Enhancement of Lower Value Tropical Wood Species Acetylation for Improved Sustainability & Carbon Sequestration

Ferry Bongers[1], Roger M. Rowell[2], Matt Roberts[3]

ABSTRACT

Wood, having the lowest embodied energy of any mainstream building material, is carbon neutral. As such, wood, our only naturally renewable construction resource, helps combat global warming by absorbing carbon from the atmosphere and storing it away for the life of the wood product. Not only is wood renewable, but it is also biodegradable and sustainable. Nature is programmed to recycle wood back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. Once broken down, these elements contribute to the circle of life by providing nutrients or biomass energy for the growth of new plant life which will grow and, in turn, absorb carbon atmospheric carbon.

The rate of recycling depends on the natural durability of the wood species. Many tropical hardwoods are known for their durability characteristics. However, a large number of higher yield sustainable tropical species do not have inherent durability, dimensional stability and other valued characteristics and thus rank only low market prices. By altering the wood cell wall polymers at the molecular level, the properties of wood species with low durability could be enhanced. Acetylation is well known to increase the resistance of wood against wood decaying fungi and destructive insects as well as improving the dimensional stability in moist circumstances. Acetylation of wood creates opportunities to improve the utilization of low value tropical wood species and to extend the balance of carbon sequestration capabilities of otherwise non-durable species.

KEYWORDS

Acetylation, dimensional stability, decay resistance, carbon sequestration, low durable wood species

[1] Product Development Manager, Titan Wood Ltd.., Westervoortsedijk 73, 6827 AV, Arnhem, The Netherlands, phone +31 26 366 4122, ferry.bongers@titanwood.com.

[2] Professor Emeritus, University of Wisconsin, Madison, WI phone +1 608-231-1821, rmrowell@wisc.edu and Chief Wood Scientist, Titan Wood Ltd.., Westervoortsedijk 73, 6827 AV, Arnhem, The Netherlands, roger.rowell@titanwood.com.

[3] Technical Sales Manager, Americas , Titan Wood Ltd, 5000 Quorum Dr. #620, Dallas, Texas 75254 USA, phone +1 972 233 6565 x2216, matt.roberts@titanwood.com

1. INTRODUCTION

1.1 Wood's nature

Wood is a renewable, biodegradable and sustainable matrix of cellulose, hemicelluloses, lignin, extractives and inorganics. Nature is programmed to recycle it, in a timely way, back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradation processes. Most problems are associated with wood destroying fungi under high humidity conditions. This leads to strength loss and destruction of the wood. Furthermore, wood changes dimension with changing moisture content because the cell wall polymers contain hydroxyl groups that attract moisture through hydrogen bonding. Moisture swells the cell wall which expands until it is saturated with water (fiber saturation point, FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further swelling. This process is reversible, and the fiber shrinks as it loses moisture below the FSP. Wood exposed to moisture frequently is not at equilibrium, having wetter areas and drier areas within the same board. This exacerbates the moisture problem resulting in differential swelling followed by cracking and/or compression set. Further wood exposed outdoors undergoes photochemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, but after the lignin has been degraded, the poorly bonded carbohydrate-rich fiber surface easily erodes which exposes new lignin to undergo further degradation reactions. In time, this "weathering" process causes the surface of the composite to become rough and can account for a loss in surface fibers. Further, wood exposed outdoors is subject to discoloration due to mold and blue stain fungi.

The rate of recycling depends on the natural durability of the wood species. Many tropical hardwoods are known for their durability characteristics. However, a vast majority of the world's wood species do not posses inherent durability, dimensional stability and other valued characteristics. The world's supply of durable wood suitable for long term performance in outdoor applications is becoming more and more scarce. Furthermore, environmental regulations on the use of toxins to enhance the durability of wood species is increasing. An environmentally friendly alternative is the chemical modification of wood which results in improved wood performance. By altering the wood matrix on a molecular level, the properties of wood species with low durability can be enhanced. Acetylation is well known to increase the resistance of wood against wood decaying fungi and destructive insects as well as improving the dimensional stability in moist circumstances.

