

## 1. Summary

This study investigates the bonding properties of modified wood by considering three different aspects: water related characteristics, mechanical performance and optical (fluorescence microscopy and X-ray micro-computed tomography) observation of adhesive penetration into modified wood structure. In recent years, the new wood modifications have become more commercially available in the market for both exterior and interior applications due to improved properties that modification can bring to the wood e.g. the improved biological durability, dimensional stability, hardness and weathering resistance of the wood as well as the environmentally friendly nature of the wood modification processes (Militz and Hill 2005). Besides these advantages, modification can affect some technological aspects of the wood such as its bonding performance. For example, it can alter the strength of adhesion as a result of changes in chemical, physical and structural characteristics of the wood. For example, the less polar and less porous modified wood surfaces can result in reduced adhesion due to formation of less free -OH groups for bonding leading to poorer adhesive wetting of the wood surface and weaker chemical bonds between the two adherents (Hunt et al. 2007). As modified wood becomes a more demanded material for different applications, there is a need to study its bonding performance where the challenge is to bond different modified materials as their physical and chemical characteristics are substantially changed by modification.

In this thesis, measurements of capillary water uptake, contact angle and surface energy were used to determine the water related properties and hydrophobic behavior of furfurylated (FA40 and FA70, which represent 65 and 75 % WPGs) and N-methylol melamine (NMM) (10, 20 and 30%) modified Scots pine and thermally treated Scots pine and beech (modified through an industrial scale vacuum press dewatering method at 195 and 210 °C). The capillary water uptake results indicated a considerable reduction of water uptake for all modifications in all directions



both after short (24 h) and long contact times (168, 336 h). Contact angle measurement data revealed an increased hydrophobicity of modified wood. However, some exceptions were observed, mainly for thermally -treated wood. Modifications provided radial and tangential surfaces with a non-polar character. Penetration of adhesives into the wood structure plays an important role in the production of glued wood-based panels and products by affecting the bond quality (Frihart 2005, Kamke and Lee 2007). The gross penetration of emulsion polymer isocyanate (EPI), polyurethane (PU) and polyvinyl acetate (PVAc) adhesives into modified wood, both with and without pressure, were determined by using fluorescence microscopy based on measurements of effective (EP) and maximum penetration (MP). Without application of pressure, the EP of EPI adhesive reduced after NMM modification and furfurylation (FA70) and also PU adhesive after NMM modification while the EP of PVAc adhesive increased into furfurylated and NMM modified (10 and 20%) wood. For thermally treated Scots pine, increasing the treatment temperature improved EP of all adhesives. Among used adhesives, PU penetrated much deeper into thermally -treated wood for both treatment temperatures. Comparison of penetration of adhesive with and without pressure revealed that with the exception of EP of PU and EPI adhesives into NMM-modified wood and PVAc into thermally treated beech at 195°C, application of pressure led to rather different results as compared to the EP data when no pressure was applied. Visual observation and analysis of fluorescence microscopy photomicrographs provided more detailed information on modality of penetration. Due to the large and deep penetration of PU adhesive into thermally treated Scots pine observed in both studies (with and without pressure), the 3D pattern of penetration of this adhesive was obtained by X-ray micro-computed tomography indicating the pathways which were used by this adhesive for penetration. In another study, the bonding shear strength of the same modified wood materials glued with the same adhesives was also investigated. For all adhesives used, the shear strength significantly

reduced after furfurylation and NMM modification of Scots pine samples, mainly due to the brittle nature of the wood after modification rather to the failure of the bondline. Bonding strength of both Scots pine and beech was also negatively affected by thermal modification and the bondline was found to be the weakest link in thermally modified wood. The EP of adhesives and the bondline thickness did not relate to the shear strength of all modified wood materials. It was indicated that the lower shear strength of modified wood could be attributed to other factors, such as the decreased chemical bonding or mechanical interlocking of adhesives, and the reduced strength of brittle modified wood substrate.

