



# Benchmarking and State of the art for Modified wood

Pia Larsson Brelid

SP Technical Research Institute of Sweden

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SP Technical Research Institute of Sweden  
Box 857, 501 15 Borås, Sweden (headquarters)

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## Abstract

### Benchmarking and State of the art for Modified wood

With an increased awareness of the fragility of our environment and the need for durability in wood products, new technologies have been developed to increase the service life of wood materials without the use of toxic chemicals. Issues of sustainability, carbon sequestration and performance converge in this search for environmentally friendly methods of wood preservation.

For wood to be used in exterior applications, dimensional stability and fungal resistance is of crucial importance. There are really only three routes that can be considered as a complement to traditional pressure impregnation or naturally durable wood species, namely acetylation, furfurylation and thermal treatment.

Reductions in hygroscopicity, increased dimensional stability and decay resistance of thermally treated wood depend on decomposition of a large portion of the hemicelluloses in the wood cell wall. In theory, these hemicelluloses are converted to water and furan-type intermediates that can polymerize in the cell wall. Furfuryl alcohol is a low-viscosity liquid that can be impregnated into wood and swells the wood cell walls. It reacts strongly with itself at low (acid) pH to form a dark, highly-resistant, hard, cross-linked polymer. Recent studies have shown that the FA also covalently bonds to the wood cell wall during polymerization. Reductions in hygroscopicity and improved dimensional stability of acetylated wood depends on esterification by means of reacting the cell wall polymers with acetic anhydride, reducing hydrogen bonding with water, and bulking the cell wall back to its green volume. The cell wall moisture content is too low in acetylated wood to support fungal attack so the initial enzymatic attack starting the colonization does not take place.

Strength properties are reduced in thermally treated wood as a result of the degradation of the cell wall matrix, while strength properties are not significantly changed in furfurylated and acetylated wood.

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Appendix: A summarizing bench marking table for the different technologies

# 1 Introduction

The most common way to protect wood from moisture sorption and weathering is by applying different coatings, such as oil-based or latex-based paints, stains or vanishes. Coatings on exterior wooden claddings are subjected to environmental stresses such as sunlight, moisture, temperature variations, microorganisms and pollutions. Thus, coating will not prevent moisture sorption by the wood cell wall polymers over an extended period of time (Larsson Brelid 1998).

## 1.1 Wood impregnation

Wood is treated with preservatives to increase its resistance to decay caused by insect attack, micro-organisms and damage caused by marine wood-boring animals (Larsson Brelid 1998). The modern wood preservation industry commenced in the 1830s, when sleepers and poles of railroads were pressure impregnated by a heterogeneous mixture of polycyclic aromatic hydrocarbons PAH, creosote, (Rowell 2005). Wood preservatives can be divided into two general classes: Oil type (creosote) and waterborne salts for example chromated copper arsenate (CCA) and alkaline copper quaternary ammonium ACQ (Rowell 2005). Each active ingredient which is incorporated into wood preservative formulations has its own mode of action (Eaton and Hale 1993). The toxicity of heavy metals has been widely used to fight fungal decay of wood. Some of the mechanisms of toxicity involve denaturation of proteins, inactivation of enzymes, cell membrane disruption, inhibition of respiration and inhibition of protein synthesis (Eaton and Hale 1993; Rowell 2005). The primary mode of action of CCA is most likely absorption of solubilized CCA into hyphae but evidence also demonstrate inhibition of cellulose decomposing systems (Chou et al. 1974).

There are two general types of wood preservation processes: non-pressure processes and pressure processes (Eaton and Hale 1993). The most commonly used pressure processes are full cell (wood is impregnated in a closed vessel under pressure), modified empty cell or empty cell (Eaton and Hale 1993). There are many non-pressure processes and they differ in their retention and penetration of the preservative (Eaton and Hale 1993). Examples of non-pressure processes include surface application of preservative by brief dipping or brushing, diffusion processes of waterborne preservatives and vacuum treatment (Eaton and Hale 1993).

## 1.2 Wood modification

Wood modification is an alternative to protection of wood with toxic chemicals. Wood modifications do not have a toxic mode of action as is the case for preservative treated wood (Hill 2006). The modified wood should itself be non-toxic under service conditions, and there should be no release of any toxic substances during service, or at the end of service life (Hill 2006). The wood constituents can be physically altered and/or the wood structure can be chemically altered. Both of these changes can lead to more durable wood (Hill 2006). There are several ways to chemically modify the wood cell wall polymers and the most abundant single site for reactivity is the hydroxyl groups (Rowell 2005). The hydroxyl groups in the wood polymers (i.e cellulose, hemicellulose and lignin) are the most reactive sites in the wood. They are also responsible for the dimensional instability through their hydrogen bonding to water (Larsson Brelid 1998). Chemical modification of the wood by reacting the hydroxyl groups with a stable, covalently bounded, less hydrophilic group, leads to an increased dimensional stability (Larsson Brelid 1998). The sites of unsaturation in the lignin

structure may also play a role (Rowell 2005). Many reactive chemicals capable of forming covalent bonds have been studied in order to chemically modify wood.

To make the modification permanent, the bond created between the wood polymers and the reagent is of great importance. The major important types of covalent bonds formed by chemical modification of the wood are ethers, acetals and esters (Larsson Brelid 1998). Currently, little is known about the mode of action of modified wood but some general hypotheses have been put forward (Hill 2006):

- 1) The equilibrium moisture content (EMC) is lowered in modified wood, and hence it is harder for fungi to get the moisture required for decay.
- 2) There is a physical blocking of the entrance of decay fungi to micropores of the cell walls.
- 3) Inhibition of action of specific enzymes.

Some examples of commercial wood modifications are thermal modification (Tjeerdsma et al. 1998; Sailer et al. 2000), furfurylation (Schneider 1995; Westin 1995; Westin 1996; Lande et al. 2008), modification with DMDHEU (dimethylol dihydroxy ethylene urea) (Militz 1993) and acetylation (Militz 1991; Larsson Brelid et al. 2000).

## **2 Modified wood**

### **2.1 Acetylated wood**

The acetylation of wood was first performed in Germany by Fuchs (1928), using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40%, which meant that he decrystallized the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn (1928) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. Suida and Titsch (1928) acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30 to 35 percent after 15 to 35 days at 100 °C. Tarkow (1945) first demonstrated that acetylated balsa was resistant to decay. Tarkow (1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

Acetylation of wood using acetic anhydride has mainly been done as a liquid phase reaction. The early work was done using acetic anhydride catalyzed with either zinc chloride or pyridine. Through the years, many other catalysts have been tried both with liquid and vapor systems. Some of the catalyst used include urea-ammonium sulphate, dimethylformamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride and  $\gamma$ -rays. The reaction has also been done without catalyst and by using an organic co-solvent. Gas phase reactions have also been reported using both ketene and acetic anhydride, however, the diffusion rate is very slow so this technology has only been applied to thin veneers (Rowell 2005).

