Effect of chemical modification on dimensional stability of Pinus radiata D. Don using acetic anhydride

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Abstract: Chemical modification is used to efficiently improve some properties of wood to make it suitable for specific end uses. Modification using acetic anhydride (AA) is found suitable to make the wood more stable dimensionally. Pinus radiata wood samples treated with pyridine catalyzed AA were exposed to four different treatment methods comprising vacuum dipping and full cell method (cured with and without chemical). Physical properties like weight percentage gain (WPG), bulking coefficient, swelling coefficient (S) due to the chemical, water absorption and anti-swelling efficiency (ASE) were assessed for a comparative analysis. Results indicated a significant reduction in water absorption of acetylated wood. The swelling coefficients of all the treatments were found in the range of 3.86–4.96, which was twice to three times less than in the control (11.72) attributing 55–64% improvement in dimensional stability. Samples treated with full cell method and cured in the chemical mixture showed minimum swelling coefficient and best anti-swelling efficiency. All the four treatment methods chosen for the study returned significantly better dimensional stability as compared to untreated wood.

Keywords: Anti-swelling efficiency (ASE); dimensional stability; swelling coefficient; water absorption; weight percentage gain (WPG)

Wood is an exceptional building material made up of cellulose, hemicellulose and lignin comprising a large number of hydroxyl groups (Singh et al. 1992; Devi, Maji 2012). The presence of these hydroxyl groups in wood results in many unwanted behaviours of wood in use. Chemical modification of wood is one way of achieving desired improvement in properties like dimensional stability, biological durability, surface hardness and wear, hygroscopic nature, fire retardancy and colour (Hansmann et al. 2005). It also helps in achieving stability towards UV-radiation and improvement of weathering performance of wood (Donath et al. 2004). Chemical modification of wood is the reaction of a chemical reagent with the wood polymeric constituents, resulting in the formation of a covalent bond between the reagent and the wood substrate (Hill 2007). The principle of modification is by altering hydrophilic OH-groups into larger more hydrophobic groups (Rowell 2005a). Various types of chemical compounds like anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles and epoxides have been used for this very purpose (Rowell 1983; Donath et al. 2004). Chemical modification can result in increased dimensional stability by two-way cross-linking of the chemical with the hydroxyl group of cellulose present in wood (Yan et al. 2014) or by causing the cell wall bulking (Rowell 1982). This bulked up state reduces the increase in volume when the wood comes into contact with moisture. Likely, the reaction of acetic anhydride takes place with cell wall polymeric hydroxyl groups to form an ester bond, while acetic acid is produced as a by-product (Hill 2006) (Figure 1).

Anhydride may be used in vapour or liquid phase for reaction with wood. The efficiency of acetylation depends on wood density. High-density wood...
is difficult to acetylate as the penetration of acetyl molecules is more difficult, blocking a lesser number of free hydroxyl (–OH) groups compared to low-density wood (Ajdinaj et al. 2013). The degree of esterification of modified wood with anhydrides is evaluated by an increase in weight, acid value and saponification value of the product (Matsuda 1987). Acetic anhydride provides decay resistance and dimensional stability to the modified wood, which depends on sufficient distribution of reacted chemicals in water accessible regions of cell walls (Rowell 1982). Acetic acid, the by- product of acetylation, causes acidic conditions in the wood which catalyse the removal of acetyl groups. Acid hydrolysis of cellulose causes a loss in strength and acetic acid also corrodes metal fasteners (Rowell 1983). Concentration of acetic acid lower than 10% accelerates the reaction and the opposite happens with higher concentration (Ajdinaj et al. 2013).

The Accoya™ production plant at Arnhem in the Netherlands is already involved in commercial production of acetylated radiata pine using liquid phase reaction (Hill 2007). Pinus radiata, native to North America, is the world’s most extensively planted softwood. The total plantation area in the world covered by radiata pine is 3.7 million hectares (ha), majorly in New Zealand (1.2 million ha), Chile (1.3 million ha), Australia (740 000 ha) and Spain (260 000 ha). Radiata pine is a versatile, fast-growing, medium-density softwood, very suitable for a wide range of end uses. The timber can be readily sawn, peeled, has good nail-holding power and can be easily stained. Further, when treated with preservatives suitable for particular end uses, it is suitable for several applications with the significantly longer service life span (Forestry Corporation 2016). India imports radiata pine logs from Australia and New Zealand through ports like Kandla and Tuticorin and the same gets distributed to North and South India for further conversion and uses. Kandla can discharge Pinus radiata logs at a rate of 4 000 m³ per day while Tuticorin can discharge logs at a rate of 500 to 600 m³ per day.