1.2 Wood acetylation

Acetylation has been studied extensively and is shown to be one of the most promising methods for improvement of technical properties of low durable wood species. The first wood acetylation trial was done in 1928 by Fuchs on small blocks using acetic anhydride and sulfuric acid as a catalyst. Since then many others have performed research on the acetylation of wood, in respect to the process as well as the material properties of acetylated wood. A comprehensive background of acetylation and wood modification in general is given by Hill (2006) and Rowell (1983, 1984, 2005, 2006).

In the last decade most work has been done with uncatalyzed acetic anhydride. The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall to acetyl groups with the formation of byproduct acetic acid (see Fig. 1). The durability and dimensional stability of a wood species can be improved considerably by acetylation (Beckers and Militz, 1994; Beckers et al., 1994; Goldstein et al., 1961; Larsson-Brelid et al., 2000; Militz, 1991; Rowell et al., 1989; Singh et al., 1992).

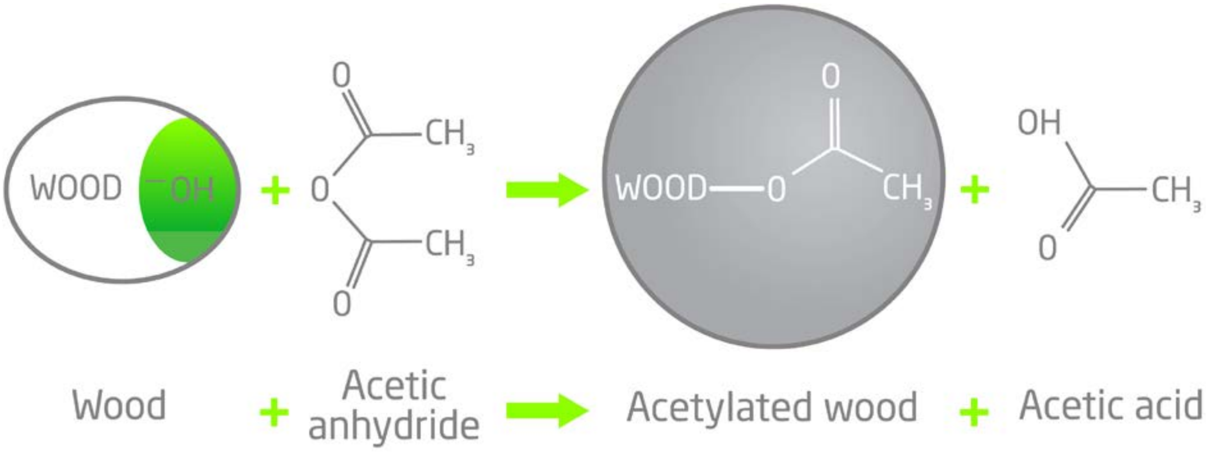

Figure 1. *Schematic reaction of acetic anhydride with wood.*

1.3 Commercial production

In spite of the vast amount of research on chemical modification of wood, and, more specifically, on the acetylation of wood, commercialization has not come easily. Besides the complexity in controlling the acetylation process and dealing with the variability and complex nature of wood, alternative products such as durable tropical hardwood species were available on the market in sufficient supply. Nowadays, the markets have changed and there is need for enhancing low valued wood species for use in high end applications. In this respect Titan Wood Ltd. (www.titanwood.com) has built a commercial-scale production facility to acetylate approximately 30,000 m^3 wood per annum. Titan Wood has developed an acetylation process for radiata pine (*Pinus radiata* D. Don) up to 100 mm lumber thickness. Currently a production facility, based on Titan Wood's technology, is being built by Diamond Wood in Asia with a capacity of 100.000 m^3 per annum.

In the large scale production of acetylated wood, lumber is stickered and placed in a high pressure vessel using advanced handling equipment for efficiency. Acetic anhydride is introduced into the vessel and the temperature is raised to the reaction temperature. After the reaction is complete, the excess anhydride is recycled and the by-product acetic acid is processed back into anhydride. The acetylated wood is then dried, removed from the vessel and stored until shipment. As part of the quality control of the product, the degree of acetylation, expressed as acetyl content, is measured by novel chemical analysis methods. The entire process has minimal by-products, which have ready end-uses, and is environmentally benign. When combined with the use of sustainably grown wood from certified sources as input, acetylated wood provides an improved building material that addresses a range of environmental factors.

