

Chemical Modification of Beech Wood

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ABSTRACT

Beech wood after drying and milling was reacted with alkylating and acetylating agents. Untreated beech wood meal was reacted with benzyl chloride in the presence of sodium hydroxide. Also beech wood meal in another experiment was pulped with ethylene glycol as pulping liquor for removing lignin and the delignified beech wood was reacted with benzyl chloride in the presence of NaOH. Untreated wood and delignified wood after benzylation show thermal flowability as determined by thermal mechanical analysis (TMA). The benzylation products of untreated and delignified wood were acetylated with acetic acid and acetic anhydride mixture. The thermal flowability of acetylation products were measured by TMA analysis. ¹H NMR and FTIR spectra of products were also recorded.

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Key Words:

beech wood;
benzylation;
acetylation;
chemical modification;
ligno cellulose.

INTRODUCTION

Industries that use wood as raw material generate a large amount of by-product wastes such as sawdust, during product manufacturing. These wood wastes are burned sometimes and its chemical energy is converted to electricity. By chemical

modification of wood wastes, they can be converted to useful products. Natural wood has some reactive functional groups, such as, hydroxyl, carbonyl, ether, acetal. Each reagent that is capable to react with these functional groups, can react with

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wood. For example, most reagents that react with -OH group of cellulose can react with wood [1]. Introduction of a substituent to wood alter the three-dimensional network of wood and some thermoplasticities induced in it. Shiraishi and his coworkers [2-4] have worked on thermoplasticization of wood by introduction of small and large groups in wood. For example, when about one-third of the hydroxyl groups in the wood have been lauroylated, the lauroylated wood meal reveals clear melting with the disappearance of wood tissue. If different substituent groups are introduced into wood, the apparent melting point (flow temperature) will be different. If wood meal is benzylated, the benzylated wood meal with 43% ether content gives a transparent film. Further increase in the ether content results in a steady decrease in the melting temperature, which finally reaches about 200°C with ether content of more than 60%.

Thiebaud and his coworkers [5-6] described a method for esterification of oak sawdust using fatty acid chlorides without addition of organic solvent. A number of derivatives were prepared using fatty acid chlorides of different length of carbon chain. Thermoplasticity was indicated from the decrease in apparent melting temperature with an increase in chain length of the alkyl substituent.

Chemically modified wood can be applied for the preparation of films, sheets and other mouldings and also products prepared from wood and unsaturated substituents can be used for the preparation of three-dimensionally cured plastic-like wooden boards [2].

In this paper untreated beech wood and delignified beech wood were reacted with benzyl chloride in alkaline condition. For the preparation of new class of chemically modified wood, products of benzylation were then acetylated. Thermal and spectral properties of products were characterized.

EXPERIMENTAL

Materials

Beech wood was used after drying and mealing. Benzyl chloride, methanol, acetic acid, acetic anhydride and sulphuric acid, all were from Merck Inc. (Germany).

Measurements

FTIR spectra were recorded on a Shimadzu FTIR - 4300(Tokyo, Japan) as KBr disks. ¹H NMR spectrum

was recorded on a Bruker AC-80. Chloroform-d₁ and TMS were used as solvent and internal standard, respectively.

TMA thermograms were recorded on a V5.1A Dupont 2000 thermomechanical analyzer. Samples with dimensions of 3×5×5mm that were fabricated by hot pressing at 140°C and 150 kg/cm² were used for TMA analysis [2]. The temperature increment was 5°C/min and temperature range was 20°C to 200°C.

Water absorption of the raw material and the products were estimated by equilibrium swelling of the samples in distilled water at 20°C for 24 h. Water content (wt%) was calculated from the relative weight increase of the samples after their immersion in water.

Reactions

Benzylation of Beech Wood Meal

Oven dried beech wood, meal 50 g, was placed in a 1000 mL round-bottomed flask together with 350mL benzylchloride and 350mL 40% by weights NaOH solution. The flask was equipped with a condenser and magnetic stirrer and the contents were refluxed for 6 h (the refluxing temperature was about 110°C) [2]. After this period, the liquor was decanted and the solid mass was refluxed twice with methanol. The product was washed with hot and cold water successively and then it was dried in oven. As a result 83.3 g benzylated beech wood (BBW) was obtained.

