CHAPTER 1 GENERAL INTRODUCTION

1 Introduction

The application of wood and wood products has a long history and tradition. Wood is an environmentally friendly material, because it is recyclable, CO_2-neutral and sustainable. It is versatile applicable and is of high natural aesthetics.

Wood is a heterogeneous, anisotropic and hygroscopic material (Kollmann 1951). In comparison to other materials such as plastic or metal, wood particularly used at high moisture conditions and in outside exposure, has many limitations such as shrinking and swelling at alternating moisture conditions, limited biological resistance and UV-stability and a tendency to surface discoloration. Due to these material properties, the use of the economically important wood species such as Scots pine (*Pinus sylvestris* L.), Spruce (*Picea abies* L.) and Beech (*Fagus sylvatica* L.) in central and northern Europe is limited for outside applications (EN 350-2 1994). In the past, these limitations were overcome by either using tropical wood species with a high natural durability or the treatment of home growing wood species with biocidal wood preservatives. The use of tropical wood species has contributed to the tropical deforestation resulting in a decrease of the quality and the quantity of available species. Furthermore the use of wood preservatives containing toxic metal compounds is limited nowadays because of its high environmental and health relevance (Jermer and Englund 1990, Wöss 1990). Therefore, new strategies of wood protection are in the main focus which includes biocide treatments of lower toxicity and wood modification processes.

1.1 Wood protection

Wood species with a low natural durability and resistance against degradation by microorganisms which are exposed outside or at high moisture conditions have to be protected against wood inhabiting microorganisms. Beside the performance of the construction (wood protection by design), chemical treatments are often necessary. A preservative chemical treatment of wood should achieve the following requirements:

- High efficacy against wood inhabiting organisms
- Nonhazardous to humans and other non-target organisms
- Environmentally friendly including disposal and recycling at the end of the life cycle of the product
- Permanent and stable for the life cycle of the product

To protect wood in service, different strategies have been described. In the last decades very efficient biocidal treatments have been used. Conventional wood preservatives contain toxic substances which inhibit the degradation of wood by inhabiting microorganisms. These active ingredients of preservative formulations have a direct impact of the target organisms. These include the denaturation of proteins, inactivation of enzymes and cell membrane disruption (Eaton and Hale 1993). Within the last years, basic compounds of efficient conventional wood preservatives have been restricted for most applications due to their high mammalian and environmental toxicity such as pentachlorophenol (PCP), formulations including mercury or arsenic and creosotes (ChemVerbotsV 1993). Further additives such as chromates are under discussion due to new regulations for the registration and use of biocides and chemicals. These new regulations such as the **B**iocidal **P**roduct **D**irective (BPD) and the **R**egistration, **E**valuation and **A**uthorisation of **CH**emicals (REACH) aim for a harmonization of the EU market for biocidal products and their active substances as well as a degree of protection for humans, animals and the environment. Therefore, the development of efficient biocidal wood preservatives with less toxicity is in the main focus. Beside the development of less toxic wood preservatives, new strategies for wood protection have been developed in the last years. These new strategies of wood protection focus on modifying the wood properties itself without biocides to prevent biological degradation, improve dimensional stability and weathering resistance. These techniques are termed as wood modification (Hill 2006).

1.2 Wood modification

Wood modification includes chemical and thermal treatments (Schmid et al. 2001, Hill 2006). The objectives of wood modification are the improvement of wood properties particularly the dimensional stability, the resistance against degradation caused by biological attack and weathering agents (Rowell 1983, Militz et al. 1997).

Different modification methods were in the focus of scientific research within the last years which are partly available on the market nowadays. Heat treatment, acetylation, furfurylation, modification with 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU), melamine and different silane and silicone formulations were intensive investigated (Rowell 1983, Beckers et al. 1994, Militz 1997, Westin et al. 1997, Leithoff and Peek 1998, Welzbacher and Rapp 2002, Donath 2004, Weigenand 2006, Ghosh 2009).

Wood modification is based on the inclusion of chemicals in the wood cell walls. In wood, the hydroxyl groups of the cellulose, hemicelluloses and lignin are the main reactive parts. Modification agents can be chemically bonded or fixed mechanically within the cell wall (Militz et al. 1997, Rowell 2005, Hill 2006). Wood modification in the broadest sense also includes treatments without any reaction with the cell wall polymers. Generally, wood modification can be categorised according to the localisation of the chemicals within the wood cells (Militz and Mai 2008):

1. Localisation in the wood cell wall, bonding of the chemical to the cell wall polymers, mainly by OH-groups
2. Localisation in the lumen of the wood cells, filling and partly fixation
3. Localisation in the wood cell wall, impregnation of the cell wall and partly fixation

The inclusion and fixation of chemicals in the wood cells affects the wood properties such as decay resistance, mechanical strength properties, dimensional stability, weathering resistance and resistance against mould and staining fungi. However, none of the different modification systems and processes is beneficial to all properties. Hence the selection of chemicals and processes has a great importance for the application of modified wood and furthermore for the investigations of specific wood properties such as resistance against wood degrading fungi as well as mould and staining fungi. Therefore, the main focus was on the following points for the chemical selection within this study:

- Localisation of chemicals within the wood cells, chemicals which are bonded to the cell wall polymers or localised in the cell lumens
- Potential to affect the growth patterns of mould and staining fungi and improve the resistance against these fungi

DMDHEU, an oligomeric siloxane and water glass were selected as modification chemicals. DMDHEU reacts with the cell wall polymers, mainly via OH-groups and is located in the wood cell wall predominantly. Siloxane and water glass are mainly located in the cell lumens. Furthermore the selected treatments improve the resistance against wood degrading organisms (van Acker et al. 1999, Krause et al. 2004, Donath et al. 2006, Dellith 2006, Bollmus 2010) and might potentially improve the resistance against mould and staining fungi.