1.4 Development of acetylation processes

Currently Titan Wood is working on the development of commercially viable acetylation processes for wood species other than radiata pine, which is already commercially produced and sold under the name Accoya® (www.accoya.info). Included in this research program are various wood species sourced from throughout the world including, but not limited to, those of southern yellow pine (USA), scots pine (EU), beech (EU) and masson pine (China). Generally all wood species which are easily impregnatable and have a low to intermediate density (300 to 700 kg/m3) have high potential for the acetylation process to successfully upgrade the dimensional stability and durability (resistance against fungi). Furthermore, in respect to commercial production, the available volume, quality, and pricing of the wood species are important considerations. In addition to process development, detailed studies are performed on the wood characteristics, economics and market opportunities.

1.5 Acetylation of non-durable tropical wood species.

Most acetylation research on non-durable tropical woods is done on rubber wood (*Heavea brasillensis*) and oil palm (*Elaeis guineemsis*). Research has been concentrated on acetylation of fibers for stable composite boards (Dhamodaran 1995, Hadi et al. 1995, Harun 1995). The results show that the dimensional stability and durability can be improved considerably for these non-durable tropical wood species.

Titan Wood has performed some initial acetylation trials on the non-durable tropical hardwood species from Brazil in co-operation with a FSC certified forest owner. The following wood species were studied on their suitability for the acetylation process: marupa (*Simarouba spp*.), breu vermelho (*Protium altosonii*.), breu branco (*Protium spp*.), jacareuba (*Calophyllum angularis*), piquirana (*Caryocar glabrum*), tauari vermelho (*Cariniana micrantha*) and tento (*Ormosia paraensis*). Promising results in respect to the achieved acetylation content are obtained for tauri vermelho. In the next phase of the project more detailed process development is performed, wood characteristics are determined and economic and market studies are done.

2. MATERIAL PROPERTIES ACETYLATED WOOD

The properties presented in this paper are mainly based on acetylated radiata pine. These properties have been determined for certification of Titan Wood's acetylation process and to demonstrate the suitability of acetylated radiata pine for use in joinery, cladding and decking. All described testing work has been performed by a series of independent research institutes. Current process development within Titan Wood and studies by many other researchers show that acetylation could be successfully performed on many other wood species like southern yellow pine, aspen and beech.

2.1 Durability

Radiata pine, which has been acetylated to various degrees, has been investigated according to EN 113 and ENV 807 in which the resistance against fungal decay by brown-, white-, and soft rot fungi is studied. Prior to the testing the samples have been leached in water according to EN 84.

In the EN 113 the following fungi species were tested:

- *Coniophora puteana* (brown rot: cellar fungus, wet rot fungus, cellar rot fungus)
- *Coriolus versicolor* (white rot: Turkey tail fungus, shelf fungus)
- *Gloeophyllum trabeum* (brown rot: conifer mazegill)
- *Poria placenta* (brown rot: pore fungus)
- *Serpula lacrymans* (brown rot: true dry rot fungus)

The samples were placed in culture vessels, which contained sterilized culture medium (agar) which was inoculated with one of the wood destroying fungi. In each culture vessel, two acetylated samples and one reference sample (scots pine sapwood) were placed. These culture vessels were placed in a culture chamber (22 °C, 70% RH) for a period of 16 weeks. After the exposure period, the mass loss, as result of fungal decay of the samples, was determined (see Figure 3).

