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# A study of strength, hardness and deformation of acetylated Scandinavian softwoods

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In this work, properties such as bending strength (expressed as modulus of rupture and modulus of elasticity), hardness, and deformation under cyclic relative humidity have been studied for acetylated Scandinavian pine and spruce. The acetylation was performed with a limited amount of liquid acetic anhydride without addition of catalyst or organic cosolvent. The weight gain due to acetylation was 19.1% for the pine samples. Two kinds of spruce samples were acetylated to 18.2% (narrow annual rings) and 23.3% (broad annual rings), respectively. The results indicated that only small changes in strength were obtained. For pine, modulus of rupture decreased with about 6%, and increased with about 7% for spruce. The modulus of elasticity also decreased for pine but increased for spruce. For practical applications, these properties can be considered unaltered. Acetylated pine wood showed increased Brinell hardness. Acetylated spruce wood did not tend to deform as much as unmodified wood when exposed to moisture cycled between 40 and 90% relative humidity.

*Festigkeit, Härte und Verformung von acetyliertem skandinavischem Kiefern- und Fichtenholz*

An acetylierten Proben von skandinavischem Kiefern- und Fichtenholz wurden mechanische Eigenschaften (MOE, MOR), Härte und Verformung unter zyklischen Feuchtebedingungen gemessen. Die Acetylierung erfolgte mit reduziertem Anteil an flüssigem Acetanhydrid und ohne Zugabe eines Katalysators oder anderer organischer Lösemittel. Der Gewichtszuwachs betrug bei Kiefernholz 19,1%, bei Fichtenproben 18,2% (enge Jahrringe) bzw. 23,3% (weite Jahrringe). Nur geringfügige Veränderungen der Festigkeitswerte wurden beobachtet. Die MOR-Werte fielen bei Kiefernholz um 6% ab; bei Fichtenholz stiegen sie um 7%. Die MOE-Werte verhielten sich ähnlich. Für praktische Zwecke kann man die mechanischen Eigenschaften als unverändert ansehen. Die Brinellhärte des Kiefernholzes stieg nach der Acetylierung an. Die Verformungstendenzen unter zyklischem Wechselklima (40/90) wurden durch die Behandlung verringert.

## 1 Introduction

Wood is classified as a hygroscopic material because the hydroxyl groups in the cell wall polymers attract water through hydrogen bonding. Consequently, its dimensions change with changes in the relative humidity of the surrounding air. Moisture uptake swells the cell wall and, since the process is reversible, the cell wall shrinks when it loses moisture. Wood is biologically degraded by organisms with very specific enzyme systems capable of hydrolyzing polymers in the cell wall into digestible units. When the polymers responsible for strength are degraded, the mechanical properties of the wood decrease (Rowell 1984).

Chemical modification through acetylation involves reaction of accessible hydroxyl groups in the wood polymers with acetic anhydride, forming acetyl groups in the wood and giving acetic acid as a by-product. Acetylation gives a material in which hygroscopicity is considerably reduced. Hence, the material exhibits a high degree of dimensional stability (Rowell et al. 1986a, b). At the same time, acetylated wood shows greatly improved resistance to tunneling bacteria and brown, white, and soft rot decay fungi (Nilsson et al. 1988).

This property enhancement makes acetylated wood an excellent building material, provided that the strength properties remain equal to those of unmodified wood. The objective of this work was to determine how acetylation influences properties such as bending strength, hardness and deformation in cyclic relative humidity when applied to Scandinavian pine and spruce.

Only a few studies have been made investigating changes in the mechanical properties of wood that result from acetylation. Goldstein et al. (1961) examined impact strength and wet compressive strength for ponderosa pine and southern yellow pine samples acetylated in a mixture of acetic anhydride and xylene (1:4). They found that the impact strength of the acetylated wood was not decreased by the treatment, and that the wet compressive strength was doubled. Dreher et al. (1964) used the same acetylation method in a study of mechanical properties of acetylated ponderosa pine, red oak and sugar maple and found that compressive strength and hardness were increased for all wood specimens. Modulus of rupture was increased by 10 percent for pine, but decreased by 10 percent for oak and maple. The modulus of rupture remained unchanged.