Delignification of Beech Wood Meal with Ethylene Glycol

Dried beech wood meal of 50 g was placed in a 1000-mL round-bottomed flask together with 500mL ethylene glycol and 10 mL 40% NaOH solution [7]. The flask was equipped with condenser and magnetic stirrer and the contents were refluxed for 2 h. The temperature during refluxing was about 160-170°C. After refluxing the delignified beech wood was washed several times with water and it was dried. The delignification yield was 52%.

Benzylation of Delignified Beech Wood Meal

Dried Delignified Beech Wood Meal of 20g was benzylated according to procedure 1 and after purification and drying 32.3 g benzylated delignified beech wood (BDBW) was obtained.

Acetylation of BBW

Dried BBW of 5 g was placed in a 250 mL-Erlenmeyer flask together with 25 mL glacial acetic acid. The flask

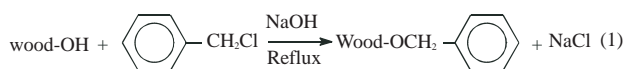
was equipped with magnetic stirrer and it was placed in a water bath at 50-55°C for 30 min. After this period a mixture of 16mL acetic anhydride and 1mL concentrated sulphuric acid was added to flask, and the mixture was stirred for 1.5 h at 55°C. After this, the liquor was decanted and acetylated product was washed several times with water and was stabilized through boiling in 100 mL 0.01% H₂SO₄ solution [8]. The stabilized product, benzylated acetylated beech wood (BABW), was dried in oven at 60°C.

Acetylation of BDBW

BDBW of 5 g was acetylated through procedure 4 above and benzylated acetylated delignified beech wood (BADBW) was obtained.

RESULTS AND DISCUSSION

Although the main component of wood, that is, cellulose, is a linear polymer, it acts as a thermoset material due to its strong interchain hydrogen bonds. Consequently, it decomposes on heating, because before those interchain bonds are broken, the backbone bonds, that is, carbon-carbon and carbon-oxygen bonds are broken and the polymer thermally is degraded. With substitution of H-atom of hydroxyl group in cellulose molecule with non-polar groups, thermoplasticity is bringing into cellulose. On the basis of this idea, beech wood was reacted with benzyl chloride in the presence of 40% NaOH solution.



During this reaction a small substituent (H atom) is replaced with a large substituent (benzyl group) and

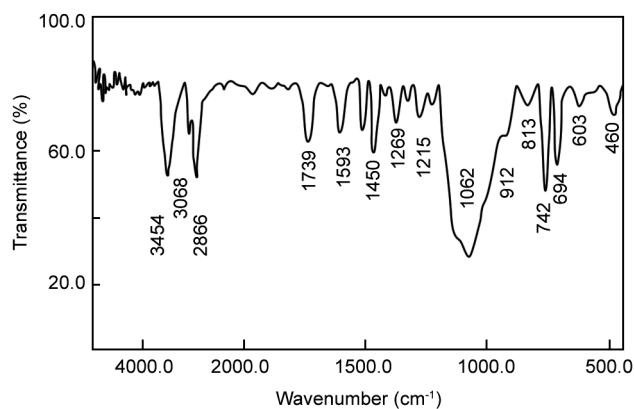


Figure 1. FTIR spectrum of BBW.