With its utility established already, several studies have been conducted in New Zealand and India for suitability of radiata pine for the Indian building codes in the tropical climatic conditions of India. New Zealand also funded independent studies at the Indian Council of Forestry Research and Education (ICFRE) to have Pinus radiata products assessed for inclusion in building code specifications (Midgley et al. 2007).

Keeping in mind the literature and studies mentioned above, the present study was performed with the aim to understand the effects of the combination of acetic anhydride and acetic acid on dimensional stability of Pinus radiata by pressure treatment and vacuum dipping treatment during the curing stage in chemical modification.

MATERIAL AND METHODS

Seasoned planks of Pinus radiata D. Don of New Zealand origin were procured from Green Gold Timbers Pvt. Ltd. Dehradun, Uttarakhand, India. Samples were prepared from seasoned planks, free from knots, mould, stain and any other defects. Sanding of selected samples was done by 120 grit size sandpapers.

Acetylation: Chemical modification. Pinus radiata samples of size 2 × 2 × 6 cm³ (tangential × radial × longitudinal) were oven dried at 105°C till constant weights were achieved. The oven dry weights and dimensions of the samples were recorded. A chemical mixture of acetic anhydride and pyridine, as catalyst (90/10 ratio w/w), was used for modification (Hansmann et al. 2005).

A total of 30 samples were used in the study, the samples were divided into two sets each consisting of 12 samples and the remaining 6 samples were used as control. Samples of Set I were soaked overnight in a cold acetic anhydride-pyridine solution under vacuum of 38 cm Hg. These samples were then further divided into two different subgroups each consisting of 6 replicates, depending on curing to estimate the effect of formed acetic acid: (i) Samples of the first subgroup were heated in the chemical mixture at 120 °C (T1) for 8 hours (Obataya, Yamauchi 2005), (ii) Samples of the second subgroup were heated without chemical mixture at 120 °C (T2) for 8 hours.
Set II samples were subjected to a cycle of vacuum 63 cm Hg for 30 min and pressure of 7 kg·cm⁻² for 60 min and again vacuum of 63 cm Hg for 30 min (the full cell process). These samples were divided into two subgroups of 6 replicates each and were given the following treatments:

(i) One subgroup of samples was heated in the chemical mixture at 120 °C (T3) for 1 hour,
(ii) The other subgroup was heated without chemical mixture at 120 °C (T4) for 1 hour (Figure 2).

Weight percent gain (WPG). The WPG of each specimen was calculated by Equation 1:

\[
WPG = \left(\frac{W_t - W_o}{W_o}\right) \times 100
\]  

(1)

where:

\(W_o, W_t\) – oven-dried weight of unmodified and chemically modified wood samples, respectively.

Percentage volume increase (bulking coefficient). Percentage volume increase after modification of samples was calculated by Equation 2:

Bulking coefficient = \left(\frac{V_m - V_u}{V_u}\right) \times 100

(2)

where:

\(V_u, V_m\) – oven-dried volumes of unmodified sample and chemically modified wood samples, respectively.

Swelling coefficient (S) due to chemical. Volumetric swelling coefficient S due to chemical (Sc) was determined by Equation 3:

\[Sc \text{ (%) } = \left(\frac{V_w - V_o}{V_o}\right) \times 100\]

(3)

where:

\(V_w\) – volume of saturated chemically modified sample,
\(V_o\) – volume of oven-dried modified sample.

Water absorption. Water absorption was also calculated by the repeated water soaking method for ten cycles. Water absorption percentage was determined by (Devi, Maji 2012) Equation 4:

Water absorption (%) = \left(\frac{W_t - W_d}{W_d}\right) \times 100

(4)

where:

\(W_t\) – weight of wood sample soaked in water,
\(W_d\) – oven-dried weight of sample.

