

Fiberboard made of miscellaneous wood fibers oxidized by laccase mediator system

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Received April 5, 2015

Laccase was applied to wood processing due to its special significance in the ecological environment security. According to the synergic effect of nature mediator and artificial mediator, miscellaneous wood fibers were modified by the laccase mediator system (LMS) to press medium density fiberboard. Based on response surface methods, the best technological parameters were 60 U/ml of laccase activity, 0.28 mmol/L of ABTS concentration, 1.66 mmol/L of vanillin concentration and 55 min of treatment time. The study of the mechanism showed that increasing covalent bonds and hydrogen bonds between the fibers were the root cause for the mechanical properties. Moreover, the reaction of lignin and laccase with the mediator was competing. Excessive mediators restrained the oxidation reaction of lignin, and the amount of mediators was related to the amount of lignin. There is good industrialization prospect to press medium density fiberboard by LMS without adhesive.

Key words: laccase mediator system, miscellaneous fiber, medium density fiberboard.

INTRODUCTION

Laccase was applied to wood treatment authentically in the mid-1990s. After that, many countries carried out research on activation processes, adhesive, decoloration, bioremediation, etc. The binding force was mainly due to covalent bond between fibers and polymerization of lignin (Felby, 2002; Zhu, 2004; Felby, 2004). The movement of free radicals would hinder the generation of lignin (Barsberg, 1999). The bonding strength was related with the quantity of cellulose and lignin (Duan, 2007). On account of non-phenolic lignin, low molecular weight compound was introduced as redox mediator (Srebotnik, 2000; Xu, 2000; Camarero, 2007; Camarero, 2005). Therefore, we have undertaken investigations into the performance and bonding mechanism in medium density fiberboards (MDF) made from LMS treated and untreated miscellaneous wood fibers.

MATERIALS AND METHODS

Test materials

Miscellaneous wood fibers were supplied by Heilongjiang Nancha Fiberboards Co. Ltd. Enzyme activity was 4060 U/g. Artificial mediator is ABTS supplied by Sigma-Aldrich Co. Vanillin is nature mediator supplied by Adamas Reagent Co. All other chemicals were with the highest purity of

analytical grade from commercial vendors.

Medium density fiberboard (MDF) preparation

First of all, fibers were pretreated by UV light to modify functional groups. The distance between fibers and UV light was 50 cm. The intensity of UV light was 150 W/m². Irradiation time was 24 h. Then, fibers were treated by laccase mediator system (LMS), Table 1 shows the technological parameters. The control wood fibers were treated for 60 min without laccase and mediators at 4% consistency as a suspension in demineralized water. After that, the moisture content of the fibers reached 20±3%, and then fiberboards of dimensions 150 mm×150 mm×3.2 mm were made by hot pressing. Target density for the boards was 800 kg/m³. The hot pressing was divided into drying process and plasticizing process. Drying process was a cycling drying method with two steps. The first step was at 12 MPa for 60 s and 4 MPa for 40 s, and the second step was at 12 MPa for 40 s and 4 MPa for 60 s. Plasticizing process was performed at 12 MPa for 200 s. The temperature during the whole process was 180°C

Fiberboard properties

For each treatment, the fiberboards were tested for moisture content, density, modulus of rupture (MOR), internal bond strength (IB) and water absorption (WA) following a 24 h cold water (20±2°C) soak. All testing was done according to

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RG7-20A, except that the fiberboard samples were equilibrated at 65% RH and 21 °C prior to testing.

FTIR analysis

The fibers in the interior of MDF were removed using a razor blade and analyzed by direct transmission (KBr pellet technique) (Pandey and Pitman, 2002). All spectra were measured at a resolution of 4 cm⁻¹ and 30 scans were recorded per sample. Peak heights of IR bands were measured using OMNIC software according to previously published methods.

XPS analysis

X-ray photoelectron spectra were obtained with a physical electronics (England) ESCALAB MK instrument equipped with a monochromatic Mg K_α X-ray source. A Gaussian curve fitting program was used to deconvolute C1 carbon (C-C, C-H and C=C functional groups) signal at 285 eV as an internal standard. The chemical shifts relative to C1 used in the deconvolution were 1.7 ± 0.2 eV for C2 (C-O), 3.1 ± 0.2 eV for C3 (C=O or O-C-O), and 4.3 ± 0.2 eV for C4 (O-C=O groups).

