Moisture Repellent Effect of Acetylation on Poplar Fibers

B. Mohebby and R. Hadjihassani

ABSTRACT

Fibers of poplar wood (Populus nigra L.) were prepared and oven dried. Afterwards, they were acetylated with acetic anhydride without a catalyst. Acetylation was carried out for different durations at 120°C. Different weight percentage gains (WPGs) were achieved based on the operating conditions. Acetylated fibers were exposed to varying levels of relative humidity to determine equilibrium moisture contents (EMC). IR-spectra were also taken from the fibers to indicate substitution of the hydroxyl groups by the acetyl groups. Results showed that the acetylation decreased moisture absorption in the fibers. It was revealed that a WPG of about 10% had a proper moisture repellent effect on fibers. IR-spectra confirmed fully the substitution of the acetyl groups.

Keywords: Acetylation, EMC, IR-spectroscopy, Moisture repellent effect, Populus nigra L.

INTRODUCTION

Any changes in the chemistry of wood cell wall polymers affect the physical and mechanical properties of wood or composites made from the wood. These properties can vary from color changes to major changes in modulus properties, strengths, gas permeability, moisture sorption and water repellence, bioreistance and dimensional stability in wood and wood-based composites such as fiberboards, particleboards, etc. Improvement in those technical properties is an encouragement to technologists to modify wood cell walls through chemical modification.

Acetylation is a type of chemical modification by which hydroxyl groups on the cell wall polymers are substituted with acetyl groups from acetic anhydride [8, 17, 10, 11]. Fiberboard is a fiber-based product. Changes in the moisture sorption of the fiber cell walls have a major effect on the mechanical properties and dimensional stability of the fiberboard as well as its bioreistance [19, 9, 2, 7, 12]. At moisture contents from oven dry to fiber saturation point, any changes in the moisture content has an effect on the major properties of the fiberboard. It therefore, is expected that any decrease in the moisture sorption or increase in the water repellence properties of the fibers would affect the major properties of the boards. Hydroxyl groups on fiber cell wall polymers are mostly responsible for moisture sorption. Any decrease in those groups is associated with improvement of the board's properties [16]. Substitution of the hydroxyl groups with the hydroxyl groups due to the acetyl of the fibers; gives a great chance of improving the technological properties of the fiberboard.

The current research has been aimed to acetylate poplar fibers, a commonly used wood species in Iran, with acetic anhydride to study its influences on the moisture sorption and the moisture repellent properties in the fibers prior to manufacture of the board.

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MATERIALS AND METHODS

Fiber Preparation

Poplar (Populus nigra L.) chips were prepared by using a laboratory chipper, Pallman 430×120. They were sieved to achieve uniform sizes (2×20×25mm). Afterwards, they were dipped in water for few hours and steamed at 175ºC for five minutes. The steamed chips were refined using a laboratory single disk refiner. Refining was carried out five times. The fibers were oven dried at 103±2ºC for 24 hours.

Acetylation

The dry fibers were weighed and placed in aluminum capped beakers and the acetylation was carried out for 0, 30, 60, 90, 120, 150, 180, 360 and 2,520 minutes at 120ºC under an atmospheric pressure without a catalyst by using acetic anhydride. The acetylated fibers were rinsed in water to remove the acetic acid and excess of acetic anhydride until no acid smell leaked out. The washed fibers were oven dried at 103±2ºC for 24 hours.

IR-spectroscopy

Attenuated Total Reflection (ATR) Infra-red Spectroscopy was carried out to prove the acetylation reaction in the fibers. A Few milligrams of the oven dried acetylated fibers were put on a detector prism and IR spectra were collected directly from the fibers by using an FTIR Bruker Vectra 22 equipped with a DuraSample IR II™ detector.

Background spectra were collected by using an empty detector. Both the samples’ and background spectra were collected with 60 scans at a spectral resolution of 4cm⁻¹. A rubber band method was used for the baseline correction. The band for CO₂ was excluded to make a suitable baseline correction [10, 11].

