Journal of Tropical Forest Science 30(Anniversary Issue): 488–495 (2018)
https://doi.org/10.26525/jtfs2018.30.5.488495

STABLE AND DURABLE WOOD PRODUCTS BASED ON MOLECULAR MODIFICATION

Rowell RM[1,] * & RE Ibach[2]

[1]*Biological Systems Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA*
[2]*Forest Products Laboratory, USDA Forest Service, One Gifford Pinchot Drive, Madison, Wisconsin 53726, USA*

* *rmrowell@wisc.edu*

Received April 2018

Stable and durable wood products can be produced by chemical modification at the molecular level. One modification that is effective in achieving these properties is by reacting both hardwoods and softwoods with acetic anhydride. The reaction takes place in the most accessible hydroxyl groups in the cell wall polymers. Lignin reacts the fastest followed by the hemicelluloses. Both are highly substituted. As the level of bonded acetyl increases, dimensional stability increases and attack by fungi decreases. The threshold of fungal resistance is approximately 18% acetyl. The moisture in the cell wall may be too low to support fungal growth. This is a summary of several independent projects on the mechanism of property enhancement that were previously published in proceedings.

Keywords: Hardwoods, softwoods, modification, acetylation, stable, durable, swelling, shrinking, decay, performance

INTRODUCTION

Wood has been used since the first humans walked the earth for fuel, shelter, weapons, tools and for decoration. It is considered easy to work, and is renewable, sustainable and widely available. For the most part, it has been used without modification. Wood is valued and used all over the world not only for its aesthetics but also for its low cost and recyclability. However, using untreated wood in tropical outdoor climates raises concerns about its low stability and durability. There are more and more restrictions on the use of toxic wood preservatives and the use of durable tropical timbers.

Since wood is hygroscopic, it sorbs moisture from its environment and swells. It shrinks as that moisture is lost. This is a problem for furniture makers in tropical countries that ship the finished product to countries with low humidity. Joints loosen when the product adjusts to the new lower moisture content.

The performance at the solid wood level (swelling/shrinking, biological attack and strength) are derived from the properties at the cell wall matrix and polymer level. Swelling/shrinking, rotting, weathering, burning and strength properties are all a result of properties at the molecular level (Rowell 2012b, 2015a, 2016a). If we want to change performance, it is best done at the molecular level.

The properties of any resource are, for the most part, a result of the chemistry of the resource (Rowell 1975). If you change the chemistry, you change properties, and if you change properties, you change performance. Stable and durable properties of wood can be modified by changing at the molecular level the chemistry of the cell wall polymers and the matrix they are in. This can be done through several chemical systems (reviewed by Kumar 1994; Hon 1996, Hill 2006, Rowell 2012a). These chemicals include anhydrides such as phthalic, succinic, malaic, propionic and butyric anhydride, acid chlorides, ketene, carboxylic acids, many different types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthaldehydic acid, dimethyl sulfate, alkyl chlorides, β-propiolactone, acrylonitrile, epoxides (e.g. ethylene, propylene and butylene oxide), furfural alcohol, dimethyloldihydroxyethylenurea (DMDHEU) and difunctional epoxides.

The acetylation of wood was first performed 1928 (Fuchs 1928, Horn 1928, Suida & Titsh 1928) and the first patent on wood acetylation was in 1930 (Suida 1930). Tarkow (1945) was the first to demonstrate that acetylated balsa was resistant

to decay. Tarkow et al. (1946) first described the use of wood acetylation to stabilise wood from swelling in water. Many laboratories in the world have done research on wood acetylation (reviewed by Kumar 1994; Hon 1996, Hill 2006, Rowell 2012a).

All woods contain acetyl groups, which comprise 0.5–1.7% and 2–4.5% of soft- and hardwoods respectively. Increasing the cell wall acetyl level changes properties and performance in proportion to the level of bonded acetyl. Wood that has been acetylated to an acetyl level above about 18% has very high dimensional stability, decay resistance, improved coating performance, wet strength and stiffness (Rowell 2006).

