

Modification of wood by chemical processes: A review

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Abstract: Very important developments in the area of wood modification have been made during the last five decades. These developments can be attributed to the increased environmental concerns, the escalating demand for a high quality of wood products, and the rising prices of the durable tropical timbers, as affected by the illegal logging. As a consequence, a number of wood modification techniques such as chemical and impregnation modifications, by chemical processes, have been introduced, and some of these technologies have reached the industrial level. This review paper discusses the most important chemical processes of wood modification as of today.

Keywords: Wood modification, Acetylation, Furfurylation, Resin impregnation, Impregnation modification of wood, Monomer impregnation

1. Introduction

Wood has been utilized by humans for many centuries, mainly for fuel, shelter, weapons, tools, and furniture. As a material, wood is considered to be easy-to-work, renewable, readily available, and sustainable. For the most part, it has been used without any modification (Rowell 2014). Solid timber and lumber long have been treated for decay and fire resistance, as recorded in ancient, historic sources. Nonetheless, most modern applications of wood involve little treatment, mostly limited to coatings or finishes (Rowell 2016).

Humans have learned to use wood, accepting that it changes dimensions with changing moisture content, or in contact with water (Mantanis *et al.* 1994). It can be degraded by a wide variety of microorganisms, it burns, and it is decomposed by ultraviolet energy (Stamm 1964; Rowell 1983). With an increased awareness of the fragility of the environment and the need for durability in wood products, new technologies have been developed to increase the service life of wood without the use of toxic chemicals (Rowell 1983, 1984; Miltz 1991; Westin 1996; Hill 2006; Rowell *et al.* 2009; Rowell 2012; Gérardin 2016). Issues of sustainability and carbon sequestration converge in this search for new 'green' technologies to improve durability, stability, and performance of wood, especially in exterior applications (Rowell 2016).

In addition, the progress of regulations in Europe, North America, and elsewhere, on the use of biocide products, has led to novel developments in the field of wood modification (Gérardin 2016). This has led to an increasing attention for non-biocide treatments including chemical modification, thermal modification, or impregnation modification, in an attempt to face the forthcoming prohibition of biocide-treated products (Hill 2006; Rowell 2012). Through chemical modification of wood, low-durability species can be upgraded to new modified wood products with advanced properties, without any deleterious effects to the natural environment or to the human beings (Hill 2006; Rowell 2014).

It should be noted in here that most of the processes developed, or today being under experimentation, in the area of wood modification have full or partial origins based upon the pioneering research and seminal work of Dr. Alfred J. Stamm and his co-workers of the Forest Products Laboratory at Madison, Wisconsin, back in the '40s and '50s.

This work reviews on the present technologies of wood modification by chemical processes and focuses mostly on the two processes which have reached in the industrial-scale level.

2. Modification of wood by chemical processes

Chemical modification of wood takes place when a chemical reaction of a reagent occurs with the polymeric constituents of wood (lignin, hemicelluloses, or cellulose), resulting thus in the formation of a stable covalent bond between the reagent and the cell wall polymers (Rowell 1982, 1983; Hill 2006).

In general, chemical modification of wood can be regarded as an active modification because it results in a distinct chemical change in the macromolecules of the cell wall. Currently, much is known about the modes of action of modified wood, which includes the following: i) the equilibrium moisture content is lowered in modified wood, and hence it is harder for fungi to obtain the moisture required for decay; ii) there is a physical blocking of the entrance of decay fungi to micropores of the cell walls; and/or, iii) inhibition of the action of specific enzymes (Hill 2006; Rowell *et al.* 2009; Rowell 2012). These three are only parts of the whole mechanism (Mantanis 2017).

Several chemical technologies of wood modification are reviewed, and briefly discussed in the following sections.

2.1. Acetylation of wood

The first recorded experiment of wood acetylation was carried out in Germany by Fuchs (1928) using the chemical agent acetic anhydride, with sulphuric acid as a catalyst. Horn (1928) also acetylated beech wood, but in order to remove hemicelluloses in a similar lignin isolation procedure. Tarkow was actually the first scientist who described the use of acetylation process in an attempt to stabilize wood from swelling in the water (Tarkow 1946; Tarkow *et al.* 1946). Since the '40s, many laboratories worldwide have performed experiments on the acetylation of wood in a variety of different ways, and by using various wood species and agricultural resources (Rowell 1983, 1984).

Early attempts to commercialise the process of wood acetylation failed in the USA (Koppers Inc. in 1961), Russia (1977), and Japan (Daiken Inc. in 1984) due to the high production costs involved (Rowell 2012). Pioneering work in scaling-up laboratory acetylation to the semi-industrial level, was successfully carried out at Stichting Hout Research (SHR, The Netherlands) by Prof. H. Militz and his coworkers during the '90s (Militz 1991; Beckers and Militz 1994; Beckers *et al.* 1994).

Wood acetylation, using primarily acetic anhydride, has been initially carried out as a liquid phase reaction (Rowell 1983, 1984). The early work was initiated using acetic anhydride catalyzed by zinc chloride or pyridine (Tarkow 1946). Through the years, many other catalysts have been evaluated, both with liquid and vapour systems. Some of the catalysts used include sodium acetate, potassium acid, urea-ammonium sulphate, magnesium persulfate, and dimethylformamide (Rowell 1983). Most acetylation reactions today are realized without the use of a catalyst (Rowell 2012; Larsson-Brelid 2013).