Equilibrium Moisture Content (EMC)

About three grams of the acetylated and non-acetylated fibers were placed in a climate chamber at varying levels of relative humidity. The moisture content of the fibers was determined using a moisture sensitivity tester at a temperature of 25ºC and a constant relative humidity of 65%.

Equation for Weight Percent Gain (WPG)

The weight gains (WPGs) were calculated on the basis of the following equation:

\[ \text{WPG} \% = \frac{(W_{\text{act}} - W_{\text{od}})}{W_{\text{od}}} \times 100 \]

where:

- \( W_{\text{act}} \) = Dry weight after acetylation (g),
- \( W_{\text{od}} \) = Dry weight before acetylation (g).

Equation for Weight Percent Gain (WPG)

\[ y = 2.9935 \ln(x) - 4.3486 \]

\[ R^2 = 0.9448 \]

\[ n=3 \]

Figure 1. Weight gains of non-catalysed acetylation in the poplar fibers at an atmospheric pressure.
humidity at 25ºC. At certain relative humidities, the absorbed moisture content of the fibers was calculated to determine EMCs. Based on the EMCs, the moisture repellent effect (MRE) of the acetylation was calculated in the acetylated fibers (Equation 2).

\[
\text{MRE}(\%) = \frac{\text{EMC}_{\text{non}} - \text{EMC}_{\text{act}}}{\text{EMC}_{\text{non}}} \times 100
\]

where:
- \(\text{MRE}\): Moisture repellent effect at a certain relative humidity (%);
- \(\text{EMC}_{\text{non}}\): Equilibrium moisture content of non-acetylated fibers (%),
- \(\text{EMC}_{\text{act}}\): Equilibrium moisture content of acetylated fibers (%).

**RESULTS AND DISCUSSION**

The weight percentage gains (WPGs) achieved in the acetylated fibers are shown in Figure 1. Results revealed that the rate of the acetylation reaction in the fibers followed an exponential trend. It was higher during the first hours of the reaction, and a weight gain of 10% was achieved after 120 minutes at atmospheric pressure without any catalyst; whereas, achieving higher WPGs required quite longer time. For example, a weight gain of 18% was achieved after 42 hours (Figure 1).

The IR spectra of the acetylated fibers are shown in Figure 2. It was revealed that at wave numbers of between 3,500-3,300 cm\(^{-1}\) (1), the intensities were decreased due to the acetylation. This peak has been assigned for OH stretching of the water absorbed to the cell wall polymers [6, 15, 13, 10]. The magnitude of the peak was increased with raised WPGs. This indicates that the number of OH groups was decreased due to the substitution of the acetyl groups during the acetylation in the fiber walls. Reports have suggested that acetylation improves water repellence in wood as a result of decreased OH groups [17].

A peak that is assigned for CO\(_2\) (2), was increased at wave number 2,358 cm\(^{-1}\) with raised WPGs. This peak was excluded from the spectra during the base line correction and was not considered in this research.

It was revealed that there were prominent peaks at the finger print region (wave numbers 1,800-600 cm\(^{-1}\)) where their intensities were increased due to the acetylation with its
raised WPGs. An assigned peak (3) at wave number 1,730 cm⁻¹ is related to an unconjugated C=O stretch in xylan [19, 18, 14, 10, 11]. The intensity of this peak was increased by a raised WPGs in the fibers (Figure 2). This peak has been shifted slightly to higher wave numbers (1,730-1,739 cm⁻¹) in the acetylated fibers (Table 1). Another peak (4) at wave number 1,363 cm⁻¹, which has been assigned to C-H deformation in cellulose and hemicelluloses, was increased due to the acetylation [3, 13, 15, 1, 10, 11]. Its intensity was also increased by raised WPGs in the poplar fibers. A prominent peak (5) at wave number 1,236 cm⁻¹ was increased due to the acetylation. This peak has been assigned for C-O stretching and C=O deformation in lignin and xylan [4, 5, 14, 10]. Its intensity was increased by raised WPGs. This peak was shifted slightly to other close wave numbers (1,226-1,236 cm⁻¹) due to the substitution of the acetyl groups (Table 1). The peak was shifted slightly to lower wave numbers by the raised WPG.