Dimensional stability. Dimensional stability was determined by estimating S and ASE by the repeated water soaking method (Figure 3). Samples are vacuum impregnated with deionized water for 30 min, then released for 1 hour; vacuum is reapplied for 30 min and then released for 24 hours (Rowell and Ellis 1978; Pandey et al. 2009). Excess water was drained, weights and volumes were measured. Specimens were again oven dried for 48 hours, and their weights and volumes were determined. The same process was carried out for ten cycles to ascertain the particular value of S and ASE till the difference becomes insignificant.

Volumetric swelling coefficient (S) was determined by (Rowell, Ellis 1978) Equation 5:

\[S \text{ (%) } = \left(\frac{V_s - V_o}{V_o}\right) \times 100\]

(5)

where:

\(V_s\) – volume of soaked sample,
\(V_o\) – volume of oven-dried sample.

Figure 2. Layout of the chemical modification plant (1 – treatment plant, 2 – heating rod, 3 – insulating jacket, 4 – temperature sensor, 5 – vacuum/pressure pump, 6 – chemical mixture storage tank, 7 – temperature controller unit, 8 – spacer, 9 – connecting pipes) (Hom 2019)
ASE was determined by (Rowell, Ellis 1978) Equation 6:

\[
ASE \, (\%) = \left(\frac{S_u - S_m}{S_u}\right) \times 100 \tag{6}
\]

where:

\(S_u, S_m\) – swelling coefficients of unmodified and chemically modified wood samples, respectively.

All the data were subjected to the Duncan homogeneity (\(\alpha = 0.05\)) test using SPSS 15 (IBM, Armonk, USA).

RESULTS AND DISCUSSION

Weight percent gain, percentage volume increase, volumetric swelling coefficient due to chemical treatment

The means and standard error (SE) for weight percentage gains along with increase in volume and swelling coefficient (due to chemical) of the samples treated with acetic anhydride-pyridine mixture when heated with and without chemical are given in Table 1.

Samples of Pinus radiata subjected to T3 treatment showed maximum WPG of 32.95 ± 0.88% and T4 treated samples showed the lowest WPG of 23.94 ± 0.87%. The results document that the samples heated in the chemical gained more weight as compared to the samples heated without chemical. Earlier study showed the WPG of 20–25% in Southern pine specimens using a xylene and acetic anhydride mixture without catalyst with similar treatment conditions like those of T3 (Rowell 1982). The WPG of 19.7% observed for T4 was higher than that of Populus ussuriensis for acetic anhydride modification when heated without chemical at 120 °C (Chai et al. 2017). It was also reported that the upper limit of WPG (30%) due to acetylation is irrespective of the reaction time. Liquid phase acetylation with acetic anhydride and 10% pyridine as catalyst resulted in a 26% increase in WPG for Picea abies (Hansmann et al. 2005). A better result was obtained by T2 and T1 treatment of Pinus radiata when compared with results of Obataya and Yamauchi (2005), who reported WPG of 19.8% to 20.7% by applying vacuum dipping and then heating at 120 °C for 8 hrs to Cryptomeria japonica D. Don. Using the Duncan homogeneity (\(\alpha = 0.05\)) test it was observed that WPG for T3 was significantly better than for all the other treatments, WPG of T4 and T1 were significantly different from each other but T4 and T2 showed a non-significant difference. From the study it is evident that the effect of curing without chemical mixture was significant in both vacuum dipping and full cell method. It was found out that the presence of the chemical mixture during curing affected WPG for both treatments as there was a significant difference between T1–T2 (vacuum dipping) and T3–T4 (full cell process).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>WPG (%) (Mean ± SE)</th>
<th>Change in volume (%) (Mean ± SE)</th>
<th>Sc (%) (Mean ± SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T4</td>
<td>23.94 ± 0.87\textsuperscript{c}</td>
<td>10.35 ± 0.43\textsuperscript{b}</td>
<td>4.65 ± 0.04\textsuperscript{b}</td>
</tr>
<tr>
<td>T3</td>
<td>32.95 ± 0.88\textsuperscript{a}</td>
<td>14.26 ± 1.60\textsuperscript{a}</td>
<td>5.52 ± 0.09\textsuperscript{c}</td>
</tr>
<tr>
<td>T2</td>
<td>24.12 ± 0.29\textsuperscript{a}</td>
<td>9.17 ± 0.32\textsuperscript{b}</td>
<td>2.16 ± 0.14\textsuperscript{a}</td>
</tr>
<tr>
<td>T1</td>
<td>27.44 ± 0.40\textsuperscript{b}</td>
<td>9.51 ± 1.01\textsuperscript{b}</td>
<td>4.56 ± 0.18\textsuperscript{b}</td>
</tr>
</tbody>
</table>