In this work, the acetylation was performed with a limited amount of liquid acetic anhydride without addition of catalyst or organic cosolvent according to a simplified procedure (Rowell et al. 1986). Using the same acetylation procedure, Militz (1991) reported an increase of about 10% in compressive strength and a decrease of about 5% in modulus of elasticity for acetylated beech wood when compared to unmodified beech wood.

## 2 Experimental

### 2.1 Specimen preparation

Two different Scandinavian wood species, pine (*Pinus silvestris* L.) and spruce (*Picea abies* Karst.) have been used in this study. Eighteen pine sapwood specimens (30 × 30 × 480 mm; radial × tangential × longitudinal) were cut from a single board (moisture content 10%) with the grain parallel to the tangential side. Each specimen was cut in half and planed (28 × 13 × 480 mm; $r \times t \times l$). One half was acetylated and the other half was kept as a control.

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In this way, the specimens were matched, and the influence of differences in the wood could be minimized.

Spruce specimens ($30 \times 20 \times 500$ m; $r \times t \times l$) mainly composed of sapwood, were cut from lumber possessing either broad or narrow annual rings. The specimens were cut green and conditioned at 20°C and 65% RH. Twelve specimens of each kind were acetylated. Four control specimens of the same size, adjacent to each side of the acetylated specimen, were taken.

## 2.2 Acetylation



The acetylation was carried out in a stainless steel reactor. The specimens were separated by small wood pieces, placed in the reactor, and impregnated with acetic anhydride under vacuum for 1 hour. This was followed by impregnation under pressure (10 bar) for 1 hour. The excess acetic anhydride was drained off, and the temperature was raised to 120°C. After 6 hours, unreacted acetic anhydride and by-product acetic acid were removed by means of vacuum for 2 hours, while the reactor was still heated. The specimens were finally oven dried at 105°C for 48 hours to remove the last traces of chemicals.

## 2.3 Bending strength

For measurement of bending strength, the pine specimens were tested with a 430 mm span between the two supports. A centrally placed load was applied to the tangential surface of the specimen and perpendicular to the grain. The load was increased at a constant rate of deflection, and the rupture occurred after about 120 seconds. The spruce specimens were tested with a 500 mm span between the supports. Two loads at 100 mm distance, centered around the middle point of the test specimen, were applied to the tangential surface and perpendicular to the grain. The load was increased at a constant rate of deflection, and the rupture occurred after about 40 seconds. Bending strength was calculated assuming a linear, symmetrical distribution of stresses. Shear stresses were neglected in the calculation of the modulus of elasticity.

## 2.4 Hardness

The wood hardness was measured on the pine specimens according to a Brinell hardness test. A steel ball of 10 mm diameter was pressed into the wood specimens at a normal load of 50 kp. The maximum load was reached within 15 seconds, remained constant over a period of 30 seconds, and then reduced to zero within another 15 seconds. By measuring the impression diameter of the steel ball, the Brinell hardness could be calculated.

## 2.5 Deformation test

The test specimens, spruce ($30 \times 20 \times 500$ mm), were placed in a climate room (20°C) and stickered on 40 cm centers. Relative humidity was cycled between 90% (10 days) and 40% (10 days). After three cycles, deformation was measured as flat bending (bow), edge bending (crock) and twisting. The measurements were performed with an accuracy of 0.5 mm per 400 mm.

# 3 Results and discussion

## 3.1 Acetylation

The pine specimens were acetylated to an average weight gain of 19.1% calculated on oven-dried wood. For spruce, the average weight gain was 18.2% for the specimens with narrow annual rings, and 23.3% for the specimens with broad annual rings (Tables 1 and 2). The difference in weight percent gain between the two types of spruce specimens may be explained by the higher amount of early wood in the specimens with broad annual rings which makes these specimens easier to acetylate. Table 1 shows that the pine samples increased in volume by 11.5% after acetylation. Together with the weight gain, this results in an increase in density of about 7%. The equilibrium moisture content (EMC) of the acetylated specimens was much lower than that of the unmodified wood. For example, the moisture content was 9.8% for the untreated pine samples and only 4.1% for the acetylated specimens at 20°C and 65% relative humidity (RH).