The reaction of acetic anhydride with wood polymers results in the esterification of the accessible hydroxyl groups in the cell wall (Rowell 1983), with the formation of a by-product, acetic acid (Fig. 1). The by-product is, for the most part, removed from the final modified material (Lankveld 2017) as the human nose is quite sensitive to the odour of acetic acid. Like untreated wood, acetylated wood is comprised only of carbon, hydrogen, and oxygen, and it contains absolutely nontoxic constituents (Hill 2006). In fact, acetylation of wood is a single-addition chemical reaction (Rowell 1984; Rowell *et al.* 1994) which means that one acetyl group is on one hydroxyl group without any polymerisation (Fig. 1).

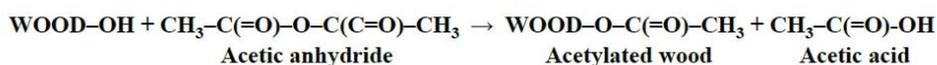


Figure 1. The main acetylation reaction of wood with acetic anhydride (Rowell 1983)

Many scientists today believe that wood acetylation reduces the number of hydroxyl groups (-OH) that can sorb moisture by hydrogen bonding so the equilibrium moisture content and fibre saturation point are largely reduced. Hence, the dimensional stabilisation of wood increases with increasing weight gain due to acetylation reaction (Rowell *et al.* 1994, Rowell *et al.* 2009, Larsson-Brelid 2013, Rowell 2016). Other scientists like Prof. Hill and others (Papadopoulos and Hill 2003, Hill 2006, Jones and Hill 2007, Papadopoulos 2010) favour another mechanism, that is: by modifying wood with acetic anhydride, it is observed that the dimensional stabilisation is related closely to the weight percentage gain (WPG) or bulking of the cell wall. As a consequence, the extent of OH- substitution is rather irrelevant.

As far as it concerns the biological resistance, several theories have been proposed to explain the high resistance of acetylated wood to fungal attack. One theory, that has gained large acceptance, is based on the fact that enzyme penetration is prevented by physical blocking of the cell-wall micropores (Papadopoulos and Hill 2002, Hill 2006, Hill 2009). In an agreement with the above, Highley *et al.* (1994) have showed that the smallest enzyme of a brown-rot fungus is too large to penetrate the cell wall of wood.

On the contrary, Prof. Rowell has postulated that the mechanism of decay resistance in acetylated wood is clearly based on 'moisture exclusion' owing to the fact that the equilibrium moisture content of a highly modified wood is too low to support fungal attack, i.e., there are not enough water molecules at the site of a glycosidic bond, which the fungal enzymes need for hydrolysis (Rowell 2006, Rowell *et al.* 2009). Rowell (2014) in his recent review, supports the idea that in the case of brown-rot fungal attack, the reduced moisture of acetylated wood prevents the fungus from initiating the breakdown of the hemicelluloses as an energy source. Mohebbi (2003) in his interesting doctorate work, speculated a third possible mechanism, that is: there are possibly very small regions in the cell wall that are not acetylated owing to the size of the acetate group itself. In consequence, these regions are accessible to the free radicals generated by the fungi. Hill (2009) in his review concluded that the substrate recognition effects were very unlikely to be of importance given the inherent lack of enzyme accessibility; thus, the reduced cell-wall water content was considered to be the most likely mechanism for the high biological resistance of acetylated wood.

However, recent research works (Ringman *et al.* 2015, Alfrendsen *et al.* 2015) have demonstrated that the mechanism of substrate recognition by the fungus should be considered as very important, in combination with the lowered moisture content as distributed within the wood matrix.

According to Prof. Rowell, during the acetylation process, wood material at 100 to 120°C reacts with acetic anhydride in the absence of catalyst, and at an acetyl weight gain of 16% to 19%, approximately 90% of the lignin is esterified and 25% of the hemicellulose (Rowell *et al.* 1994; Rowell 2012). As expected, 100% of the hydroxyl groups in the hemicelluloses, which are readily accessible, are substituted. It has been shown that lignin is the most reactive constituent of the cell wall during the acetylation reaction (Rowell *et al.* 1994).

Acetylated wood is presently commercialised by the company Accsys Technologies in Arnhem, The Netherlands. It is marketed under the commercial name Accoya®, utilizing mainly the species radiata pine (*Pinus radiata*) and alder (*Alnus* sp.), and technically, on the average, has a 20% acetyl weight gain. Annually, approximately 40,000 m³ acetylated timber is produced by Accsys (2017), while the company will increase its capacity to 60,000 m³ in the year 2018 (Mantanis 2017). Accoya wood is today available in many countries, and its main uses are for exterior windows and doors, decking, cladding, and civil construction mainly in outdoors, above- and in-ground contact (Mantanis 2017).

Today, the acetylation process, as applied in liquid phase, yields chemically modified timber that has considerably improved physical, mechanical, and biological material properties (Hill 2006; Jones and Hill 2007; Rowell *et al.* 2009; Larsson-Brelid 2013; Alexander *et al.* 2014; Gérardin 2016), which are presented below.