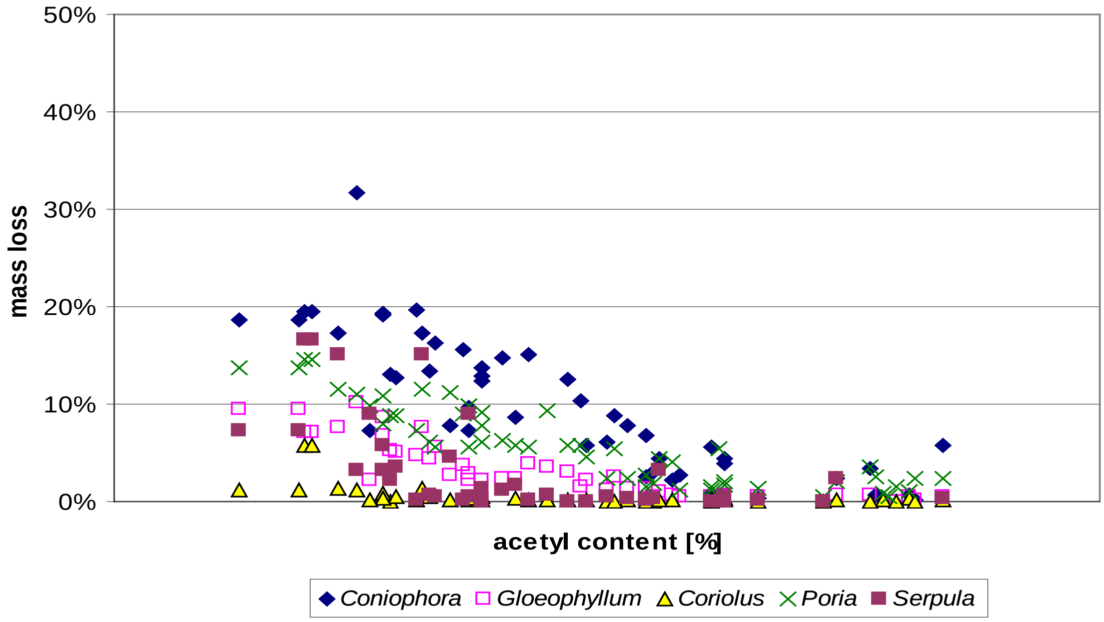

Figure 1. *Mass loss of acetylated radiata pine caused by basidiomycetes (EN 113 test) in relation to the acetyl content.*

The ENV 807 method II test was performed with acetylated samples of the same boards that were selected for the EN 113 test. Scots pine sapwood (*Pinus sylvestris*) was used as reference. The samples were placed in containers with specially prepared soil of known moisture content and water holding capacity. These containers were placed in a (dark) culture chamber (27 °C, 95% RH). After an exposure period of 12 weeks, additional scots pine sapwood samples (virulence control samples) indicated a more than sufficient mass loss to validate the test. The mass loss, as result of fungal decay, was determined for all samples (see Figure 4).

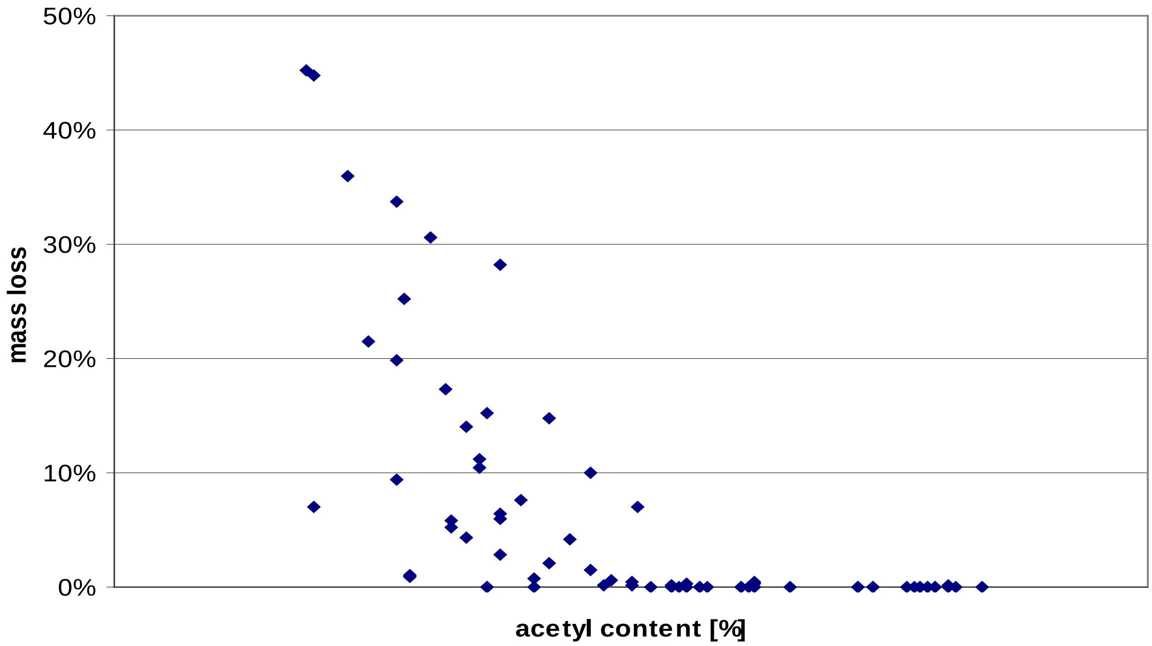

Figure 4. *Mass loss of acetylated radiata pine caused by soft rot decay (ENV 807 test) after 12 weeks soil exposure in relation to the acetyl content.*