The effect of two important bonding variables, wood moisture content and open assembly time on penetration of PU adhesive into thermally modified wood (195 and 210 °C) was also studied. The equilibrium moisture content (EMC) level of 8.6% was found to be the optimum for an effective penetration of PU adhesive in thermally modified Scots pine treated at 195°C. In most of the cases, penetration of PU adhesive did not change significantly by increasing the open assembly time, which suggested using a shorter open assembly time of 15 min than 30 min for bonding of thermally modified Scots pine with PU adhesive, in order to save time and reducing the production costs. For samples treated at both treatment temperatures and after shorter open assembly time, the highest MP values observed at moderate EMC levels of 8.6 and 8.2% and the lowest at the higher EMC levels of 13.2 and 12.5%.

In another study, the effect of phenol formaldehyde (PF) treatment on bonding performance of beech glued with PVAc and phenol resorcinol formaldehyde (PRF) adhesives was also investigated. The results of both dry and wet conditions indicated higher shear strength for samples bonded with PRF than PVAc. With the exception of 25% PF treated wood bonded with PVAc, the PF modified wood can be glued with both adhesives satisfactorily under dry condition, while under wet condition only the 25% PF modified samples bonded with PRF provided



acceptable bonding. For both adhesive systems, PF modification caused a reduction of adhesive penetration into wood structure, especially in the case of higher load treatment.

The development of bonding strength of modified birch veneers glued with hot curing phenol formaldehyde (PF) adhesive was investigated in different pressing (20 s , 160s) and open assembly times (20s , 10 min). Generally, the bonding strength improved by extending the pressing time. In 20 s pressing, increasing assembly time did not change the bonding strength in most of the cases while at 160 s pressing, prolongation of assembly time developed a better bonding for controls, NMM modified and thermally treated veneers at 180°C. The combination of 10 min assembly time and 160 s pressing time provided the highest bonding strength for controls, NMM modified and thermally treated veneers at 180°C while furfurylated samples achieved the highest values in 20 s assembly and 160 s pressing times. In general, modification affected negatively the bonding performance of the veneers, especially for furfurylated and NMM modified samples. In General, the overall results obtained in this thesis showed that modified wood has lower bonding ability and performance than unmodified wood as result of the decreased water related properties, less penetration of adhesive into wood structure and decreased bonding strength after modification. However, the increased dimensional stability and low water uptake of modified wood might lead to better performance in long term.



## **2. Introduction**

### **2.1. Wood and adhesion**

#### *2.1.1. Wood; a natural, renewable raw material*

Wood is the most frequently used building material in the world for centuries. It is a widely distributed, renewable and multifunctional substance, with a high aesthetic value, strong owing to its high strength to weight ratio and easy to process. Wood is a porous and anisotropic material with various anatomical features. It is varied in species, characteristics and uses. Due to wide range of wood applications, it can be found in our modern living environment almost everywhere and it can be produced and used in a sustainable manner according to its renewable nature. Wood products are made using tools, nails and screws and also by cutting wood into smaller size components and re-joining by adhesives or combining with other materials. They can be ranged from simple handmade wooden furniture to highly engineered wood products manufactured in a highly automated production site.

#### *2.1.2. Furniture and building constructions*

Among different wood products, the glued wood products have an important share in furniture and construction markets and adhesive bonding of the wood is known as the most important joining technique to connect wooden elements to each other in modern wood construction and timber engineering (Kamke and Lee 2007). A quick look to the vast applications of the glued wood products in interior and exterior decoration e.g. in production of facades, wood partition walls, cabinets and in production of the home and office furniture, chairs and tables, closets, library shelves and in building constructions e.g. structural wood columns, prefabricated walls,

stairs, fencing, decking and flooring, attics, garages, window frames, doors, kitchen design, and isolation boards indicates the importance of the adhesion and bonding matter of the wood.

