

Improvement of Durability of Wood by Maleic Anhydride

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Abstract—Wood as a natural renewable material is vulnerable to degradation by microorganisms and susceptible to change in dimension by water. In order to effectively improve the durability of wood, an active reagent, maleic anhydride (Man) was selected for wood modification. Man was first dissolved into a solvent, and then penetrated into wood porous structure under a vacuum/pressure condition. After a final catalyst-thermal treatment, wood modification was finished. The test results indicate that acetone is a good solvent for transporting Man into wood matrix. SEM observation proved that wood samples treated by Man kept a good cellular structure, indicating a well penetration of Man into wood cell walls. FTIR analysis suggested that Man reacted with hydroxyl groups on wood cell walls by its ring-ether group, resulting in reduction of amount of hydroxyl groups and resultant good dimensional stability as well as fine decay resistance. Consequently, Man modifying wood to improve its durability is an effective method.

Keywords—Wood, porous structure, durability improvement, maleic anhydride

I. INTRODUCTION

WOOD as a natural material of biological origin has been an essential material for human survival. However, it is vulnerable to degradation by microorganisms [1] and susceptible to change in dimension by humidity [2], which greatly reduce its durability and thus limit its service life. Researchers have proved that, to a certain degree, the above defects should be ascribed to a large number of hydroxyl groups within wood cell walls which provides suitable environment by absorbing water for microorganism's survival, as well as changes dimension of wood by absorbing water and releasing water with changing of outer conditions. Thus, durability improvement of wood should focus on the elimination of hydroxyl groups on wood matrix.

One of most popular methods to improve the durability of wood is chemical modification by some small chemical reagents. Among these reagents, acid anhydrides, inorganic acid esters, acid chlorides, chloroethers, aldehydes, lactones, reactive vinyl compounds, epoxides and isocyanates are most

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useful compounds. In this research, maleic anhydride was selected for its active ring-anhydride group, which is capable of easily reacting with hydroxyl groups on wood matrix without reversed effect on environment and resultantly reducing amounts of hydroxyl groups. And the reagent wasn't sufficiently studied in wood modification. Consequently, it's a promising way to improve the wood durability.

II. MATERIAL AND METHODS

A. Material

Maleic anhydride (Man) was received from Shanghai Chemical Reagent Factory (Shanghai, China), and also re-crystallized before use. Wood samples of poplar lumber (*Populus ussuriensis* Kom) selected for this study were obtained from the original plantation areas in Maershan located in the northeast of China. The prepared samples with different sizes were oven-dried at 105°C to a constant weight and stored in a vacuum desiccator for further testing.

B. Methods

Man was first dissolved in a solvent accounting for 20% by weight, added with a catalyst. Then the wood samples with different sizes were immersed in the mixed solution under conditions of a vacuum of approximate 0.08MPa for 20min, and a following pressure of approximate 0.8MPa for 20min, which was determined based on previous studies [3,4]. The impregnated samples were further wrapped in aluminum foils and heated to 110°C~130°C for 2~4h. The dry condition was found to be appropriate for complete reaction of impregnated samples, for there was almost no obvious exothermic and/or endothermic peak in the temperature range 25-160°C. The Man-Wood composites were eventually obtained after vacuumizing the above treated samples to constant weights under room temperature.

C. Analytical Techniques

The equipment for impregnation treatment was available at Northeast Forestry University. Environmental scanning electron microscopy (ESEM) tests were done with a QUANTA200 machine (FEI Inc, America). Fourier transformed infrared (FTIR) analysis was made with the spectrometer Magna IR560 (Nicolet Inc, Madison, USA). The samples for FTIR analysis were made by grounding solid samples into powders with a disintegrator and passing a 100-mesh screen, followed by extracting with acetone for 24 hrs, and toluene for 24 hrs, and then subsequently drying to constant weight.