- The biological durability of wood (EN 350: 2016) is improved to the highest durability class ('class 1'), which corresponds to the very durable tropical species teak (*Tectona grandis*) and merbau (*Intsia* spp.), as originating from the natural tropical forests. Acetylated wood exhibits considerably increased biological resistance to brown- and white-rot fungi (Larsson-Brelid *et al.* 2000; Papadopoulos and Hill 2002; Mohebbi 2003; Mohebbi and Militz 2010; Rowell 2012; Larsson-Brelid 2013; Alexander *et al.* 2014; Rowell 2016).
- Acetylated wood, at ca. 20% loading, obtains a fiber saturation point below 15%; thus, the cell wall becomes highly hydrophobic (Papadopoulos and Hill 2003; Hill 2006; Rowell 2012). Consequently, swelling and shrinkage properties are reduced by 70% to 75% as compared to untreated wood (Jones and Hill 2007; Rowell 2012). The reason for that is simply because the cell wall is filled with chemically bonded acetyl groups that take up space within the cell wall (Rowell 1983; Rowell *et al.* 1994; Hill 2006; Jones and Hill 2007).
- Accoya wood at high acetyl loading is very resistant to subterranean and Formosan termites (Alexander *et al.* 2014). This field study against termites verified the high resistance of acetylated material to attack by termites.
- Acetylated pine wood with high acetyl loading (>20% acetyl weight gain) has been shown to provide excellent resistance to borer attacks even after 11 years of field exposure; *i.e.*, in better order than chromium copper arsenate (CCA) impregnated pine wood (Westin *et al.* 2016). It is believed that acetylated wood at high loading can be confirmed as marine-borer resistant timber for long periods of time.
- An increase of 15% to 30% of hardness of the material can be reached (Rowell 2012).
- The acetylation treatment has no negative impact on the strength properties of wood (Jorissen and Luning 2010; Bongers *et al.* 2013; Larsson-Brelid 2013).
- Acetylated wood is marketed today as a 'green' product with several environmental benefits (Jones and Hill 2007; Lande *et al.* 2008; Van der Lugt *et al.* 2016). According to a recent study of Van der Lugt *et al.* (2016), acetylated wood has considerably lower carbon footprint than steel, concrete, and unsustainably sourced azobé. In fact, Accoya wood does have CO₂ negative life-cycle-analysis over a full-life cycle.

Recently in Germany, Accoya wood has gained acceptance for use in exterior windows by the German Association of Windows and Facades (VFF).

2.2. Furfurylation of wood

Research relating to chemical modification of wood with furfuryl alcohol (C₅H₆O₂), which has been referred to in the literature as 'furfurylation of wood', was initiated by Goldstein and Stamm (Goldstein 1959; Stamm 1977). By using cyclic carboxylic anhydrides, mainly maleic anhydride, as key catalysts, furfurylated wood, having properties superior to those produced with the early developed systems, was achieved by Prof. M. Schneider (1995) in Canada. Novel research was also carried out by Dr. M. Westin and his coworkers (Westin 1996; Westin *et al.* 1998; Lande *et al.* 2004a, 2004b) at SP Sweden, which led to a new technology based on stable solutions with good impregnating capacity, as well as some promising properties such as resistance to decay.

Furfuryl alcohol is a liquid produced from agricultural wastes such as sugar cane and corn cobs. Furfurylation is accomplished by impregnating the wood with a mixture of furfuryl alcohol and catalysts, and then heating it to cause polymerization (Schneider 1995; Westin 1996). The purpose of furfurylation is to improve some physical, mechanical, and biological properties of the lignocellulosic material (*e.g.*, resistance to biological degradation, dimensional stabilization, resistance to weathering, and hardness) by applying a proprietary furfuryl alcohol polymer, which notably is nontoxic (Lande *et al.* 2004b, 2008).

The polymerization of furfuryl alcohol polymer in the wood is a rather complex chemical reaction. The question of whether wood furfurylation is a true chemical modification of the cell wall remains unanswered by the scientific community. Some scientists believe that it comprises a chemical modification process, since the furfuryl alcohol polymer reacts with itself and possibly reacts with lignin in the cell walls (Nordstierma *et al.* 2008; Lande *et al.* 2008; Li *et al.* 2016; Gérardin 2016). Hence, the furfuryl alcohol complexes are predominantly deposited in the wood cavities, and also in the cell walls (Fig. 2). Polymerization takes place in the microscopic cell cavities, which is easily detected using several microscopic techniques (Thygesen *et al.* 2010). The study of Thygesen *et al.* (2010) also revealed that when higher amounts of catalyst were added to the impregnation liquid, a red-shift in the fluorescence from the furfurylated wood was seen, corresponding to an increased conjugation length of conjugated poly-(furfuryl alcohol) formed within the cell wall of wood.

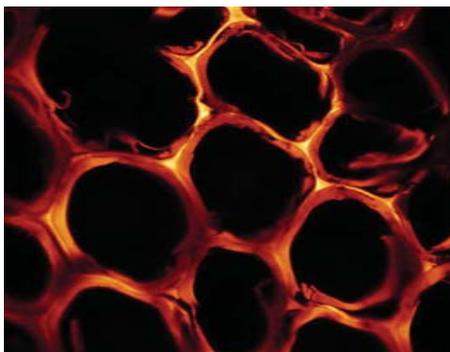


Figure 2. Cross section of radiata pine (*Pinus radiata*) wood with cell walls containing furan polymer. Image through fluorescence microscopy (courtesy: L. Garbrecht Thygesen, RVAU, Copenhagen)

Recent nanoindentation studies demonstrated improvements in indentation modulus and hardness of furfurylated wood cells demonstrated. The work indicated that furfuryl alcohol indeed penetrated wood cells during the modification process (Li *et al.* 2016). Another perception is that furfurylation leads to permanent ‘bulking’ of cell wall, meaning that the cells are swollen in a permanent way. One possible explanation is that the furfuryl alcohol polymer inside the cell wall occupies some of the space normally filled with water molecules, when wood is under swelling in humid conditions (Lande *et al.* 2008).