### *2.1.3. Adhesion background and theories*

Adhesion is defined as the situation, in which two surfaces of adherents are kept together by interfacial forces e.g. valence forces, interlocking action, or both (Vick 1999). The history of adhesive bonding dates back to early mankind and Egyptians were cited as the first mankind who bonded wood (Skeist and Miron 1990, River 1994, Keimel 2003, Frihart 2005). There are several mechanisms involved in adhesion such as mechanical interlocking, covalent bonding and secondary interactions e.g. hydrogen bonds and the process of adhesive bond formation in the wood is divided into flow, transfer, penetration, wetting, and solidification steps. The flow is described as spreading of the liquid adhesive along the external wood surface. The transfer refers to the movement of the liquid adhesive to the next wood surface during assembly time and penetration happens due to capillary forces within the cell lumens and bulk flow as result of applied pressure. Wetting, the relative ability of liquid glue to perform interfacial affinity for an adherent, applies on wood surface and causes a uniform flow of adhesive along the walls of the cell lumens. In the last step, which is called solidification, the adhesive transforms into a rigid polymer through polymerization process (Marra 1992, Sernek et al. 1999). As suggested by Marra (1992), an adhesive bond can be also supposed as a chain-link including nine attached links where the maximum strength of the bondline is determined by the weakest link of the chain (Figure 1). According to this plot, link 1 represents the pure adhesive part which is located in middle of the bondline, links 2-3 exhibit the nonhomogeneous and partly cured boundary layer of adhesive, and links 4-5 stand between this boundary layer and the wood material. These later two links represent the adhesion mechanism, e.g. mechanical interlocking, covalent bonding, or

secondary chemical bonds as mentioned before. Links 6-7 represent the wood substrate affected by the wood surface preparation or bonding processes, and links 8-9 represent the non-interacted wooden material. Penetration of adhesive affects links 4 through 7, and consequently all possible adhesion mechanisms. The volume including both wood cells and adhesive is called interphase region and the two adherent substrates, each with its own interphase, and the interface between the substrates, form the bondline (Kamke and Lee 2007).

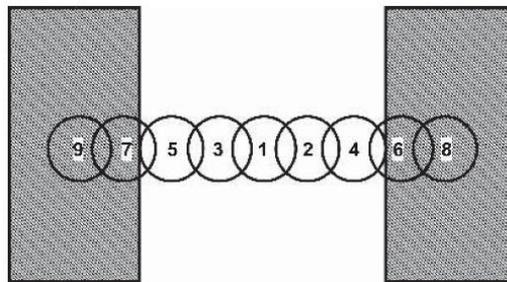


Figure 1: Chain link plot suggested by Marra for an adhesive bond in wood (Kamke and Lee 2007)

Table 1 exhibit the accessibility of the main wood constituents, cellulose, lignin, and hemicellulose to the adhesive for bonding and their involvement to the hydrogen bonding. As can be seen in this table, although hemicellulose is a less abundant constituent of the cell wall, it is quite accessible for bonding and hence it has more contribution than cellulose and lignin.



Table 1: Accessibility of the main wood constituents and their involvement to hydrogen bonding

	<b>Constitution of cell wall (%)</b>	<b>Accessibility for bonding (%)</b>	<b>Involvement in bonding (%)</b>
<b>Cellulose</b>	50	35	17.5
<b>Hemicellulose</b>	24	100	24
<b>Lignin</b>	26	30	7.8

(Salehuddin 1970, River 1991)

#### 2.1.4. Influencing factors on bonding

The influencing factors on bond quality are mainly classified in three groups: wood (e.g. species, cutting direction, free surface energy and moisture content of the wood), adhesive (e.g. type, formulation, molecular weight and viscosity) and process related factors (e.g. open assembly time, pressing time, pressure and temperature). These bonding variables have an interplay effect on each other, which determines the final cost of production and the ultimate bonding quality. For example in many cases, higher load or temperature of pressing might lead to higher bonding quality which can also increase the production costs. Therefore, it is essential to have an optimal combination of these bonding factors, both to meet customer's needs by increasing the quality of the product and also to decrease production costs. Service related factors can be also considered as another group of bonding variables. More detailed information are given in Table 2 (Frihart 2005).