The technology involves the reaction of wood with acetic anhydride and is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no

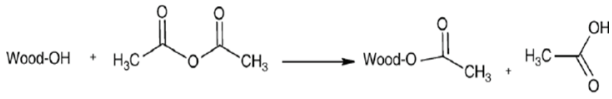


Figure 1 Reaction of wood with acetic anhydride

polymerisation (Figure 1). The reaction rate is based, in large part, on the rate of chemical penetration to the reactive site, and the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked since it is a single site reaction and with polymerisation (Rowell et al. 1986). The shape of the reaction curve depends on the reaction time and temperature (Figure 2, Rowell 2014a). After some time, the reaction slows and levels off indicating that the reaction is 'complete'. Since the acetyl group is larger than a water molecule, some hydroxyl groups will still be available for hydrogen bonding after the reaction is 'complete' (Rowell 2014a).

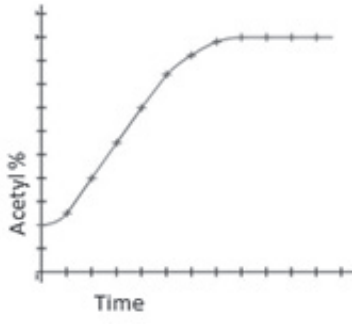


Figure 2 Rate of reaction of acetic anhydride with wood

The reaction is taking place with the most accessible hydroxyl groups, which are the hydroxyl groups that are mainly involved in the binding of water in the cell wall (Rowell 2011). Lignin is the fastest to react but since there are more hemicelluloses in wood as compared to lignin (by weight), the hemicelluloses react to a higher degree (Rowell 1982, Rowell et al. 1994). Eighty nine percent of the hydroxyl groups are substituted on lignin and 25% on the holocellulose at an acetyl weight gain of 16–19%. The hemicelluloses are much more reactive (accessible) than cellulose and very little, if any, of the crystalline cellulose reacts.

The hemicelluloses are also the most hygroscopic so it is critical to react as many hydroxyl groups in this group of polymers as possible. The hemicelluloses are the major moisture pipeline in the cell wall so acetylation of these polymers not only reduces the amount of moisture in the cell wall but also restricts the movement of moisture in the cell wall (Rowell 2015c).

We have been studying the rate of reaction and acetyl content of softwoods and hardwoods, the relationship between cell wall acetyl content and dimensional stability, and the relationship between acetyl content and decay resistance. While brown-rot fungi account for only about 6% of the total fungal population, these fungi cause the most damage, especially in softwoods (Rowell et al. 2009).

This paper is a summary of several independent projects that were previously published in proceedings. Research objectives were to determine for acetylated wood samples of selected soft- and hardwood species: (1) equilibrium moisture content (EMC) as a function of bonded acetyl, (2) dimensional stability (reported as anti-shrink efficiency or ASE) as a function of acetyl content, (3) the stability of bonded acetyl during a cyclic humidity test, (4) decay resistance as a function of acetyl content and EMC, (5) swelling and weight loss during fungal cellar test, (6) losses of weight, acetyl content and sugars after exposure to brown-rot fungus in soil block tests.

MATERIALS AND METHODS

The studies are described below. For all studies, three replicates were prepared for each sample tested. The acetyl content was determined for oven-dried specimens using gas chromatography according to the procedure outlined by Rowell et al. (2013).

(1) Softwood *Pinus radiata* (radiata pine), *Picea abies* (spruce), *Pinus sylvestris* (Scots pine), and hardwood *Fagus sylvatica* (beech), *Quercus rubra* (oak) and *Populus tremuloides* (aspen) blocks measuring 2.5 cm × 2.5 cm × 1.5 cm (radial × tangential × longitudinal), in a timed acetylation study, were reacted with acetic anhydride at 120 °C for 0.25, 0.5, 1.0, 2.0 and 4.0 hours (Rowell 2011). The acetyl content was determined for the samples and reported as weight percent gain (WPG). The results of reaction time vs WPG are reported in Table 1.

