J. Agric. Sci. Technol. (2008) Vol. 10: 157-163

Moisture Repellent Effect of Acetylation on Poplar Fibers

B. Mohebby[1]* and R. Hadjihassani[1]

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 120ºC. 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, bioresistance 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 bioresistance [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.

1. Department of Wood and Paper Science, Faculty of Natural Resources and Marine Science, Tarbiat Modares University, P. O. Box: 46414-356, Noor, Islamic Republic of Iran.
* Corresponding author, e-mail: Mohebbyb@modares.ac.ir

[DOR: 20.1001.1.16807073.2008.10.2.4.8]

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 minuets 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 and weighed to determine their weight gains (WPGs). The weight gains (WPGs) were calculated on the basis of the following equation:

$$WPG\ (\%) = (W_{act} - W_{od}) / W_{od} \times 100 \qquad (1$$

where:

WPG= Weight percent gain (%);

W_{act}= Dry weight after acetylation (g),

W_{od}= Dry weight before acetylation (g).

IR-spectroscopy

Attenuated Total Reflection (ATR) Infrared 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 CO_2 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

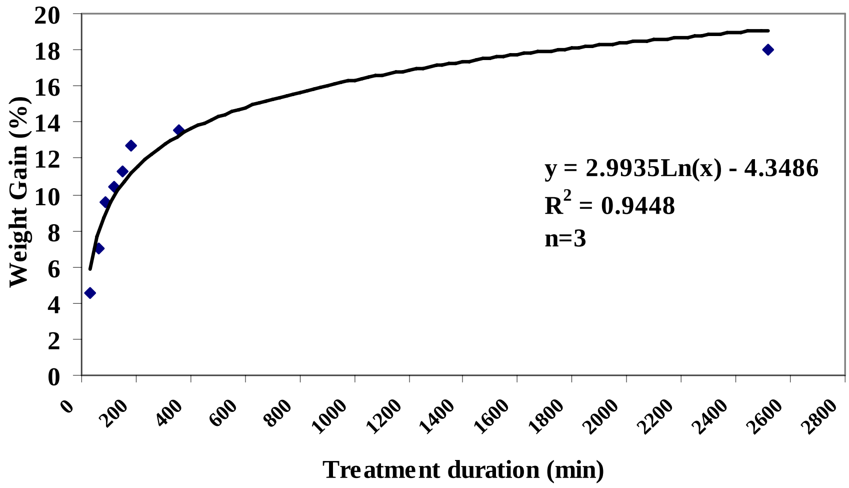

Figure 1. Weight gains of non-catalysed acetylation in the poplar fibers at an atmospheric pressure.

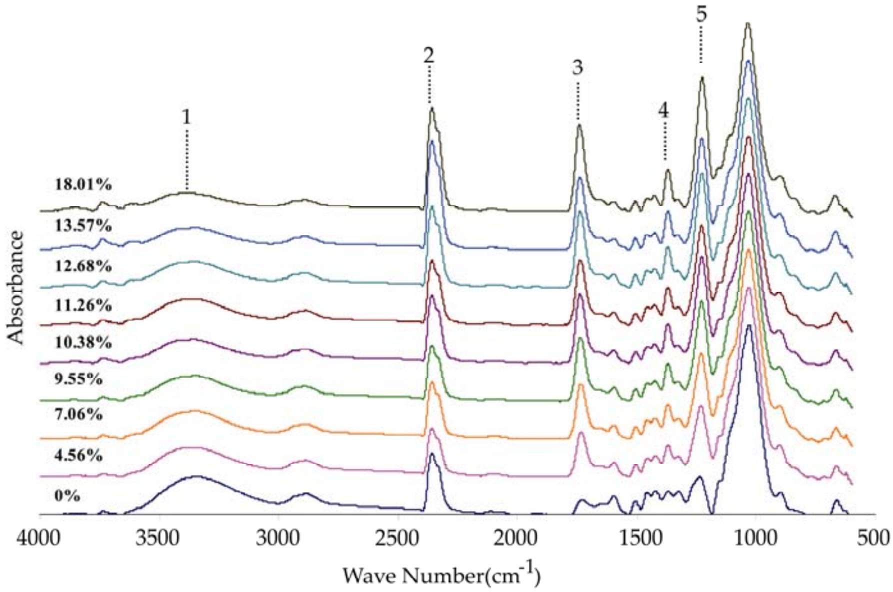

Figure 2. IR-spectra of the acetylated poplar fibers.

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).

$MRE(\%)= (EMC_{non}–EMC_{act})/ EMC_{non}\times100$ (2

where:

MRE= Moisture repellent effect at a certain relative humidity (%);

EMC_{non}= Equilibrium moisture content of non-acetylated fibers (%),

EMC_{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.