D. Performance Evaluations

Three indexes such as Volume Swelling Efficiency (VSE), Anti Swelling Efficiency (ASE) and Resistance of Water Absorption (RWA) are used to represent dimensional stability. Volume Swelling Efficiency is calculated according to the following equation 1:

$$VSE = \frac{V_i - V_0}{V_0} \times 100\% \quad (1)$$

Where: VSE represents volume swelling efficiency; V_i represents volume of impregnated samples after immersing in solvent; V_0 represents weight of samples before any treatment.

Anti Swelling Efficiency is calculated according to the following equation 2:

$$ASE = \frac{VSE_i - VSE_0}{VSE_0} \times 100\% \quad (2)$$

Where: ASE represents anti swelling efficiency; VSE_i represents volume swelling efficiency of Man-wood; VSE_0 represents volume swelling efficiency of untreated wood.

Resistance of Water Absorption (RWA) is calculated according to the following equation 3:

$$RWA = \frac{W_i - W_0}{W_0} \times 100\% \quad (3)$$

Where: RWA represents resistance of water absorption; W_i represents weight gain efficiency of Man-wood; W_0 represents weight gain efficiency of untreated wood.

III. RESULTS AND DISCUSSION

A. Selection for solvent

As maleic anhydride is solid, it's necessary for Man being dissolved in a solvent so that the resultant solution can easily enter into wood matrix and Man can approach larger number of hydroxyl groups for further reaction. The selected solvents in this research contain 8 solvents all capable of dissolving Man, i.e., benzene, methanol, ethanol, acetone, N, N-dimethyl formamide, 1, 4-dioxane, dimethylsulfoxide, and pyridine.

Wood samples with 20×20×20mm in sizes were respectively dissolved in the 8 solvents, and the volumes of each wood sample at different time were measured. The mean volume swelling rate of five wood samples in each solvent at different immersing time was shown in Fig.1. From Fig.1, it can be seen that after 442 hours immersion, the solvents in order of increasing volume swelling rate are dimethylsulfoxide, N, N-dimethyl formamide, pyridine, methanol, ethanol, acetone, 1, 4-dioxane, and benzene. This suggests that the bigger the volume swells, the larger the number of Man enter into wood matrix. However, both dimethylsulfoxide and N, N-dimethyl formamide resulted in shrinking of wood samples, and pyridine resulted in yellow color of white wood samples. Furthermore, both methanol and ethanol may theoretically take side effect on reaction of Man with wood matrix. Consequently, acetone was finally selected for its easy evaporation without any side effect on reaction of Man and hydroxyl groups.

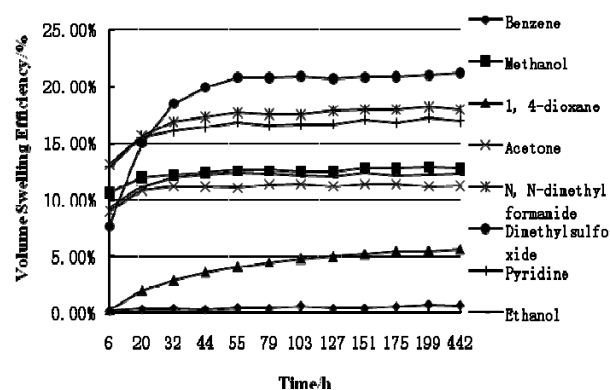


Fig. 1 relation of volume swelling rate of wood samples in each solvent and immersing time

B. Structure Characterization with SEM

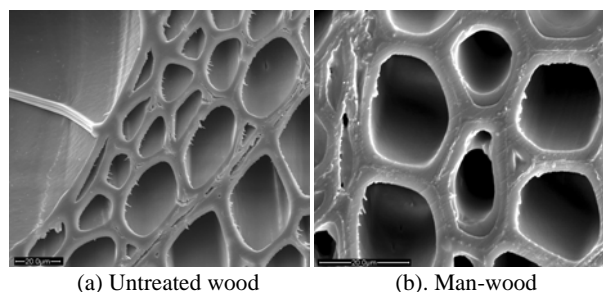


Fig. 2 SEM morphologies of untreated wood and Man-wood

Fig. 2 shows the SEM morphologies of untreated wood and Man-wood. Untreated wood possesses a porous structure consisting of wood cell walls (i.e., wood matrix). Man-wood also have a cellular structure without obvious difference with untreated wood, which indicates that large number of Man may enter into wood matrix and thus fewer number of Man leaved in the ring-spaces, resulting in Man-wood with a porous structure.