Table 2: Influencing factors on bonding

<b>Resin</b>	<b>Wood</b>	<b>Process</b>	<b>Service</b>
Type	Species	Adhesive amount	Strength
Viscosity	Density	Adhesive distribution	Shear modulus
Molecular weight	Moisture content	Relative humidity	Swell—shrink resistance
Mole ratio of reactants	Plane of cut: radial, tangential,	Temperature	Creep
Cure rate	Heartwood vs. sapwood	Open assembly time	Percentage of wood failure
Total solids	Juvenile vs. mature wood	Closed assembly time	Failure type
Catalyst	Earlywood vs. latewood	Pressure	Dry vs. wet
Mixing	Reaction wood	Adhesive penetration	Modulus of elasticity
Tack	Grain angle	Gas-through	Temperature
Filler	Porosity	Press time	Hydrolysis resistance
Solvent system	Surface roughness	Pretreatments	Heat resistance
Age	Drying damage	Posttreatments	Biological resistance: fungi, bacteria, insects,
pH	Dirt, contaminants	Adherend temperature	Finishing
Buffering	Extractives pH		Ultraviolet resistance marine organisms
	Buffering capacity Chemical surface		

(Frihart 2005)

### 2.1.5. Evaluation methods

Bonding performance of the wood can be examined considering different aspects e.g. by investigation of the physical, chemical and water related properties of the surface of wooden adherent, via mechanical testing of the adhesive joints and glued assemblies and by optical observation of the bondline and adhesive penetration into wood structure. In each category, various methods can be employed to evaluate bonding properties. The physical and chemical conditions of the wood surface are very important to reach a satisfactory bonding performance since adhesives join to the wood by surface attachment. Polarity, surface energy and the amount of extractives on the wood surface have influence on wettability of the wood surface and hence its bonding (Nussbaum 1999, Vick 1999). For example, according to the wetting or adsorption theory the less polar and in some cases less porous wood surfaces can lead to reduced adhesion as result of poorer adhesive wetting of the wood (Hunt et al. 2007). The wettability of wood can be



determined through measurement of the contact angle, surface free energy and work of adhesion using parameters which describe the molecular polar or non-polar interactions between liquids and solids (Mantanis and Young 1997, de Meijer et al. 2000, Wålinder and Bryne 2006). Contact angle measurement is a useful method to appraise the solid-liquid interfacial forces. It can be performed by using the Wilhelmy, the rising height, and the sessile drop methods (Pétrissans et al. 2003, Bryne and Wålinder 2010). Estimation of the water uptake and water vapor sorption ability of the wood is another useful method to predict the similar uptake of the liquid adhesive by the wood tissue due to its porous nature and capillary forces. Using different methods, water uptake and water vapour sorption properties of the wood have been investigated in several studies (Donath et al. 2006, Ghosh et al. 2009, Scholz et al. 2009, Johansson and Kifetew 2010, Xiao et al. 2010, Xie et al. 2010, Ghosh et al. 2013, Pries et al. 2013).

Generally, it is expected that an adhesive should be able to keep materials together and to transfer the loads from one adherent to the other one. Mechanical testing of the bonded joints and assemblies are used in order to predict the performance of wooden structures under long term stress and can be divided into four major stressing modes; shear, tensile, cleavage, and peel (Vick 1999). Among mentioned modes, shear mode was taken into consideration in several studies and usually is expressed along with the amount of wood failure of the bondline (Vick and Rowell 1990, Frihart et al. 2004, Brandon et al. 2005, van der Zee et al. 2007, Kurt et al. 2008, Sahin Kol et al. 2009).

The wood–adhesive interface, bondline and adhesive penetration can be monitored in several ways e.g. by optical microscopy of cross-sections and micro-slides (Johnson and Kamke 1992, Sernek et al. 1999), scanning electron microscopy (Koran and Vasishth 1972, Saiki 1984), energy-dispersive X-ray analysis (Smith and Côté 1971, Bolton et al. 1988), scanning thermal microscopy (Konnerth et al. 2008), UV-microscopy (Gindl et al. 2002), energy loss spectroscopy