On the contrary, other scientists insist that furfurylation of wood is an impregnation modification process in which the properties of the furfurylated material appear more like those of a polymer-filled cell wall rather than a reacted cell wall (Rowell 2012; Larsson-Brelid 2013). However, it may be possible that a branch from the polymer chain forms a connection to the wood polymers *via* the lignin hydroxyls (Thygesen *et al.* 2010; Gérardin 2016).

The technology for industrially producing furfurylated wood is presently applied by the Norwegian company Kebony AS (formerly Wood Polymer Technologies). The industrial process of wood furfurylation consists of the following production steps (Lande *et al.* 2004a):

- ✓ Storage and mixing of chemicals: The treating solutions are mixed in a separate mixing tank where different chemicals (furfuryl alcohol, initiators/catalysts, buffering agents, surfactants, water) are added. The mixed solution is pumped to one of the buffer tanks.
- ✓ Impregnation: The wood material (i.e. treatable softwoods or hardwoods) is vacuum pressure impregnated with the treating solution by a full-cell process with a vacuum step, a pressure step, and a short post-vacuum step.
- ✓ Reaction/curing: In-situ polymerisation of the chemicals and grafting reactions with the wood polymeric components occur during this step. The curing chamber is heated with direct injection of steam, where the temperature achieved depends on the product use. The chamber is operated as a closed system during the curing period except for a ventilation period at the end. The ventilation gas is cooled, and the condensate is separated from the gas. Condensate goes back to the condensate tank for re-use.
- ✓ Drying: Final drying of the wood material in a kiln dryer is essential to minimize emissions and to obtain desirable final moisture content.
- ✓ Cleaning: The emissions during the process are managed by cleaning the ventilated gases.

By using cyclic anhydrides as catalysts, the impregnation solution is stable at room temperature. The polymerization reaction is initiated by heating. In the initial phase of polymerization, there are two competing condensation reactions (González *et al.* 1992). The possible cross-linking patterns of furfuryl alcohol polymer chains have been proposed by González *et al.* (1992), who demonstrated that the high amount of permanent wood cell-wall bulking in the furfurylated wood is evidence of the grafting reactions at early polymerization stages. In addition, it has been concluded (González *et al.* 1992; Lande *et al.* 2004b) that with the catalytic systems used for furfurylation of wood it is more likely that grafting to hemicelluloses and most of all to lignin is dominant. As a consequence, a possible grafting reaction between the furfuryl alcohol and a guaiacyl unit of lignin (the predominant unit in softwood lignins) is evidently probable. Gérardin (2016) in his recent review work reported that the furfurylation of wood as a process is based on the *in-situ* polymerization of furfuryl alcohol, with the main chemical reactions demonstrated in Fig. 3.

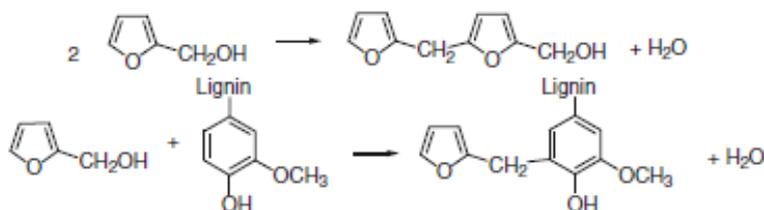


Figure 3. Main reactions involved in the polymerization of furfuryl alcohol (Gerardin 2016)

According to the literature (Lande *et al.* 2004a; Lande 2008; Lande *et al.* 2008; Rowell 2012; Larsson-Brelid 2013; Mantanis and Lykidis 2015), the furfurylation process results in a modified wood product that has significantly improved material properties and characteristics, which are summarized below.

- The biological durability of wood is upgraded to ‘class 1’ (Gérardin 2016) according to EN 350 (2016). Results from decay resistance test ongoing for 9 years, have shown that furfurylated wood of moderate loading, *e.g.*, at 30to35% of weight percentage gain (WPG), has comparable biological resistance with that of pine wood treated with copper chromium arsenate (Lande *et al.* 2008; Larsson-Brelid 2013).
- The mechanical properties of wood, except for impact resistance, are enhanced when wood is treated with the furfuryl alcohol polymer. As a matter of fact, furfurylated wood is characterized by greater hardness, elastic and rupture moduli, as compared to untreated wood but, on the other hand, it is more brittle (Larsson-Brelid 2013).
- Furfurylated wood at a loading >35% exhibits very good dimensional stability (Lande *et al.* 2008), and resistance to weathering (Mantanis and Lykidis 2015). It was reported that furfurylation leads to an anti-shrink efficiency of 60%, at a WPG of approximately 35% (Lande *et al.* 2008).
- Furfurylated wood is resistant to marine borers (Westin *et al.* 2016) only when the WPG is very high (>50%). Not really satisfactory results were obtained after 16-year exposure at reasonable loadings of 30to35% (*i.e.*, slight or moderate wood failure to marine borers was observed at these levels of WPG or lower).
- Recent studies regarding ecotoxicology of furfurylated wood and leachates from furfurylated wood have shown no significant ecotoxicity, while its combustion did not release any volatile organic compounds or polyaromatic hydrocarbons above the normal levels of wood combustion (Pilgård *et al.* 2010a, 2010b).
- Furfurylated wood is a ‘green’ wood product that holds an ecological label in the Scandinavian market, named ‘Swan’. Furfurylation of wood is, therefore, believed to be a safe process for the environment (Gérardin 2016).

