1 Introduction

1.1 Wood Polymer Composites (WPC)

The term Wood Polymer Composites or Wood Plastic Composites describes a new class of hybrid material that has different definitions and a broad range of constituents and applications. Different definitions cover the synthetic polymers (thermoplastic and/or thermosetting), the used natural based polymer (wood and/or agricultural crops) and the processing technique required to manufacture the composite (Kirsch and Daniel 2004; Smith and Wolcott 2005; Vogt et al. 2005; Klyosov 2007; Oksman 2008). During the last decades WPC were developed and optimized to combine the advantages of the individual components. Thus, water uptake and biological durability of the composite are superior to solid wood products (Glasser et al. 1999; Clemons 2002). The stiffness and heat stability of the thermoplastic matrices are improved after mixing it with the wooden component (Wolcott and Englund 1999; Valle et al. 2007). In general, the properties of WPC are mainly influenced by the wood content, the manufacturing process and the additives used (Mankowski and Morrell 2000; Hristov et al. 2004; Kumari et al. 2007). Almost 80% of WPC applications are polyolefin based. There are many investigations and research work on processing and formulation optimization (Clemons 2002). During the last years PVC became more important for applications with higher technical requirements. Compared to PE and PP matrices, PVC shows enhanced stiffness, creep behavior, weatherability and flame retardancy. Thus, PVC based composites can be used in building construction applications such as doors, windows or facades (Jiang and Kamdem 2004). PVC based composites need to meet high requirements in order to be applicable. Still, the compatibility of PVC and wood is higher than that of polyolefin ones, it is insufficient to reach important mechanical properties such as impact strength for the application in window frame elements. In the following, analyses of the components were conducted to understand WPC and the interactions of its constituents.

1.1.1 Wood

Wood is a complex substance that consists of lignin, hemicelluloses and cellulose (Kollmann 1951). These components are connected in a three-dimensional network and build up the wooden cell wall (Fig. 1). The cellulose-chains are organized in micelles via hydrogen bridge bonds, forming micro- and macro-fibrils. The tensile strength of the cells increases as the cellulose content increases (Niemz 1993). The hemicelluloses, composed of various 5- and 6-carbon sugars, cover the cellulose and serve as a coupling agent between cellulose and lignin (Fengel and Wegener 1989). Lignin is an amorphous macromolecule that consists of bonded hydroxyl- and methoxy-substituted phenylpropane units. It is less polar than cellulose and hemicelluloses and improves the compression strength and stiffness of the wooden cell wall (Rowell 2005).

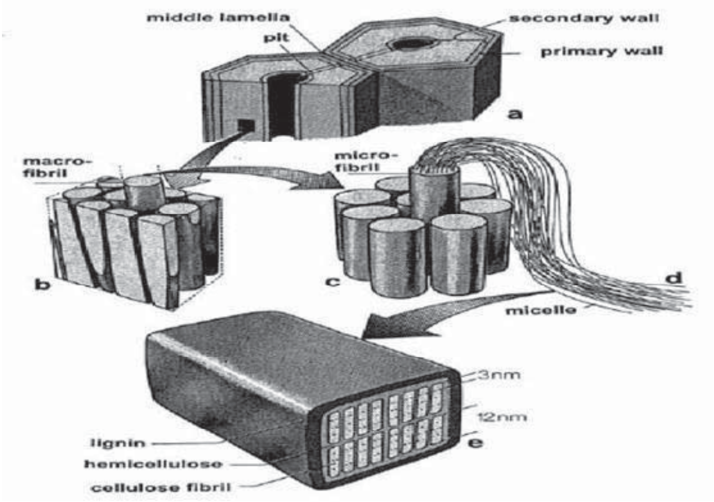

Fig. 1: Anatomical and chemical composition of the wooden cell wall (Kettunen 2006)

The hygroscopic nature of wood is due to the occurrence of free hydroxyl groups in all components, whereas hemicelluloses and amorphous parts of cellulose have higher equilibrium moisture content than the lignin (Fengel and Wegener 1989; Rowell 2005).

The moisture absorption behavior of wood makes it susceptible to fungal attack and degradation. The biological durability depends on the wood species and chemical composition, respectively. Norway spruce *(Picea abies)*, that is used in this study, has low resistance against wood destroying fungi (Fengel and Wegener 1989).

The thermal degradation behavior of wood is mainly influenced by temperature, moisture content and exposure time to high temperatures. Rowell (2005) detected onset thermal degradation of wood at approx. 250°C via thermogravimetric analysis (TGA). Hemicelluloses and Cellulose are decomposed at 400°C, the lignin content follows a more linear decomposition, starting between 200-250°C and ending above 800°C, depending on chemical structure and used thermal degradation method (Shafizadeh 1982; Brebu and Vasile 2010; Gasparovic et al. 2010). Thus, wood particles are used only in polymers that are processed at temperatures less than about 200°C (Oksman 2008).