The results show that the higher the degree of acetylation the better the resistance against fungal decay. By comparing the acetylated wood to the unmodified reference wood species, scots pine sapwood, a durability classification can be made according to EN 350-1. The test results show that the most aggressive fungus for acetylated radiate pine is the brown rot fungus *Poria placenta*. Based on regression the minimum degree of acetylation (acetyl content) to classify acetylated radiata pine as durability class 1 can be determined (see Figure 5).

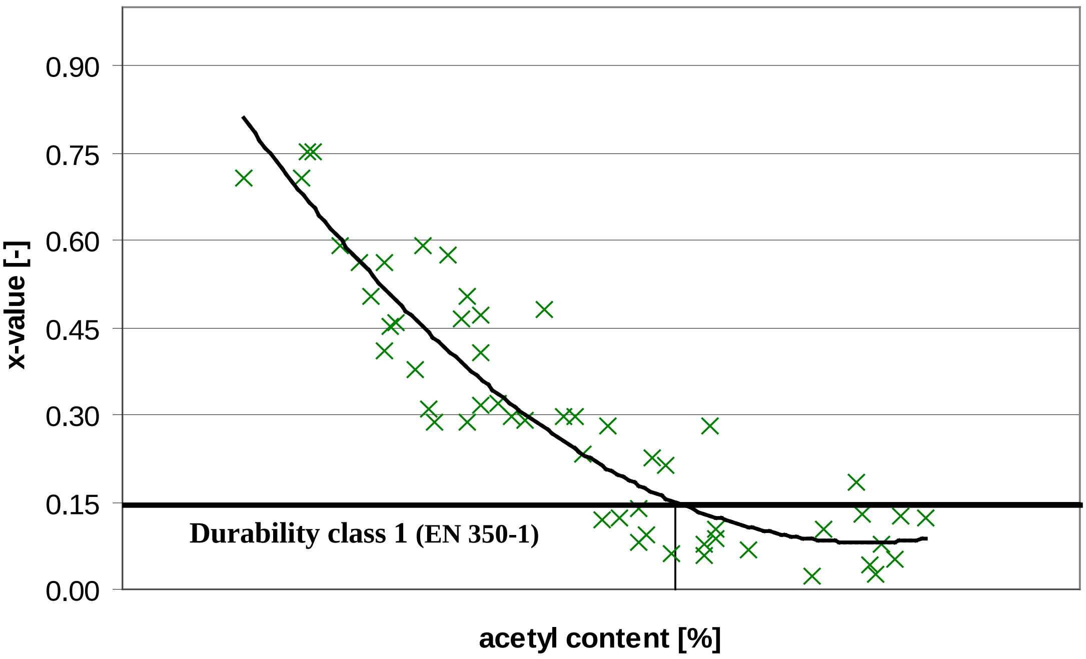

Figure 5. *X-values of acetylated radiata pine in relation to the acetyl content, based on the EN 113 test with Poria placenta.*

<u>2.2 Dimensional stability</u>

Unmodified and acetylated radiata pine samples were conditioned at the following climates: oven dry, 25, 35, 50, 65, 80, 95% relative humidity and water saturated (all at a temperature of 20 °C). In this order (adsorption sequence), as well as in the reverse order (desorption sequence). The weight and dimensions (radial and tangential) of the samples were determined for each of the conditions. Based on the weight measurements, the relation between the relative humidity (of the air) and the corresponding equilibrium moisture content (EMC) of the wood was determined for both the adsorption and desorption sequence. The corresponding shrinking and swelling was measured in the radial and tangential orientations of the wood structure. The results are expressed in Figure 6. The results illustrate that the equilibrium moisture content of acetylated radiata pine has been significantly be reduced. Further the dimensional stability is improved considerably.