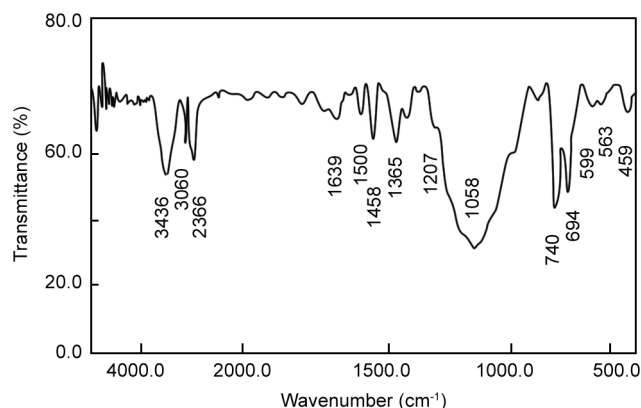


Figure 2. FTIR Spectrum of BDBW.

therefore, the weight of product is increased. The percent of weight increase was calculated as follows:

$$\text{Percent of weight increase} = \frac{W - W_0}{W_0} \times 100$$

where, W is the weight of product and W₀ is the weight of initial wood meal. For the wood meal the percentage weight increase was 66.6%. In the other reaction, beech wood meal initially was delignified with ethylene glycol (yield of delignification was 52%), and then it was reacted with benzyl chloride. The percent of weight increase for this reaction was 6106. The comparison of the two weight increase percents for untreated and delignified wood shows that as well as cellulose, other components, that is, hemicelluloses and lignin, are subjected to benzylation reaction to a lesser extent.

Figures 1 and 2 show the FTIR spectra of benzylated beech wood (BBW) and benzylated delignified beech wood (BDBW), respectively. The difference

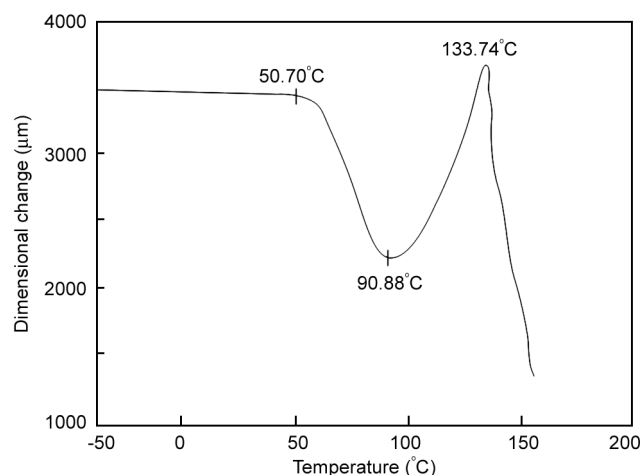


Figure 3. TMA Thermogram of BBW.

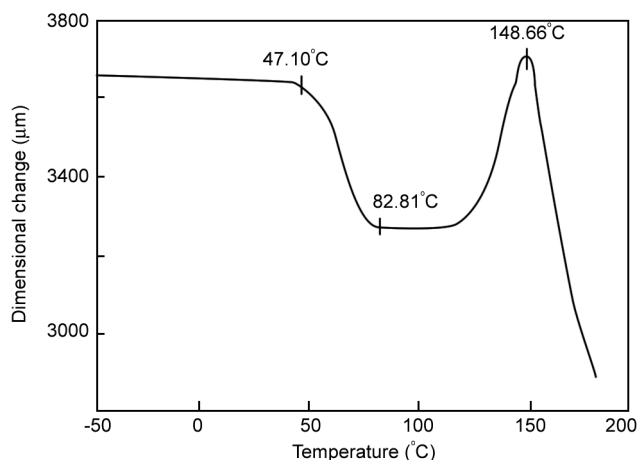


Figure 4. TMA Thermogram of BDBW.

between two spectra is in intensity of lignin moiety at 1728 cm^{-1} and 1593 cm^{-1} , that in BDBW spectrum has lower intensity. In two-spectrum benzyl group absorption appears at $1600\text{--}2000\text{ cm}^{-1}$.

Figures 3 and 4 show the TMA thermograms of BBW, and BDBW, respectively. The softening point of BBW was at 157°C and that of BDBW was at 180°C . These data show that lignin and hemicelluloses in untreated wood act as external plasticizer and therefore, the softening point of BBW was decreased.

