1997; Muasher 2006)
High-density Polyethylene (HDPE)	(Woodhams 1984; Maiti 1986; Vu-Khanh 1987; Venkatraman 1989; Raj 1989a; Raj 1989c; Raj 1990; Raj 1991; Maldas 1992; Hedenberg 1995; Stark 1997a; Bledzki 1998a; Balma 1999; Nabi Saheb 1999; Stamboulis 1999; Falk 2000; Lundin 2001; Pendleton 2002; Clemons 2002b; Manning 2003; Stark 2003; Wolcott 2003; Raukol 2004; Simonsen 2004; Simonsen 2004; Gnatowski 2005; Lopez 2005; Lu 2005; Schirp 2005; Stark 2005; Fink 2006; Muasher 2006; Stark 2006a; Stark 2006b; Dawson-Andoh 2007; Gardner 2007; Sewda 2007; Stark 2007; Zhang 2007; Fabiyi 2008; Ikeda 2008; Mengeloglu 2008; Migneault 2008; Wolkenhauer 2008; Ashori 2009; Li 2009)
Polyvinylchloride (PVC)	(Matuana-Malanda 1996; Fiaz 1998; Bledzki 1998b; Ochiai 1999; Mantuana 2000; Chetanachan 2001; Mantuana 2002; Haihong 2004; Grossman 2006; Shi 2007; Wirawan 2009; Jiang 2010)
Polystyrene, normal (PS) impact modified (PS)	(Kokta 1983; Maldas 1989; Raj 1989b; Couturier 1996; Kosonen 2000; Bakraji 2003; Doroudiani 2004) (Loos 1968; Hedenberg 1995; Wolcott 2003; Fink 2006)
Polylactidacid (PLA)	(Patil 1999; Khan 2001; Fink 2006; Xu 2008)
Polymethylene-methacrylate (PMMA)	(Loos 1968; Chia 1985; Boey 1986; Teoh 1986; Boey 1989; Chan 1989; Couturie 1996; Ng 1999)
Recycled thermoplastics	(Yam 1990; Sain 1993; Maldas 1995; Gregorova 2004; Raukol 2004; Khalil 2006; Najafi 2007; Ashori 2009)
Other thermoplastics	Polyester (Singh 1996; Khan 2000; Hill 2000b; Prak 2001; Ganan 2004; John 2004; Mehta 2005) Polybutyleneadipate-terephthalate (Le Digabel 2004) Acrylonitrile butadiene styrene (Shi 2007) Polyamide 6 / Polyamide 12 (Klason 1984) Chlorinated Polyethylene (Maldas 1995) Mixtures of Polymers (Hedenberg 1995)

Thermoplastics such as polyethylene (PE), polyvinyl chloride (PVC), and polypropylene (PP) are mainly being utilized for a variety of commercial products (Wolcott 2001; Clemons 2002a). Polystyrene (PS) (Bledzki 1998b), acrylonitrile-butadiene-styrene (ABS) (Clemons 2002a), Polyamide (PA) 11/12, and Lignin and starch (Bledzki 1998a; Bledzki 1998b) are also being used. Adcock (1999) reported that small amounts of thermoset resins such as phenol-formaldehyde or diphenyl methane diisocyante are also used in highly wood filled composites. Due to the limited thermal stability of wood, only thermoplastics that melt or can be processed at temperatures below 200°C are commonly used in Wood Polymer Composites (Bledzki 1998b; Clemons 2002a; Bledzki 2003; Radovanovic 2007)

Polypropylene

Polypropylenes are a high-volume commodity polymer processing characteristics of special materials and have a history of technical innovations. This polymer has numerous grades for specific end uses, and the catalyst is a complex system resulting from major technological achievements. The catalyst's sophistication allows the manufacturing process to be simple, economical, flexible, and environmentally friendly. Continuing catalyst developments, such as homogenous catalysis, have great potential for generating new types of polypropylene with expanded applications. Although technically incorrect, the term polypropylene is widely accepted to mean highly isotactic propylene homo-polymers, propylene-ethylene-copolymers, and other co- and terpolymers of propylene that are produced in commercial quantities. Isotactic polypropylene is an important polymer not only commercially, but also scientifically, because of its different morphological behavior. On the crystal lattice level, iPP exhibits three different morphological forms; α,β, and γ, distinguished by the arrangement of the chains. Another form of iPP with a degree of order between crystalline and amorphous phases was first reported by Natta, who named it the "smectic" form. Polypropylenes have a specific density of 0.90-0.91 g/cm^3, which is approximately equal to that of very low-density polyethylene (Awaya 1988; Elias 1997; Salamone 1999; Vasile 2005; Klyosov 2007; Radovanovic 2007; Wypych 2008).
Therefore it is chosen to be used in the following investigations.