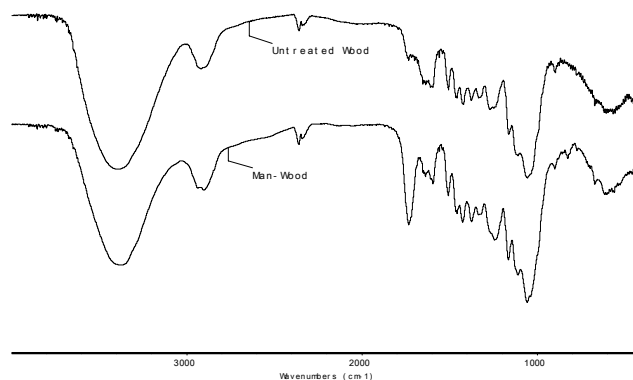
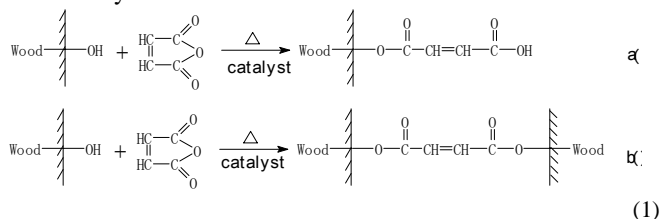


Fig. 3 FTIR spectra of untreated wood and Man-Wood

A. Reaction Analysis with FTIR

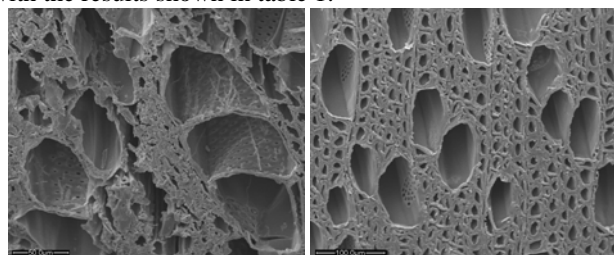
Fig. 3 illustrated that compared with untreated wood, the band intensity of Man-Wood at 1733cm⁻¹ for carbonyl stretching vibration was sharp and quite strong, indicating the carbonyl groups from Man grafting onto wood matrix.

The fact was also proved by slightly lower band intensity of Man-wood at 3370cm⁻¹ for hydroxyl group vibration and slightly higher band intensity at 1100cm⁻¹ for ether group vibration, respectively compared with those of untreated wood. Thus, FTIR spectra indicated that Man grafted onto wood matrix by reaction of Man with hydroxyl groups. The possible reaction style was shown in scheme 1:



B. Decay Resistance

The testing results of decay resistance according to mass loss rate for both untreated wood and Man-wood were shown in table 1. The results indicate that after 3 months decay attacking, both masses of untreated wood and Man-wood are loss. Compared with untreated wood without acetone extracting, the mass loss of untreated wood with acetone extracting is slightly higher, reaching 81.71%, which is induced by some extracts in wood porous structure against decay attacking. For Man-wood, no matter whether acetone extracting or not, the mass losses are quite lower than those of untreated wood, respectively. The mass loss of Man-wood with acetone extracting is slightly higher than that with acetone extracting, which indicates that Man in wood without reacting with hydroxyl groups is quite few, i.e., Man almost reacted with wood matrix under the adopted treatment conditions. No matter of whether acetone extracting or not, the decay resistance of Man-wood was improved more than 2 times than untreated wood, which suggests that the durability of wood can be effectively improved by reaction of Man with wood. Fig.4 shows the SEM morphologies of both materials after decay attacking. Fig.4a shows that the untreated wood matrix has been collapsed, while Fig.4b illustrates that Man-wood kept good porous structure, which are in accordance with the results shown in table 1.



