ENZYMATIC HYDROLYSIS LIGNIN DERIVED FROM CORN STOVER AS AN INTRINSTIC BINDER FOR BIO-COMPOSITES MANUFACTURE: EFFECT OF FIBER MOISTURE CONTENT AND PRESSING TEMPERATURE ON BOARDS' PROPERTIES

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Binderless fiberboards from enzymatic hydrolysis lignin (EHL) and cotton stalk fibers were prepared under various manufacturing conditions, and their physico-mechanical properties were evaluated. Full factorial experimental design was used to assess the effect of fiber moisture content and pressing temperature on boards' properties. In addition, differential scanning calorimetry (DSC) was used to obtain the glass transition temperature (T_g) of EHL. We found that both fiber moisture content and pressing temperature had significant effects on binderless fiberboards' properties. High fiber moisture content and pressing temperature are suggested to contribute to the self-bonding improvement among fibers with lignin-rich surface mainly by thermal softening enzymatic hydrolysis lignin. In this experiment, the optimized pressing temperature applied in binderless fiberboard production should be as high as 190°C in accordance with the EHL T_g value of 189.4°C, and the fiber moisture content should be limited to less than 20% with a higher board density of 950 kg/m^3 to avoid the delamination of boards during hot pressing.

Keywords: Enzymatic hydrolysis lignin; Agricultural residues; Self-bonding; Fiberboard

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INTRODUCTION

An increasing concern for air pollution and health risks has given impetus to research to reduce formaldehyde emissions from wood composites made from formaldehyde-based resins. The possibility of using replacement materials for formaldehyde-based resins (such as isocyanate, soy protein-based adhesive, etc.) and excluding synthetic resins from wood composites are considered as the most effective solutions to this problem. In this regard many researchers have investigated the production of binderless boards from various origins since the 1980s (Jain and Handa 1982; Suzuki et al. 1998; Widyorini et al. 2005; Hashim et al. 2010). The results of these studies have shown that lignin from lignocellulosic materials plays an important role in the expression of binderless board performance (Okuda et al. 2006a, b).

Lignin, a phenolic polymer, is the second most abundant component of renewable biomass in nature and constitutes about 15 to 30% of the dry mass of wood and vascular plants. It acts as a binder in the cell walls of plants, consolidating the polysaccharide matrix and holding the hemicellulose and cellulose microfibres (Kumar et al. 2009). This offers potential for higher value-added applications of lignin generated from the papermaking and emerging cellulosic ethanol industries in renewable polymeric materials development. Several kinds of lignin, such as kraft lignin and lignosulfonate, have been added directly for binderless board manufacture and show that mechanical properties of binderless boards can be greatly improved (Anglès et al. 2001; Velásquez et al. 2003; Dam et al. 2004).

Enzymatic hydrolysis lignin (EHL) is a by-product of bio-ethanol production from lignocellulosic materials. Both the cellulosic and hemicellulosic fractions of biomass can be converted to simple sugars that can subsequently be fermented to ethanol. Therefore, current research and development attention has been focused on producing bio-ethanol from wood and agricultural residues. However, lignin, one of the major three components of lignocellulosics, plays a role as a barrier to enzymatic saccharification of cellulose and is considered as a waste product generated from the cellulosic ethanol processes. According to the survey, nearly 1 ton of residues is generated during the production of 1 ton bio-ethanol from lignocellulosic materials, of which 40 to 50% consists of enzymatic hydrolysis lignin (EHL). It is anticipated that the future lignocellulosic ethanol industry will generate large quantities of EHL (Zhu and Pan 2009). Value-added utilization of EHL not only can help offset the cost of bio-ethanol production and boost the economic viability of the bioethanol industry but also provide a source of renewable materials. EHL will likely be more active than that produced from conventional pulp mills due to enzymatic hydrolysis, which offers potential for higher value-added applications in renewable polymeric materials development. However, there is little information available on its value-added applications so far.

To explore the potential value-added applications of enzymatic hydrolysis lignin (EHL), binderless fiberboards from cotton stalk fibers with adding EHL as the intrinsic binder have been developed. In a previous study, the better properties of boards were achieved with an EHL addition amount of 10% based on the weight of oven-dried fibers. As part of a comprehensive research project, the effect of fiber moisture content and pressing temperature on binderless fiberboards' properties was investigated in this study, so that manufacturing conditions of binderless fiberboard from enzymatic hydrolysis lignin and cotton stalk fiber can be optimized.