For obtaining the new double derivatives of wood and characterization of new products the benzylated products of untreated and delignified beech wood meal, that is, BBW and BDBW, were subjected to acetylation reaction (only single derivatives of wood have been prepared and characterized by other authors) [9]. For acetylation, an acetylating mixture including acetic acid and acetic anhydride was used. The FTIR spectrum of acetylated product of BBW is shown in

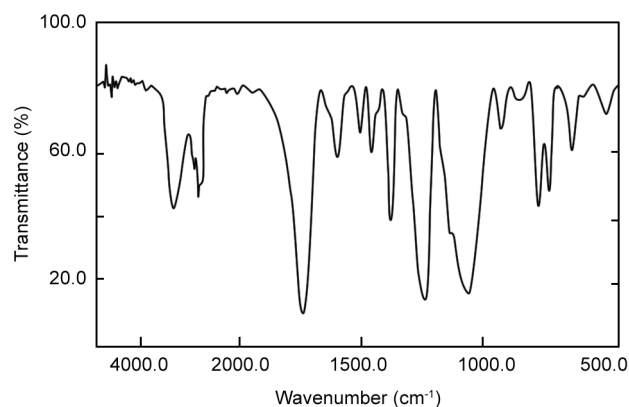


Figure 5. FTIR Spectrum of BABW.

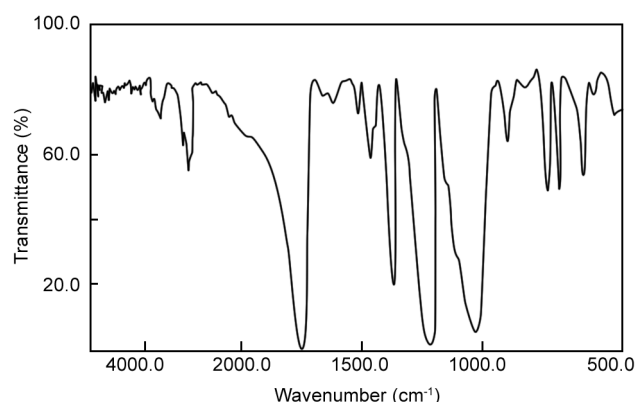


Figure 6. FTIR Spectrum of BADBW.

Figure 5. The carbonyl group absorption of acetyl moiety appears at 1749 cm^{-1} . In the acetylated product of BDBW, the carbonyl group absorption appears at 1753 cm^{-1} (Figure 6). The comparison of two spectra shows that the hydroxyl group intensity in BABW (benzylated acetylated beech wood) is higher than BADBW (benzylated acetylated delignified beech wood). The reason for this observation is that in BABW the concentration of OH-group containing components are high because of existence of hemicelluloses and lignin.

Figures 7 and 8 show the ^1H NMR spectrum of BABW and BADBW, respectively. In two spectra the CH_3 protons of acetyl moiety appear at $\delta = 1.99\text{ ppm}$, phenyl protons of benzyl group appear at $\delta = 7.26\text{ ppm}$ and CH_2 protons of benzyl group and protons of glu-

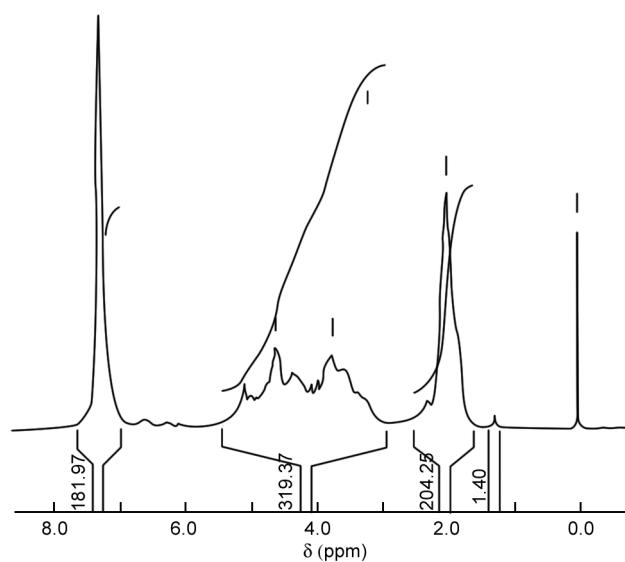


Figure 7. ^1H NMR Spectra of BABW.