## 3.2 Strength properties

As shown in Table 1, acetylation led to a small reduction in both modulus of rupture (MOR) and modulus of elasticity (MOE) for the pine specimens. The MOR-value decreased from 115 MPa for untreated wood to 109 MPa for the acetylated pine wood specimens, while MOE decreased from 13.5 to 11.2 GPa.

Table 1. MOR and MOE for acetylated and unmodified pine sapwood

| Weight gain (%) | Swelling[1] (%) | Density[2] (kg/m$^3$) | Moisture[3] content (%) | MOR (MPa) | MOE (GPa) |
|---|---|---|---|---|---|
| 19.1(2.0) | 11.5(1.1) | 629(16) | 4.1(0.2) | 108.9(10.6) | 11.2(3.0) |
| 0 | - | 587(17) | 9.8(0.1) | 115.0 (9.9) | 13.5(1.3) |

[1] Swelling measured from oven-dried, unmodified to oven-dried, acetylated condition
[2] Density calculated from weight and volume of oven-dried samples
[3] Moisture content during strength test (20°C, 65% RH)

Table 2. MOR and MOE for acetylated and unmodified spruce wood

| Type of wood | Weight gain (%) | Density[1] (kg/m$^3$) | Moisture[2] content (%) | MOR (MPa) | MOE (GPa) |
|---|---|---|---|---|---|
| Broad | 23.3(1.5) | 380(46) | 2.8(0.8) | 52.5(13.4) | 8.8(1.5) |
| annual rings | 0 | 325(33) | 12.0 - | 48.9(8.5) | 8.5(1.4) |
| Small | 18.2(4.3) | 475(73) | 2.7(0.4) | 70.3(15.8) | 13.0(1.9) |
| annual rings | 0 | 440(36) | 12.0 - | 65.5(11.2) | 12.3(2.0) |

[1] Based on weight of oven-dried samples and volume of water saturated samples
[2] Moisture content during strength test (20°C, 65% RH)

Spurce specimens, on the other hand, showed a slight increase in both MOR and MOE (Table 2). For the specimens with narrow annual rings, representing trees grown in natural forest, the MOR-value increased from 65.5 MPa for untreated wood to 70.3 MPa for the acetylated specimens and the MOE-value from 12.3 to 13.0 GPa. Specimens with broad annual rings, representing fast-growing trees, showed an increase in MOR from 48.9 to 52.5 MPa, and in MOE from 8.5 to 8.8 GPa. Several factors are believed to influence strength properties of acetylated wood. The acetylation process includes heat treatment under acidic condition that could cause a certain degree of wood degradation and subsequent strength reduction. Acetylation also swells the wood, resulting in fewer load-bearing fibers within a given cross-sectional area. The increase in density is not believed to increase strength properties to any great extent, since the acetyl groups form side groups on the existing wood polymers which are thereby forced further apart with a splitting of hydrogen bonds.

The moisture content is considerably less for acetylated wood than for unmodified wood. Many mechanical properties of wood (unmodified) are affected by changes in the moisture content below the fiber saturation point, and a decrease in moisture content is known to cause an increase in most strength properties (Kollman and Coté 1986; Wood handbook 1987). However, no such clear increase was observed. The positive effects of reduced moisture content which might result from acetylation are probably evened out by strength losses caused by acidic and thermal degradation and swelling due to acetylation.

Differences in moisture content are probably the reason for the differences in strength properties between pine and spruce. The acetylated pine specimens had a moisture content of 4.1%, while that of the controls was 9.8%. The acetylated spruce wood, on the other hand, had a moisture content of 2.8% while that of the controls was as high as 12%. This resulted in a relatively higher strength of acetylated spruce and a relatively lower strength of the spruce controls, as compared with pine. For both species, the difference in mechanical properties of acetylated and unmodified wood is, however, within the limits of error considering the standard deviation.