EXPERIMENTAL

Raw Materials and Preparation

EHL was extracted from corn stover residues, which were derived from the production of bio-ethanol in the pilot plant in Hei Longjiang Province, with sodium hydroxide solution (Liu and Cheng 2007). Then EHL was ground and screened to an average diameter of 20 μm and kept at a stable moisture content of 8%.

Cotton (*Gossypium hirsutum*) stalk was harvested in an agricultural field of northern Jiangsu Province in China. From the sample stalk collected, its husks and other impurities were cleaned and its branches were removed. Then its stem was chipped and screened to an average size of 25×10×5 mm for fiber preparation. Chips were soaked in tap water overnight and then softened in a pressure tank with a steam pressure of 1.2 bar. The steamed chips were then fiberized rapidly using a laboratory atmospheric refiner. Refining was necessary with regard to the morphology and size of fibers. The fiber size distribution was determined by a PTI Fiber Classifer as illustrated in Fig. 1. The fibers were gradually collected and oven dried at 100 ^{o}C to a moisture content of 9.9%, 14.3%, and 18.2%, respectively for producing fiberboards.

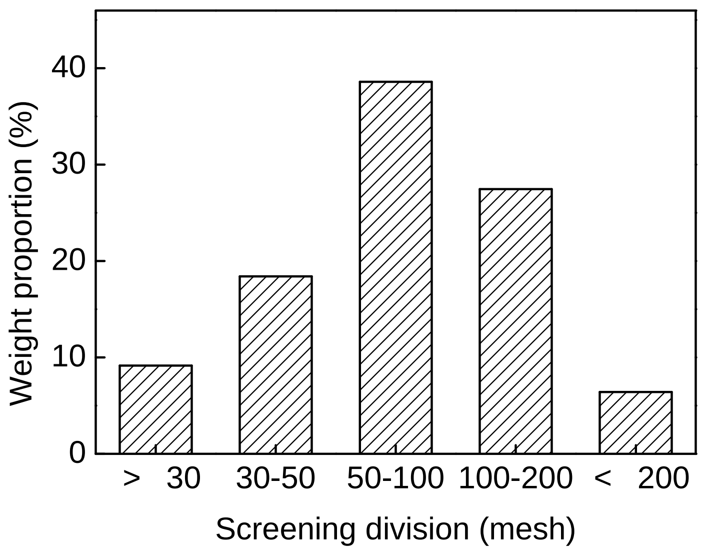

Fig. 1. Screening distribution of the cotton stalk fiber

DSC Measurement

A differential scanning calorimeter (DSC; 200F3, Netzsch, Germany) with high purity nitrogen as carrier gas was used to evaluate the thermal behaviors of the EHL with the heating rate of 10K/min. Five samples were tested. For each scan, about 6 mg of EHL was added to an aluminum capsule. The capsule was sealed and then heated from room temperature to 220 ^{o}C. Calculated data involved automatic output through the system of Proteus Analyzer. The DSC curves were used to determine glass transition temperature (T_g) of the sample using the step analysis method.

Binderless Fiberboards Manufacture

The prepared cotton stalk fibers were mixed with EHL in the proportion of 10% based on the weight of oven-dried fibers, since better properties of boards had been achieved with this addition amount in our previous study. Then the mixture was shaped using a forming box (300 mm in length and 300 mm in width). 4 mm thick cotton stalk fiberboard mats were prepared with a target density of 950 kg/m^3. After forming, the mats were loaded into a hot-press, and the two platens were closed to the target mat thickness that was controlled by thickness gauge. The pressing temperature was set at 170, 190, and 210 ^{o}C, respectively. Full factor experimental design was used to determine the effect of fiber moisture content and pressing temperature on boards' properties, as shown in Table 1. The pressing time and the initial pressing pressure were kept constant at 60 s/mm and 5.0 MPa respectively. For each condition three replicates were used, resulting in a total of 27 fiberboards.

Table 1. Full Factorial Experimental Design With Two Factors and Three Levers for Board Manufacture

Run	Moisture content of fibers (wt%)	Pressing temperature (^{o}C)
1	9.9	170
2	9.9	190
3	9.9	210
4	14.3	170
5	14.3	190
6	14.3	210
7	18.2	170
8	18.2	190
9	18.2	210

Physical and Mechanical Properties of Fiberboards

Prior to the evaluation of the mechanical and physical properties, the boards were conditioned at 25°C and 65±5% relative humidity (RH) until the boards reached equilibrium moisture content for properties examination. The boards were characterized according to the Chinese National Standard for Medium Density Fiberboard (MDF) (GB/T 11718-2009) for internal bonding strength (IBS), modulus of rupture (MOR) and thickness swelling (TS).