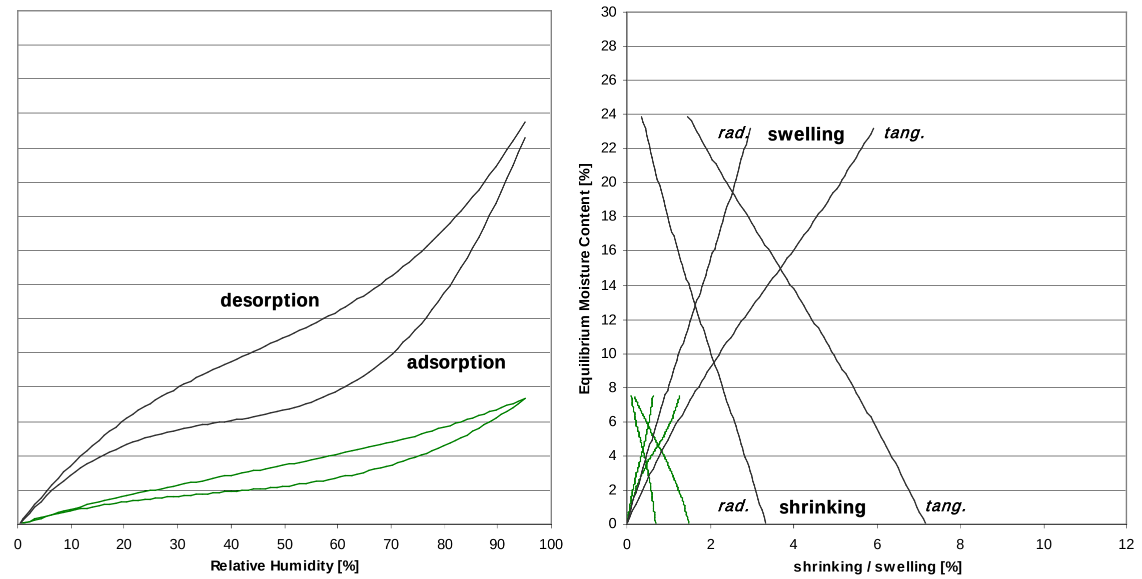

Figure 6. Hygroscopic behavior (left) of acetylated radiata pine (green line) and (unmodified) radiata pine (black line) under different moisture conditions and the corresponding swelling and shrinking behavior.

2.3 Insect resistance

Testing to date with a range of acetylated wood species that are not naturally resistant to insect attack has shown strong results. For example, testing of acetyalted ® radiata pine for termite resistance following AWPA E1 choice test protocals yielded appearance ratings always $\geq$ 9 (Light Attack) versus control sample averages of 3.5 (worse than Heavy Attack). Weight loss averaged 1.43% for acetylated radiata versus control sample averages of 32.06%.

2.4 Mechanical properties

2.4.1 Bending stiffness and -strength

In Jorissen et al. (2005) the bending stiffness (MOE) and bending strength (MOR) of acetylated and unmodified radiata pine in structural sizes are reported. The results are given in table 1. The table shows strength properties are retained even after acetylation.

Table 1. *Bending stiffness (MOE) and bending strength (MOR) of unmodified and acetylated radiata pine.*

	Density* [kg/m^3]	**MOE [N/mm^2]**	**MOR [N/mm^2]**
Acetylated	492	8788	39
Unmodified	417	9664	43

**conditioned at 65% RH and 20°C.*

2.4.2 Janka hardness

The Janka hardness of unmodified and acetylated radiata pine has been determined according to ASTM D143. In Table 2 the results are shown. It can be concluded that the acetylation process significantly increases the Janka hardness of radiata pine. The average Janka hardness of acetylated radiata pine in radial, tangential and end grain orientation has been increased by 44%, 53% and 80% respectively, compared to unmodified radiata pine.

Table 2. *Average Janka hardness of unmodified and acetylated radiata pine.*

	Janka hardness		
	Radial [N]	**Tangential [N]**	**Cross cut [N]**
Acetylated	4050	4190	6600
Unmodified	2750	2750	3640

2.4.3 Impact bending strength

The impact bending strength of unmodified and acetylated radiata pine has been determined according to DIN 52189. The results (see Table 3) show that the impact bending strength of acetylated radiata pine is not significantly different from that of unmodified radiata pine.