At present, the company Kebony AS in Norway produces two distinct furfurylated wood products, namely:

- i) ‘Kebony Clear’: a highly-loaded, dark, hard furfurylated wood currently used for flooring that simulates tropical hardwood. The wood species used for this are radiata pine (*Pinus radiata*), southern yellow pine (*Pinus sp.*), and maple (*Acer sp.*). Typically, the mean WPG of this product is approx. 35%.
- ii) ‘Kebony Character’: a more lightly-loaded furfurylated wood presently used as decking, siding, roofing, and outdoor furniture mainly sold in the Scandinavian markets. This wood material is produced today from Scots pine (*Pinus sylvestris*) wood; it has an average WPG of ca. 20% (Mantanis 2017).

In addition, Kebony wood has been recently used in the production of exterior windows. Following a series of extensive quality tests in Germany (Bollmus *et al.* 2012), furfurylated wood has been recommended by the German Association of Windows and Facades. Results from a project, entitled ‘Winfur’, indicated that the use of furfurylated wood in windows has not caused any problems, fulfilling the criteria for the Scandinavian *P-mark* and the German *RAL* certificates (Bollmus *et al.* 2012).

Today, the company Kebony AS (Norway) produces the above-listed modified products at approximately 22,000 m³ annually (as in 2017). It is expected to increase its production capacity by building a new factory in Belgium (Mantanis 2017).

2.3. Modification of wood with thermosetting resins

Historically, the first experiments on impregnation modification of wood using formaldehyde-based resins were carried out by Dr. A. Stamm and co-workers during the 1940s. Their initial research work included impregnation of wood with phenol-formaldehyde resins to up to 100% resin addition, which resulted in an improved dimensional stability (anti-shrink efficiency, ASE up to 58%) and improved resistance to biodeterioration against fungi, termites, marine borers. Initial experiments using wood veneers by applying impregnation with phenol-formaldehyde (PF) resins, and also heat and compression, have been made by Stamm and Seborg (1955) leading to the production of products called *Compreg* and *Impreg*.

Manufacture of *Compreg* is currently taking place in a number of industrial sites in the USA, Pakistan and India under different brand names. *Compreg* and related products (Fibron, *Permal*, *Dymonwood*, *C-K Composites*) have very good dimensional stability, and high strength properties like hardness, abrasion resistance and compression strength (Hill 2006). Products resulting from these impregnation treatments have been used in the manufacture of knife and tool handles, musical and electrical instruments but not directly for preservation purposes (Gérardin 2016). The volumes of these products are today very low (Hill 2006).

Research on the impregnation modification of wood with melamine-formaldehyde (MF) resins has been increased in the recent decades, especially in Europe, with positive results in respect to dimensional stability and biological resistance to brown-rot fungi (Kielmann *et al.* 2012). Main drawbacks still remain are the high production cost and the tendency of such wood products to cracking under humid-dry cycle conditions. In nowadays, none of these impregnation modification methods has reached the full scale level.

2.4. Modification of wood with DMDHEU

This technology was transferred from the treatment of non-wood systems. As a matter of fact, it involves the impregnation of pine wood, a known highly porous species, with the reagent 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). This reagent (Fig. 4) was well utilised in the industry of textiles until the 1980s in an attempt to manufacture wrinkle-free fabrics. Wood modification with DMDHEU has been shown to improve dimensional stability and durability, and to slightly reduce the moisture uptake of wood (Militz 1993).

Militz (1993) was the first scientist to successfully report on the use of DMDHEU in treating wood, with very positive results. Prof. Militz tested beech wood treated with DMDHEU and demonstrated its effectiveness by using a variety of catalysts. It was finally found that temperatures of 100°C were necessary for the effective curing of the resin system. Noticeably, the anti-shrink efficiency (ASE) value of DMDHEU-treated wood was found to be ca. 75%.

Since then, the process has been undertaken considerable improvements by Militz and co-workers (Krause et al. 2003, Xie et al. 2005), from which commercial application has been finally achieved in Germany. This impregnation modification process is marketed today by the German company BASF under the commercial name *Belmadur*® (Fig. 4).

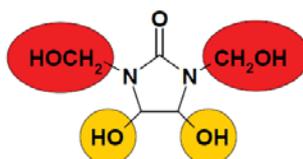


Figure 4. The reagent 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU).

This technology is considered to be an innovative modification process under which pine wood, typically Scots pine, is impregnated under high pressure (12-14 atm) and polymerised by curing. The whole process is based on simple production stages. The first stage consists of penetrating the wood with a proprietary DMDHEU solution, that is, an aqueous solution of a chemical agent (Militz 1993). The air is removed from the cell structure by applying a vacuum to ensure that the agent can reach the innermost cells when the solution is applied under pressure. The next stage consists of the drying of impregnated wood at a slow rate at a temperature of 100-120°C under humid conditions. This causes the agent molecules to cure by polycondensation, and water is released (Krause et al. 2003, Krause & Militz 2009).

The modified product has highly reduced hygroscopic properties (Krause & Militz 2009, Papadopoulos and Mantanis 2012, Larsson-Brelid, 2013). The ASE values of up to 70% can be achieved (Krause and Militz 2009), but normally is in the range of 30-40% (Krause et al. 2003). The mechanisms of the reaction between DMDHEU and the cell wall polymers are still not clear (Hill 2006, Larsson-Brelid 2013). It has been shown that the modification of wood with DMDHEU produces a bulking effect, while results from Dieste et al. (2009) have shown indications that DMDHEU reduces the pore size of the samples by occupying the void space present in the cell walls.