(2) *Pinus sylvestris* and *P. tremuloides* samples were submitted for sugar analysis as given in Rowell 2012a). The values are presented in Table 2. Green wood samples of these two woods, measuring 3.5 cm × 3.5 cm × 2.0 cm (radial × tangential × longitudinal), were used in an acetylation study. They were oven-dried overnight at 105 °C then reacted with acetic anhydride at 120 °C for 4 hours. Green wood volumes of the blocks were measured, oven dried over night (105 °C) and dry volume calculated. The dry wood was then acetylated. These values were used to calculate percent volume loss in drying and volume gained in acetylation. The results of these experiments are shown in Table 3 (Rowell 2011).

(3) *Pinus sylvestris* and *P. tremuloides* control and acetylated specimens were exposed to a cyclic humidity test (Rowell et al. 1992). Acetyl analysis was run on oven-dry control and acetylated specimens and placed in a 30% RH room and conditioned for 3 months. Acetyl analysis was again run and the specimens were placed in a 90% RH room for an additional 3 months. The 30% RH to 90% RH cycle was continued for 33 cycles. The results are shown in Table 4.

(4) *Pinus radiata* and *F. sylvatica* wood blocks measuring 2.5 cm × 2.5 cm × 1.5 cm (radial × tangential × longitudinal), used in studies determining EMC and ASE, were reacted with acetic anhydride at 120 °C, then placed in a constant humidity room for 21 days at 27 °C and 90% relative humidity (RH). After 21 days the specimens were weighed to determine the EMC and ASE. These values were calculated as given in Rowell 2012a. The results are presented in Figure 3.

(5) SYP wood blocks measuring 2.5 cm^3, used in ASTM D1413 standard soil block tests determining EMC and losses of weight, acetyl content and sugars; and in the fungal cellar test, were reacted with acetic anhydride at 120 °C, then placed in a constant humidity room for 21 days at 27 °C and 90% RH.

   (a) All the soil block tests exposed wood samples to the brown-rot fungus *Gloeophyllum trabeum* for 12 weeks. In the first soil block test, samples with acetyl contents of 0, 6.0, 10.4, 14.8 and 17.8% were used and samples were weighed at 12 weeks to determine EMC (Ibach et al. 2000). In the second test, samples with acetyl contents of 0.6 and 18.6% were used, and acetyl content and weight loss determined at 12 weeks (Rowell 2011). In the third soil block test, samples had initial acetyl contents of 0 and 15%, and their sugar content was determined using HPLC (following Rowell et al. 2013) at 12 weeks (Rowell 2011). Scanning electron micrographs were taken of control and acetylated samples before and after brown-rot fungal attack.

   (b) In the fungal cellar test, samples with acetyl contents of 0, 7.3, 11.5, 13.6 and 16.3% were exposed to non-sterile soil containing brown-, white-, and soft-rot fungi and tunnelling bacteria for 36 months (Rowell et al. 2007). Samples were visually assessed at 2, 3, 4, 5, 6, 12, 24 and 36 months and the degree of fungal/bacterial attack was rated as: 0 = none, 1 = slight, 2 = moderate, 3 = heavy, 4 = destroyed. Swelling of the samples, if observed, was also recorded.

RESULTS AND DISCUSSION

Table 1 shows the rate of reaction of three softwoods and three hardwoods. The softwoods react faster and to a higher level of bonded acetyl as compared to hardwoods. This may be due to the higher content of pentosans in the hemicelluloses in hardwoods as compared to softwoods. Pentosans have no primary hydroxyl group and may account for the slower reaction rate and lower final acetyl content (Rowell 2011, 2015b).

Table 2 shows the sugar content of *P. sylvestris*, *Q. rubra* and *P. tremuloides*. The pentose (xylan) content of oak (19.0%) is much higher than for pine (7.6%).