Wood and natural fibers

Wood

The growth and development of higher plants is governed by cell division; wood is formed during the growth of certain plants. Wood is obtained from stems, roots, and branches of trees (Wagenführ 1999). Wood is a natural composite material of elongated cells, which are mostly oriented on the longitudinal direction of the stem. The cells are connected with each other through openings, called softwood pits. The wood cells vary in their shape according to their specific function and provide the necessary mechanical strength to the tree, and also act as liquid transport pathways in the living tree and also as food storage (Sjöström 1981; Fengel 2003).

To define them botanically, softwoods are those woods that belongs to the gymnosperms (mainly conifers), and hardwoods are woods belong to the angiosperms (flowering plants) (Rowell 2005).
Biologically seen softwood are older and therefore less specified compared to the younger hardwoods with a higher level of specification of the cells (Wagenführ 1999). Considering these different cells softwoods have a much simpler structure compare to hardwoods due to the presence of only two cell types and only little miscellaneousness in the structure of these cell types. Hardwoods itself have a greater structural complexity, due to their greater number of cell types and a higher degree of the variation within these cell types (Fengel 2003; Rowell 2005).

Anatomical structure

The main species, which are used in Europe are spruce (*Picea abies L.*) and pine (*Pinus sylvestris L.*) wood for the production of Wood Polymer Composites (Maine 2004; Vogt 2005). Due to that, the following chapter will only deal with softwoods, its structure and properties.
Figure 2 shows the three anatomical directions of wood and can be recognized on the sections cut in the three main planes (used for the anatomical characterization of wood) (Wagenführ 1999; Fengel 2003; Rowell 2005):

- the cross or transfers section
- the tangential section
- the radial section

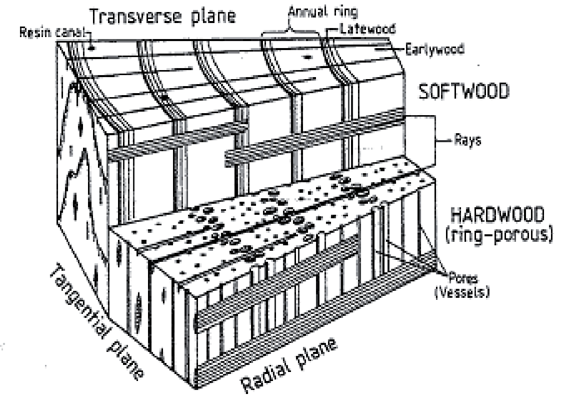

Figure 2: Models of a softwood and a hardwood block, showing the main cutting planes for anatomical studies, and anatomical structures visible without optical aids (Fengel 2003)

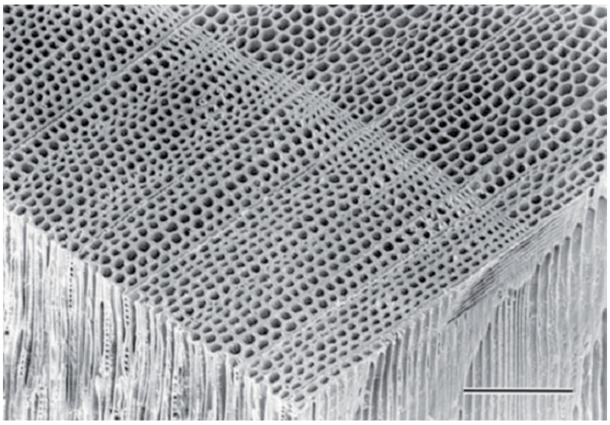

Figure 3: Three-dimensional view of a coniferous wood (*Chamaecyparis obtuse*) showing the structure of softwood; transverse (top), tangential longitudinal (left) and radial longitudinal (right) face (scale bar = 200µm) (Huang 2003)