Most acetylation reactions done today are done without the use of a catalyst, by reacting wood with acetic anhydride which results in esterification of the accessible hydroxyl groups in the wood cell wall with the formation of the by-product acetic acid (Rowell et al. 1994).

Acetylation is a reaction where acetic anhydride forms ester bonds to wood (Rowell 2005). All of the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked (Rowell 2005).

Acetylated wood shows an increase in biological resistance (Larsson Brelid et al. 2000), and reduction in hygroscopicity of the wood material (Rowell 1991). It shows an anti-shrinking/swelling efficiency of up to 80% (Goldstein 1961; Rowell and Plackett 1988), with very little change of the mechanical strength and modulus of elasticity (Goldstein et al. 1961; Militz 1991; Akitsu et al. 1993; Eaton and Hale 1994; Larsson Brelid 1998). Acetylated wood also shows low toxicological effects (Van Eetvelde et al. 1998). Today there are two producers of acetylated wood, Titan Wood Ltd and Eastman Chemical Company. The Titan wood product is called Accoya® and was originally acetylated radiata pine, although they are now also acetylating other wood species for the Chinese market. A new plant has also been designed for their Chinese daughter company, Diamond Wood China Ltd. Acetylated wood from Eastman Chemical Company is launched by the name of PERENNIAL WOOD™. Even though, the state of technology is high for both companies the market introduction was rather recent and the production capacity is below 50 000 m<sup>3</sup>/year. Key applications are window joinery and load bearing constructions such as bridges. They have also gone through all testing needed for approval for load bearing construction application. Accoya's advantage over other modified wood materials is, in some applications, the bright colour. Drawbacks are that it is very susceptible to mould growth (may look worse than unmodified wood) and sensitive to alkali (e.g. contact with concrete and many detergents). Current cost for a small end user is 1500-2000 €/m<sup>3</sup> and for a large end user less (depending on volume purchased) (personal communication).



**Figure 1.** Bridge made from Accoya (from: Conterporist 20090203) and decking and garden furniture made from Perennial wood (<http://www.perennialwood.com>).

## 2.2 Thermally modified wood

Thermal modification is a thermal treatment of wood, by mild pyrolysis, to physically increase its durability (Militz 2002; Hakkou et al. 2006).



Heating wood to improve its performance dates back many thousands of years. In the 11<sup>th</sup> century, the Viking shipbuilders used heat for bending of ship parts (Olsen and Crumlin-Pedersen 1967) and in the early part of the 20<sup>th</sup> century it was found that drying wood at high temperature increased dimensional stability and caused a reduction in hygroscopicity (Tiemann, 1915, Stamm and Hansen 1937). Burmester (1973) studied the effect of temperature, pressure and moisture on wood properties. He found that the optimum conditions for pine were 160 C, 20-30% moisture and 0.7 MPa pressure. He reported high dimensional stability and resistance to brown-rot fungi attack and minimal loss of strength. He named his process as FWD (Feuchte-Wärme-Druck).

More recently, Norimoto et al. (1993) and Ito et al. (1998) heated wet wood to improve dimensional stability. Inoue et al. (1993) heated wet wood to fix compression set in wood. Different hypotheses for the mechanisms of increased durability have been reported (Tjeerdsma et al. 1998; Boonstra et al. 1998; 2007; Kamdem et al. 2002; Hakkou et al. 2006). Evidence supporting the theory of improved decay resistance due to generation of fungicidal components of the wood was not found. Instead the durability is mainly attained by lowering of the EMC (Boonstra et al. 2007). The thermally modified wood also shows low toxicological effects (Van Eetvelde et al. 1998) and life cycle assessment (LCA) has shown superior environmental performance compared to wood impregnated with creosote and CCA (Hill 2006). A clear negative correlation between decay resistance and mechanical properties has been found (Millett and Gerhards 1972). This is due to the loss of wood constituents at the elevated process temperatures required to obtain decay protection.

Many different methods for thermal modification exist with different temperatures, different pressure conditions and with or without oil (Tjeerdsma et al. 2002; Venås 2008). The treatment temperature and atmosphere are critical variables and the thermally induced chemical changes in the wood differ between various processes (Tjeerdsma et al. 2002). Thermally modified timber is not recommended for use that requires contact with the ground (Welzbacher and Rapp 2007).

Thermally modified wood is by far the modified wood available in largest volumes and the lowest cost. Like other novel products cost estimations are uncertain and the cost can vary from approximately 4-500 Euro/m<sup>3</sup> to almost the double. There are many producers, many of which are members of the International ThermoWood Association. ThermoWood is the dominating process but there are other processes resulting in similar products, e.g. PlatoWood. Total production capacity will soon reach 150 000 m<sup>3</sup>, but the total current production volume is less than 100. 000 m<sup>3</sup>. ThermoWood has been on the market for over 12 years but there is still a need for more and the key applications are cladding, decking, cupboard doors, cabinets and saunas. One issue with thermally modified wood is the poor performance in contact with ground or at permanent wetting. Another issue is the rapid weathering in out-door applications if the product is un-coated.



**Figure 2.2.** Examples of applications of Thermowood  
(<http://www.moelven.com/Thermowood>).

## 2.3 Furfurylated wood

Furfurylated wood is lumber modified with furfuryl alcohol (FA) which is a bioderived chemical. The modification of wood with FA is accomplished by impregnating wood with a polymerizable mixture of FA and catalyst and then heating to polymerize. The purpose of furfurylation is to improve physical and biological properties such as resistance to moisture and decay (Lande et al. 2008, Schneider et al. 2009).

Early research concerning modification of wood with furfuryl alcohol, was initiated by the “pioneer of wood modification”, Dr. Alfred Stamm, in the early 1950’s. (Goldstein 1955, Goldstein 1960, Goldstein and Dreher 1960, and Stamm 1977). In the early 1990s, Schneider and Westin simultaneously developed similar new catalytic systems for furfurylation of wood (Schneider 1995, Westin 1995, Westin et al. 1996). They used cyclic carboxylic anhydrides, mainly maleic anhydride, as key catalysts. These catalysts were soluble in FA without the addition of water, and they have similar molecular size and polarity to FA. Therefore they penetrate with the FA and a catalyst concentration gradient does not develop. These novel systems are stable solutions with good impregnating properties that produce furfurylated wood with several outstanding properties (Lande et al. 2004b, Epmeier et al. 2004). Furfuryl alcohol molecules can, due to its polarity, penetrate into the wood cell wall and polymerize in situ. This results in a permanent swelling of the wood cell walls (Stamm 1977). Furfurylation of wood leads to high protection against bio degradation by fungi, bacteria, and marine borers (Lande et al. 2004a) and it also improves the hardness, lowers the equilibrium moisture content (Epmeier et al. 2004) and significantly improves the dimensional stability of the wood (Westin 2004) while the leachates from furfurylated wood has little toxicological effects (Epmeier et al. 2004; Lande et al. 2004b; Lande et al. 2004c; Treu et al. 2009; de Vetter et al. 2009; Pilgård et al. 2010a; Pilgård et al. 2010b). Anti-shrinking/swelling efficiency has been reported to range from 30 to 80% depending on chemical formulations and wood species used (Homan and Jorissen 2004; Westin 2004; Lande et al. 2004b). A moderate loading of FA polymer in wood provides biodeterioration resistance suitable for ground contact or marine use (Epmeier et al. 2004, Lande et al. 2004b & a, Hadi et al. 2005, Westin et al. 2006, Westin & Alfredsen 2007, Venås 2008). Its rich, brown colour is attractive and makes it possible for light- coloured woods to simulate dark, expensive woods. Its moisture resistance makes it suitable for applications

that can be flooded with water from time to time, such as wet-room floors, countertops and furniture surfaces (Figures 3-5). Low loading gives sufficient biodegradation protection for above-ground, outdoor uses (Alfredsen & Westin 2009) (personal communication).