Table 3 shows the results of the change in volume in *P. sylvestris* and *P. tremuloides* from green to oven dry to acetylated wood. Oven-drying pine results in a shrinkage of 10.6% and acetylating to 21.7% acetyl brings the dry acetylated volume back to the original green volume. Oven-dry aspen results in a shrinkage of 11.8% and acetylating to 18.4% brings the dry acetylated volume back to the original green volume. This bulking of acetyl in the cell wall is the mechanism of dimensional stability. However, since the water molecule is smaller than an acetyl molecule, some cell wall hydroxyl groups are still accessible to moisture so the ASE value is never 100%.

Figure 3 shows the equilibrium moisture content (EMC) and anti-shrink efficiency (ASE) of *P. radiata* and *F. sylvatica* wood samples with different bonded acetyl levels. The decrease in moisture content is proportional to the increase in acetyl content. Hardwoods show a lower EMC at the same acetyl content as compared to the softwoods (Rowell 2014b). The increase in ASE is proportional to the increase in acetyl content. As with the EMC, the hardwoods show a higher ASE at the same acetyl content as compared to softwoods.

Table 1 Per cent acetyl content of soft- and hardwoods reacted with acetic anhydride over time

Wood sample		Reaction time (hours)				
		0.25	0.5	1	2	4
Softwood	*Pinus radiata*	13.4	15.2	19.7	21.8	24.8
	Picea abies	13.5	14.8	18.7	20.5	23.8
	Pinus sylvestris	13.7	15.4	19.5	20.7	24.9
Hardwood	*Fagus sylvatica*	10.6	11.9	15.4	16.3	17.5
	Quercus rubra	11.9	13.9	17.2	17.8	17.7
	Populus tremuloides	12.6	14.0	15.6	16.4	17.0

Table 2 Percentage of sugars found in wood samples of *Pinus sylvestris*, *Quercus rubra* and *Populus tremuloides*

Wood sample	Sugar (%)				
	Glucose	Xylose	Galactose	Arabinose	Mannose
P. sylvestris	44.0	7.6	3.1	1.6	10.0
Q. rubra	41.0	19.0	1.2	0.4	2.0
P. tremuloides	49.0	17.0	2.0	0.5	2.1

Table 3 Changes in volume of *Pinus sylvestris* and *Populus tremuloides* green wood upon drying and acetylation, and final acetyl content, with volume change (%) in brackets

Wood sample	Volume (cm^3) of wood			Acetyl content (%)
	Green	Oven-dried	Acetylated	
P. sylvestris	24.5	21.9 (-10.6)	24.3 (+9.9)	21.7
P. tremuloides	24.5	21.6 (-11.8)	24.4 (+11.5)	18.4

Table 4 shows the results of the cyclic humidity test on *P. sylvestris* and *P. tremuloides* going from 30% relative humidity (RH) and 90% RH. This shows that the acetyl (ester) bond is very stable to changes in cell wall moisture content (Rowell 2016b).

Table 5 shows the weight loss in the first 12-week soil block test using the brown-rot fungus *G. trabeum* on *P. sylvestris* (Ibach et al. 2000, Ibach and Rowell 2000). The control lost 61% weight in the test and the specimen was destroyed (see Figure 3b). As the level of bonded acetyl increased, resistance to fungal attack went down and weight loss decreased. The threshold acetyl level for resistance to attack was approximately 18% bonded acetyl. As the control sample was so deteriorated after the test and so covered with hypha, it was not possible to isolate a sample for determining the EMC. In all cases, the EMC was lower after the test showing that what was lost was more hydrophilic than the remaining specimen.

Figure 4 shows electron micrographs of the control sample before the test (a) as well as the control sample (b) and acetylated (c) *P. sylvestris* after the first 12-week test. The control sample after test was almost completely covered with fungal hypha with a destroyed cell wall (b). The acetylated sample showed a few hypha (c) growing on the inner cell wall but no weight loss was detected. Note the hypha growing on the S_3 layer of the inner cell wall (arrow Figure 4c).