Softwoods are simple in structure and mainly composed of only one cell type, the so called tracheids. Tracheids constitute approximately 90-95% of the wood (by volume) (Wagenführ 1999; Fengel 2003; Stokke 2003; Rowell 2005). Tracheids are long and slender cells with flattened or tapered closed edges (Fengel 2003). The tracheids are arranged in radial files, and their longitudinal extension are oriented in the axes of the stem (Fengel 2003; Rowell 2005). Softwood tracheids are typically between 3…4 mm long and have an average diameter of 30…40 µm; therefore the aspect ratio (length to diameter ratio) is approximately 100:1 (compare *Aspect ratio*) (Fengel 2003; Stokke 2003). In evolving from earlywood to latewood the cell diameter become smaller while the cell walls become thicker. In the latewood the cell wall becomes thicker, and in the earlywood the cell lumina is bigger (Figure 3) (Fengel 2003).
Softwood also contains specialized cells and so called parenchyma cells, small food storage cells; most of these parenchyma cells are organized into aggregate structures known as rays. These rays form ribbon-like radial conduits for flow and storage of food in the living tree (Fengel 2003; Rowell 2005).

The concentric arrangement of the cell wall layers are caused by the differences in the chemical composition and by different orientations of the structural elements; between the individual cells there is a thin layer. This thin layer is called middle lamella, which glues the single cells together to form tissues. This layer is mainly cellulose free. The transition from the middle lamella to the adjacent cell wall layers is not very clear (Sjöström 1981; Fengel 2003; Rowell 2005).

In the primary wall (P) the cellulose fibrils are arranged in thin crossing layers. The subsequent wall layer is the secondary wall 1 (S1) with a gentle helical slope of the fibrils. The thickest layer is the secondary wall 2 (S2), within this layer the fibrils are oriented in step angels, whereas changes in the angle and differences in the packing of the fibrils result in a lamellar structure of the S2. The last fibrillar layer at the luminal border is the tertiary wall (T). The fibrils are arranged under a gentle slope but not in a strict order. In certain cases, e.g. the tracheids of spruce and pine, the luminal surface is covered with warts (W) (Fengel 2003). Figure 4 models the cell wall structure of softwood.

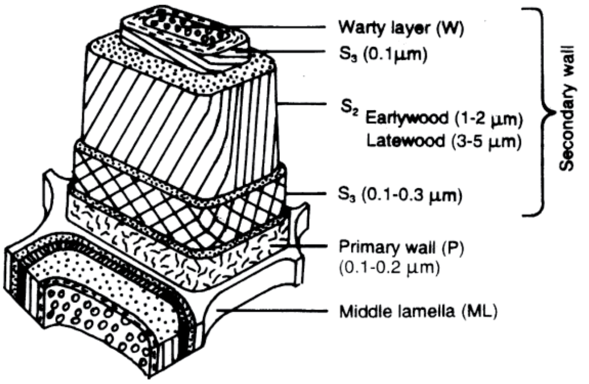

Figure 4: Model of the cell wall structure of softwood tracheids (hardwood libriform fibers), ML=middle lamella, P=primary wall; S1=secondary wall 1; S2=secondary wall 2; T=tertiary wall; W= wart layer (Fengel 2003; Huang 2003)

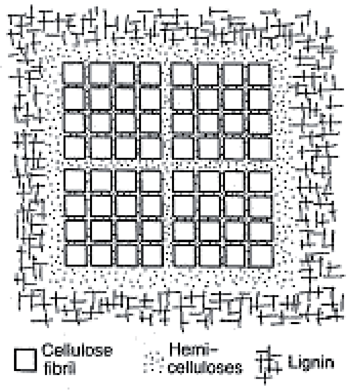

Figure 5: Fengel's (1970) model which defines the smallest fibrillar units of cellulose (Ø3nm) separated by monomolecular layers of hemicellulose, the largest units (Ø25nm) surrounded by hemicellulose and lignin (Eaton 1993)

The main portion of the cell wall is caused by the secondary cell wall, and reaches an extremely high percentage with approximately 90% in the latewood tracheids of softwoods. The thickness and the percentage of the wall layers vary within a species and between early and latewood sections within a single stem (Sjöström 1981; Fengel 2003; Rowell 2005).