Furfurylated wood has greater hardness, elastic and rupture moduli than untreated wood but are on the other hand more brittle. These properties increase with polymer loading of the wood (Epmeier et al. 2004 & 2006, Lande 2008).

Furfurylated wood has been produced on commercial scale by Kebony ASA in Norway since 2003. The process is based on a full cell (vacuum/pressure) impregnation with a chemical solution followed by an intermediate vacuum drying step before steam curing and drying/post curing. The impregnation liquid is a waterborne solution containing 40% furfuryl alcohol, buffer agents, maleic anhydride and citric acid catalysts (Pilgård et al. 2010a).



**Figure 2.3.** Moderately-loaded furfurylated maple (photos by courtesy of Kebony ASA).



**Figure 2.4 .** Moderately-loaded furfurylated Scots pine (photo by courtesy of Kebony ASA).

## 2.4 Other modification methods

### 2.4.1 DMDHEU modified wood (Belmadur<sup>®</sup>)

DMDHEU modification is a wood modification with a water solution of dimethylol dihydroxy ethylene urea. DMDHEU was originally developed for the textile industry as a wrinkle resistant finish. Wood modification with DMDHEU has previously been shown to improve dimensional stability and durability and to slightly reduce the moisture uptake of wood (Nicholas and Williams 1987; Militz 1993; Yasuda and Minato 1994; Yusuf et al. 1994; Militz et al. 1997; van der Zee et al. 1998; Van Acker et al. 1999; Krause et al. 2003; Schaffert et al. 2005; Wepner and Militz 2005; Krause et al. 2008; Verma et al. 2009). An anti-shrinking/swelling efficiency of up to 70% can be achieved (Militz 1993; Yusuf et al. 1995) but normally it is in the range of 30 to 40% (Krause et al. 2003). Indications of cross linking with the cell wall polymers are found but the mechanisms of the reaction between DMDHEU and the wood cell wall are unknown (Yasuda et al. 1994; Krause et al. 2003). It has been shown that the modification of wood with DMDHEU produces a bulking effect (Yusuf et al. 1995; Krause et al. 2003). Results from Dieste et al. (2009) showed indications that DMDHEU reduces the pore size of the samples by occupying the void space present in the cell wall.

The production of Belmadur is still very small, more to be regarded as a test introduction phase. The producer belongs to the BASF group and has so far focused on the German market. In many ways the product is similar to Kebony. Key applications so far have been decking and garden furniture. The resistance to marine borers is very good so there will be trials to enter markets for marine application. Drawbacks are brittleness, that modification chemicals are currently petroleum based and emissions of formaldehyde from the product (personal communication).

### 2.4.2 KeyWood<sup>®</sup> (by Arch Timber Protection, recently bought by Lonza)

The product, that resembles furfurylated wood, was developed within an EU-project (*Ecobinders*). In a way, the whole process was a way for the coordinator of the project, TransFuran Chemicals, to go around Kebony's patents by using an adduct between furfuryl alcohol and formaldehyde (Bis-hydroxymethyl furan, BMHF) as modification chemical. The reactant (that may contain small amounts of tri-hydroxy-methyl furan, THMF, and furfuryl alcohol, FA) is more water soluble than FA and easily penetrates the wood cell walls. After curing of the BHMf-impregnated wood, the polymer formed within the cell wall, resembles the polymer formed by FA. However, unlike in furfurylated wood, no covalent bonds to the cell wall polymers (lignin, hemicelluloses and cellulose) could be detected in the analytical studies within the project. Furthermore, due to higher amount of remaining hydroxyls in the polymer, compared to FA-polymer, and no bonds to the lignin the product had higher equilibrium moisture contents (EMCs) than furfurylated wood at the same relative air humidity. The decay resistance is due to this fact slightly poorer than furfurylated wood at the same treatment level (expressed as Weight Percent Gain). Furthermore, kiln-drying temperatures of 125°C is needed for sufficient curing and this temperature causes problems with cracking and brittleness. Anyhow, the technology was sold to Arch in 2009 but the production volumes seem to be very small. A qualified guess is that Arch (now Lonza) bought the technology in order to have a back-up technology in case their main business, wood preservatives, should become less profitable due to possible restrictions and environmental tax of preservative treated wood in the future (personal communication).

### **2.4.3 Naturally high quality wood (mainly tropical wood species)**

The consumption of tropical timber in Europe alone is more than 6 million m<sup>3</sup>/year. The application areas in the official statistics are furniture (26%), windows (26%), doors (16%), stairs (6%), flooring (3%) and other (6%) including decking application. However, the consumption of tropical timber for decking application is difficult to estimate since a lot of timber for this application is simply registered as “hardwood”. Some tropical wood species have very good properties both concerning durability and mechanical properties, and customers are willing to pay a lot for these. However, it is not sustainable to continue with such a large consumption of tropical wood from an environmental perspective. Plantations of precious wood species such as teak have been started in tropical regions around the world. The problem is that the quality of the plantation-grown teak is inferior to the teak from the rainforest. Altogether, this means that there is a huge potential market for products replacing tropical wood products (personal communication).

### **2.4.4 Preservative treated wood**

The far most common method to protect wood from biological degradation is impregnation with Copper containing preservatives. The production of preservative treated wood in Europe is approximately 6 million m<sup>3</sup>/year and in North America over 25 million m<sup>3</sup>/year.

However, this market is more price-driven than performance-driven and many customers of preservative treated wood will not consider paying the cost for modified wood. What will make possible to take market shares from these products, would instead be legislation (environmental tax, bans or further restrictions). There has been a debate over the last couple of years to have environmental tax or restrictions on the use of copper, and if this would come true it would increase the possible market for modified wood overnight. However, I don't believe that this will happen in the near future (within the next 5 years) (personal communication).