![Figure 3. Equilibrium moisture content (EMC) in the acetylated poplar fibers.](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Weight percent gain (%)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N.a. 456 7.06 9.55 10.30 11.20 12.60 13.50 18.01</td>
<td>OH stretching (bonded)[6]</td>
</tr>
<tr>
<td>2</td>
<td>2358 2358 2358 2358 2358 2358 2358 2358</td>
<td>C=O stretching due to presence of carbon dioxide [18, 19]</td>
</tr>
<tr>
<td>3</td>
<td>1730 1731 1733 1735 1737 1735 1737 1737 1739</td>
<td>C=O stretching in acetyl groups, increased due to acetylation in xylan [18, 19]</td>
</tr>
<tr>
<td>4</td>
<td>1363 1363 1363 1363 1363 1363 1363 1363 1363</td>
<td>C-H deformation in CH₃ from acetyl groups due to acetylation in hemicelluloses and cellulose [3, 13, 15, 14, 1]</td>
</tr>
<tr>
<td>5</td>
<td>1236 1232 1230 1228 1228 1228 1226 1226 1226</td>
<td>Stretching of C-O &amp; C=O deformation in the ester bond formed during acetylation [14, 4, 5]</td>
</tr>
</tbody>
</table>

*Peaks number

*Non-acetylated
Results indicated that acetylation affected the moisture sorption in the poplar fibers and that it was decreased by raised WPGs (Figure 3). A decreased moisture sorption was rated as high at higher relative humidities than at lower ones. A study of the moisture repellent effect (MRE) of the acetylation showed that this property was increased by raised WPGs with the same rates at different relative humidities (Figure 4). Results revealed that the acetylation had a higher rate of WRE at WPGs below 10% and about 50% of WRE was achieved in this range. However, the increased rate of the WRE was slowed down at higher WPGs.

**CONCLUSION**

From the current study, it may be concluded that the fibers react with the acetic anhydride and that a substitution of the hydroxyl groups by the acetyl groups occurs over time. This reaction was proved by IR spectroscopy. A moderate and an efficient acetylation occur in first minutes when the reaction starts. Any increase in the WPG affects the moisture sorption and the water repellence in the fibers. The moisture sorption decreases when the WPG increases. The moisture repellent effect of the acetylation increases when the WPG arises. Consequently, an improvement of dimensional stability in manufactured products could be expected when the WPG is increased in the fibers.

**ACKNOWLEDGEMENT**

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**REFERENCES**


اثر بازدارندهٔ جذب رطوبت توسط استیلاسیون بر روی الاف صنور

ب. محي و ر. حاجي حسني

چکیده

الاف صنور (Populus nigra L.) نه و در آون خشک شدن. سپس توسط اندرید استیک و بدون کاتالیست استحکام استیلاسیون در دمای 120 درجه های زمانی متفاوت انجام شد. بر اساس
Moisture Repellent Effect of Acetylation... ____________________________

شرايط اعمال شده، شدت هاي مختلف وزني (WPGs) به دست آمده‌ند. الاف استيله شده در معرض رطوبت هاي نسبی متغيري قرار گرفتند تا به رطوبت تعادل (EMC) معيين دست یافته شود. طیف ماده هاي فرمز از الاف به گرفته شد تا گروهگري گروه هاي هيدروکسيلي را با گروه هاي استيلی نشان بدهد.

نتایج نشان دادند که استراکتان اصلاحات رطوبت را در الاف كاهش مي دهد. مشخص گردید که شدت افزایش وزن 10% اثر باردارانگي خوبي بر روی الاف دارد. طیف سنگین ماده فرمز نيز به خوبي گروهگري گروه هاي استيلی را تأييد نمود.