Preparation and Evaluation of Green Composites Using Modified Ammonium Lignosulfonate and Polyethylenimine as a Binder

Yuan Yuan, Minghui Guo,* and Fangyan Liu

Modified ammonium lignosulfonate (MAL) and polyethylenimine (PEI) were combined and used as a binder in the manufacture of a wood-based green composite. The effects of hot pressing temperature (150 ºC to 190 ºC), hot pressing time (3 min to 11 min), binder content (10 wt.% to 30 wt.%), and MAL/PEI weight ratio (1:1 to 1:9) on the physico-mechanical properties of the composites were investigated. The composites met the mechanical property requirements for furniture grade medium density fiberboard (MDF-FN REG) under the following parameters: hot pressing temperature of 170 ºC, hot pressing time of 7 min, binder content of 20 wt.%, and MAL/PEI weight ratio of 7:1. Under optimum processing, although the X-ray diffraction analysis showed that the addition of either unmodified ammonium lignosulfonate (UMAL) or MAL did not change the crystalline structure, this addition markedly improved the relative crystallinity of the composites in comparison to that of pure wood fiber. The DMA results indicated that the MAL/PEI composites had higher storage modulus and tanδ values than did the UMAL/PEI composites. Moreover, SEM analysis showed that the MAL/PEI composites had better bonding strength characteristics than did the UMAL/PEI composites.

Keywords: Ammonium lignosulfonate; Oxidized treatment; Polyethylenimine; Physico-mechanical properties; XRD; DMA; SEM

*Contact information: Key Lab of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin, 150040, China; *Corresponding author: gmh1964@126.com*

INTRODUCTION

As a consequence of increasing environmental and health concerns, the trend of the global panel marketplace has developed towards the use of fiberboards or particleboards with little or no adhesive from non-renewable petroleum, a method that decreases the emission of toxic volatiles (Widyorini *et al.* 2005). “Green composites’’ is the term often used for composites prepared from both natural fibers and a bio-based matrix (Pfister and Larock 2013). As potential composites, green composites offer several advantages, such as renewability, biodegradability, and lower cost while retaining the desired properties.

Lignin, the most abundant aromatic (phenolic) polymer found in nature, is the second most abundant natural polymer in the world, after cellulose (Lora and Glasser 2002). A number of recent studies have investigated the use of industrial lignin alone (Duval *et al.* 2013; Hu *et al.* 2012; Jin *et al.* 2011; Mancera *et al.* 2011; Privas and Navard 2013; Sahoo *et al.* 2013) or in combination with cross-linking agents such as polyethylenimine (PEI) (Geng and Li 2006; Liu and Li 2006; Sun 2009), furfuryl alcohol (Schneider and Phillips 2004), and polyaminoamide-epichlorohydrin (Li and Geng 2004) for use as formaldehyde-free adhesives. These studies are still in the exploratory stages because of barriers such as low lignin content and the high cost of cross-linking agents. In terms of industrial lignin, lignosulfonates are water-soluble anionic polyelectrolytes containing a large number of functional groups that provide unique colloidal properties for many applications (Vishtal and Kraslawski 2011).

However, the low reactivity of industrial lignin due to its chemical structure has inhibited its commercial use, and lignin is thus limited in adhesive applications. Since the 1970s, efforts have been made to improve the reactivity of industrial lignin through chemical modifications, including methylolation, phenolation, and oxidation. Of those options, H_2O_2-oxidation is a environmentally safe and effective method (Hu *et al.* 2011). Several studies have investigated the use of modified lignosufonate as a natural binder in manufacturing binderless fiberboard, but these panels have weaker properties than required by the market. However, few studies have reported on the combination of modified technical lignin and PEI in fiberboard manufacturing.

This study investigated whether a combination of MAL and PEI would be able to serve as a formaldehyde-free binder for green wooden composites, and, additionally, sought to optimize manufacturing conditions and to examine the effects of independent variables on the physico-mechanical properties of the MAL/PEI composites. Under the optimum processing conditions, UMAL/PEI and MAL/PEI composites were characterized by X-ray diffraction (XRD), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Industrial wood fibers were supplied by Greater Khingan Range Hengyou Furniture Co., Ltd. They consisted of a blend of soft- and hardwoods of different maturities with the fiber mesh of 20 to 80 mm. All the wood fibers were further oven-dried at 80 ºC to a moisture content of about 4% and stored in plastic bags for the later manufacturing of the composites. The ammonium lignosulfonate was purchased from Shenyang Xingzhenghe Chemical Co., Ltd. and was used without further purification. Its composition was as follows: 4.8% moisture, 10.8% ash, 51.7% total lignin, and 26.9% carbohydrates. Polyethylenimine (PEI) with a molecular weight (M_w) of 75,000 (50 wt.% aqueous solution) was purchased from Shanghai UN Chemical Co., Ltd.