### **2.4.5 Wood plastic composites (WPC)**

Today WPCs consist of 50-60% wood fibre/particles in thermoplastic polymer. The global annual production of WPC products has increased from practically zero to 1 million m<sup>3</sup> over the last 15 years. The main application has been decking, thereby taking 20% of the US decking market from preservative treated wood, despite a cost that is double or triple. The first generation WPC had huge problems with performance resulting in many large so called class action lawsuits. The newer, slightly more expensive, WPC products contain biocides (usually zinc borate), coupling agents, UV-absorbers and other additives. However, WPC for decking have had difficulties to enter the European market. And the inclusion of biocides and other additives has complicated the environmental arguments for the product. These products actually have a poorer carbon footprint and LCA than preservative treated wood in the few studies made on the topic (personal communication).





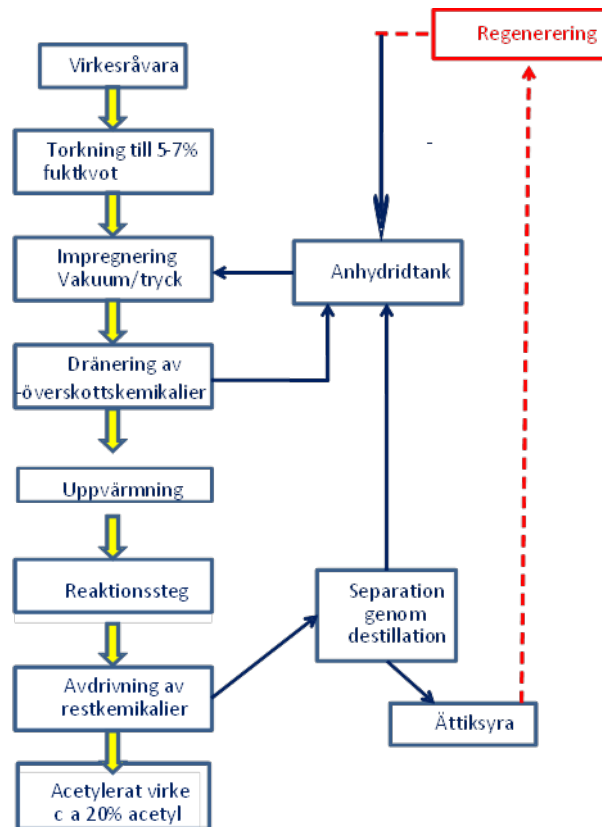
**Figure 2.5.** Examples of products produced from Wood plastic composites.

### **3 Modification processes**

All of the processes for wood modification described in this report are conducted batchwise in closed vessels that can withstand both vacuum and pressure e.i. autoclaves.

#### **3.1 Acetylation process**

Wood, preferably pine sapwood or other permeable wood species, is placed in a stainless steel autoclave and vacuum pressure impregnated with acetic anhydride. Excess chemicals are drained off and the impregnated wood is heated. The reaction is carried out at elevated temperature. After reaction, unreacted acetic anhydride and by-product acetic acid are removed by means of vacuum while the autoclave is still heated. A schematic picture, of an acetylation process, presented in figure 3.1. also, reveals possible regeneration of acetic acid back to acetic anhydride.

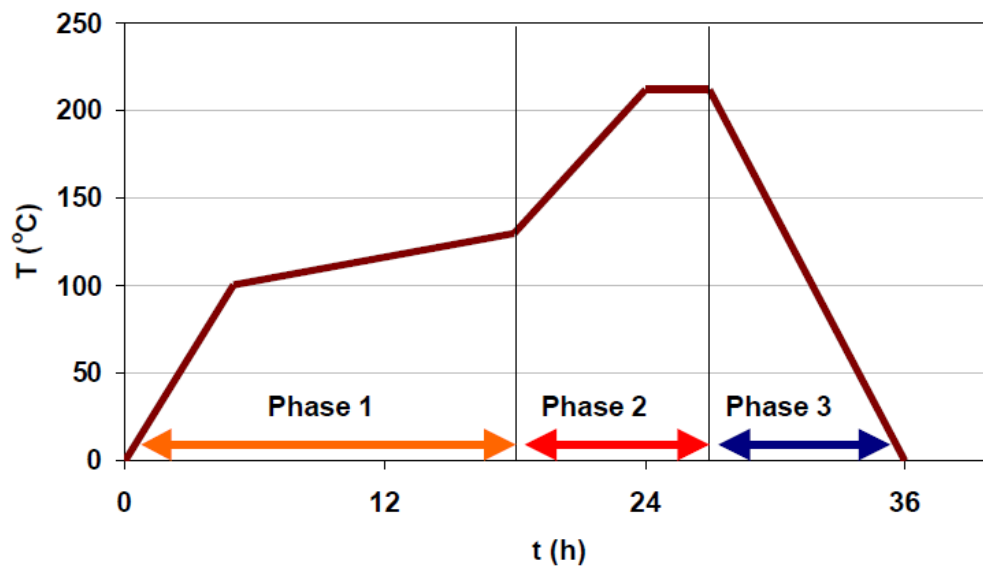


**Figure 3.1** Schematic picture of an acetylation process

## 3.2 The Thermowood process

When it comes to thermally treated wood there is a variety of methods using different reaction temperature and pressure conditions. In this report the Thermowood process will be presented since it is by far the most common in the Scandinavian countries. Thermowood is manufactured using a method developed by VTT. A schematic picture of the process is presented in Figure 3.2. In Phase 1 the temperature is raised to 100° C. Thereafter, the temperature is increased to 130° C and high temperature drying is taking place leading to a decrease in wood moisture to nearly zero. During the high-temperature drying (phase 2), the temperature is increased to between 185° C and 215° C and kept there for 2 to 3 hours depending on the end-use application. In phase 3, the cooling step, the temperature is decreased by using water spray. After the final moisture conditioning, the wood contains about 4-7% moisture.

Thermowood distinguishes between two products Thermowood D and Thermowood S. Thermowood D is processed at a higher temperature, resulting in a product with higher dimensional stability, lower strength, higher durability and a darker colour, compared to Thermowood S (cf. Figure 3.3)



**Figure 3.2** The Thermowood process (from: Thermowood handbook, by the Finnish Thermowood Association)

Softwoods (pine and spruce)			Hardwoods (birch and aspen)		
	Thermo-S	Thermo- D		Thermo-S	Thermo- D
Treatment temperature	190 °C	212 °C	Treatment temperature	185 °C	200 °C
Weather resistance	+	++	Weather resistance	no change	+
Dimensional stability	+	++	Dimensional stability	+	+
Bending strength	no change	-	Bending strength	no change	-
Colour darkness	+	++	Colour darkness	+	++

**Figure 3.3.** The different Thermowood standard treatment classes process (from: Thermowood handbook, by the Finnish Thermowood Association)