### 3.3 Hardness

Table 3 shows the Brinell hardness for acetylated and unmodified pine wood. The hardness was increased in both directions for the acetylated pine specimens, as compared with the unmodified specimens. For tangential surface, hardness increased from 1.82 to 2.28 and for radial surface from 2.47 to 2.96, due to acetylation. The increase in hardness is probably more related to the lower moisture content of acetylated wood than to the increase in density for reasons indicated above.

### 3.4 Deformation test

Figures 1 and 2 show the degree of deformation after three cycles of conditioning between 40 and 90% relative humidity for unmodified and acetylated spruce wood. No consideration is taken of the type of deformation; bow, crook and twist are just summed up as deformation. In Fig. 1, it is shown that the deformation was greatly reduced for the acetylated specimens. Both for the specimens with broad annual rings and for the specimens with narrow annual rings, the deformation was reduced to about half of what was observed for unmodified controls. It can also be noticed that specimens with narrow annual rings tended to deform more than specimens with broad annual rings, both for acetylated and unmodified wood. Twist was the most common type of deformation, irrespective of if the specimens were acetylated or not.

The presence of knots is a factor of great importance with regard to deformation. It dominates substantially over other parameters, such as the type of wood (fast growing or wood from natural forests), amount of heartwood/sapwood or irregularities of grain. If only specimens without knots are studied (Fig. 2), the

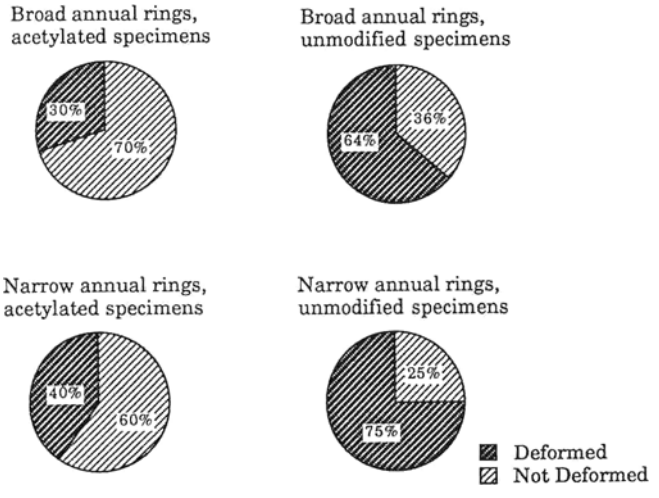


Fig. 1. Deformation of acetylated and unmodified specimens including the effects of knots.
Bild 1. Verformung aller acetylierten und unbehandelten Proben.

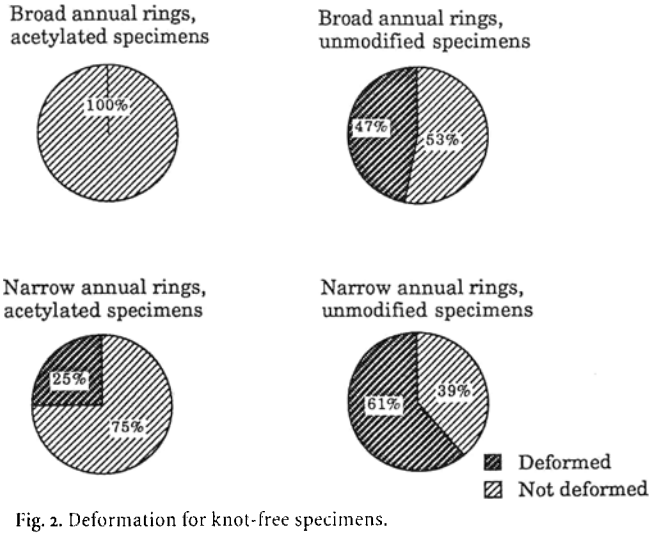


Fig. 2. Deformation for knot-free specimens.
Bild 2. Verformung der astreimen Proben

Table 3. Brinell hardness for acetylated and unmodified pine sapwood

| Weight gain (%) | EMC, when tested (%) | Density, oven dry (kg/m$^3$) | Brinell hardness (kp/m$^2$) | |
|---|---|---|---|---|
| | | | Tangential surface | Radial surface |
| 0 | 9.8 | 587 | 1.82 | 2.47 |
| 19.1 | 4.1 | 629 | 2.28 | 2.96 |

effect of acetylation is even more distinct. The smaller tendency of acetylated wood to deform as compared with unmodified wood can also be ascribed to its lower EMC-value and, consequently, its lower swelling and shrinkage on variation in relative humidity of surrounding air.