Preparation of the MAL/PEI Binder

Ammonium lignosulfonate was oxidized using H_2O_2 in accordance with a previously published procedure (Hu *et al.* 2012). Lignosulfonate (50 g) was mixed with 100 g of water, and the pH of the resulting mixture was adjusted to 10 using a sodium hydroxide solution (30 wt.%). Then, a 30% H_2O_2 dosage (on the basis of dry weight to lignosulfonate) was added. The mixture was heated to 60 ºC and stirred for 30 min. The obtained modified ammonium lignosulfonate (MAL) was a dark homogeneous liquid. The solution was kept in an 80 ºC oven for 6 h, reaching a concentration of 20 wt.%, and then cooled to ambient temperature. The MAL/PEI binder was prepared by stirring mixtures of 20 wt.% MAL solutions and 20 wt.% PEI solutions according to the MAL/PEI weight ratio of the experimental design. The mixing time, which includes the previous processing, was 30 min.

Manufacturing of Green Composites

The wood fibers were mixed in different proportions with the MAL/PEI binders using a SHR-10A high-speed blender. After being air-dried at 20% moisture content, 190 g of the mixture was manually formed into a mat of dimensions 200 mm × 200 mm in a wooden box. The mat was pre-pressed at 1.5 MPa for 30 s and then hot-pressed at a pressure of 4 to 10 MPa until it reached the target thickness of 5 mm. The density of the green composites is very important (Laemsak and Okuma 2000), and all panels in this study had a target density of 0.80 g/cm^3. Each group of conditions was replicated three times. The manufacturing conditions were as follows: hot pressing temperature, 150 °C to 190 °C; hot pressing time, 3 min to 7 min; binder content, 10 wt.% to 30 wt.%; and MAL/PEI weight ratio, 1:1 to 9:1.

Evaluation of Physical and Mechanical Characteristics

Physical and mechanical properties, including the modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding strength (IB), and thickness swelling (TS), are very important specifications for green composites. After they had been equilibrated at 20 ± 2 °C and at 65 ± 5% relative humidity (RH) to reach a constant moisture content of around 8%, the green composites were cut into three test samples for each test, in accordance with the China National Standards (1999). The mechanical properties were tested on an AG-10TA multi-function mechanical testing machine with a load cell capacity of 10 kN; the loading speed was 5 mm/min for the MOR and MOE tests and 2 mm/min for the IB test. The measured dimensions of the test samples were 50 mm × 150 mm for the MOR and MOE tests and 50 mm × 50 mm for the IB test. For the TS test, the fiberboards were cut into 50 mm × 50 mm squares and soaked in water at 20 ± 1 °C for 24 h. The thickness of each test sample was measured before and immediately after soaking. The TS was calculated as the ratio of the thickness after soaking to the thickness before soaking. The China National Standards (1999) for these properties are as follows: MOR $\geq$ 28 MPa, MOE $\geq$ 2600 MPa, IB $\geq$ 0.6 MPa, and TS $\leq$ 35%.

Fourier Transform Infrared Analysis (FTIR)

A Magna-IR 560 FTIR Spectrometer (Nicolet, USA) was used to obtain the spectra of the UMIL and MAL. Each spectra was recorded in the range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}, and 40 scans per sample were conducted. Background spectra were collected before each sample.

X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) with a wide angle was carried out to investigate the crystallographic structure and orientation of the pure wood fiber and the composites. An X-ray diffractometer (D/MAX 2200) was used with a Cu-K$_{\alpha1}$ radiation source generated at an operating voltage and a current of 40 kV and 30 mA, respectively. A 2θ angle range from 10° to 40° in reflection mode was scanned at 4 °/min. The crystallinity index was calculated in accordance with the method used in a previous study (Segal *et al.* 1959) and was used to quantify the relative crystallinity of the samples. The measured dimensions of the test samples were 15 mm × 15 mm × 3.2 mm.

Dynamic Mechanical Analysis (DMA)

The samples of the UMAL/PEI and MAL/PEI composites were studied using a DMA-242 model thermal mechanical instrument. A three-point bending mold was employed for the test. The dimensions of the samples were 50 mm × 8 mm × 3.2 mm. A fixed displacement mode with an amplitude of 50 mm and an oscillation frequency of 5 Hz was used. The temperature program began with an equilibration waiting period at room temperature, followed by an increase in temperature at the constant rate of 5 °C/min until 250 °C was reached. DMA instrumental analysis was used to obtain the rigidity (storage modulus, E') and tan delta (δ, E''/E') curves.

Scanning Electron Microscopy (SEM)

SEM images were acquired using a Sirion 200 (FEI, the Netherlands) to investigate the morphological changes of the UMAL/PEI and MAL/PEI composites under hot pressing. A 5-mm-radius sample was taken from each binderless particleboard. Each small sample was mounted on an aluminum stub using carbon tape. The samples were coated with a thin layer of gold using a sputter coater. Images were taken at a beam voltage of 12.5 kV.

RESULTS AND DISCUSSION

Physico-mechanical Properties of Green Composites

Effects of hot pressing temperature

The effects of the hot pressing temperature on the MOR and MOE of the composites are shown in Fig. 1a. At all hot pressing temperatures studied, except for the hot pressing temperature of 150 °C, the MOR exceeded the minimum China National Standards (2009) requirement of 26 MPa (horizontal solid line) for MDF-FN REG. The average MOR value increased by 49.1% as the hot pressing temperature increased from 150 °C to 170 °C, and then decreased smoothly when the temperature was further increased from 170 °C to 190 °C. Figure 1a shows that the MOE exceeded the minimum MDF-FN REG requirement of 2600 MPa (horizontal dashed line). The MOE increased by 34.9% when the hot pressing temperature increased from 150 °C to 170 °C, and then decreased when the temperature was further increased from 170 °C to 190 °C. The average MOE value (4231 MPa) at 170 °C was significantly higher than that at all other temperatures. These findings were in agreement with those of Hu and Guo (2013).