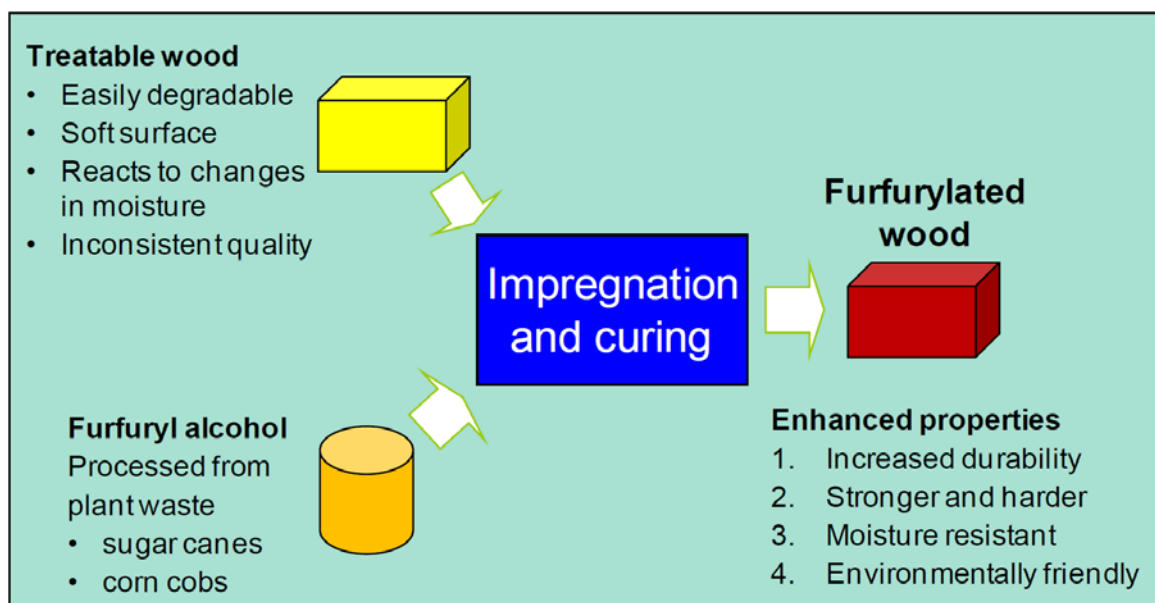
### 3.3 The furfurylation process

Wood furfurylation is carried out by impregnating wood with monomeric furfuryl alcohol either neat or in a water solution and then polymerizing the furfuryl alcohol, FA (Figure. 3.4). To treat lumber, a vacuum and pressure process is used. Curing is done by heating to approximately 100°C.

Diluting FA with water allows loading to be controlled by solution concentration. The water distributes the FA within the wood and then evaporates. The FA is polymerized, resulting in a uniform, low polymer concentration in the wood.



Polymers made from furfuryl alcohol are very dark brown. The darkness it imparts to wood depends upon the loading of the wood. As a result of polymerized furfuryl alcohol color, furfurylated wood ranges from slightly browner than untreated wood to very dark brown. Heavily-loaded furfurylated wood can appear to be black. FA swells the wood cell wall because of its small molecular size and hydroxyl group. The FA cures to a hard polymer in the wood causing it to remain permanently swollen. As a result, subsequent moisture-induced shrinkage and swelling is greatly reduced. Recent studies have shown that the FA also covalently bonds to the wood cell wall during polymerization, therefore furfurylation is true chemical modification of wood (Nordstierna et al. 2008).