Mechanical properties of MDF

Regression models of MOR, IB and WA were analyzed by the method of descent. Response surface is shown in Fig.1. MOR, IB and WA achieved the ideal value since the laccase activity was between 59.08 U/ml and 70U/ml, mediator concentration was between 1.94 mmol/L and 2.33 mmol/L, and time was controlled between 54.98 min and 90 min. Lignin was the catalytic object of LMS, but overmuch laccase possibly hindered the reaction due to steric hindrance. Mediators could promote oxidation reaction of non-phenolic lignin, but excess mediator could restrain oxidation reaction of non-phenolic lignin. Reaction time was important factor to guarantee complete reaction, but longer time could reduce mechanical properties due to the hydrolysis of lignin. The best technological parameters were 60 U/ml of laccase activity, 0.28 mmol/L of ABTS concentration, 1.66 mmol/L of vanillin concentration and 55 min of treatment time.

Table 1. Technological parameters of LMS treated fiber.

ABTS(mmol/L)	Vanillin(mmol/L)	Laccase(U/ml)	Time(min)	Temperature(°C)	pH value
0.25	1.5	50	30	50	5
0.3	1.8	60	60		
0.35	2.1	70	90		

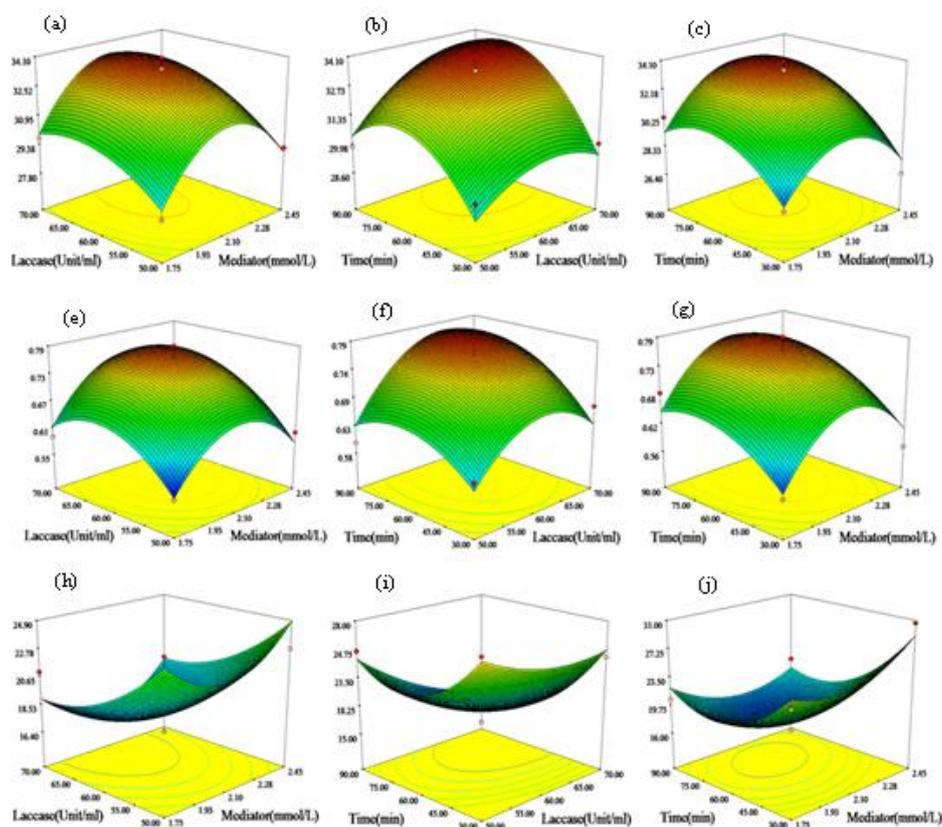


Fig. 1. Response surfaces of MOR, IB and WA interacted by laccase, mediator and time