The effects of hot pressing temperature on the internal bond strength (IB) and thickness swelling (TS) values of the composites are shown in Fig. 1b. The IB values exceeded the minimum requirement of 0.6 MPa (horizontal solid line) for MDF-FN REG at all hot pressing temperatures. The IB value increased significantly, by 77.8%, when the hot pressing temperature increased from 150 °C to 170 °C. In the range of 170 °C to 190 °C, the IB value did not change significantly. The maximum IB value was 1.09 MPa at 170 °C.

As Fig. 1b shows, the TS decreased significantly when the hot pressing temperature increased from 150 °C to 180 °C, and then increased as the temperature was further increased from 180 °C to 190 °C . The TS met the minimum requirement of 35% (horizontal dashed line) for MDF-FN REG at temperatures exceeding 170 °C. The minimum TS value was 25.3% at 180 °C. Overall, considering the properties of the composites, 170 °C appeared to be the best hot pressing temperature and was used in the subsequent evaluation.

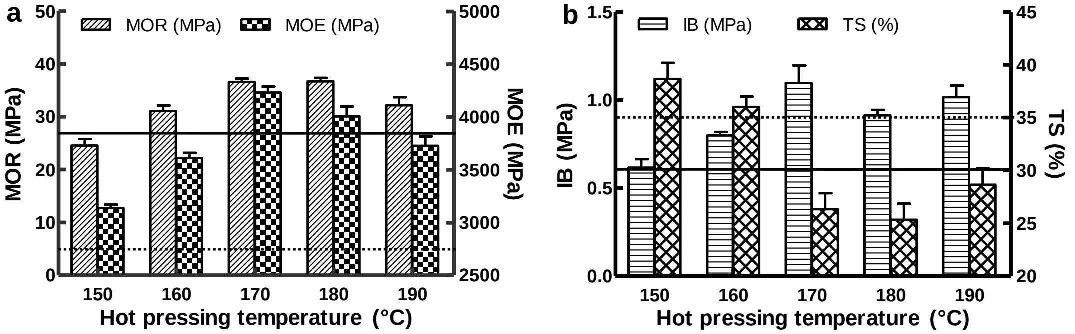


Fig. 1. Effects of hot pressing temperature on (a) the MOR and MOE, and (b) the IB and TS of composites. (Hot pressing time, 5 min; binder content, 20 wt.%; MAL/PEI weight ratio, 5:1. Data are the means of three replications, and the *error bar* represents one standard error of the mean.)

Effects of hot pressing time

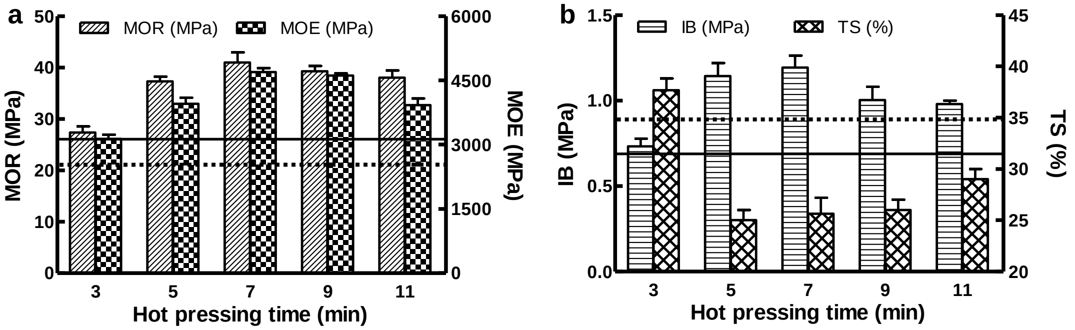


Fig. 2. Effects of hot pressing time on (a) the MOR and MOE, and (b) the IB and TS of composites. (Hot pressing temperature, 170 °C; binder content, 20 wt.%; MAL/PEI weight ratio, 5:1. Data are the means of three replications, and the *error bar* represents one standard error of the mean.)

The effects of hot pressing time on the MOR and MOE of the composites are shown in Fig. 2a. The MOR increased by 50.1% when the hot pressing time was lengthened from 3 min to 7 min. The MOR did not significantly change when the hot pressing time was lengthened from 7 min to 11 min. The MOR exceeded the minimum requirement (horizontal solid line) at all hot pressing times studied. As shown in Fig. 2a, the MOE exceeded the minimum requirement (horizontal dashed line). The MOE increased and reached its maximum value (4695 MPa) when the hot pressing time was lengthened from 3 min to 7 min, and then decreased markedly when the hot pressing time was further increased from 7 min to 11 min.