Two static bending specimens (200 mm×50 mm) were prepared from each board for MOR testing. The three-point static bending test was conducted over an effective span of 150mm, at a loading speed of 10mm/min. Six internal bonding strength (IBS) specimens (50 mm×50 mm) and four thickness swelling (TS) (24h immersion in 20°C water) specimens (50 mm×50 mm) were cut from each board for testing. The density of each specimen for MOR, IBS, and TS were also measured before testing for the purpose of statistical analysis.

The actual densities of the specimens vary around the target density due to the horizontal density variation of boards, resulting from mat forming. As is well known, density has a significant effect on board performance. Hence, the board properties must be adjusted to the same density level before comparison. All of the experimental values obtained were corrected to the target board density of 0.95g/cm^3 based on the linear regression between board density and properties (Xing et al. 2006).

RESULTS AND DISCUSSION

Effect of Fiber Moisture Content and Pressing Temperature on IBS

The internal bonding strength (IBS) refers to the strength of the bonding between fibers, which is an important consideration to ensure that the board will not delaminate during post-processing. The fiber moisture content and the pressing temperature play important roles in the development of inter-fiber bonds during hot-pressing. The results of ANOVA revealed that both fiber moisture content and pressing temperature were very significant factors for IBS, as shown in Table 2. As depicted in Fig. 2, the IBS increased significantly with increasing pressing temperature and fiber moisture content. At the low pressing temperature of 170 ^{o}C, the lowest IBS value of boards was observed with the low fiber moisture content of 9.9%, while the IBS was improved to about twice of the lowest one when the pressing temperature and the fiber moisture content were raised to 210 ^{o}C and 18.2%, respectively.

Table 2. ANOVA Table of Fiber Moisture Content (MC) and Pressing Temperature (T) in Relation to IBS

Factor	SS*	df*	MS*	F*	P*
MC	0.0815	2	0.0408	14.156	0.0002
T	0.0302	2	0.0151	5.241	0.0161
T×MC	0.0276	4	0.0069	2.398	0.0883
Error	0.0518	18	0.0029		
Total SS	0.1912	26			

* SS: sum of squares; df: degree of freedom; MS: mean of square; P: probability; F: F value. P<0.01, very significant factor; 0.01<P<0.05, significant factor; 0.05<P<0.2, not significant factor

The internal bonding between lignocellulosic fibers without synthetic adhesives is mainly due to: hydrogen-binding between fibers, condensation reaction in lignin (Okuda et al. 2006a, 2006b), and lignin-polysaccharides cross-linking reactions, such as lignin–furfural linkages (Suzuki et al. 1998). Moreover, the formation of covalent bonds between the lignocellulose polymers results in intermolecular forces that are much stronger than those created by hydrogen bonds (Back 1991). Recent investigations have demonstrated that fibers with lignin-rich surfaces could improve the mechanical properties of binderless boards by mechanical entanglement of the softened lignin molecules under pressure and temperature, possibly accompanied by the formation of covalent bonds (Okuda et al. 2006a, 2006b; Quintana et al. 2009). Our previous results proved that better properties of binderless fiberboards from cotton stalk could be obtained with the addition of EHL at a 10% level. As a plastic material, lignin would be fused together under pressure and temperature. Therefore, high pressing temperatures increase the lignin fluidity on fibers, improving lignin distribution and forming better inter-fiber bonds. In addition, it is obvious that increasing fiber moisture content will promote hydrogen bonds between fibers, and it is of great benefit to thermal softening of the lignin, which is expected to be particularly important for binderless fiberboard manufacture and has been suggested to contribute to the self-bonding improvement (Okuda et al. 2006a; Baldwin and Goring 1968).

Effect of Fiber Moisture Content and Pressing Temperature on MOR

The effect of fiber moisture content and pressing temperature on the modulus of rupture (MOR) of binderless fiberboards is shown in Table 3 and Fig. 3. The smaller probability values in Table 3 show that fiber moisture content and pressing temperature were very significant factors for MOR. Under a lower fiber moisture content of 9.9%, the boards did not exhibit satisfactory bending strength. Meanwhile, the MOR was not improved dramatically with increasing pressing temperature. However, the MOR was improved remarkably with raising of the fiber moisture content. The highest MOR value was 20.75 MPa, which was achieved with the fiber moisture content of 18.2% and a pressing temperature of 210 ^{o}C, resulting in behavior similar to IBS.