WPG – weight percent gain, SE – standard error, Sc – volumetric swelling coefficient due to chemical treatment
The maximum increase in volume due to chemical treatment was recorded in T3 samples, i.e. 14.26 ± 1.60%, and the minimum of 9.17 ± 0.32% was observed due to T2 treatment. The volume increase by 10.35 ± 0.43% for T4 is comparable to the 10.1% volume increase in Southern pine with 22.8% WPG (Rowell 1982). A significant difference was observed in percentage volume increase due to the chemical for T3 from the other treatments, but an insignificant difference was observed between T4, T2 and T3 treatments. Unlike the results obtained in WPG, the presence of the chemical mixture affected a volume increase only in the full cell process as there was a significant difference between T3 and T4. But volume increases for T1 and T2 treatments (vacuum dipping) were insignificantly different from each other referring to an insignificant effect of the chemical mixture during curing.

Volumetric swelling coefficient due to treatment (S¢ %) followed the same pattern; T3 samples showed maximum S¢ of 5.52 ± 0.09% and minimum S¢ of 2.16 ± 0.14% was found for T2 samples, showing a significant difference from all the other treatments. But T1 and T4 samples were insignificantly different from each other having the S¢ values of 4.65 ± 0.04% and 4.56 ± 0.18%, respectively. The result shows that the presence of the chemical mixture during curing affects the volumetric swelling coefficient for both processes as there was a significant difference between T1 & T2 (vacuum dipping) and T3 & T4 (full cell process).

T3 was significantly different form all the other treatments and although T4 showed lower WPG than T2 and T1, using the Duncan homogeneity (α = 0.05) test, it was observed that there was no significant difference in the percentage change in volume due to the chemical between these three treatments. Similarly T1 and T4 showed an insignificant difference in S¢ whereas the S¢ value for T2 was significantly lower than in the other two treatments. This may be due to the acetyl group because T1 and T2 treatment does not get chemically fixed to the cell wall as much as T4. The WPG and S¢ for processes, i.e. full cell process and vacuum dipping, were influenced by the presence of the chemical mixture (acetic anhydride and acetic acid) during curing and had a significant effect on the physical properties.

**Water absorption percentage**

The results of treated and untreated samples are shown in Figure 4. Both treated and untreated samples showed an increase in water absorption with each water soaking cycle although almost a constant uptake was also observed in some cycles. Untreated or control samples absorbed more water than the treated samples. From the previous studies it has been established that the water accessible area in the cell wall decreases as the WPG increases, representing a proportion of sites being occupied by the acetyl groups and therefore reducing water sorption (Rowell 1982). Acetylation cannot completely prevent water absorption, but may reduce the absorption for a longer period of time (Lahtela et al. 2014). Rowell (1983) stated that at the higher level of chemical modification, the acetylated wood shows

![Figure 4. Water uptake by different treatments (C – untreated/control sample, T1 – vacuum dipped samples were heated in the chemical mixture for 8 hours at 120 °C, T2 – samples heated for 8 hours at 120 °C without chemical mixture, T3 – full cell treated samples were heated in the chemical mixture for 1 hour at 120 °C, T4 – full cell treated samples heated for 1 hour at 120 °C without chemical mixture)](image_url)
a reduction in water absorption by 35%. The present study showed a contradicting result in water absorption. Among the treatments, T3 with maximum WPG absorbed most water as compared to the other treatments. In softwoods, the tracheids are closed at the ends and the flow of the liquid between adjacent tracheids is through the pits between the cell walls in a transverse direction which are considered to have the most significant influence on flow properties (Messner et al. 2003).