Table 3. *Average impact bending strength of acetylated and unmodified radiata pine.*

	Impact bending strength [kJ/m^2]
Acetylated	50
Unmodified	50

2.4 Other properties

Many other properties have been determined in order to be able to prepare a final product (for instance joinery, cladding and decking) with acetylated radiata pine. Tests have been performed on glueing, painting, mounting and processing of acetylated wood. A 10-year old field test with coated acetylated and unmodified panels showed significantly improved coating performance on the acetylated wood. Whilst the coating layer on the unmodified wood was seriously cracked and flaked and in some cases almost completely eroded, the coated acetylated samples were still in good shape. It was concluded that “If a coating system is adapted to be used on acetylated wood and the application is done in the appropriate way, it is expected that the maintenance frequency can be once every ten years or even lower” ((Bongers et al. 2005). Schaller and Daniel (2007) concluded that part of the lignin is more resistant to UV degradation in acetylated radiata pine.

3. APPLICATIONS

The enhanced durability and dimensional stability resulting from acetylation makes acetylated wood highly suitable for demanding applications such as joinery, cladding, decking and other outdoor applications. Currently, acetylated radiata pine is commercially produced for the Dutch, German and UK market. In this phase of introducing acetylated wood to the market, independent research companies are involved in the regular inspection of realized projects. One project of particular importance is the production of a heavy duty (60 ton) wooden bridge of 40 meter span (Tjeerdsma et al. 2007). Acetylated radiata pine was selected as the building material of choice due to its superior strength-to-weight ratio, durability, dimensional stability and low maintenance costs. Additionally, the use of acetylated wood in place of traditional materials such as steel further contributes to the sustainable nature of the project. In this project many research companies and test institutes have been involved to realize a dream. The bridge is build in Sneek (NL) and will be installed in November 2008.

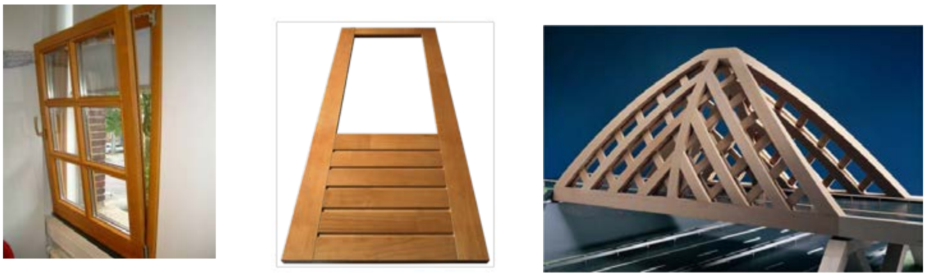

Figure 5. *Examples of acetylated wood applications (windows, doors and Sneek bridge).*

4. CONCLUSIONS

Acetylation of wood significantly improves the base species' dimensional stability and durability and has minor impact on strength properties. As a result, acetylated wood is highly suitable for demanding applications such as joinery, cladding, decking and other outdoor applications.

Acetylation technology provides an environmentally safe method of protecting sustainable non-durable woods resulting in a new generation of value-added products with increased stability and durability without the use of toxic chemicals. This method of chemical modification can relieve demand pressure of endangered tropical hard wood species that have traditionally been the only means of meeting durability requirements.

REFERENCES

ASTM D143 (1994). Standard Test Methods for Small Clear Specimens of Timber. Section 13 – Hardness. ASTM International, West Conshohocken, USA.

Beckers, E.P.J. and Militz, H. (1994). Acetylation of solid wood. Initial trials on lab and semi industrial scale. In: Second Pacific Rim Bio-Based Composites Symposium, Vancouver, Canada, November 6-9 1994, 125-133.

Beckers, E.P.J., Militz, H. and Stevens, M. (1994). Resistance of acetylated wood to basidiomycetes, soft rot and blue stain. In: International Research Group on Wood Preservation, Document no. IRG/WP 94-40021.

Bongers, F., Creemers, J., Kattenbroek, B. & W. Homan (2005). Performance of coatings on acetylated scots pine after more than 9 years outdoor exposure. In: Miltz, H.& C. Hill (eds.). Wood Modification: Processes, properties and commercialisation. Proceedings of the Second European Conference on Wood Modification. ECWM 2005, 6-7th October 2005, Göttingen, Germany, p. 125-129.