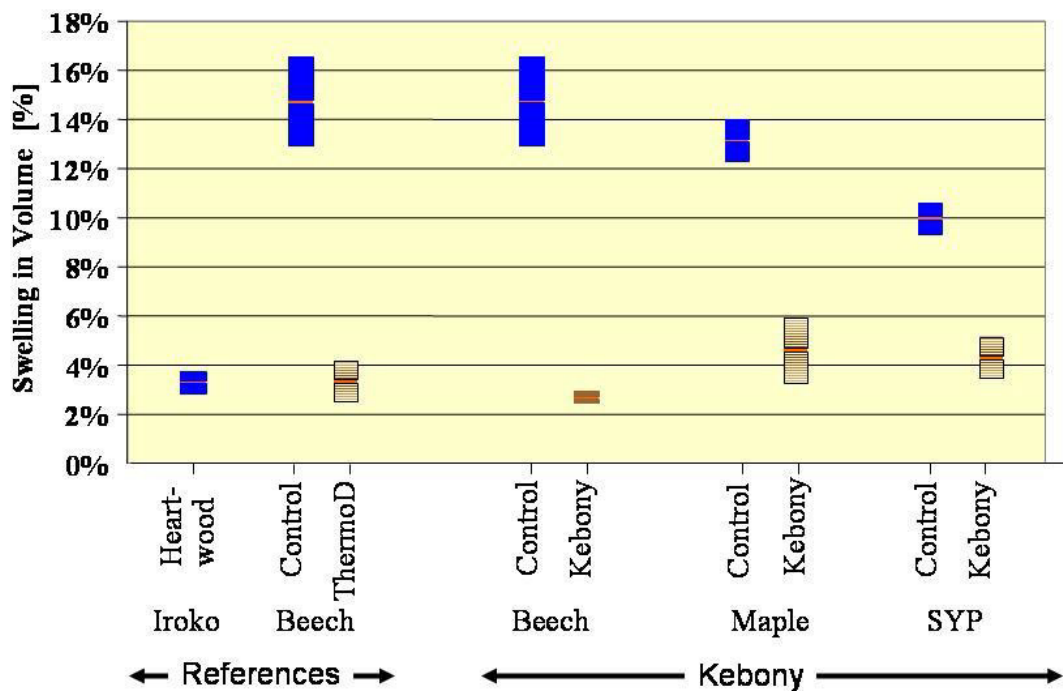


**Figure 3.4.** Method of producing furfurylated wood. Diagram by courtesy of Kebony ASA.

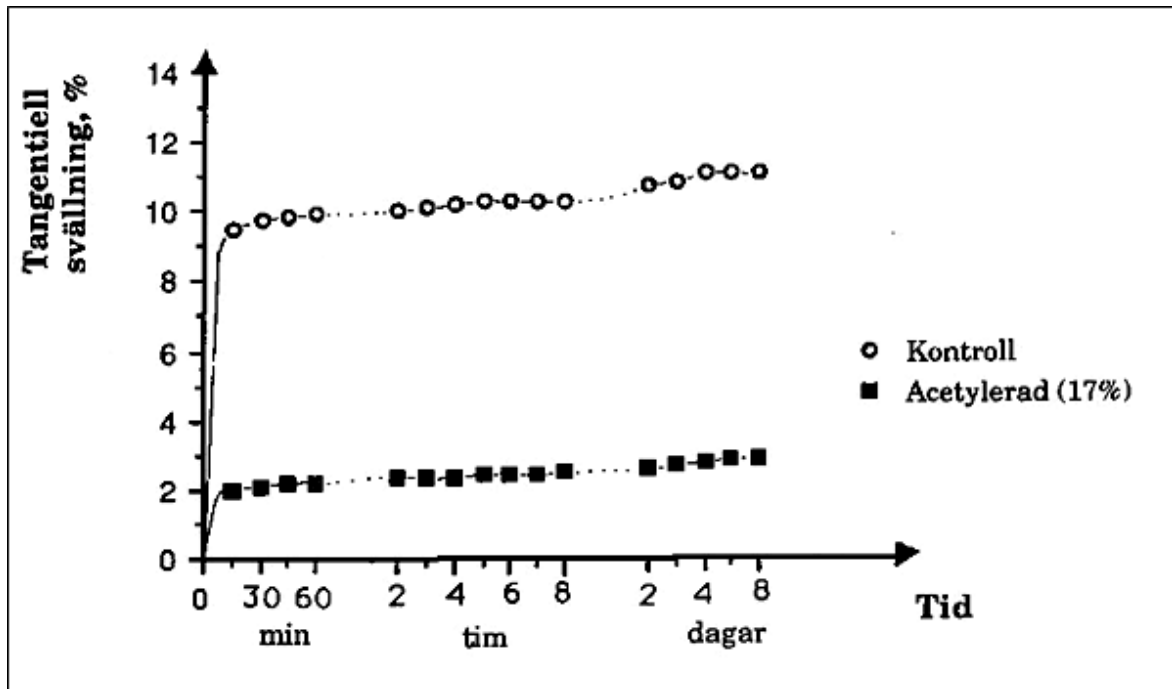
## 4 Properties of modified wood

### 4.1 Dimensional stability

All three modification routes result in products with enhanced dimensional stability. In figure 4.1 results from volumetric swelling between dry climate (30% RH) and relatively moist climate (85% RH) show that the dimensional stability of Kebony is similar to that of beech Thermowood D and the tropical timber Iroko which is commonly used for window and door joinery. In Figure 4.1 the dimensional stability is expressed as tangential swelling in water. The longitudinal swelling of a small wood block is more or less neglectable under these circumstances, meaning that the two figures are comparable. Figure 4.2 reveals that for acetylated pine sapwood the dimensional stability is even higher.



**Figure 4.1.** Volumetric swelling between dry climate (30% RH) and relatively moist climate (85% RH) for furfurylated wood (Kebony) and heat treated wood (Thermo D) [results from Ecobinders 2005-2008 and EcoBuild phase 1 2007-2009]



**Figure 4.2.** Tangential swelling in water for pine sapwood samples 1 x 1 x 1 cm ( from: own results).

By earlier experience, It has also been know that the dimensional stability of acetylated pine, expressed as antiswelling efficiency is approximately 70% which is similar to that of iroko and Kebony. However, Kebony black (Kebony beech with 100% WPG) has ASE higher than 80%. The dimensional stability of DMDHEU-treated wood is similar to melamine resin modified wood which has lower ASE than acetylated and Kebony wood. Pressure impregnation with preservatives does not result in dimensional stabilisation, except for chromium containing preservatives that gives a slight stabilising effect.

**Table 4.1.** Dimensional stability of various woods as a result of heat treatment

Wood species	Conditions	ASE (%)	Reference
<i>Pinus pinaster</i>	170 °C WL <sup>1</sup> 2%	50	Esteves et al. 2006
<i>Eucalyptus globulus</i>	190 °C WL 2%	77	Esteves et al. 2006
<i>Eucalyptus globulus</i>	200 °C WL 10%	60	Esteves et al. 2006
<i>Pinus sylvestris</i>	220 °C	40	Rapp Sailer 2001

<sup>1</sup>WL = Weight loss

**Table 4.2.** Dimensional stability, expressed as antishrink efficiency for several types of acetylated wood.

Species	WPG	ASE (%)	Reference
<i>Pinus elliotti</i>	15	60	Rowell 1983
<i>Pinus sylvestris</i>	20	70	Epmeier et al. 2004
<i>Pinus strobus</i>	22	70	Rowell 2005

The practical effect of a more dimensional stable wood material shows at variation in surrounding moisture through:

- Decreased deformation
- Decreased crack formations
- Decreased delamination for glued products

The dimensional stability results in decreased maintenance costs for painted products is here visualized by figure 4.3, showing acetylated and unmodified wooden boards painted with acrylic paint and exposed outdoor for 5 years. A longer intervals maintenance could be a strong reason for choosing a more expensive wood material.



**Figure 4.3.** Acetylated and unmodified wood fine wood panels, exposed outdoor for 5 years ( from: own unpublished study)

## 4.2 Strength properties

Numerous studies have been conducted on the strength performance of modified wood. In this report a selection of these data will be highlighted.

In a study on acetylated pine and spruce, conducted by Larsson and Simonson (1994), it was concluded that although the acetylation process includes heat treatment under acidic conditions, the change in strength for pine and spruce specimens due to acetylation was small and for practical applications the strength properties can be regarded as unaltered compared to those exhibited by unmodified wood. Acetylated pine samples also showed a somewhat higher hardness than did controls when measured as Brinell hardness. This is probably attributed to the lower equilibrium moisture content in acetylated wood compared with unmodified wood. Acetylation of wood reduces the number of hydroxyl groups that can sorb moisture by hydrogen bonding so the equilibrium moisture content (EMC) and fiber saturation point (FSP) are reduced and the dimensional stabilization increases with increasing weight gain due to acetylation (Rowell 2005). Figure 4.1. shows the reduction of equilibrium content as a result of acetylation. Acetylation also results in a significantly increased wet shear strength as compared with unmodified controls.

**Table 4.1.** Reduction of equilibrium moisture content as a result of acetylation.

Species	WPG	Reduction in EMC	Reference
<i>Pinus sylvestris</i>	20	50	Minato et al. 2003
<i>Pinus elliotti</i>	20	50	Hillis 1984
<i>Populus tremula</i>	20	50	Rowell 2005
<i>Pinus sylvestris</i>	20	70	Epmeier et al. 2004

For heat treated wood Stamm et al. (1946) were the first to report a loss of mechanical properties as a result of the treatment of wood. They heated wood at 320 °C for one minute or 150 °C for a week and found a 17 % reduction in modulus of rupture (MOR) when heated in molten metal and 50 percent when heated in air. Under the same conditions, there was less loss in modulus of elasticity (MOE).

Rapp and Sailer (2001) heated pine and spruce at 180 to 220 °C for various times in air and in oil and determined MOR and MOE in a three point bending test. The highest MOE was 11,000 N/mm<sup>2</sup> in oil heating and little loss in MOE in both air and oil heating. MOR, however, decreased 30% in oil heating and impact bending strength decreased and the wood became brittle. Oil-heated wood lost about 50% and air-heating lost over 70% of the impact strength compared to controls. Table 4.3. shows changes in strength as a result of heat treatment for various woods.