These pits become aspirated during drying and the permeability of an unaspirated membrane increases as compared to the aspirated pit due to the presence of the open margo structure (Wang, DeGroot 1996). The reasons for pit aspiration are hydrogen bonding between adjacent cellulose chains and presence of resinous compounds (Messner et al. 2003). In general, deaspiration is promoted when the liquid lacks the ability to form hydrogen bonds (Lehringer et al. 2009).

In case of T3 treatment the rate at which air can escape from wood as water displaces air in the lumen is higher compared to the other treatments. This may be due to a reduction in the formation of hydrogen bonds between water and wood hydroxyl groups and higher leaching of extractives. This increases the water flow in the cell lumen and not inside the cell wall of wood with T3 treatment. In case of other treatments, the water flow is reduced due to the formation of hydrogen bond causing a reduction in the rate of deaspiration and decreasing the water flow between adjacent tracheids. T1 shows minimum absorption but there was an insignificant difference in water uptake percentage between T2 and T1.

As capillary structures present in the wood are not blocked after acetylation, modified wood absorbs water in the coarse capillary similarly to untreated wood although less water enters the cell wall (Tarkow et al. 1955). The present study also supports that with an increase in time, the capillaries and void spaces become saturated with water, which increases the water absorption capacity (Devi, Maji 2012). Water absorption is almost constant after 4th cycle in case of T3 as the capillaries become saturated, but for T4, T2 and T1 it becomes constant from 3rd to 6th cycle and then from 7th to 9th cycle.

This variation in water absorption for T4, T2 and T1 may be due to too high leaching of extractives after 6th cycle affecting the water absorption. The presence of the acetic anhydride and acetic acid mixture during curing affects the water absorption but only in case of full cell treatment and not vacuum dipping as the water absorption for T3 is significantly different from T4, whereas water absorption for T1 is insignificantly different from T2.

**Dimensional stability**

The dimensional stability of the modified samples was determined by calculating S and anti-swelling efficiency ASE after each soaking cycle and the results are given in Table 2. The effect of the presence of the acetic anhydride and acetic acid chemical mixture of (formed as a by-product) was observed only in full cell treatment and not in vacuum dipping. S value for all the ten cycles was calculated and it was observed that T3 showed the lowest swelling coefficient and T2 the maximum one. There was a significant difference in the swelling coefficient of all the treatments only in the first cycle, after which the effect of curing in the chemical mixture was evident for full cell treatment and not for vacuum dipping. T3 was significantly better than T4 but T1 and T2 showed an insignificant difference (Figure 5).

T3 samples showed the best results for ASE, which ranged between 78.27 ± 0.22% for the first cycle to 64.19 ± 0.17% for the tenth cycle. T2 showed the lowest ASE and it ranged from 64.22 ± 0.36% to 55.15 ± 0.17%. Even though T4 had minimum WPG of 23.94 ± 0.87%, it showed an insignificant difference in ASE with respect to T1 and T2. The ASE for T4 was comparable with the result obtained by CHAI et al. 2017 for *Populus ussuriensis* wood modified with acetic anhydride and heated without chemical at 120 °C. It was from 74.13±0.61% to 55.71 ± 0.36%, ASE for T1 was 69.82 ± 0.87% to 55.28 ± 0.13% (Figure 6).

An increase in S and a decrease in ASE were observed throughout the ten cycles but this difference was insignificant after the fifth cycle for all the treatments irrespective of the presence of the acetic anhydride and acetic acid mixture. The WPG, S and ASE for T4 are better than the results obtained by Rowell 2005 (b) for pine wood, with WPG of 22.5 and ASE of 70.3%, but the change in ASE from the first cycle to the fifth cycle was higher. WPGs for T4, T2 and T1 were also similar to the WPG of pressure-treated wood and wood heated in the chemical by Rowell 2005 (b), but the decrease in ASE value was greater with each cycle, and this may be due to the leaching of non-bonded chemicals. The influence of the absence of the acetic anhydride and acetic acid mixture during...
Table 2. Volumetric swelling coefficient (S) and anti-swelling efficiency (ASE) for different treatments