With regard to the use in WPC, the geometry of wood particles is important in order to optimize a desired property. Wood particles can be applied in the form of fibers (aspect ratio >50), chips or flour (Jiang and Kamdem 2004; Klyosov 2007). It is reported that wood fibers reinforce the polymer matrix, whereas chips and flour act as filler and increase the stiffness of the composite (Vogt et al. 2005; Schirp and Stender 2010).

1.1.2 Polyvinyl chloride (PVC)

PVC is an amorphous, thermoplastic polymer (Fig. 2). The degree of Vinyl chloride polymerization influences the properties of PVC. With increasing molecule weight, described as K-value, mechanical properties and viscosity are increased (Osswald and Menges 1996).

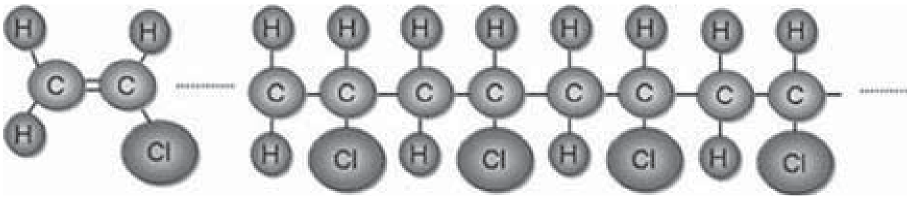

Fig. 2: Vinyl chloride and isotactic PVC (Baudrit 2007)

Besides Polypropylene (PP) and Poylethylene (PE), PVC is the third most important polymer used for WPC providing a wide range of properties and applications. The addition of plasticizer divides PVC in plasticized PVC (PVC-P) and un-plasticized PVC (PVC-U). PVC-U has a larger market share than PVC-P and is mainly used for extrusion of window- or pipe profile (Wilkers et al. 2005). Compared to polyolefins, PVC shows enhanced stiffness, creep behavior, weatherability, flame retardancy and melt strength (Becker and Braun 1985). In contrast, the thermal stability is limited. Between 160-205°C the polymer plasticizes and parameters such as the free matrix volume are regulated. The free matrix volume decreases with increasing processing temperature, leading to a more brittle polymer with decreased impact strength (Cora et al. 1999; Baudrit 2007). Above 205°C a rapid degradation of the polymer occurs, whereas the main decomposition is caused by chain stripping and dehydrochlorination of PVC (Starnes 2002).

Compared to polyolefin based composites, the wood content in PVC based WPC is limited to 50-60 weight per cent because of the higher melt viscosity of the polymer. Moreover, there are various additives required to manufacture PVC (Jiang and Kamdem 2004).

1.1.3 Additives

The most important additives in order to process PVC-U are heat stabilizers and lubricants. Due to the previously mentioned poor heat stability of PVC, organometallic-stabilizers are used to neutralize free hydrochloric acid and reduce the thermal degradation of the polymer (Wilkers et al. 2005; Baudrit 2007). Lubricants are divided into internal and external ones. While internal lubricants such as fatty acids and metallic stearates reduce the friction between the polymer chains, external lubricants such as PE-waxes reduce the friction between the melt and the processing equipment (Richter 2004; Oksman 2008). The amorphous structure of PVC-U leads to brittle fracture properties at service temperature. Impact modifiers based on chlorinated polyethylene (CPE), ethylene vinyl acetate (EVC), methacrylate-butadiene-styrene (MBS) or acrylic elastomer (ACR) are mixed with the matrix to absorb impact loads (Gomez 1984). Fillers (mainly calcium carbonate) are used to reduce the costs and increase the stiffness of the PVC-U products. The usage of the filler amounts to roughly 10 weight per cent. After hot-cool mixing, compounded neat polymer and additives are called PVC dry-blend. Since PVC and additives are mixed in the form of powder, it is favorable to use fine wood flour for WPC-processing in order to reach homogenous distribution of the components.

Besides the mentioned PVC-additives, there are coupling agents to improve the adhesion between polymer and wood particles. The most extensively used coupling agents for polyolefin based composites are maleic anhydride (MA) in modified versions, mainly grafted on a polymer backbone with various origins such as polypropylene (MAPP) and polyethylene (MAPE) (Hill 2000; Grüneberg 2010).

1.2 Wood modification

In the field of wood modification, many research activities have been conducted and practical applications of the obtained products have been explored during the last decades. The main goal of wood modification is the improvement of biological durability and various technological properties such as swelling and shrinking behavior by application of non-toxic substances. Furthermore, modified wood is expected to substitute durable tropic wood species that are harvested non-sustainable (Hill 2006; Militz and Mai 2008).