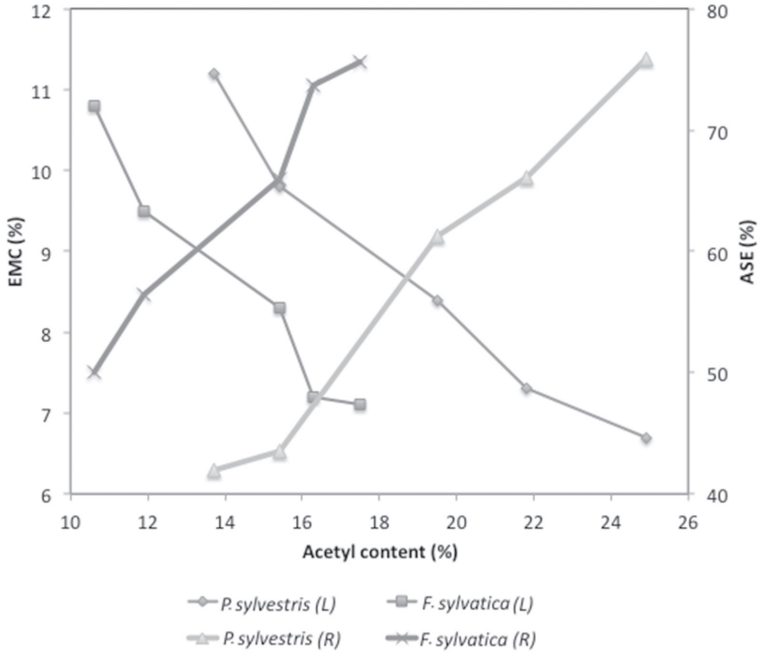


Figure 3 Equilibrium moisture content (EMC) and anti-shrink efficiency (ASE) of *Pinus radiata* and *Fagus sylvatica* wood samples with different bonded acetyl levels

Table 4 Stability of acetyl groups in *Pinus sylvestris* and *Populus tremuloides* flakes after cyclic exposure between 90 and 30% relative humidity

Wood sample	Acetyl content (%) after cycle			
	0	13	21	33
Pinus sylvestris	18.6	18.2	16.2	18.0
Populus tremuloides	17.9	18.1	17.1	17.8

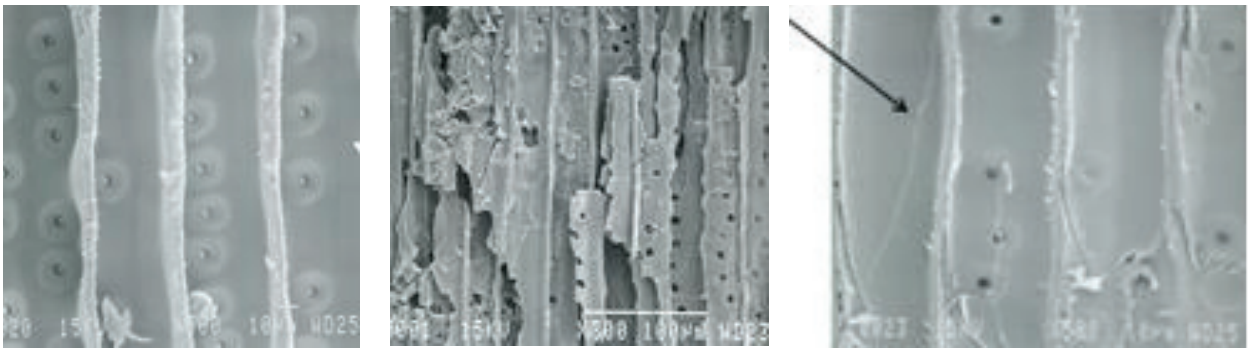
Table 5 Equilibrium moisture content (EMC) and weight loss of acetyl-bonded *P. sylvestris* stakes exposed to *Gloeophyllum trabeum* for 12 weeks

Acetyl content (%)	EMC		Weight loss (%)
	0 week	12 weeks	
0 (control)	20.2	-	61.3
6.0	16.5	11.8	34.6
10.4	13.0	10.3	6.7
14.8	11.4	9.7	3.4
17.8	8.6	7.2	< 2

In the second 12-week soil bock test using *P. sylvestris*, there was only a 3% weight loss and the acetyl content went from 18.6% before the test to 17.7% after the test (Table 6). This shows that what was lost in the test had the same acetyl content as the starting specimen. The weight loss was very small, almost within experimental error.