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Variable (Mean ± SE)</th>
<th>Variable (Mean ± SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WPG</td>
<td>$S_1$</td>
</tr>
<tr>
<td>C</td>
<td>–</td>
<td>11.85 ± 0.09$^c$</td>
</tr>
<tr>
<td>T4</td>
<td>23.94 ± 0.87</td>
<td>2.99 ± 0.06$^b$</td>
</tr>
<tr>
<td>T3</td>
<td>32.95 ± 0.88</td>
<td>2.51 ± 0.13$a$</td>
</tr>
<tr>
<td>T2</td>
<td>24.12 ± 0.29</td>
<td>4.14 ± 0.30$^a$</td>
</tr>
<tr>
<td>T1</td>
<td>27.44 ± 0.40</td>
<td>3.49 ± 0.93$^c$</td>
</tr>
</tbody>
</table>

WPG – weight percent gain, $S_i$ – volumetric swelling coefficient estimated from initial oven dry (OD) volume and first water swollen volume, ASE$_i$ – anti-swelling efficiency based on $S_i$, $S_j$ – estimated from second water swollen volume and re-oven dry volume, ASE$_j$ – anti-swelling efficiency based on $S_j$, $S_k$ – estimated from third water swollen volume and second re-oven dry volume, ASE$_k$ – anti-swelling efficiency based on $S_k$, $S_l$ – estimated from fourth water swollen volume and third re-oven dry volume, ASE$_l$ – anti-swelling efficiency based on $S_l$, $S_m$ – estimated from fifth water swollen volume and fourth re-oven dry volume, ASE$_m$ – anti-swelling efficiency based on $S_m$, $S_n$ – estimated from sixth water swollen volume and fifth re-oven dry volume, ASE$_n$ – anti-swelling efficiency based on $S_n$, $S_{10}$ – estimated from seventh water swollen volume and sixth re-oven dry volume, ASE$_{10}$ – anti-swelling efficiency based on $S_{10}$, $S_{11}$ – estimated from eighth water swollen volume and seventh re-oven dry volume, ASE$_{11}$ – anti-swelling efficiency based on $S_{11}$, $S_{12}$ – estimated from ninth water swollen volume and eighth re-oven dry volume, ASE$_{12}$ – anti-swelling efficiency based on $S_{12}$, $S_{13}$ – estimated from tenth water swollen volume and ninth re-oven dry volume, ASE$_{13}$ – anti-swelling efficiency based on $S_{13}$, different letters denote significantly different groups.
curing was significant for pressure treatment but the pressure-treated samples cured without chemical mixture resulted in similar dimensional stability as that of vacuum dipped wood samples with and without chemical mixture.

CONCLUSION

*Pinus radiata* reacted very well towards acetic anhydride modification. Different treatments showed an evident increase in the weight of wood due to chemical modification that caused swelling due to chemical treatment resulting in cell wall bulking. Water uptake of acetylated wood was much lower than in untreated wood. Improvement in dimensional stability was also observed as the swelling coefficient for all the treatments ranged between 4.18 and 5.24 while the control samples showed the swelling coefficient of 11.68 at the end of the experiment. The results of curing the pressure-treated wood without chemical (T4) were similar to the results of vacuum dipped wood with (T1) or without chemical (T2).

Soaking the wood in cold acetic anhydride and heating it when the entire sample is saturated with chemical minimized the formation of acetic acid on the surface that might dilute the reaction mixture and that may slow down or stop the reaction.
Hence, pressure-treated wood and heated in the chemical mixture (T3) showed minimum swelling coefficient and best anti-swelling efficiency of 64%. This may be attributed to the reason that the entire sample was saturated with acetic anhydride and curing in the chemical mixture provided more acetyl groups to replace hydroxyl groups of wood as compared to pressure-treated wood and heated without chemical (T4), which lacked availability of more acetyl groups than present in the wood or vacuum dipping where samples were not completely saturated to show the effect of the presence of the acetic anhydride and acetic acid mixture during curing.

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