The effects of hot pressing time on the IB and TS values of the composites are shown in Fig. 2b. The IB value increased significantly when the hot pressing time was lengthened from 3 min to 7 min, and then decreased as the time was further lengthened to 11 min. Figure 2a also shows that the IB values met the minimum requirement (horizontal solid line) at all hot pressing times studied. The TS value decreased by 32.4% when the hot pressing time was lengthened from 3 min to 5 min, showed no marked changes when the time was lengthened from 5 min to 9 min, and then increased when the time was further lengthened from 9 min to 11 min. The TS values met the minimum requirement (horizontal dashed line) at all hot pressing times except for at 3 min. This indicated that MAL/PEI binder not fully cured after 3 min (Liu and Li 2006), but longer pressing time might have negative effect (over curing and degradation) on the development of strength properties of the composites. Thus, 7 min was deemed to be the optimum hot pressing time for use in subsequent investigations.

Effects of binder content

The effects of binder content on the MOR and MOE of the composites are shown in Fig. 3a. The MOR increased significantly when the binder content was increased from 10 wt.% to 20 wt.%, decreased when the binder content was further increased from 20 wt.% to 25 wt.%, and then did not change significantly when the binder content was increased from 25 wt.% to 30 wt.%. The MOR values exceeded the minimum requirement (horizontal solid line) at all binder contents except for at 10 wt.% and 15 wt.%. The MOE increased significantly when the binder content was increased from 10 wt.% to 20 wt.%, but did not change significantly when the binder content was increased from 20 wt.% to 30 wt.% (Fig. 3a), indicating that a higher amount of lignin might negatively affects the board's physico-mechanical properties (Velásquez *et al.* 2003). At all the tested levels of binder contents, the MOE exceeded the minimum requirement (horizontal dashed line).

The effects of binder content on the IB and TS values of the composites are shown in Fig. 3b. The IB trend was the same as that of MOR. The IB values exceeded the minimum requirement (horizontal solid line) at all binder contents except for at 10 wt.% and 15 wt.%. The TS value significantly decreased when the binder content was increased from 10 wt.% to 25 wt.%, and then increased when the binder content was further increased from 25 wt.% to 30 wt.%. The TS values met the minimum requirement (horizontal dashed line) at all binder contents except for at 10 wt.%. Overall, considering the costs, 20 wt.% was deemed to be the optimal binder content for use in subsequent evaluations.

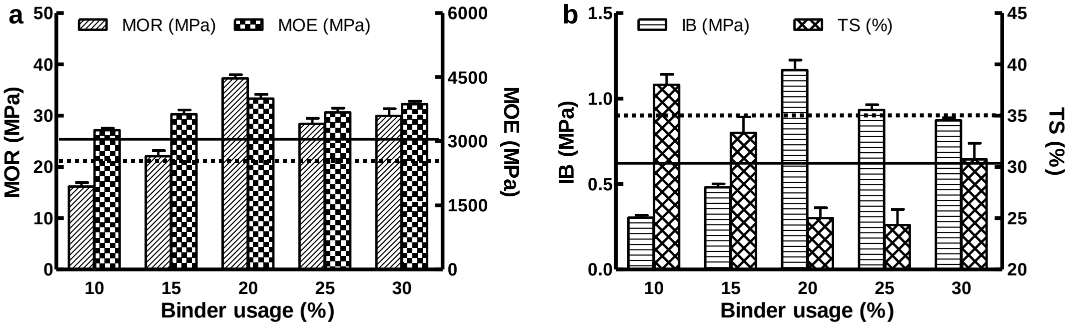


Fig. 3. Effects of binder content on (a) the MOR and MOE, (b) the IB and TS of composites. (Hot pressing temperature, 170 °C; hot pressing time, 7 min; MAL/PEI weight ratio, 5:1. Data are the means of three replications, and the *error bar* represents one standard error of the mean.)

Effects of MAL/PEI weight ratio

The effects of the MAL/PEI weight ratio on the MOR and MOE of the composites are shown in Fig. 4a. The MOR value did not change significantly when the MAL/PEI weight ratio was increased from 1:1 to 3:1. The average MOR value increased by 35.5% when the MAL/PEI weight ratio was increased from 3:1 to 7:1, and then decreased markedly with further increases in the MAL/PEI weight ratio. At all the MAL/PEI weight ratios studied, except for at 1:1 and 3:1, the MOR value exceeded the minimum requirement (horizontal solid line). The trend for MOE was the same as that for MOR, with a maximum value of 4588 MPa. At all MAL/PEI weight ratios tested, the MOE exceeded the minimum requirement (horizontal dashed line).

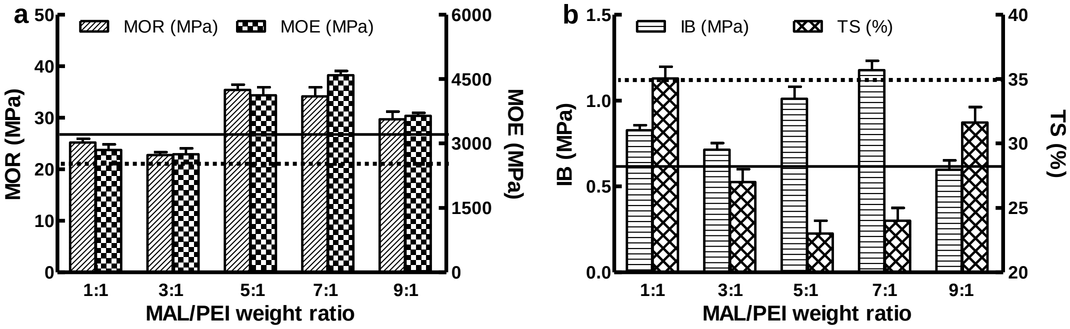


Fig. 4. Effects of MAL/PEI weight ratio on (a) the MOR and MOE, (b) the IB and TS of composites. (Hot pressing temperature, 170 °C; hot pressing time, 7 min; binder content, 20 wt.%. Data are the means of three replications, and the *error bar* represents one standard error of the mean.)