Chemical wood structure

Rowell (2005) defines:

> *"Wood chemically as 3-dimensional biopolymer composite composed of an interconnected network of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganic materials. The major chemical component of a living tree is water, but on a dry-weight basis, all wood cell walls consist mainly of sugar-based polymers (carbohydrates, 65…75%) that are combined with lignin (18…35%)."*

In general, the coniferous species (softwoods) have a high cellulose (40…45%), high lignin (26…34%), and lower hemicelloluse (7…14%) content (Wagenführ 1999; Fengel 2003; Rowell 2005). Figure 5 shows the interaction between the chemical wood components on cell wall level.

Holocellulose

Encompasses cellulose and hemicellulose accounts usually for 65…70% of the dry wood weight (Rowell 2005). These polymers are composed out of mostly simple sugars, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid, and few amounts of other sugars such as L-rhamnose and D-fucose. These polymers are rich in hydroxyl groups that are mainly responsible for moisture sorption through hydrogen bonding (Sjöström 1981; Fengel 2003; Rowell 2005).

Cellulose

Cellulose is the structural basis of the plant cells (Fengel 2003) and is a long-chain and unbranched polymer of β-D-glucose in the pyranose form linked together by 1,4' glycosidis bonds to form cellobiose residues which are the repeating units in the cellulose chain (Schniewind 1989). The cellulose consists of crystalline and amorphous regions. The cellulose is predominantly located in the secondary cell wall (Sjöström 1981). The degree of polymerization for the cellulose molecules ranges between 7,000…10,000 DP (Sjöström 1981; Fengel 2003; Rowell 2005), but can strongly decrease when stressed in further processing (Fengel 2003). The cellulose is mainly responsible for the tensile strength in the wood structure.

Hemicelluloses

Hemicellulose fraction of woods consists of a collection of polysaccharide polymers with a lower degree of polymerization as the cellulose with an average of 100…200 DP and containing mainly different types of sugars (Sjöström 1981; Fengel 2003). Compared to the cellulose polymer chain, the hemicellulose chain is branched. Hemicelloluse are intimately associated with cellulose and contribute to the structural components of the tree. Some hemicelluloses are present in very large amounts when the tree is under stress, e.g. compression wood has a higher D-galactose content as well as a higher lignin content (Schniewind 1989; Fengel 2003). Hemicelluloses are intimately associated with cellulose and contribute to the structural components of the tree, and are chemically bonded to the lignin component (Sjöström 1981; Rowell 2005).

Lignin

Lignin is amorphous, highly complex, mainly aromatic polymers of phenylpropane units that are considered to be an encrusting substance. The 3-dimensional polymer is made up of C-O-C and C-C linkages. The precursors of lignin bio-synthesis are *p*-coumaryl-alcohol, coniferyl alcohol, and sinapyl alcohol. Also lignin does not have a single repeating unit of the hemicellulose like cellulose does, but instead consists of a complex arrangement of substituted phenolic units (Rowell 2005). Lignin can be classified in several ways, but are usually divided according to their structural elements (Sjöström 1981). Lignin of softwoods are mainly a polymerization product of coniferyl alcohol and are called guaiacyl lignin (Rowell 2005). Lignin increases the compression strength properties to such an extent, that huge plants remain upright (Fengel 2003).

Extractives

As the name implies, extractives are chemicals in the wood structure which can be extracted by using solvents. Hundreds of extractives have been identified and classified on their role in the tree. The functions of these extractives are well understood, whereas the role of some extractives are still not fully understood (Rowell 2005). The extractives are a group of cell wall chemicals mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, sugars, and many other minor organic compounds, such as minerals. These chemicals exists as monomers, dimers, and polymers; generally the extractives content in softwoods is higher compared to hardwoods, but located in both cases in the heartwood and responsible for smell, color, and durability (Sjöström 1981; Wagenführ 1999; Fengel 2003; Rowell 2005).

Mechanical properties of softwood

The source of strength in solid wood is the fiber itself. Wood is basically a composite of tubelike cells glued together. Each cell wall is composed of various quantities of the above mentioned polymers (cellulose, hemicellulose, and lignin). Cellulose is the strongest polymer in the cell wall and therefore mainly responsible for tensile strength due to its high degree of polymerization. The hemicellulose acts as support matrix for the cellulose and increases the packing density of the cell wall; lignin does not only hold wood cells together but also binds carbohydrate (Fengel 2003; Rowell 2005).