**Table 4.3.** Change in MOR as a result of heat treatment of various woods.

Species	Treatment	MOR (%)	Reference
<i>Betula pendula</i>	Vapor, 200 °C	-43	Johansson and Moren 2005
<i>Beech, spruce</i>	Vapor 200 °C	-50	Yidiz et al. 2006
<i>Pinus sylvestris</i>	OHT 220 °C	-30	Rapp and Sailer 2001
<i>Pinus pinaster</i>	O <sub>2</sub> 180-200 °C	-6 to -25	Esteves et al. 2006

In a strength study conducted on furfurylated wood, within the European project, EcoBinders it was found that the bending strength is more or less unchanged compared to the unmodified wood whereas the modulus of elasticity (MOE) is increased with approximately 50%. The energy needed to break the test specimens expressed as WTF (work to failure) was reduced by 15-25% depending on wood specie. Decreased WTF is correlated to increased brittleness.

In both an industrial strength grading machine (Precigrader) and in 4-point bending in a conventional rig, full size Kebony beech decking boards had 20% lower strength compared to unmodified beech boards. However the MOE was practically the same which is more important for the application. Concerning brittleness, furfurylated, DMDHEU modified and melamin resin modified wood have approximately equal increase in brittleness compared to unmodified control. Acetylation only leads to slight increase in brittleness. Impregnation with wood preservatives does not change the brittleness.

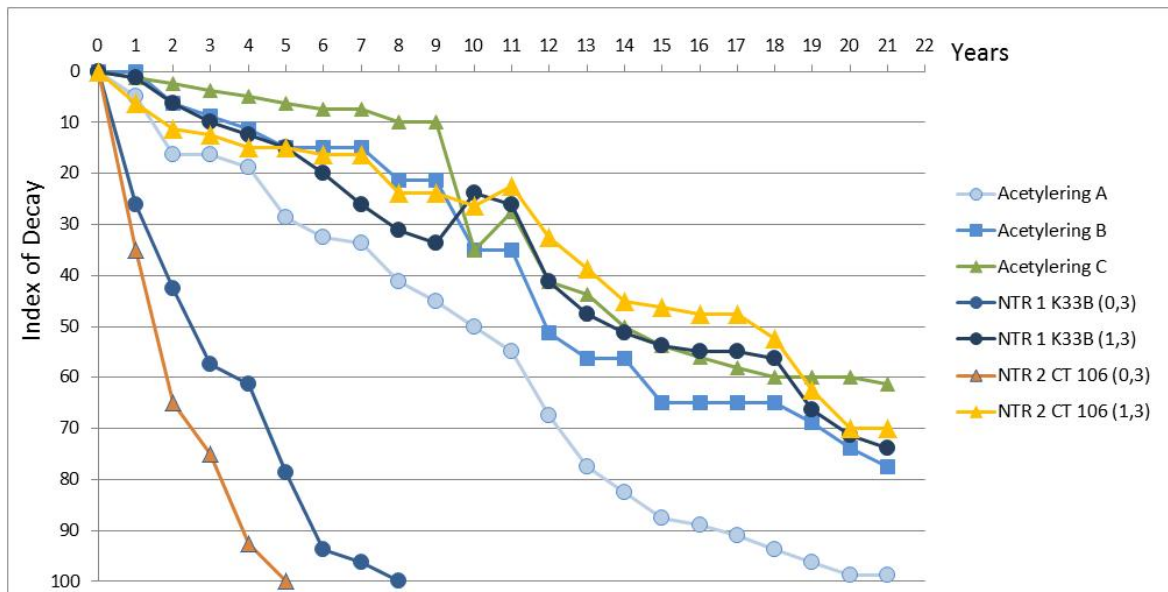
An important strength parameter in long-term loading of wood is creep. Epmier et al (2006) stated that when studying the creep deformation under constant load and during cyclic climate changes for modified wood, acetylated wood had the lowest creep deformation, followed by furfurylated wood wood compared to unmodified wood. Preservative treated wood had the same creep deformation as untreated wood and thermally modified wood had only slightly lower creep deformation than unmodified wood.

### 4.3 Durability

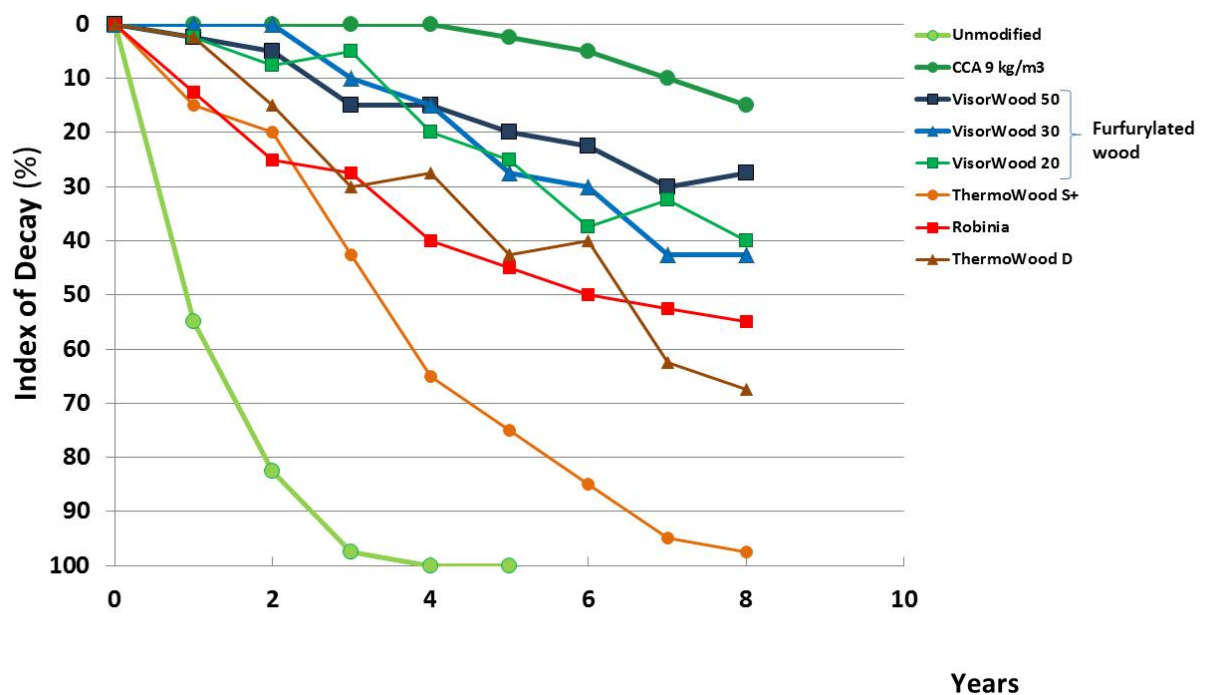
The three modification methods investigated all gain enhanced decay resistance. Results from different studies are presented below and the most severe test is the EN 252 standard, (durability in ground contact).