The effects of the MAL/PEI weight ratio on the IB and TS values of the composites are shown in Fig. 4b. First, the IB value decreased when the MAL/PEI weight ratio was increased from 1:1 to 3:1, and then increased significantly when the MAL/PEI weight ratio was increased from 3:1 to 7:1. The IB value decreased markedly as the ratio was increased to 9:1. The maximum IB value (1.17 MPa) was obtained at the MAL/PEI weight ratio of 7:1. Figure 2a also shows that the IB values met the minimum requirement (horizontal solid line) at all the MAL/PEI weight ratios studied except for at 9:1. The TS value decreased significantly when the MAL/PEI weight ratio was increased from 1:1 to 5:1, and then increased when the ratio was further increased from 5:1 to 9:1. The TS values met the minimum requirement in the MAL/PEI weight ratio range of 3:1 to 7:1 (horizontal dashed line, Fig. 4b). Therefore, the optimum MAL/PEI weight ratio to be used in further study was deemed to be 7:1.

The green composites were compared with composites made using unmodified ammonium lignosulfonate under the optimized conditions of the manufacturing variables (hot pressing temperature, 170 °C; hot pressing time, 7 min; binder content, 20 wt.%; MAL/PEI weight ratio, 7:1), and the results of the analysis of the physico-mechanical properties of the samples are shown in Table 1.

Table 1. Physico-Mechanical Properties of UMAL/PEI Composites and MAL/PEI Composites

Samples	Density (g/cm^3)	MOR (MPa)	MOE (MPa)	IB (Mpa)	TS (%)
UMAL/PEI composites	0.89	22.45	2667	0.41	36.7
MAL/PEI composites	0.86	35.70	4696	1.23	24.3

The properties shown in Table 1 were better in the MAL/PEI composites than in UMAL/PEI composites. Moreover, the MAL/PEI composites fully met the China National Standards (2009), whereas the UMAL/PEI composites only partially satisfied these standards.

Fourier Transform Infrared Analysis (FTIR)

To better compare the structural changes of UMIL and MAL due to the modification process, the FTIR spectra of UMIL and MAL are presented in Figs. 5 a and 5 b. Characteristic vibrational modes were observed at 3400 cm^{-1} (aromatic and aliphatic hydroxyl groups), 3250 cm^{-1} (hydroxyl groups of lignin), 1710 cm^{-1} (carbonyl group), 1595 cm^{-1}, 1510 cm^{-1} and 1422 cm^{-1} (aromatic ring vibrations), 1460 cm^{-1} (methoxyl groups), 1042-1044 cm^{-1} (sulfonate group), 1225 cm^{-1} (phenolic hydroxyl group). The dramatic differences between UML and MAL were the intensities of the methoxyl group and the sulfonate group, which both decreased greatly, indicating these two groups were easily cleaved under the presence of H_2O_2 (Hu *et al.* 2013). The intensity of phenolic hydroxyl group and carbonyl group was found to be higher for MAL, while the intensity of aromatic ring vibrations and sulfonate group greatly decreased. Thus the UMIL was degraded and activated to MAL by H_2O_2 (Hu *et al.* 2011), and higher reactive activity of MAL can react with PEI as a new binder for composites, which may improve the physico-mechanical properties of the composites (Hu and Guo 2013).

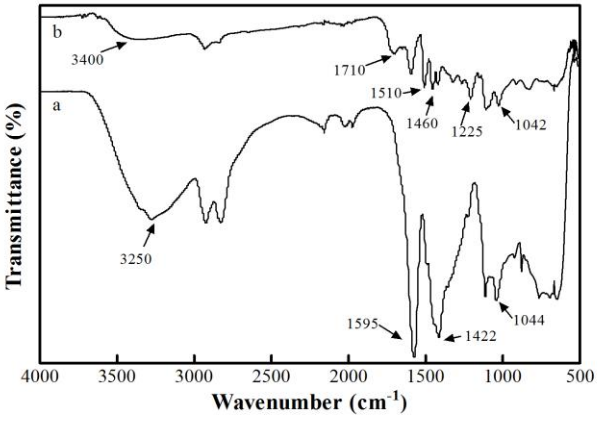


Fig. 5. FTIR spectra of UMAL (a) and MAL (b)