Dhamodaran, T.K. (1995). Chemical modification of rubberwood by acetylation and its effect on dimensional stability and physical and mechanical properties. IUFRO XX World Congress, 6-12 August 1995, Tampere, Finland.

DIN 52189 (1981). Prüfung von Holz; Schlagbiegeversuch; Bestimmung der Bruchschlagarbeit. DIN Deutsches Institut für Normung, Berlin, Germany.

EN 84 (1997). Wood preservatives - Accelerated ageing of treated wood prior to biological testing - Leaching procedure. European Standard.

EN 113 (1996). Wood preservatives – Test method for determining the protective effectiveness against wood destroying Basidiomycetes – determination of toxic values. European Standard.

EN 350-1 (1994). Durability of wood and wood-based products – Natural durability of solid wood – Part 1: Guide to the principles of testing a classification of the natural durability of wood. European Standard.

ENV 807 (2001). Wood preservatives - Determination of the effectiveness against soft rotting micro-fungi and other soil inhabiting micro-organisms. European Standard.

Fuchs, W. (1928). Acetylation of pine wood. Genuine lignin I, Ber. 61B:948-51.

Goldstein, I.S., Jeroski, E.B., Lund, A.E., Nielson, J.F. and Weaver, J.W. (1961). Acetylation of wood in lumber thickness. Forest Products Journal, 11(8), pp.363-370.

Hadi, Y.S., Darma, I.G.K.T., Febrianto, F., Herliyana, E.N. (1995). Acetylated rubberwood flakeboard resistance to bio-deterioration. Forest Products Journal 45(10), pp. 64-66.

Hill, C.A.S. (2006). Wood modification: chemical, thermal and other Processes. John Wiley & Sons, Chichester, England, 239 pp.

Harun, J. (1995). Acetylation and dimensional stability of oil palm (*Elaeis guineensis Jacq*.) trunk and empty fruit bunch composite boards. IUFRO XX World Congress, 6-12 August 1995, Tampere, Finland.

Jorissen, A., Bongers, F., Kattenbroek, B. & W. Homan (2005). The influence of acetylation of radiata pine in structural sizes on its strength properties. In: Miltz, H.& C. Hill (eds.). Wood Modification: Processes, properties and commercialisation. Proceedings of the Second European Conference on Wood Modification. ECWM 2005, 6-7th October 2005, Göttingen, Germany, p. 108-115.

Larsson-Brelid, P., Simonson, R., Bergman, O. and Nilsson, T. (2000). Resistance of acetylated wood to biological degradation. Holz als Roh- und Werkstoff, 58, pp. 331-337.

Militz, H. (1991). Die Verbesserung des Schwind- und Quellverhaltens und der Dauerhaftigkeit von Holz mittels Behandelung mit unkatalysiertem Essigsäureanhydrid. Holz als Roh- und Werkstoff, 49, pp. 147-152.

Rowell, R. M. (1983). Chemical modification of wood: A review, Commonwealth Forestry Bureau, Oxford, England, 6(12), pp. 363-382.

Rowell, R. M. (1984). The Chemistry of Solid Wood, Advances in Chemistry Series No. 207, American Chemical Society, Washington, DC, 458 pp.

Rowell, R.M. (2005). Handbook of Wood Chemistry and Wood Composites, Taylor and Francis, Boca Raton, FL, 487 pp.

Rowell, R.M. (2006). Chemical modification of wood: A journey from analytical technique to commercial reality, Forest Products Journal, 56(9), pp. 4-12.

Rowell, R.M., Imarura, Y., Kawai, S. and Norimoto, M. (1989). Dimensional stability, decay resistance, and mechanical properties of veneer-faced low-density particleboards made from acetylated wood. Wood and Fiber Science, 21(1), pp. 67-79.

Schaller, C., Daniel, R. (2007). Light Stabilization of Modified Wood Species. ECWM 3, 15-16th October 2007, Cardiff, Wales, UK.

Singh, S.P., Dev, I. and Kumar, S. (1992) Chemical modification of wood with acetic anhydride. Journal of the timber Development Association of India 38(1), pp. 5-8.

Tjeerdsma, B., Kattenbroek, B., Jorissen, A. (2007). Acetylated wood in exterior and heavy load-bearing constructions. Building of two timber traffic bridges of acetylated radiata pine. ECWM 3, 15-16th October 2007, Cardiff, Wales, UK.