There is a wide range of chemicals and/or processes that are used to modify the wooden structure. Depending on the modification, several modes of actions can be classified (Fig. 3). The first one (3a) describes the filling of the cell lumens without changing the chemical structure of the cell wall. Typical filling of the lumen can be applied by penetrating the wood with oils and waxes (Scholz et al. 2010). In contrast the cell wall itself can be filled with modification agents (3b). Cell wall filling is required to ensure reaction (3c) and/or cross-linking (3d) between free hydroxyl groups of lignin, hemicelluloses and cellulose and the modification agent. A structural and chemical change of the cell wall is established using reactive cell wall fillers (Militz et al. 1997). To ensure a throughout penetration of the cell wall, vacuum-pressure impregnation is typically applied for solid wood. The penetration of wood flour or fibers can be realized via spraying and mixing. Chemicals used as cell wall fillers have mostly a monomeric structure during the penetration step and polymerize and/or react with the hydroxyl groups during the curing step (Krause 2006; Hundhausen et al. 2009).

Another process of wood modification is thermal treatment (3e). Hereby a decomposition of the constituents, especially the hemicelluloses, occurs and leads to a reduced amount of hydroxyl groups and therefore decreased moisture absorption and swelling (Militz 2002; Rowell 2005).

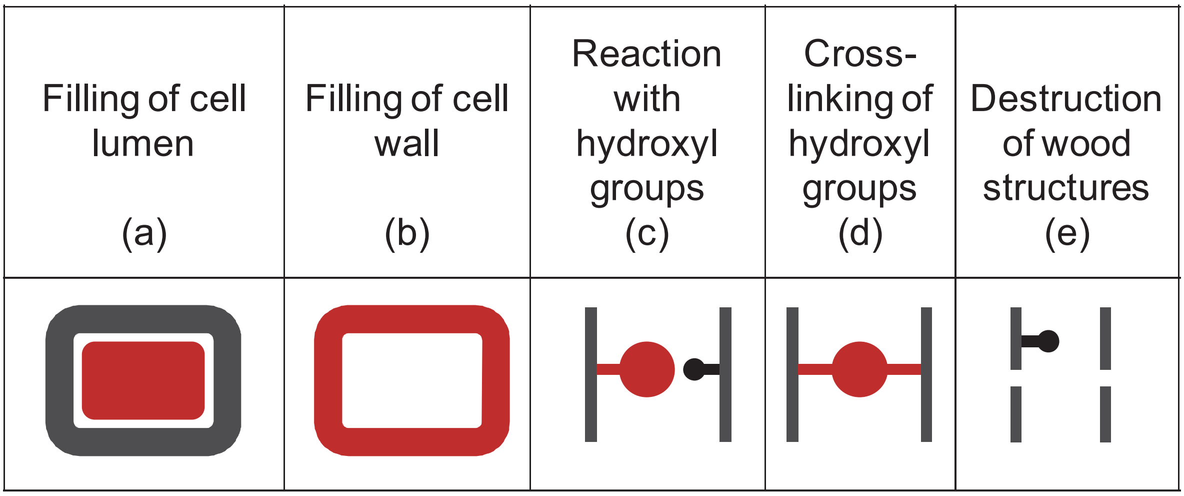

Fig. 3: Different modes of actions of wood modification: (a) Filling of cell lumen, (b) Filling of cell wall, (c) Reaction with hydroxyl groups, (d) Cross linking of hydroxyl groups, (e) Destruction of wood structures.

1.2.1 Acetylation

Acetylation causes a reaction of acetic anhydride with the hydroxyl groups of the wood constituents forming acetyl-groups and acetic acid (Beckers et al. 1994). Thus, acetylation belongs to the cell wall filling methods (3b) and leads to reactions with hydroxyl groups (3c) without polymerization of the modification agent. The acetylated groups are less susceptible to water molecules. After the reaction step, the wood is in a steady swollen state that increases the dimensional stability. Several studies reveal positive effects on water absorption and biological durability (Rowell et al. 1989; Takahashi et al. 1989; Militz 1991; Beckers et al. 1998; Brelid et al. 2000). As a function of the used degree of acetylation, the resistance to wood destroying and discoloring fungi is increased with increasing degree of acetylation (Hill et al. 2005).

1.2.2 Melamine-treatment

Reduced water absorption and increased dimensional stability can also be achieved by using methylated melamine-formaldehyde resin. The monomer is able to penetrate the cell wall structure (Rapp et al. 1999; Gindl et al. 2003). Curing of the resin depends on temperature and pH-value. During curing melamine monomers condensate, whereas methanol, water and formaldehyde molecules are split off (Jones et al. 1994; Lukowsky 2002). Since leaching effects are negligible, the thermoset remains in the cell wall (Rapp and Peek 1996). Similar to the acetylation, the melamine-treatment is known as cell wall filling method, whereby it is also detected on the lumen surfaces after curing. Treatments with melamine formaldehyde resin improve dimensional stability and biological durability of solid wood (Inoue et al. 1993).