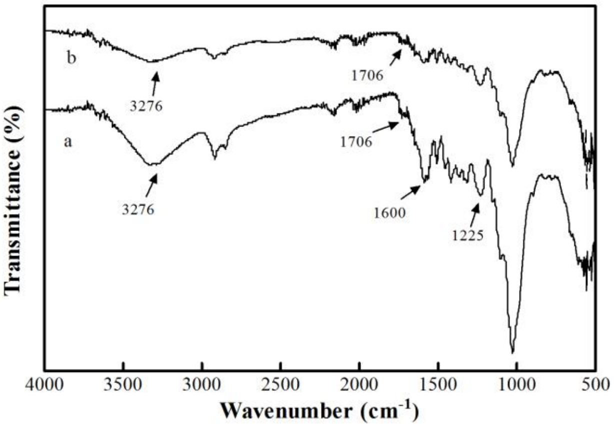


Fig. 6. FTIR spectra of (a) MAL-PEI mixtures at 20 °C; (b) MAL-PEI mixtures for 170 °C for 7 min

The FTIR of spectra of the MAL-PEI mixtures (the MAL/PEI weight ratio, 7:1) are shown in Fig. 6. When MAL and PEI were mixed at 25 °C, the shoulder peak of carbonyl groups at 1706 cm^{-1} could still be seen. After the MAL-PEI mixture was heated at 170 °C for 7 min, the intensity of the carbonyl peak significantly decreased (Fig. 6), which was contrary to the intensity increase of the peak at 1710 cm^{-1} for MAL alone (Fig. 5). After heating the mixture, the intensity of amino groups at 3276 cm^{-1} and phenolic hydroxyl group at 1225 cm^{-1} also were dramatically decreased. This indicated that covalent bonds such as amide linkages were found. All these results also suggested the curing mechanisms of MAL-PEI between carbonyl groups in MAL and amino groups in PEI, which are similar to the DKL-PEI adhesive (Liu and Li 2006).

X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a non-destructive technique that is widely used in material characterization, particularly to determine crystallographic structure and orientation. Crystallinity is a major factor that determines the mechanical properties of composites. The XRD diffraction patterns and crystallinity of the pure wood fiber (Sample A) and the composites (Samples B and C) under optimum conditions are shown in Fig. 7. The characteristic diffraction peaks at $2\theta = 16.5°$ and $2\theta = 22.6°$ were respectively assigned to the (101) and (002) planes of cellulose I. Transformations of crystalline structures of the samples were not observed under the hot pressing condition, and the samples exhibited diffraction peaks similar to those of natural cellulose (Chen *et al.* 2010). Following the instructions proposed by Segal *et al.* (1959), the relative crystallinities of samples A, B, and C were found to be 61.7%, 70.5%, and 73.1%, respectively, as shown in Fig. 7. The crystallinities of samples B and C were higher by over 14% than that of sample A. The crystallinities of the composites containing either UMAL or MAL were significantly enhanced in comparison to that of pure wood fiber. This enhancement occurred because some amorphous regions of the cellulose molecular chain were hydrolyzed under higher hot pressing temperature and time, thus shortening the chain. The relative crystallinity increased because reducing the degree of polymerization and the hydroxyl content of the cellulose resulted in the formation of hydrogen bonds during the degradation of hemicellulose and lignin (Jin 2002). Moreover, the active groups (*e.g.*, phenolic hydroxyl and aldehyde groups) in the MAL (Hu *et al.* 2013) and PEI reacted with the wood fiber to form more hydrogen or covalent bonds in the composites, thus improving the dimensional stability and mechanical properties of the composites. These results are in agreement with the given mechanical data (Figs. 1 through 4).

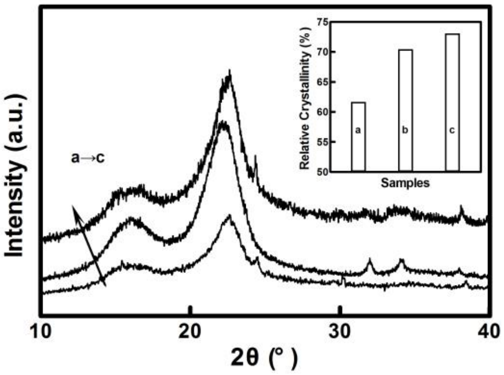


Fig. 7. XRD patterns of (a) pure wood fiber, (b) UMAL/PEI composites, and (c) MAL/PEI composites

Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of the composites were investigated using DMA. DMA tests were likewise used to investigate the effects of the additions of unmodified or modified ammonium lignosulfonate on the thermomechanical properties (the storage modulus E' and tan delta) of the composites, as shown in Fig. 8. The storage modulus was significantly enhanced in the MAL/PEI composites, unlike in the UMAL/PEI composites, indicating an improvement in the stiffness of the composites. The MAL/PEI composites reached a maximum modulus value of 5374 MPa. The observed enhancement of these properties may be attributed to the fact that the modified lignosulfonate exhibited higher activity, which, when combined with PEI, had a stronger adhesion to the wood fiber (Hu and Guo 2013). This result was in agreement with the crystallinity data (Fig. 8) and suggested that MAL/PEI significantly affects the elastic properties of the composites. The plots of tanδ *versus* temperature were used to detect molecular transitions, and the peak of tanδ was interpreted as T_g. The tanδ peaks for the composites were approximately 240 °C and did not significantly shift, indicating that treatment with modified lingo-sulfonate does not affect T_g. Moreover, unlike in the UMAL/PEI composites, the tanδ peaks increased in intensity in the MAL/PEI composites, which suggested that the addition of modified lignosulfonate promotes the mobility of wood fiber chains during hot pressing.