(a) untreated poplar wood with acetone extracting
(b) Man-Wood with acetone extracting

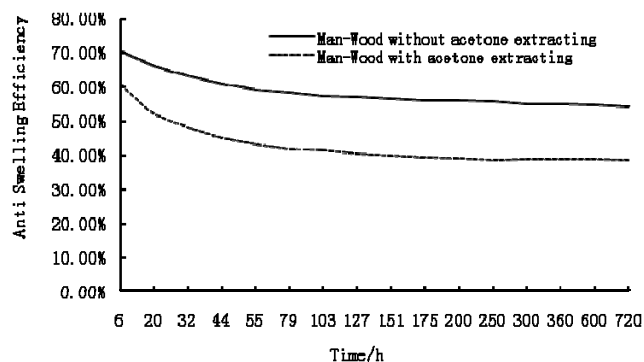
Fig. 4 SEM morphology of decay-resistant species of Man-Poplar WPC and untreated poplar wood

TABLE I
CONTRAST OF THE DECAY RESISTANCE OF UNTREATED WOOD AND MAN-WOOD

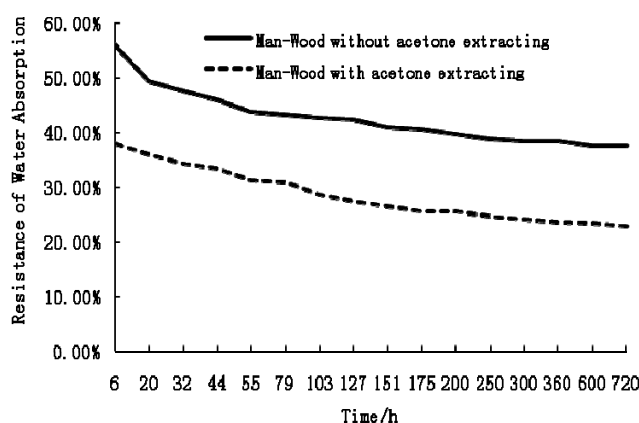
Without acetone extracting	Mass loss (%)	Improved times	With acetone extracting	Mass loss (%)	Improved times
untreated wood	79.28	-	untreated wood	81.71	-
Man-wood	23.95	2.31	Man-wood	25.17	2.25

C. Dimensional Stability

Fig.5 shows the dimensional stability towards water of Man-wood. From Fig.5a, it can be known that after immersing in water for 720h, the dimensional stability of Man-wood according to ASE is still good (>40%), although the ASE of sample with acetone extracting is lower than that without acetone extracting. The little difference induced by acetone extracting indicates that just few amount of Man didn't react with hydroxyl groups. For Fig.5b, the similar phenomenon was also seen. After 720h water immersion, RWA of samples with acetone extracting can still reach about 30%, indicating good dimensional stability for Man-wood.



(a) ASE—Time



(b) RWA—Time

Fig. 5 Variations of Anti Swelling Efficiency and Reduction in Water Absorption of Man-Poplar WPC

In a total, according to ASE and RWA, the dimensional stability of wood was greatly improved after Man treatment.

IV. CONCLUSION

- 1) Acetone is a good solvent for transporting Man into wood porous structure, and for Man successfully approaching into hydroxyl groups for their further reaction.
- 2) Man entered into wood matrix and chemically reacted with hydroxyl groups on wood cell walls, resulting in great reduction of amount of hydroxyl groups in wood cell walls.
- 3) As most of Man reacting with hydroxyl groups, the decay resistance and dimensional stability of Man-wood were greatly improved, compared with untreated wood, indicating good durability of wood being endowed by Man treatment.

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