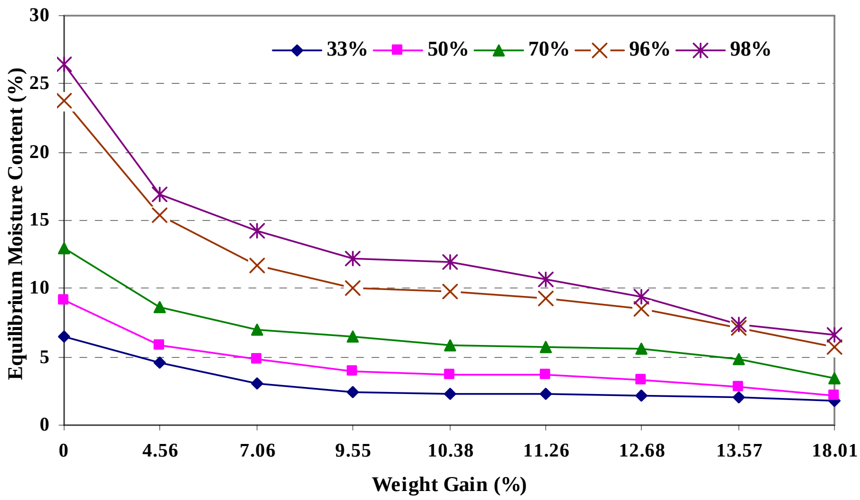

Figure 3. Equilibrium moisture content (EMC) in the acetylated poplar fibers.

Table 1. Wave numbers and their assignments in the acetylated poplar fibers.

No [a]	Weight percent gain (%) N.a. [b]	456	7.06	9.55	10.30	11.20	12.60	13.50	18.01	Assignments
1	3352	3359	3344	3348	3352	3350	3350	3340	3390	OH stretching (bonded)[6]
2	2358	2358	2358	2358	2358	2358	2358	2358	2358	C=O stretching due to presence of carbon dioxide [18, 19]
3	1730	1731	1733	1735	1737	1735	1735	1737	1739	C=O stretching in acetyl groups, increased due to acetylation in xylan [18, 19]
4	1363	1363	1363	1363	1363	1363	1363	1363	1363	C-H deformation in CH_3 from acetyl groups due to acetylation in hemicelluloses and cellulose [3, 13, 15, 14, 1]
5	1236	1232	1230	1228	1228	1228	1226	1226	1226	Stretching of C-O & C=O deformation in the ester bond formed during acetylation [14, 4, 5]

[a] Peak number
[b] Non-acetylated

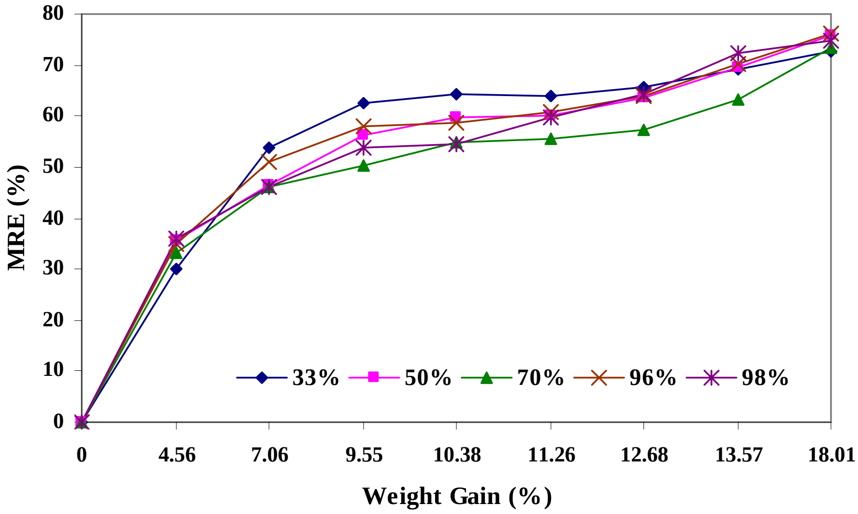

Figure 4. Moisture repellent Effect (MRE) of the acetylation on the poplar fibers at different relative Humidities.

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

We would like to express our sincere thanks to Dr. Carsten Mai of the Institute of Wood Biology and Wood Technology, Göttingen University, for his great cooperation in taking IR spectra from the fibers.

REFERENCES

1. Chang, S. T., Chang, H. T., Huang, Y. S. and Hsu, F. L., 2000: Effects of Chemical Modification Reagents on Acoustic Properties of Wood, *Holzforschung*, **54(6)**: 669-675.
2. Chow, P., H. T., Meimban, R., Youngquist, J. A. and Rowell, R. M. 1996. Effects of Acetylation on the Dimensional Stability and Decay Resistance of Kenaf (*Hibiscus cannabinus* L.) Fiberboard .The International Research Group on Wood Preservation, 19-24 May; West Indies; IRG/WP 96-40059.