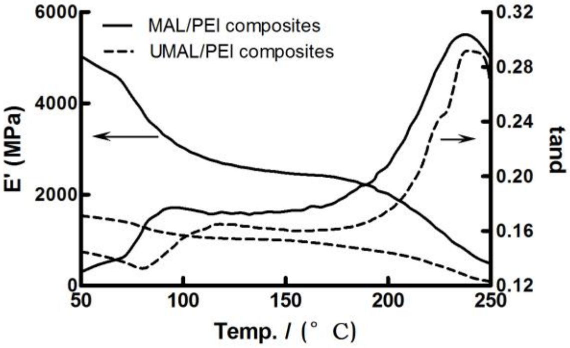
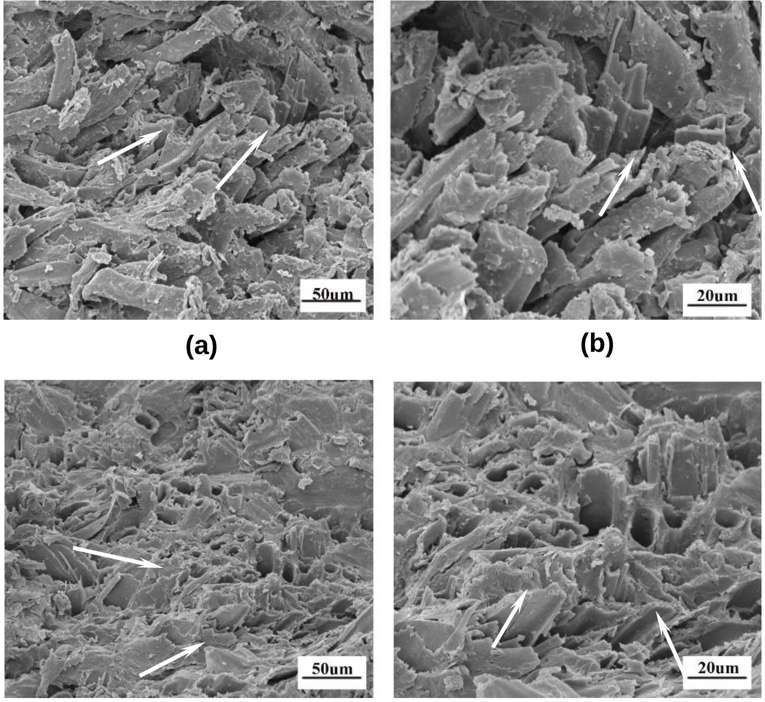


Fig. 8. Storage modulus and tan delta of the UMAL/PEI composites and MAL/PEI composites

Scanning Electron Microscopy (SEM)

The morphology of the cross sections was examined using scanning electron microscopy (SEM). Micrographs of the UMAL/PEI composites and MAL/PEI composites were compared at low and high magnifications, as shown in Fig. 9. The SEM images showed a moderate dispersion of the fiber. Without the modified lignin, the fiber cell wall almost maintained its original morphology under hot pressing conditions. The UMAL/PEI composites had more void spaces, as shown in Figs. 9a and 9b (see arrow). Moreover, fiber debonding clearly occurred because of poor adhesion in the UMAL/PEI composites. After the modified lignosulfonate treatment (as shown in Figs. 9c and 9d), the MAL/PEI composites showed a reduction in void space, which increased the compressibility of the fibers. The MAL/PEI was embedded in the matrix of wood fibers lying close to each other. The presence of the MAL/PEI during board formation facilitates the bonding of the composites with the so-called glue line (Hu and Guo 2013). This is in agreement with the mechanical data shown in Table 1. Thus, the combination of MAL and PEI can act as a formaldehyde-free binder for wood fibers with applications in green composite manufacturing.



(a) (b)

(c) (d)

Fig. 9. Micrographs of cross sections of the UMAL/PEI composites and MAL/PEI composites

CONCLUSIONS

1. It was demonstrated that a formaldehyde-free, environmentally friendly MAL/PEI binder could be used to manufacture an MDF-FN REG composite under the following variables: hot-press temperature of 170 °C, hot-press time of 7 min, binder content of 20 wt.%, and MAL/PEI weight ratio of 7:1.
2. The FTIR analysis of UMIL and MAL revealed that the UMIL was degraded and activated to MAL by H_2O_2, and higher reactive activity of MAL can react with PEI as

a new binder for composites. Evidence for covalent bonds such as amide linkages was found when the MAL-PEI mixture was heated at 170 °C for 7 min.

3. The XRD analysis of the wood fiber and the composites revealed that the addition of either UMAL or MAL did not change the crystalline structure, but it did markedly improve the relative crystallinity of the composites.
4. The DMA analysis of the composites revealed that adding MAL/PEI increased the storage modulus and tan delta, whereas no significant change in T_g occurred. The MAL/PEI composites had good viscoelastic properties.
5. The SEM of the cross sections revealed poor adhesion of UMAL/PEI, which might result in a decrease in strength (MOR and IB) of the composites. The MAL/PEI was embedded in the matrix of wood fibers with better bonding strength characteristics.