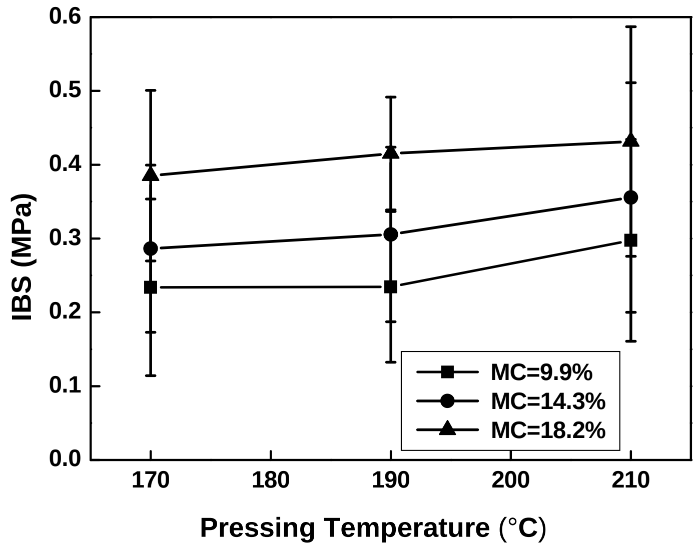

Fig. 2. Effect of fiber moisture content and pressing temperature on IBS

Table 3. ANOVA Table of Fiber Moisture Content (MC) and Pressing Temperature (T) in Relation to MOR

Factor	SS*	df*	MS*	F*	P*
MC	155.54	2	77.77	33.85	7.96E-07
T	73.23	2	36.61	15.94	0.0001
T×MC	16.05	4	4.01	1.75	0.1837
Error	41.35	18	2.30		
Total SS	286.17	26			

* SS: sum of squares; df: degree of freedom; MS: mean of square; P: probability; F: F value. P<0.01, very significant factor; 0.01<P<0.05, significant factor; 0.05<P<0.2, not significant factor

Since the value of MOR depends on the bonding strength among fibers and the individual fiber strength, better inter-fiber bonds is suggested to contribute to the bending strength improvement with the same quality of fibers. As shown by the above results, higher IBS was obtained with increasing fiber moisture content, resulting in a marked fall of the softening temperatures of lignin. Enhancing the bonding strength among fibers with EHL deposited on the surface has a beneficial effect on MOR of binderless fiberboards. In addition, higher fiber moisture content and pressing temperature result in plasticizing the fibers so that densification occurs more easily, giving rise to higher density of boards, particularly involving the surface layer which determines the MOR value. However, in the preliminary experiment, the board was found to delaminate when raising the fiber moisture content up to 20%. Therefore, the fiber moisture content had to be limited to less than 20% with a higher board density of 950 kg/m^3.