Belmadur wood production is still very small in Germany. The producing German company, Münchinger, belongs to the BASF group, and until today is focusing on the German market. Key applications so far have been decking and garden furniture. However, a laminated Belmadur product has gained acceptance by the German association of Windows and Facades (VFF) for use in exterior windows. The resistance of Belmadur wood to marine borers is very good (Larsson-Brelid 2013). However, the drawbacks are brittleness, tendency to cracking and high emissions of formaldehyde from the product. As a matter of fact, the present technical and market developments of Belmadur technology are not known.

2.5. The indurite process

The so-called 'Indurite process' has been developed from a comprehensive survey of possible reactions of wood cell walls with polymer systems. The technology was scaled-up by the company Engineered Wood Solutions in New Zealand (Hill 2006), and afterwards, it has been obtained by the company Osmose. The original concept for Indurite was undertaken to upgrade home-grown radiata pine (*Pinus radiata*) by impregnation of wood with a water-soluble polysaccharide solution (soy and corn starch).

The impregnated material is held in a covered area for some hours, and then the curing step takes place in a temperature-controlled conventional kiln with the use of certain catalysts in the solution (Hill 2006). Major advantage is that there is no need of significant equipment investment. This modified wood is claimed to be used presently in exterior applications such as cladding and decking. However, the present developments of this technology are not clear.

2.6. The keyword process

According to Larsson-Brelid (2013), a new product named *KeyWood*, that resembles furfurylated wood, was developed within an EU funded project ('Ecobinders'). The reactant that contains small amounts of tri-hydroxy-methyl furan (THMF) and furfuryl alcohol is more water soluble than furfuryl alcohol itself, and easily penetrates the cell wall. After curing of the THMF-impregnated wood, the polymer formed within the cell wall resembles the polymer formed by the Kebony process. However, unlike furfurylated wood, no covalent bonds to the cell wall polymeric constituents (lignin, hemicelluloses, cellulose) were detected in the analytical studies within the project 'Ecobinders'.

Furthermore, due to the higher amount of remaining hydroxyls in the polymer as well as to no bonds to the lignin, the *KeyWood* product has higher equilibrium moisture contents than furfurylated wood at the same level of relative humidity. Furthermore kiln drying temperatures of 125°C are necessary for sufficient curing; consequently, this temperature causes problems with cracking and brittleness. As of today, the technology was sold to the company Arch SA in 2009, but the production volumes seemed to be very small. Meanwhile, the present market developments of the *KeyWood* process are not clear and have not been disclosed publicly.

2.7. Modification processes of wood using monomers

Vinyl monomer impregnation of wood, followed by in situ polymerization, represents another promising way to enhance mechanical, dimensional and thermal stability as well as fungal and insect resistance to wood species of poor natural durability. Different commercially available vinyl monomers such as acrylonitrile, glycidyl methacrylate, methyl methacrylate, hydroxyethylene methacrylate, ethylene glycol, dimethacrylate, butyl acrylate, butyl methacrylate, styrene, acrylamide or acrylonitrile have been investigated by several scientists (Hill 2006, Rowell 2012).

According to the nature of the monomer used, polymerisation can take place either in the cell lumens, in the cell wall, or in both (Schneider 1995). Polymerisation can be initiated by different means using either thermal free radical initiator, or gamma radiation. X-rays, derived from a high-energy, high current electron beam can be also used to initiate in situ polymerisation of vinyl monomers. X-rays initiated polymerisation and penetrated through thick pieces of wood, where polymerisation took place allowing polymerisation of the monomers in the cell walls of wood. Having entered the cell walls and then being polymerised within the cell walls, these radiation-cured treatments increased the dimensional stability of treated wood (Gérardin 2016). Nevertheless, all of the above mentioned techniques have not resulted in commercial applications up to date.

3. Conclusions

This work briefly reviewed the most known wood modification technologies based upon chemical processes, up to date. These technologies have given rise to new modified products with, more or less, improved physical, mechanical, and biological properties. This fact can gradually change the mistaken perspective of customers about wood being a fragile, instable, and easily degraded construction material. For each of them, as disclosed in the literature, a very large number of quality tests have been carried out worldwide, demonstrating the technical advantages and enhanced durability of the modified timber products.

Acknowledgement

This review paper acknowledges the most respected wood scientist, namely, the late Dr. Alfred J. Stamm (Forest Products Laboratory, Madison, Wisconsin, USA) for his pioneering scientific contributions on the modification of wood in general.