Acetylated wood material exhibits a considerably increased biological resistance, and has among the studied modifications the highest biological resistance. Over the years, several authors have reported on this effect in different laboratory tests (Rowell et al. 1987, Nilsson et al. 1988, Takahashi et al. 1989)

One early field test on acetylated wood was conducted by Larsson et al. in 1992 and results from this study (figure 4.4.) show that today after 21 years of exposure in ground contact at the test site in Simlångsdalen the acetylated wood performs as well as CCA treated wood (a traditional wood preservative treated to a high loading of copper, chromium and arsenic). Both level B and level C of acetylation have a about the same index of decay as the CCA reference preservatives.



**Figure 4.4.** Decay resistance expressed as index of decay for acetylated wood exposed for 21 years in Simlångsdalen (from: authors own data)



**Figure 4.5.** Decay resistance expressed as index of decay for furfurylated and heat treated wood exposed for 8 years in the test field in Borås (from: authors own data)

A selection of results from a field test started at SP wood technology by Westin and co-workers in 1996 is presented in figure 4.5. It shows that after 8 years Thermowood S is almost totally degraded by fungi, while Thermowood D performed better. Furfurylated wood showed the best performance.

It should be pointed out the neither Kebony nor Thermowood claims that their products are to be used in ground contact (Use class 4) but are instead recommending the products for applications in Use class 3, which is above ground applications.

## **5 Concluding remarks**

In this report mainly three different modification methods have been discussed. The processes for production and the product properties have been presented. The aim has also been to give the reader a comparison between the modification methods.

In general it can be concluded that for all methods hardness, dimensional stability and durability are highly increased compared to unmodified wood whereas the strength properties are unchanged or in the case of heat treatment decreased.

In appendix 1, a summarizing bench marking table for the different technologies is presented. It should be pointed out, though, that the figures in the table are to be seen as guidance rather than absolute figures.

From the authors point of view there are great market potentials for modified wood in the near future.

**SP Technical Research Institute of Sweden**  
**SP Wood Technology**

A handwritten signature in black ink, reading "Pia Larsson Brelid". The signature is fluid and cursive, with the first name "Pia" and last name "Brelid" being more prominent than the middle name "Larsson".

Dr. Pia Larsson Brelid  
Senior researcher and Project leader



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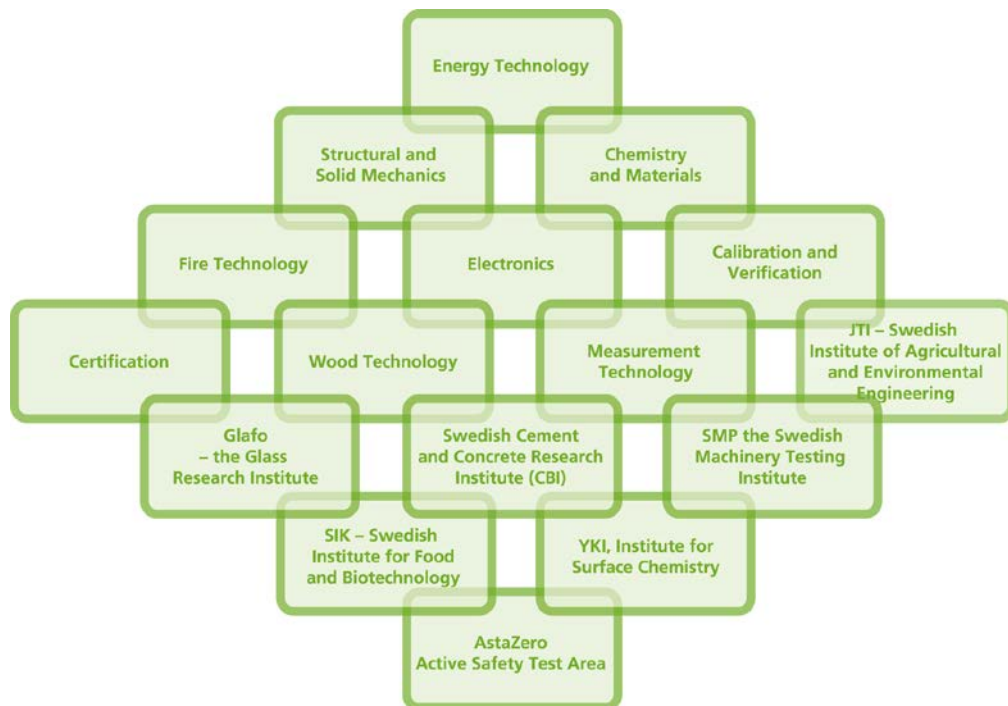
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A summarizing bench marking table  
for the different technologies

Property	Kebony Scots pine	Kebony SYP or Maple	Kebony Black	Accoya	Thermo-Wood D spruce	Belmadur (DMDHE U)	Preservative treated wood		Western red Cedar	Budget Tropical timber e.g. Cumaru	Prestigious Tropical timber e.g. teak	Wood Plastic Composite (no biocide)
	3x	5x	10x	6-7x	3x	5x?	UC3	UC4	6-7x	4x	8-20x	2-3x
Cost	++	++	+++	++	--	+	x	x	-	+	++	-
Durability UC4	++	++	+++	++	++	++	++	++	++	++	++	+
Durability UC3	+	+	+	++	+	-	+/-	+	++	+	++	-
Mould resistance	+	++	+++	++	++	+	+/-	+/-	+	+	++	+
Dimensional stability	+/-	+	++	+/-	--	+	+/-	+/-	-	+	++	-
Strength	-	-	++	+/-	--	-	+/-	+/-	+	-	+/-	++
Toughness	+	+	+++	+/-	++	+	-	-	+/-	+	+	+
Hardness	++	++	+	+	+	+/-	--	--	-	--	--	-
Environmental profile	-	-	+/-	+/-	--	-	+/-	+/-	+/-	+/-	+	++
Low risk for splinters	--	--	--	--	-	-	-	-	-	+/-	+/-	++
Not corrosive to fastener												
Colour	Dark brown	Dark brown	Black	Bright	Brown	Light brown	Blue-green	Blue-green	Orange brown	Dark brown	Dark brown	Any colour
Suitable for:												
- residential decking	Maybe	Yes				Yes	Yes	Yes	Yes	Yes		Yes
- fence-poles	Yes	Yes		Yes			Yes	Yes		Yes		
- transmission poles	Yes							Yes				
- noise shields	Yes						Yes	Yes	Yes			Yes
- boat decking		Yes									Yes	
- window and door joinery		Yes		Yes		Yes					Yes	
- bridges & jetties	Yes	Yes		Yes				Yes	Yes			Yes
- cladding	Yes											
- outdoor furniture incl public furniture		Yes		Yes		Yes					Yes	
- furniture		Yes										
- flooring incl public		Yes	Yes			Yes					Yes	

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## SP Technical Research Institute of Sweden

Box 857, SE-501 15 BORÅS, SWEDEN

Telephone: +46 10 516 50 00, Telefax: +46 33 13 55 02

E-mail: [info@sp.se](mailto:info@sp.se), Internet: [www.sp.se](http://www.sp.se)

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