In the third 12-week soil block test using *P. sylvestris*, carbohydrate analysis showed that the control specimen lost 52% total weight with a total carbohydrate loss of 86% (Table 7). There were significant losses of all carbohydrate sugars in the control specimen. In the 15% acetylated specimen, there was a mass loss of only 1.4% and a loss of total sugars of 13.2%, no loss of cellulose but some degradation did take place. There was only a weight loss of 1.4% in the acetylated specimen but a major loss of arabinose with lesser losses in galactose, mannose, rhamnose and xylose. Arabinose is the only pentose sugar in the hemicelluloses that contains a strained five-membered ring. This could be significant in the study on the mechanism of brown-rot attack on softwoods.

In the three-year fungal cellar test of control and acetylated *P. sylvestris* there was no attack on the wood until swelling was observed indicating that moisture is required before attack can take place (Table 8, Rowell et al. 2007).



(a) (b) (c)

Figure 4 Scanning electron microscope images of (a) control (unacetylated) *P. sylvestris* wood before and (b) after exposure to *Gloeophyllum trabeum* in a 12-week soil block test, and (c) acetylated wood after 12 weeks; arrow point to hypha

Table 6 Acetyl content of acetyl-bonded *P. sylvestris* exposed to *Gloeophyllum trabeum* for 12 weeks

Weight percentage gain	Acetyl content (%)		Weight loss (%)
	0 week	12 weeks	
0	0.6	0.2	65.8
19.2	18.6	17.7	3.0

Table 7 Carbohydrate and weight losses in acetyl-bonded *Pinus sylvestris* stakes exposed to *Gloeophyllum trabeum* for 12 weeks

Carbohydrate loss (%)	15% initial acetyl content	Control (no acetyl)
Arabinose	89.0	87.0
Galactose	55.2	71.9
Rhamnose	70.0	90.0
Glucose	0.0	83.8
Xylose	38.3	90.6
Mannose	42.0	92.5
Total carbohydrate loss (%)	13.2	85.8
Weight loss (%)	1.4	51.7

Table 8 Performance of acetylated *Pinus sylvestris* stakes exposed to non-sterile soil in a 36-month fungal cellar test

Acetyl content (%)	Rating of attack* at month:							
	2	3	4	5	6	12	24	36
0.0 (control)	2s	3s	3s	3s	4s	-	-	-
7.3	0s	1s	1s	2s	3s	4s	-	-
11.5	0	0	0s	1s	2s	3s	4s	-
13.6	0	0	0	0	0s	1s	2s	4s
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

* 0 = none, 1 = slight, 2 = moderate, 3 = heavy, 4 = destroyed; s = swelling observed

CONCLUSIONS

Acetylation of both soft- and hardwoods was effective in providing high levels of dimensional stability and decay resistance. At acetyl weight gains above about 18%, the dimensional stability— reported as antishrink efficiency—was approximately 80%. The bulking of the bonded acetyl groups in the cell wall is likely the mechanism of dimensional stability. As the bonded acetyl content increased, resistance to attack by fungi increased. This may be due to the low moisture content in the cell wall being below that needed for fungal attack. The threshold of fungal resistance was approximately 17% acetyl. The EMC at 90% RH, was the same before and after the brown-rot decay test indicating that the material lost had the same hygroscopic properties as the remaining wood. The acetyl content was the same before and after the brown-rot decay test indicating that the material lost had the same acetyl content as the remaining wood. There was minor weight loss (1.4%) in the 15% acetylated pine specimen after the soil block test and a total carbohydrate loss of 13.2% with arabinose the major hemicellulose sugar lost.