ACKNOWLEDGMENTS

The authors are grateful for the support of the National Science & Technology Pillar Program during the 12th Five-Year Plan Period (No. 2011BAD08B0304).

REFERENCES CITED

China National Standard. (1999). "GB/T 17657-1999. Medium density fibreboard," Standard Press of China, Beijing, China.

Chen, W., Yu, H., Liu, Y., Jiang, N., and Chen, P. (2010). "A method for isolating cellulose nanofibrils from wood and their morphological characteristics," *Acta Polymerica Sinica* (11), 1320-1326.

Duval, A., Molina-Boisseau, S., and Chirat, C. (2013). "Comparison of Kraft lignin and lignosulfonates addition to wheat gluten-based materials: Mechanical and thermal properties," *Ind. Crop Prod.* 49, 66-74.

Geng, X., and Li, K. (2006). "Investigation of wood adhesives from kraft lignin and polyethylenimine," *J. Adhes. Sci. Technol.* 20(8), 847-858.

Hu, J., and Guo, M. (2013). "Research on the preparation process and binding performance of the oxidation of modified industrial lignin-wood fiber composite material," *Scientia Silvae Sinicae* 49(4), 103-109.

Hu, J., Guo, W., Sun, X., Peng, Z., Zhan, J., and Guo, M. (2012). "Effects of oxidizing condition on properties of eco-friendly fiberboard made by modified lignin," *J. Northeast Forest. Univ.* 40(4), 55-58.

Hu, L., Pan, H., Zhou, Y., and Zhang, M. (2011). "Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review," *BioResources* 6(3), 3515-3525.

Hu, L., Zhou, Y., Liu, R., Zhang, M., and Yang, X. (2013). "Synthesis of foaming resol resin modified with oxidatively degraded lignosulfonate," *Ind. Crops Prod.* 44, 364-366.

Jin, C. (2002). "Study on processes of self-bonding composites," Ph.D. Thesis, Northeast Forestry Univ., Harbin, China.

Jin, C. D., Li, S., Liu, L., Ye, J. W., and Du, C. G. (2011). "Research of process on making bamboo particle board by laccase-treated calcium lignosulfonate," *Adv. Mat. Res.* 179-180, 1031-1036.

Laemsak, N., and Okuma, M. (2000). "Development of boards made from oil palm frond II: Properties of binderless boards from steam-exploded fibers of oil palm frond," *J. Wood Sci.* 46(4), 322-326.

Li, K., and Geng, X. (2004). "Investigation of formaldehyde-free wood adhesives from kraft lignin and a polyaminoamide–epichlorohydrin resin," *J. Adhes. Sci. Technol.* 18(4), 427-439.

Liu, Y., and Li, K. (2006). "Preparation and characterization of demethylated lignin-polyethylenimine adhesives," *J. Adhesion* 82(6), 593-605.

Lora, J. H., and Glasser, W. G. (2002). "Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials," *J. Polym. Environ.* 10(1-2), 39-48.

Mancera, C., El Mansouri, N.-E., Vilaseca Morera, F., Ferrando, F., and Salvado, J. (2011). "The effect of lignin as a natural adhesive on the physico-mechanical properties of *Vitis vinifera* fiberboards," *BioResources* 6(3), 2851-2860.

Pfister, D. P., and Larock, R. C. (2013). "Green composites using switchgrass as a reinforcement for a conjugated linseed oil-based resin," *J. Appl. Polym. Sci.* 127(3), 1921-1928.

Privas, E., and Navard, P. (2013). "Preparation, processing and properties of lignosulfonate–flax composite boards," *Carbohydr. Polym.* 93(1), 300-306.

Sahoo, S., Misra, M., and Mohanty, A. K. (2013). "Effect of compatibilizer and fillers on the properties of injection molded lignin-based hybrid green composites," *J. Appl. Polym. Sci.* 127(5), 4110-4121.

Schneider, M. H., and Phillips, J. G. (2004). "Furfuryl alcohol and lignin adhesive composition," *United States Patent* 6747076.

Segal, L., Creely, J., Martin, A., and Conrad, C. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794.

Sun, Q. (2009). "Research on preparation of non-formaldehyde adhesive by modified brown-rotted wood," M.S. Thesis, Chinese Academy of Forestry, Beijing, China.

Velásquez, J. A., Ferrando, F., and Salvadó, J. (2003). "Effects of kraft lignin addition in the production of binderless fiberboard from steam exploded *Miscanthus sinensis*," *Ind. Crops Prod.* 18(1), 17-23.

Vishtal, A. G., and Kraslawski, A. (2011). "Challenges in industrial applications of technical lignins," *BioResources* 6(3), 3547-3568.

Widyorini, R., Xu, J., Umemura, K., and Kawai, S. (2005). "Manufacture and properties of binderless particleboard from bagasse I: Effects of raw material type, storage methods, and manufacturing process," *J. Wood Sci.* 51(6), 648-654.

Article submitted: August 5, 2013; Peer review completed: September 9, 2013; Revised version received: November 30, 2013; Second revised version received and accepted: December 6, 2013; Published: December 18, 2013.