References

- Alfredsen G, Ringman R, Pilgård A, Fosdøl CG (2015). New insight regarding mode of action of brown rot decay of modified wood based on DNA and gene expression studies: a review. *International Wood Products Journal* 6(1):5-7.
- Alexander, J., Hague, J., Bongers, F., Imamura, Y., and Roberts, M. (2014). The resistance of Accoya® and Tricoya® to attack by wood-destroying fungi and termites, in: *Proceedings of the 45th Annual Meeting of the International Research Group (IRG) on Wood Protection*, 11-15 May 2014, St. George, Utah, USA, Document IRG/WP 14/40658, Section 4, pp. 1-10.
- Beckers, E. P. J., and Militz, H. (1994). Acetylation of solid wood. Initial trials on lab and semi- industrial scale, in: *Proc. of Second Pacific Rim Bio-Based Composites Symposium*, Vancouver, Canada, pp. 125-135.
- Beckers, E. P. J., Militz, H., and Stevens, M. (1994). "Resistance of acetylated wood to basidiomycetes, soft rot and blue stain," in: *Proceedings of the 25th Annual Meeting of the International Research Group (IRG) on Wood Protection*, Bali, Indonesia, Document IRG/WP 94/40021.
- Bollmus, S., Treu, A., Westin, M., Brynildsen, P., and Militz, H. (2012). "Use of furfurylated wood for the production of windows – Results from the WinFur project," in: *Proceedings of the 6th European Conference on Wood Modification (ECWM)*, Ljubljana, Slovenia, 16-18 Sept. 2012, pp. 99-107.
- Bongers, F., Alexander, J., Marcroft, J., Crawford, D., and Hairstans, R. (2013). "Structural design with Accoya wood," *International Wood Products Journal* 4(3), 172-176
- EN 350 (2016). Durability of wood and wood-based products. Natural durability of solid wood. Part 2: Guide to natural durability and treatability of selected wood species of importance in Europe, European Committee for Standardization (CEN), Brussels, Belgium.
- Fuchs, W. (1928). "Genuine lignin. I. Acetylation of pine wood," *Berichte* 61B, 948-951.
- Gérardin, P. (2016). "New alternatives for wood preservation based on thermal and chemical modification of wood - A review," *Annals of Forest Science* 73, 559-570
- Goldstein, I. (1959). "Impregnating solutions and method of impregnation therewith, Patent US No. 2,909,450, USA.
- González, R., Martínez, R., and Ortiz, P. (1992). "Polymerization of furfuryl alcohol with trifluoroacetic acid: The influence of experimental conditions," *Makromol. Chem.* 193, 1-9.

- Highley TL, Clausen CA, Croan SC, Green F, Illman BL, Micales JA (1994). Research on biodeterioration of wood: I. Decay mechanisms and biocontrol. Research Rep. FPL-RP-529, Forest Products Laboratory, Madison, WI, USA.
- Hill, C. A. S. (2006). Wood Modification – Chemical, Thermal and Other Processes, Wiley Series in Renewable Resources, Ed. J. Wiley and Sons, Chichester, United Kingdom, pp. 260.
- Hill CAS (2009). Why does acetylation protect wood from microbiological attack? *Wood Material Science and Engineering* 4(1-2): 37-45.
- Horn, O. (1928). "Acetylation of beech wood," *Berichte* 61B, 2542-2545.
- Jones, D., and Hill, C. A. S. (2007). "Wood modification - A brief overview of the technology," in: Proceedings of the 5th COST E34 International Workshop, M. Sernek (ed.), Bled, Slovenia, 6-7 Sept. 2007, pp. 1-9.
- Jorissen, A., and Luning, E. (2010). "Wood modification in relation to bridge design in the Netherlands," in: Proceedings of the 11th World Conference on Timber Engineering (WCTE 2010), Trentino, Italy, June 2010, A. Ceccottian J.-W. van der Kuilen (eds.), pp. 1-9.
- Kielmann BC, Militz H, Adamopoulos S (2012). Combined N-methylol melamine colouring agent modification of hardwoods to improve their performance under use-class 3. In: Proceeding of 6th European Conference on Wood Modification, Ljubljana, Slovenia, pp. 437-446.
- Lande, S., Westin, M., and Schneider, M. (2004a). "Properties of furfurylated wood," *Scandinavian Journal of Forest Research* 19(5), 22-30.
- Lande, S., Eikenes, M., and Westin, M. (2004b). "Chemistry and ecotoxicology of furfurylated wood," *Scandinavian Journal of Forest Research* 19(5), 14-21.
- Lande, S. (2008). "Furfurylation of wood – Wood modification by the use of furfuryl alcohol," Ph.D. Thesis. Norwegian University of Life Science, Ås, Norway.
- Lande, S., Eikenes, M., Westin, M., and Schneider, M. (2008). "Furfurylation of wood: Chemistry, properties and commercialization," in: Development of Commercial Wood Preservatives, ACS Symposium Series No. 982, pp. 337-355.
- Larsson-Brelid, P. (2013). "Benchmarking and state-of-the-art report for modified wood," SP Report No. 54, Swedish Institute of Wood Technology SP, Stockholm, Sweden, pp. 1-31.
- Larsson-Brelid, P., Simonson, R., Bergman, Ö., and Nilsson, T. (2000). "Resistance of acetylated wood to biological degradation," *Holz als Rohwerkstoff* 58(5), 331-337.
- Li, W., Ren, D., Zhang, X., Wang, H., and Yu, Y. (2016). "The furfurylation of wood: Ananomechanical study of modified wood cells," *BioResources* 11(2), 3614-3625.
- Mantanis, G., Young, R. A., and Rowell, R. M. (1994). "Swelling of wood. Part 1. Swelling in water," *Wood Science and Technology* 28, 119-134.
- Mantanis, G., and Lykidis, C. (2015). "Evaluation of weathering of furfurylated wood decks after a 3-year outdoor exposure in Greece," *Drvna Industrija* 66(2), 115-122.
- Mantanis G (2017). Chemical modification of wood by acetylation or furfurylation: A review of the present scaled-up technologies. *BioResources* 12(2), in press.
- Militz, H. (1991). "The improvement of dimensional stability and durability of wood through treatment with non-catalysed acetic acid anhydride. *Holz als Roh- und Werkstoff* 49(4), 147-152.
- Mohebby, B. (2003). "Biological attack of acetylated wood," Ph.D. thesis, Institute of Wood Biology and Wood Technology, University of Goettingen, Goettingen, Germany.
- Mohebby, B., and Militz, H. (2010). "Microbial attack of acetylated wood in field soil trials," *International Biodeterioration & Biodegradation* 64, 41-50.
- Nordstierma, L., Lande, S., Westin, M., Karlsson, O., and Furo, I. (2008). "Towards novel wood-based materials: Chemical bonds between lignin-like model molecules and poly (furfuryl alcohol) studied by NMR," *Holzforchung*, 62, 709-713.
- Papadopoulos, A. N., and Hill, C. A. S. (2002). "The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against *Coniophoraputeana*," *Holz als Rohwerkstoff* 60, 329-332.
- Papadopoulos, A. N., and Hill, C. A. S. (2003). "The sorption of water vapour by anhydride modified softwood," *Wood Science and Technology* 37(3-4), 221-231.
- Pilgård, A., De Vetter, L., Van Acker, J., and Westin, M. (2010a). "Toxic hazard of leachates from furfurylated wood: Comparisons between two different aquatic organisms," *Environmental Toxicology Chemistry* 29, 1067-1071.
- Pilgård, A., Treu, A., van Zeeland, A. N., Gosselink, R. J., and Westin, M. (2010b). "Toxic hazard and chemical analysis of leachates from furfurylated wood," *Environmental Toxicology Chemistry* 29, 1918-1924.
- Ringman R, Pilgård A, Richter K (2015). In vitro oxidative and enzymatic degradation of modified wood. *International Wood Products Journal* 6(1): 36-39
- Rowell, R. M. (1982). "Distribution of reacted chemicals in southern pine modified with acetic anhydride," *Wood Science* 15(2), 172-182.
- Rowell, R. M. (1983). "Chemical modification of wood: A review," Commonwealth Forestry Bureau, Oxford, England, No. 6, pp. 363-382.
- Rowell, R. M. (1984). "The chemistry of solid wood," in: *Advances in Chemistry Series No. 207*, American Chemical Society, Washington DC, USA, pp. 540.
- Rowell, R. M., Simonson, R., Hess, S., Plackett, D. V., Cronshaw, D., and Dunningham, E. (1994). "Acetyl distribution in acetylated whole wood and reactivity of isolated wood cell wall components to acetic anhydride," *Wood and Fiber Science* 26(1), 11-18.
- Rowell, R. M., Ibach, R. E., McSweeney, J., and Nilsson, T. (2009). "Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood," *Wood Material Science and Engineering* 1-2, 14-22.