## 4
## Conclusions

Although the acetylation process includes heat treatment under acidic conditions, the changes in strength for pine and spruce specimens due to acetylation were small, and for practical applications the strength properties can be regarded as unaltered compared to those exhibited by unmodified wood.



Acetylated pine samples showed higher hardness than did controls when measured as Brinell hardness. This is probably attributable to the lower equilibrium moisture content in acetylated wood as compared with unmodified wood.

It was also shown that acetylated spruce wood did not tend to deform as much as unmodified wood when exposed to moisture cycled between 40% and 90% RH.

## 5
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## Buchbesprechungen · Book reviews

**G. I. Torgovnikov: Dielectric Properties of Wood and Wood-Based Materials**

(Springer Series in Wood Science); 196 S. ISBN 3-540-55394-0. Springer Verlag Berlin, Heidelberg, New York. DM 160,–

Dielektrische Verfahren gewinnen zunehmend an Bedeutung zur Bestimmung der Dichte und Holzfeuchte, aber auch im Hinblick auf die Erwärmung von Holz bei der Trocknung, Konditionierung und Verleimung. Das vorliegende Werk behandelt zunächst in übersichtlicher, leicht verständlicher Form die Grundlagen des Verhaltens von Dielektrika im elektrischen Feld. Dabei nimmt der Autor Bezug auf die Vorgänge in dem komplexen, hygroskopischen Werkstoff Holz und leitet ein phsikalisches Modell aus dem Verhalten der Einzelkomponenten Zellwand, gebundenes und freies Wasser, Eis sowie Luftraum ab. Im dritten Kapitel werden die gängigen Meßverfahren vorgestellt. In diesem Zusammenhang wird besonders auf die Porblematik bei der Messung hygroskopischer Stoffe und die erforderliche Probenvorbehandlung eingegangen. In den beiden folgenden Kapiteln wird das Verhalten von trockenem und feuchtem Holz bei verschiedenen Temperaturen und Frequenzen unter Berücksichtigung von Dichte und Anisotropie behandelt. Dabei geht der Autor auf die unterschiedlichen Eigenschaften von gebundenem und freiem Wasser ein. Das Verhalten von chemisch und mechanisch vergütetem Holz wird ebenso wie die Eigenschaften von verschiedenen Holzwerkstoffen (Holzfaserplatten, Spanplatten) und Holzderivaten (Papier und Bakelite) behandelt. Dabei wird das dielektrische Verhalten auf die Eigenschaften der Bestandteile zurückgeführt. Kapitel 9 gibt Empfehlungen für die experimentelle Bestimmung und Berechnung der dielektrischen Eigenschaften von Holz. Daraus abgeleitet erhält der Leser Hinweise für die Frequenzwahl bei der HF-Erwärmung von Holz und eine Übersicht über die zulässigen Frequenzen in den verschiedenen Ländern. In einem umfangreichen Anhang sind die dielektrischen Eigenschaften von Holz und Holzwerkstoffen über einen weiten Frequenz-, Temperatur- und Holzfeuchtebereich tabellarisch dargestellt. Der Autor berücksichtigt die relevante Literatur, wobei die osteuropäischen Arbeiten, insbesondere die jenigen aus Rußland stark übergewichtet sind. Die Ergebnisse der zitierten Arbeiten werden übersichtlich dargestellt, eine Erklärung für Unterschiede fehlt dagegen häufig. Das vorliegende Buch ist, obwohl speziell auf Holz bezogen, für den Wissenschaftler ebenso wie für den Praktiker, der sich mit dielektrischen Meßverfahren oder HF-Anwendungen bei hygroskopischen Materialien beschäftigt, eine gute Grundlage.

A. Geissen