3. Evans, P. D., Micehll, A. J. and Schmalzl, K. J. 1992. Studies of the Degradation and Protection of Wood Surfaces, *Wood Sci. and Technol.*, **26**: 151-163.
4. Faix, O. 1991. Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy, *Holzforschung*, **45**(Supplementary): 21-27.
5. Faix, O., Böttcher, J. H. 1992. The Influence of Particle Size and Concentration in Transmission and Diffuse Reflectance Spectroscopy of Wood, *Holz als Roh- und Werkstoff*, **50**: 221-226.
6. Fengel, D., and Wegner, G. 1983. *Wood: Chemistry, Ultrastructure, Reactions*, New York, Walter de Gruyter: p. 613.
7. Fuwape, J. A. and Oyagade, A. O. 2000. Strength and Dimensional Stability of Acetylated *Gamelina* and Spruce Particleboard; *J. Trop. For. Prod*; **6(2)**: 184-189.
8. Goldstein I. S., Jeroski E. B., Lund A.E., Nielson, J. F. and Weaver, J. W. 1961. Acetylation of Wood in Lumber Thickness; *For. Prod. J*; **11(8)**: 363-370.
9. Militz, H. 1991. Die Verbesserung des Schwind- und Quellverhaltens und der Dauerhaftigkeit von Holz mittels Behandlung mit unkatalysierung Essigsüreanhydri; *Holz als Roh-und Werkstoff*; **49**: 147-152.
10. Mohebby, B. 2005. Infrared Spectroscopy in Acetylated Wood; JAST; *In press.*
11. Mohebby, B. 2003. Biological Attack of Acetylated Wood, Ph. D. Thesis, Göttingen University, Göttingen, Germany, 165pp.
12. Ohmae, K., Minato, K. and Norimoto, M. 2002. The Analysis of Dimensional Changes due to Chemical Treatment and Water Soaking for Hinoki (*Chamaecyparis obusta*) Wood; *Holzforschung*; **56(1)**: 98-102.
13. Pandey, K. K. 1999. A Study of Chemical Structure of Soft and Hardwood Polymers by FTIR spectroscopy, *J. Appl. Polymer Sci.*, **71(12)**: 1969-1975.
14. Pandey, K. K. and Pitman, A. J. 2003. FTIR Studies of the Changes in Wood Following Decay by Brown-rot and White-rot Fungi, *Int. Biodeteriora. Biodegrad.*, **52**: 151-160.
15. Pandey, K. K., and Theagarjan, K. S. 1997. Analysis of Wood Surface and Ground Wood by Diffuse Reflectance (DRIFT) and Photoacoustic (PAS) Fourier Transform Infra Red Spectroscopy, *Holz als Roh- und Werkstoff*, **55(6)**: 383-390.
16. Rowell, R. M. 1996. Physical and Mechanical Properties of Chemically Modified Wood; In: Chemical Modification of Lignocellulosic Materials; Hon D. N.-S.: Marcel Dekker; New York: p. 295-310.
17. Rowell, R. M. 1983. Chemical Modification of Wood, *For. Prod. Abstr.*, **4(12)**: 363-382.
18. Sundell, P., de Meijer, M. and Militz H. 2000. Preventing Light Induced Degradation of Wood by Acetylation: A Study on Lignin and Model Compounds, *Second Wood Coating Conference, Challenges and Solutions in the 21st Century*, 23-25th October, The Hague, The Netherlands.
19. Takahashi, M., Imamura, Y., and Tanahashi, M. 1989. Effect of Acetylation on Decay Resistance of Wood against Brown Rot, White Rot and Soft Rot, *International Chemistry, Congress of Pacific Basin Societies, Agrochemistry, Sub-symposium on Chemical Modification of Lignocellulosic Materials-Chemical Reactions*, p.16.

اثر بازدارندگی جذب رطوبت توسط استیلاسیون بر روی الیاف صنوبر

ب. محبی و ر. حاجی حسنی

چکیده

الیاف صنوبر (*Populus nigra* L.) تهیه و در آون خشک شدند. سپس توسط انیدرید استیک و بدون کاتالیست استیله شدند. استیلاسیون در دمای ۱۲۰°C برای دوره های زمانی متفاوت انجام شد. بر اساس

[DOR: 20.1001.1.16807073.2008.10.2.4.8]

شرایط اعمال شده، شدتهای مختلف وزنی (WPGs) به دست آمدند. الیاف استیله شده در معرض رطوبت‌های نسبی متغییری قرار گرفتند تا به رطوبت تعادل (EMC) معینی دست یافته شود. طیف مادن قرمز از الیاف به گرفته شد تا جایگزینی گروه‌های هیدروکسیلی را با گروه‌های استیلی نشان بدهد.

نتایج نشان دادند که استیلاسیون جذب رطوبت را در الیاف کاهش می دهد. مشخص گردید که شدت افزایش وزن ۱۰٪ اثر بازدارندگی خوبی بر روی الیاف دارد. طیف سنجی مادون قرمز نیز به خوبی جایگزینی گروه‌های استیلی را تأیید نمود.

[DOR: 20.1001.1.16807073.2008.10.2.4.8]