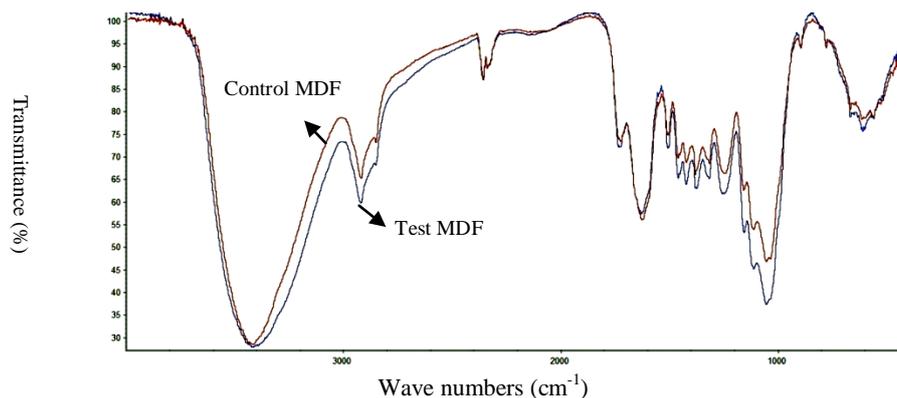


Fig. 2. FTIR spectrum of control sample and test sample.

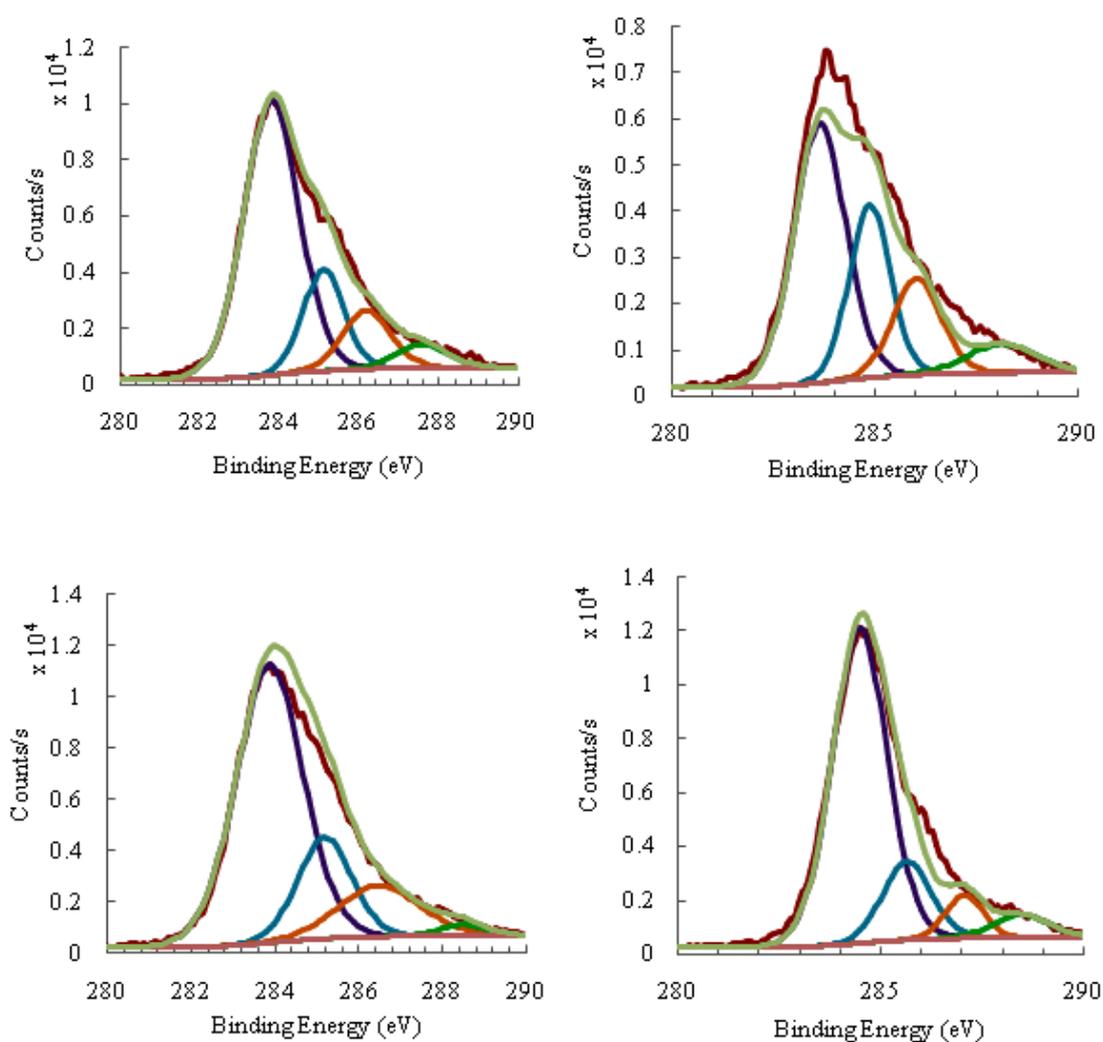


Fig. 3. XPS of control sample and test sample on the surface and in the interior: .a) XPS of control sample in the interior; b) XPS of test sample in the interior; c) XPS of control sample on the surface; d) XPS of test sample on the surface.