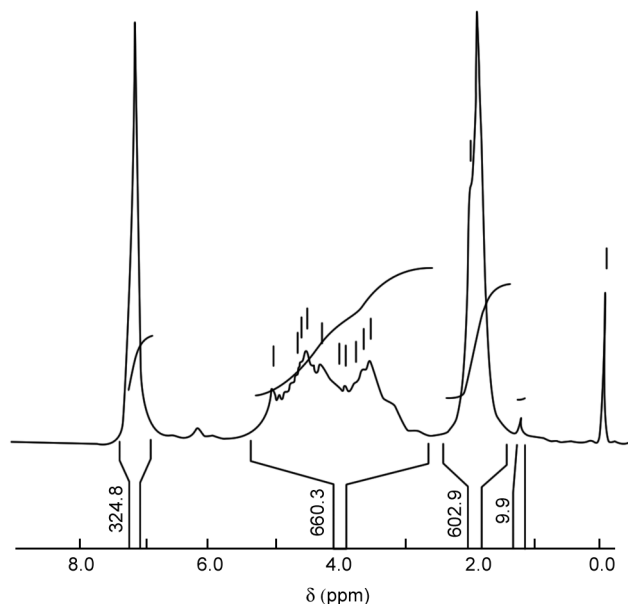


Figure 8. ^1H NMR spectra of BADBW

cose unit appear at $\delta = 3\text{-}5$ ppm as broad multiplet.

Figure 9 shows the TMA thermogram of BABW. The softening point of BABW was 94°C that shows the acetylation reaction decreases of softening point by about 60°C . By double substitution, that is, benzylation and acetylation, probably most of hydrogen bonds between chains were broken and the material behaves as a thermoplastic.

The by-products of benzylation and acetylation reactions are degradation products of cellulose, hemicelluloses and lignin during the reaction.

Both single and double substituted chemically modified woods are soluble in some organic solvents

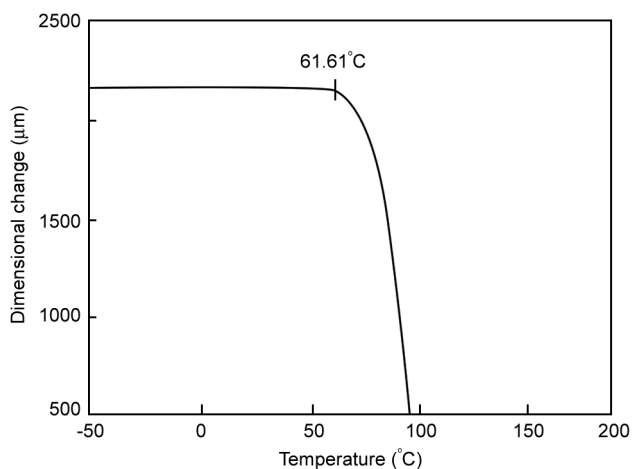


Figure 9. TMA thermogram of BABW.

Table 1. Water absorption of untreated wood and the chemically modified woods.

Sample	Water absorption(%)
Untreated wood	56
BBW	4.5
BABW	4.3
BDBW	4.2
BADBW	2.8

such as chloroform.

Table 1 shows water absorption of untreated beech wood and the products. The data show that with substitution of H-atom of hydroxyl group with benzyl or acetyl group the water absorption and hydrophilicity of chemically modified woods was remarkably decreased.

CONCLUSION

As a new method, double substitution of beech wood was carried out by benzylation and acetylation, successively. Chemically modified woods prepared by this method are soluble in some organic solvents such as chloroform and have lower hydrophilicity and water absorbancy relative to parent wood. These materials can be used for the preparation of films, sheets and other mouldings.

ACKNOWLEDGEMENT

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