Acetylation technology can be applied to tropical hardwoods to produce products with high levels of dimensional stability and decay resistance. In the reaction with hot anhydride, toxic extractives would be removed allowing the use of some woods that are too toxic for humans to handle.

Acetylated wood is now used in windows, doors, cladding and decking where both long term stability and durability are required without the use of toxic wood preservatives. Acetylated wood is also used in boat decks, musical instruments, and outdoor furniture.

REFERENCES

ASTM (American Society for Testing and Materials). 1976. ASTM D1413: Standard method of testing wood preservatives by laboratory soil-block cultures.

Fuchs W. 1928. Genuine lignin. I. Acetylation of pine wood. *Berichte der Deutschen Chemischen Gesellschaft* 61B: 948–951.

Hill C. 2006. *Wood Modification: Chemical, Thermal and Other Processes*. John Wiley and Sons, Chichester.

Hon DS.1996. *Chemical Modification of Wood Materials*. Marcel Dekker, New York.

Horn O. 1928. Acetylation of beech wood. *Berichte der Deutschen Chemischen Gesellschaft* 61B: 2542–2545.

Ibach RE & Rowell RM. 2000. Improvements in decay resistance based on moisture exclusion. *Molecular Crystal and Liquid Crystal* 353: 23–33.

Ibach RE, Rowell RM & Lee BG. 2000. Decay protection based on moisture exclusion resulting from chemical modification of wood. Pp 197–204 in *Proceedings of the 5th Pacific Rim Bio-Based Composites Symposium*. 10–13 December 2000, Canberra.

Kumar S. 1994. Chemical modification of wood. *Wood Fiber Science* 26: 270–280.

Rowell RM. 1975. Chemical modification of wood: advantages and disadvantages. Pp 1–10 in Proceeding of the American Wood Preserver's Association. 28–30 April 1975, San Francisco.

Rowell RM. 1982. Distribution of reacted chemicals in southern pine modified with acetic anhydride. *Wood Science* 15: 172–182.

Rowell RM. 2006. Acetylation of wood: a journey from analytical technique to commercial reality. *Forest Products Journal* 56: 4–12.

Rowell RM. 2011. Accessibility and reactivity of hydroxyl groups in wood. Pp 45–46 in *Proceedings of the International Academy of Wood Science Conference "Novel materials from wood and cellulose"*. 31 August–2 September 2011, Stockholm.

Rowell RM (ed). 2012a. *Handbook of Wood Chemistry and Wood Composites* (2nd edition). CRC Press, Boca Raton.

Rowell RM. 2012b. Understanding properties and performance of wood at the molecular level. Pp 8–16 in Baltrusaitis A & Ukvalbergiene K (eds)

Proceedings of the 8th Meeting of the Northern European Network for Wood Science and Engineering (WSE). 13–14 September 2012, Kaunas.

Rowell RM. 2014a. Accessibility and reactivity of hydroxyl groups in wood. Pp 149–154 in Barnes MH & Herian VL (eds) *Proceedings of the 57th International Convention of Society of Wood Science and Technology*. 23–27 June 2014, Zvolen.

Rowell RM. 2014b. Dimensional stability and fungal durability of acetylated and heat treated wood. In *Proceedings of the 68th Forest Product Society International Convention and World Conference of Timber Engineering*. 10–13 August 2014, Quebec.

Rowell RM. 2015a. Dimensional stability and fungal durability of acetylated wood: a new sustainable building material. In *Proceedings of the 1st International Scientific Conference of the Wood Technology Institute "Wood-Science-Economy"*. 5–7 October 2015, Poznan.

Rowell RM. 2015b. Understanding decay resistance, dimensional stability and strength changes in acetylated wood. In *Proceedings of the InWood 2015 International Conference "Innovations in Wood Materials and Processes"*. 19–22 May 2015, Brno.