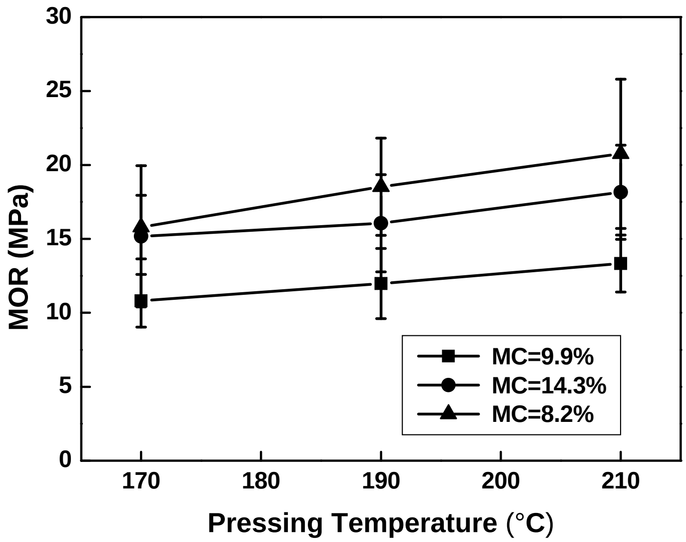

Fig. 3. Effect of fiber moisture content and pressing temperature on MOR

Effect of Fiber Moisture Content and Pressing Temperature on TS

Figure 4 shows the thickness swelling (TS) values of binderless fiberboard after 24h of immersion in water at 20°C. Binderless fiberboard made from cotton stalk fibers with a moisture content of 9.9% under lower pressing temperature presented a considerably higher TS of 86.98%, and fibers were found to be extracted from some samples, which illustrated that the fiber-fiber bonding is relatively weak under such manufacturing conditions. However, with increasing fiber moisture content and pressing temperature, the TS values were decreased significantly. The fiberboard from 18.2% MC fibers pressed under the temperature of 210°C recorded the lowest TS value of 32.35%, which was about one third of the highest one. The results of ANOVA, as shown in Table 4, also indicate that fiber moisture content and pressing temperature had very significant effects on TS.

Table 4. ANOVA Table of Fiber Moisture Content (MC) and Pressing Temperature (T) in Relation to TS

Factor	SS*	df*	MS*	F*	P*
MC	3761.03	2	1880.52	97.93	2.12E-10
T	3642.35	2	1821.17	94.84	2.76E-10
T×MC	789.56	4	197.39	10.28	0.000163
Error	345.66	18	19.20		
Total SS	8538.60	26			

* SS: sum of squares; df: degree of freedom; MS: mean of square; P: probability; F: F value. P<0.01, very significant factor; 0.01<P<0.05, significant factor; 0.05<P<0.2, not significant factor

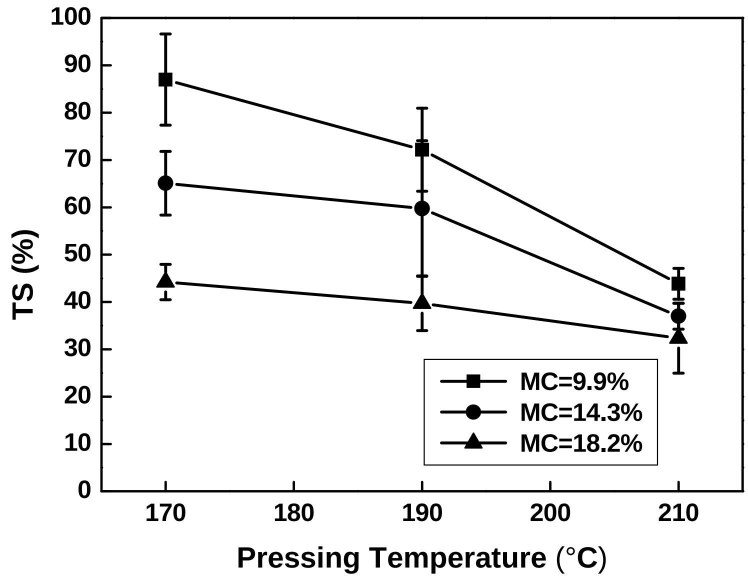

Fig. 4. Effect of fiber moisture content and pressing temperature on TS

The main causes of thickness swelling of fiberboards are recovery of compressed fibers and breakage of bonded area among fibers. Results from previous studies have shown that adding EHL can be advantageous to improve the TS of binderless fiberboard. It indicates that the reduction in hygroscopicity, due to deposition of hydrophobic EHL on the fiber surface, is one factor for the improved dimensional stability resulting from hindering the shrinkage of compressed fiber after being soaked in water. The high dimensional stability also contributed to the improvement of self-bonding among fibers under high fiber moisture content and pressing temperature.

Comparing the above results to the Chinese MDF standard (GB/T 11718-2009, IBS⩾0.55MPa, MOR⩾23MPa, TS⩽35%), which was designed for fiberboards with synthetic adhesives, we would find that IBS obtained from the cotton stalk panel products with EHL as an intrinstic binder is very low while TS is very high. It is suggested that one possible way to improve the adhesion is to chemically activate the lignin, so that binding between the fibers can be promoted during hot pressing. RF-oxygen-plasma treatment of lignin was proposed, and its effects on properties of fiberboards has been investigated. A subsequent paper should shed some light on this.

DSC Analysis

DSC defines the glass transition temperature (T_g) as a change in the heat capacity as the polymer matrix goes from a glassy state to a rubbery state. This point is determined by a change in slope in DSC curves. Determining the T_g value of EHL can help in the optimization of the pressing temperature when producing binderless fiberboards. As shown in Fig. 4, the observed T_g value for extracted enzymatic hydrolysis lignin from the production residues of bio-ethanol occurred at a temperature of 189.4°C. In general, the

T_g of lignin ranges from 127 to 193°C, depending on their source and method of isolation (Goring 1971). These ranges agree well with our data.