- Rowell, R. M. (2012). *Handbook of Wood Chemistry and Wood Composites*, 2nd Ed., CRC Press, Taylor and Francis Group, Boca Raton, Florida, USA, pp. 703.
- Rowell, R. M. (2014). "Acetylation of wood - A review," *Int. J. Lignocellulosic Products* 1(1), 1-27.
- Rowell, R. M. (2016). "Dimensional stability and fungal durability of acetylated wood," *Drewno* 59(197), 139-150.
- Schneider, M. H. (1995). New cell wall and cell lumen wood polymer composites," *Wood Science and Technology* 29, 121-127.
- Stamm AJ, Seborg RM (1955). Impreg, Compreg. Research Reports no. 1380, 1381. Forest Products Laboratory, Madison, WI, USA.
- Stamm AJ, Burr HK, Kline AA (1946). Staybwood. Heat stabilized wood. *Industrial and Engineering Chemistry* 38(6):630-634.
- Stamm, A. J. (1964). *Wood and Cellulose Science*, Roland Press, New York, USA.
- Stamm, A. J. (1977). Dimensional stabilization of wood with furfuryl alcohol," in: *Wood Technology: Chemical Aspects*, Goldstein (ed.), ACS Symposium Series, Volume 43, American Chemical Society, Washington, USA, pp. 141-149.
- Tarkow, H. (1946). "A new approach to the acetylation of wood," USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA, pp. 9.
- Tarkow, H., Stamm, A. J., and Erickson, E. (1946). "Acetylated wood," Report no. 1593, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA, pp. 29.
- Thygesen, L. G., Barsberg, S., and Venås, T. M. (2010). "The fluorescence characteristics of furfurylated wood studied by fluorescence spectroscopy and confocal laser scanning microscopy," *Wood Science and Technology* 44(1), 51-65.
- Westin, M. (1996). Development and evaluation of new alternative wood preservation treatments," Final report to The Swedish Council for Forestry and Agri. Res. (SJFR), (In Swedish with English summary), pp. 1-25.
- Westin, M., Nilsson, T., and Hadi, Y. S. (1998). "Field performance of furfuryl alcohol treated wood," in: *Proceedings of the 4th Pacific Rim Bio-Based Composites Symposium*, Bogor, Indonesia. pp. 305-331.
- Westin, M., Larsson-Brelid, P. L., Nilsson, T., Rapp, A., Dickerson, J. P., Lande, S., and Cragg, S. (2016). "Marine borer resistance of acetylated and furfurylated wood – Results from up to 16 years of field exposure, in: *Proceedings of the 47th Annual Meeting of the International Research Group (IRG) on Wood Protection*, Lisbon, Portugal, 15-19 May 2016, IRG/WP 16-40756, Section 4, pp. 1-9.
- Van der Lugt, P., Bongers, F., and Vogtländer, J. (2016). Environmental impact of constructions made of acetylated wood, in: *Proceedings of the World Conference on Timber Engineering (WCTE 2016)*, 22-25 Aug. 2016, Vienna, Austria, pp. 1-6.