Rowell RM. 2015c. Correlation between equilibrium moisture content and resistance to decay by brown-rot fungi on acetylated wood. In *Proceedings of the 8th European Conference on Wood Modification*. 26–27 October 2015, Helsinki.

Rowell RM. 2016a. Acetylated wood: a stable and durable structural building material. In Eberhardsteiner J, Winter W, Fadai A & Pöll M (eds) *Proceedings of the World Conference on Timber Engineering* (WCTE 2016). 22–25 August 2016, Vienna.

Rowell RM. 2016b. Role of cell wall specific moisture content on the brown-rot fungal attack on wood. In *Proceedings of the 47th International Research Group Annual Meeting*. IRG/WP 16-40736. 15–19 May 2016, Lisbon.

Rowell RM, Ibach RE & Nilsson T. 2007. Influence of moisture on brown-rot fungal attack. Pp 65–69 in Rikala J & Sipi M (eds) *Proceedings of the 3rd Nordic Baltic Network in Wood Material Science and Engineering*. 29–30 October 2007, Helsinki.

Rowell RM, Ibach RE, McSweeny J & Nilsson T. 2009. Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood. Pp 489–502 in *Proceedings of the 4th European Conference on Wood Modification*. 27–29 April 2009, Stockholm.

Rowell RM, Lichtenberg RS & Larsson P. 1992. Stability of acetyl groups in acetylated wood to changes in pH, temperature, and moisture. *Forest Research Institute Bulletin* 176: 33–40.

Rowell RM, Pettersen R & Tshabalala MA. 2013. Chapter 3: cell wall chemistry. Pp 9–32 in Rowell RM (ed) *Handbook of Wood Chemistry and Wood Composites* (2nd edition). CRC Press, Boca Raton.

Rowell RM, Simonson R, Hess S, Plackett DV, Cronshaw D & 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: 11–18.

Rowell RM, Tillman AM & Simonson R. 1986. A simplified procedure for the acetylation of hardwood and softwood flakes, *Journal of Wood Chemistry and Technology* 6: 427–448.

Suida H. 1930. Acetylating wood. Austrian Patent 122,499.

Suida H & Titsch H. 1928. Chemistry of beech wood: acetylation of beech wood and cleavage of the acetyl-beech wood. *Berichte der Deutschen Chemischen Gesellschaft* 61B: 1599–1604.

Tarkow H. 1945. *Decay resistance of Acetylated Balsa*. USDA Forest Service, Forest Products Laboratory, Madison.

Tarkow H. 1946. *A New Approach to the Acetylation of Wood*. USDA Forest Service, Forest Products Laboratory, Madison.

Tarkow H, Stamm AJ & Erickson ECO. 1946. *Acetylated Wood*. Report 1593. USDA Forest Service, Forest Products Laboratory, Madison.

Roger Rowell *has a PhD in biochemistry from Purdue University. He retired in 2007 as a Senior Technical Pioneering Scientist at the USDA, Forest Products Laboratory after 41 years and retired in 2007 as a professor in the Department of Biological Systems Engineering at the University of Wisconsin after 35 years. He currently serves as Professor Emeritus at the University of Wisconsin, advising graduate students in the US, Sweden, Finland, Norway, Hungary, Mexico and Japan, and teaching graduate-level courses at several universities in wood chemistry, bio-based composites and carbohydrate chemistry. He has been a visiting scholar or guest professor in several countries for various lengths of time, and a Mission Leader for the United Nations Development Project in India for six years. He has published over 450 scientific papers, 12 books and holds 26 patents.*

Rebecca E Ibach *has a PhD in wood chemistry from the University of Wisconsin, Madison. She is a Research Chemist with 31 years experience working in wood chemistry at the USDA Forest Service, Forest Products Laboratory in Madison. Her expertise is in chemical modification and lumen filling to improve the properties and overall durability of wood and composites. Her focus is on the moisture, UV, mechanical, and biological decay mechanisms that can occur when solid wood and composites are used in adverse environments and ways to improve their durability. She has presented her research nationally and internationally and published over 70 scientific papers.*