1.2.1 DMDHEU

The chemical 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) is a cyclic N-methylol compound (Figure 1) which was originally developed and used for the textile industry to modify mainly cotton and jute textiles. According Petersen (1983) DMDHEU improves the wrinkling properties of textiles, the dirt repellency and the fixation of colourants and different additives.

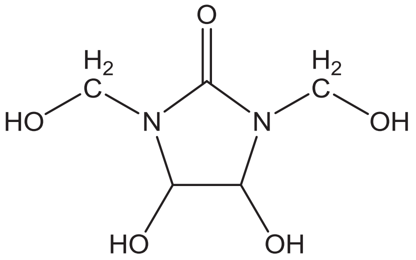

Figure 1: Dimethyloldihydroxyethylenurea (DMDHEU)

During wood modification processes in the presence of an acid catalyst (in this study magnesium chloride) the N-methylol groups of the DMDHEU react. This reaction results in a formation of a resin cross-linking with the hydroxyl-groups (OH-groups) of the wood cell wall through ester bonds (Hill 2006). Other reactions are the hydrolysis of the N-methylol groups which result in the formation of formaldehyde and amide groups (NH-groups) and the condensation of NH-groups with N-methylol groups. Due to the different reactions the DMDHEU can react with OH-groups of the wood cell walls but also forms self-polycondensates within the cell wall (Petersen 1968, van der Zee et al. 1998).

Wood modified with DMDHEU shows a permanent increase in volume characterized as bulking effect (Xie 2005, Krause 2006), which indicates a penetration of the DMDHEU into the cell wall. Furthermore the nitrogen content of wood is increased after a DMDHEU treatment, which indicates also a fixation of the chemical into the cell wall (Schaffert 2006, Wepner 2006). Untreated wood contains only traces of nitrogen.

The treatment with DMDHEU increases the dimensional stability. Different investigations showed an Anti Swell Efficency (ASE) between 35% and 70% depending on the concentration of DMDHEU and furthermore type and concentration of catalyst (Militz 1993, van der Zee et al. 1998, Krause et al. 2003). Furthermore DMDHEU treatment improves the resistance against biological attack (Militz 1993, Yasuda and Minato 1994, Sudiaynni et al. 1996, van der Zee et al. 1998, Wepner 2006, Krause et al. 2008). A DMDHEU treatment can reduce fungal colonisation and the mass loss caused by fungal decay without any biocide effect (Verma et al. 2008). The durability of DMDHEU modified Scots pine sapwood (*Pinus sylvestris* L.) and Beech wood (*Fagus sylvatica* L.) was enhanced in laboratory tests against wood destroying basidiomycetes according EN 113 and in soil bed tests according ENV 807 (van

Acker et al. 1999, Krause 2006). The specimens were treated with 10 and 20% DMDHEU and tested against the resistance of *Trametes versicolor*, *Poria placenta, Gloeophyllum trabeum* and *Coniophora puteana*. The resistance was increased with increasing concentration of DMDHEU. The mass loss after an EN 807 test against soft rotting micro-fungi was decreased (average 0.9%) for DMDHEU specimens, treated with 20% DMDHEU (van Acker et al. 1990).

DMDHEU treatment of thin veneers strips partially reduced the degradation of lignin and cellulose and stabilized the wood cell walls during artificial weathering (Xie et al. 2005). Compared to unmodified wood, less superficial damage after outside exposure was observed in wood modified with DMDHEU and coated with different systems (Xie et al. 2005a, 2008). DMDHEU modified veneers and plywood of Beech showed a decreased photo oxidative degradation, but no inhibition of these processes. The treatment revealed no influence of the growth of sapstaining fungi (Wepner 2006).

Since 2006 DMDHEU modified wood is commercial available on the market and is produced by BASF SE (Ludwigshafen, Germany). The impregnation is carried out by vacuum-pressure impregnation and a subsequent curing step under hot steam conditions. Furthermore, DMDHEU treated three dimensional shaped wood is produced by Becker KG (Brakel, Germany).

1.2.2 Silanes

Silicon compounds with the general formula Si_nH_{2n+2} are called silanes. The group of silanes contains also compounds where the hydrogen atoms are substituted by organic or inorganic groups, such as alkyl, alkoxy or chloride groups. Silanes are known as modification agents in plastic-, textile-, building- and paper-industries. They are often used for the realisation of hydrophobation against liquid water of different materials such as concrete while the material remains open to moisture exchange.

Silanes in general have a high potential for wood modification processes because of their high diversity of chemical and physical properties. A review of different silicones and silicone compounds which had been used for wood modification is given by Mai and Militz (2004, 2004a). Different types of silanes were investigated in further studies. Beside different silane systems such as ethoxy groups containing (TEOS) and alky-functional groups containing (MTES, PTEO) silane systems, amino-functional siloxanes were tested within the last years. Depending on the siloxane system different properties of treated wood will be influenced, such as fire retardance, resistance against brown and white rot and water uptake (Saka et al. 1992, Goethals and Stevens 1994, Donath 2004).