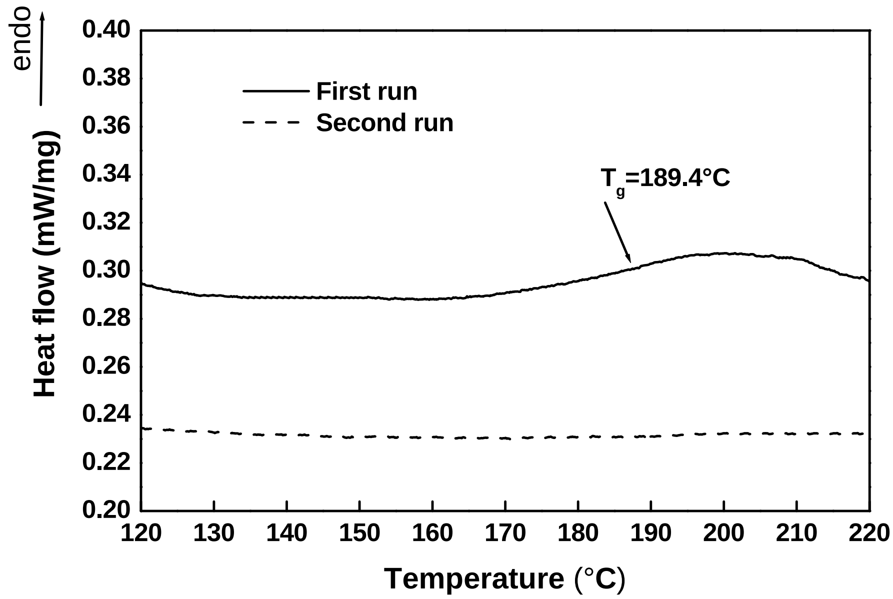

Fig. 4. DSC curves of enzymatic hydrolysis lignin (EHL). First and second heating ramp

The T_g of lignin is high compared to the T_g's of most synthetic polymers. The high T_g is probably due to hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chain. The chemical structure of lignin, particularly the aromatic ring present in the main chain, is also thought to contribute to the high T_g (Feldman et al. 2001). Enzymatic hydrolysis lignin generated through the process of steam explosion and enzymatic hydrolysis exhibits a relatively high T_g, resulting in most of the original lignin structure not being affected during this process (Kumar et al. 2009).

Bouajila has reported that the difference T - T_g (T, local temperature of board during hot pressing; T_g, local glass transition temperature) is correlated to mechanical properties of binderless fiberboards (Bouajila et al. 2005). It is obvious that poor properties of binderless fiberboards from enzymatic hydrolysis lignin and cotton stalk fiber were obtained when the pressing temperature was less than the T_g value of EHL. Thermal softening of lignin is suggested to play an important role in the expression of binderless fiberboard performance. The pressing temperature applied in binderless fiberboard production should therefore remain as high as 190°C in this experiment.

We also can find from Fig. 4 that the endotherm at 189.4°C in the first heating ramp disappeared in the second run. As a possible explanation for this, it can be presumed that the disappearance of this peak may be due to partly irreversible repolymerization reactions in lignin during hot pressing (Dam et al. 2004; Varma et al. 1986), which is essential for the development of a processing technique for binderless boards.

CONCLUSIONS

To explore the potential of enzymatic hydrolysis lignin (EHL) as an alternative to synthetic adhesives for manufacturing binderless fiberboards from agricultural residues, the effect of fiber moisture content and pressing temperature on physico-mechanical properties of binderless fiberboards from enzymatic hydrolysis lignin and cotton stalk fiber was investigated, and manufacturing conditions were optimized in this paper. The main conclusions can be summarized as follows:

(1) Both fiber moisture content and pressing temperature have significant effect on binderless fiberboards' properties. The physico-mechanical properties of boards were increased dramatically with the raising of fiber moisture content (on entering the press) and pressing temperature. It is suggested that high fiber moisture content and pressing temperature accelerate self-bonding among fibers with lignin-rich surfaces, mainly by thermal softening enzymatic hydrolysis lignin.

(2) According to the T_g value of EHL obtained from DSC curves, the optimized pressing temperature applied in binderless fiberboard production should remain as high as 190°C, and fiber moisture content should be limited to less than 20% with a higher board density of 950 kg/m^3 to avoid delamination of boards during hot pressing.

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