Evidence for Cross-linking of MDF

FTIR analysis

FTIR of control samples and test samples is shown in Fig.2. An increase at 3426 cm^{-1} and 2927 cm^{-1} showed that phenolic hydroxyl groups increased, which was due to the substitution reaction of aromatic nucleus prompted by LMS. The decrease in the characteristic absorption peak of aromatic ring in pos. 2 (781 cm^{-1}) further prove it. Moreover, the increases at 1729 cm^{-1} , 1159 cm^{-1} , 1112 cm^{-1} , 1058 cm^{-1} and 1037 cm^{-1} showed that new ether bond and carbonyl were generated in pos. 3 of aromatic ring. Accordingly, skeletal vibration of aromatic ring weakened (1625 cm^{-1}). It showed that LMS could induce the etherification and aldolization in pos. 3 of the aromatic ring. All issues considered, the increase of ether bond, carbonyl group and hydrogen bond was the dominant reason for achieving higher mechanical properties.

XPS analysis

The distribution in terms of carbon classes shows a marked increase in C2, C3, C4 and a decrease in C1 for the interior of the test sample (Fig.3 (a) and (b)). Hydroxyl group in lignin was oxidized to aldehyde or ketone under the effect of LMS, so the chances of lignin to combine with cellulose decreased. Oppositely, the chances of hydrogen generation in/among cellulose increased. So the component of C2 increased. The increase of C3 was due to the new carbonyl group, which was dominant from non-phenolic lignin oxidized by LMS. The increase of glucosidic bond generated from degraded lignin and cellulose also increased C3. The possible explanation for increased C4 was the further oxidation of aldehyde under the effect of LMS. The C1 component could give information similar to the O/C ratio and directly affect the amount of lignin. The degradation of lignin was the reason of decreased C1 component. Simultaneously, it had an increase in C1, C4 and a decrease in C2, C3 for the surface of test sample (Fig.3 (c) and (d)). There was obvious difference in compound concentration between fiberboard surface and interior. The degradation of lignin made more pores among fibers so that the lignin could easily reach fiberboard surface. More lignin lead to increased C1. The grafting reaction between cellulose and

vanillin covered the hydroxyl in cellulose, so the C2 component decreased. Semicellulose pyrolyzed under high temperature, so C3 decreased, but the product increased C4.

CONCLUSIONS

The mechanical properties of MDF corresponded to China MDF standard. The increase of covalent bond and hydrogen bond was the dominant reason for high mechanical intensity. The reaction of lignin and laccase with the mediator was competing. Excessive mediators restrained the oxidation reaction of lignin, and the amount of mediators was related to the content of lignin.

Acknowledgements: This research was sponsored by Science and Technology Support Project for the Twelfth Five-year (key technology research and demonstration of forest resource efficient utilization in Greater Hignnan Mountains: 2011BAD08B03) and the Special Funds for the Construction of Key Disciplines Funded Projects in Fujian Agriculture and Forestry University (6112C070N). The authors express our sincere thanks to coordinators for their encouragement and support during the course of this work.

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ФИБРОКАРТОН ОТ ДЪРВЕСНИ ВЛАКНА ОКИСЛЕНИ В СИСТЕМА С ЛАКАЗА КАТО МЕДИАТОР

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Постъпила на 5 април, 2015 г.

(Резюме)

Използвана е лаказа при екологичното третиране на дървесинат. Използва се синергичният ефект на естествените и изкуствените медиатори, при което лаказната медиаторна система (LMS) позволява да се получи като продукт фиброкартон със средна плътност. Най-добри технологични параметри са получени при лаказа с активност 60 U/ml, концентрация на ABTS от 0.28 mmol/L, 1.66 mmol/L ванилини, време за третиране 55 минути. Анализът показва увеличаване на ковалентните връзки и водородни връзки между влакната, които са коренната причина за механичните свойства на картоната. Освен това реакцията между лигнина при медиаторлаказа е конкурираща. Излишъкът на медиатори ограничава окислението на лигнина. Въобще, налице е добра промишлена перспектива за получаването на фиброкартон със средна плътност без адхезив.