

A Novel Formaldehyde-Free Wood Adhesive Synthesized by Straw Soda Lignin and Polyethyleneimine

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To eliminate toxic formaldehyde from wood-based panels, a new formaldehyde-free wood adhesive (named OL/PEI adhesive) was synthesized by a reaction of oxidized lignin (OL) and polyethylenimine (PEI) reaction in the presence of sodium periodate. The curing mechanism of the OL/PEI adhesive was clarified by Fourier transform infrared spectroscopy (FTIR) and solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS¹³C-NMR) spectroscopy. The results showed that the sodium periodate could selectively oxidize wheat straw lignin to produce the ortho-quinone, and then the ortho-quinone in OL could further react with amino groups in PEI to form the OL/PEI adhesive. The as-prepared poplar particleboard was investigated with regard to hot-pressing temperature, the hot-pressing time, the OL/PEI weight ratio, and the dosage of OL/PEI adhesive. Under the optimum conditions, *e.g.*, hot pressing temperature of 180 °C, hot pressing time of 13 min, the OL/PEI weight ratio of 1:1, and the dosage of 10%, OL/PEI adhesive was found to disperse evenly into the voids among the shavings of poplar particleboard, followed by the curing of OL/PEI adhesive using hot-pressing to form tightly bonds between the shavings. The resulting particleboard reached the requirement of mechanical properties (GB/T 4897.3-2003), higher water resistance properties, and better heating resistivity. This study demonstrated a new way to produce a formaldehyde-free wood adhesive with unique properties. This material could replace formaldehyde wood adhesive in wood bonding.

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Keywords: Wood adhesive; Sodium periodate; Polyethylenimine; Wheat straw lignin; Ortho-quinone

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INTRODUCTION

Wood-based panels are used in furniture, construction industries, *etc.* Wood-based panels are composite products containing wood materials (*e.g.*, fibers, flakes, particles, chips, wood powder, veneers, *etc.*) and adhesives (Hemmilä *et al.* 2017). Wood adhesive is an essential non-wood component in the industrial production of wood-based panels (Faris *et al.* 2016). At present, synthetic adhesives based on formaldehyde, such as urea–formaldehyde (UF), phenol–formaldehyde (PF), and melamine–formaldehyde resins (MF), are the most often used wood adhesives due to their excellent adhesion property and low cost (Mercer and Pizzi 1996; Dunky 1998; Hemmilä *et al.* 2017). However, the formaldehyde gases released during the production of panels are harmful for the environment and human health (Amini *et al.* 2013; Salleh *et al.* 2015). Thus, there are

emerging methods related to green and sustainable processes to replace synthetic wood-based panels, such as bio-based wood adhesives (Ando and Umemura 2020). Lignin is the second most abundant terrestrial natural resource after cellulose, and it is the most abundant aromatic polymer in nature (Boerjan *et al.* 2003; Qu *et al.* 2015). Most often, industrial lignins are obtained as byproducts from the pulping mills, *e.g.*, lignosulfonate, kraft lignin, and soda lignin. In particular, lignin can be isolated from the spent pulping liquor (black liquor) (Chen *et al.* 2009). Traditionally, the resulting industrial lignins were either burned for energy use or discarded. These disposal methods waste biomass resources and lead to environmental pollution. Recently, inspired by the plant cell wall structure, it has been found that lignin can act as an adhesive, which matches its role in holding plant fibers together (Ghaffar and Fan 2014). However, the industrial lignins differ in structure and properties compared to the natural lignin, resulting from the modification during pulping process. Industrial lignin typically has already lost some of its potential effectiveness as an adhesive due to relatively lower reactivity (Ang *et al.* 2019). Studies also showed that the use of industrial lignin individually as a wood adhesive was restricted in a sense (Velásquez *et al.* 2003; Vishtal and Kraslawski 2011). Therefore, several modification methods of industrial lignins have been developed to improve its reactivity for consideration of potential wood adhesive, for instance, demethylation, hydroxymethylation, phenolation, oxidation, and so forth (Chen *et al.* 2021). Among them, hydroxymethylation typically has been used for preparing adhesive *via* cross-linking reactions of industrial lignin in the presence of cross linker, *e.g.*, formaldehyde, such that the hydroxymethyl group is introduced into the lignin molecular (Malutan *et al.* 2008). Moreover, the hydroxymethylated lignins have been replaced the part of the phenol or urea monomers for preparing the lignin-containing PF (Wang and Chen 2014) and UF (Gao *et al.* 2020) resins, providing a lower formaldehyde emission of wood-based panels compared to the universal PF and UF resins reported by the published studies. Yet, formaldehyde as a main reactant was still used in such systems. Thus, formaldehyde-free wood adhesives based on lignin generally are not yet available on the market.

Marine mussel adhesive protein (MAP) with two functional groups, *e.g.*, amino and catechol groups, is an excellent example of a formaldehyde-free adhesive that is formed from renewable resources. In the course of the curing reaction of MAP (Waite 1990), the catechol group can be converted into an ortho-quinone by the various oxidation reactions, following that ortho-quinone was further reacted with amino groups to form a water-insoluble and three-dimensional MAP network. Li *et al.* (2004) successfully prepared the condensed tannin/PEI adhesives with very high shear strength and water-resistance properties. In addition, the demethylated industrial lignin (DKL)/PEI adhesives were also synthesized according to the MAP curing mechanism, where the catechol groups of lignin molecular were formed by the demethylation of lignin (Liu and Li 2006). However, the transformation of catechol groups to ortho-quinone in lignin molecular structure is uncertain because it is affected by many other factors. The formation mechanism of the ortho-quinones through directly selective oxidation of the free phenolic hydroxyl groups of both guaiacyl (G) and syringyl (S) building block in lignin structure has been reported (Adler and Hernestam 1955; Chang *et al.* 1975). Recently, industrial lignin was oxidized using sodium periodate, enabling the formation of the ortho-quinones group of lignin (Gosselink *et al.* 2011; Kozhevnikov *et al.* 2017; Zhang and Fatehi 2019; Chen *et al.* 2021). Moreover, the use of either industrial lignin individually or in combination with furfuryl alcohol under periodate oxidation to produce formaldehyde-free adhesives has been investigated (Gosselink *et al.* 2011; Chen *et al.* 2021). In contrast, the preparation of lignin-

based formaldehyde-free adhesives using periodate oxidized industrial lignin bonding with PEI, has been elusive.

In the present study, a novel and greener approach for valorization of industrial lignin was developed to produce the formaldehyde-free wood adhesives obtained with use of oxidized lignin (OL) and poly(ethyleneimine) (PEI), using periodate oxidation. The phenolic hydroxyl groups of wheat straw lignin were directly selectively oxidized to ortho-quinones groups using sodium periodate. The OL/PEI formaldehyde-free wood adhesive was then readily prepared according to above-mentioned MAP curing mechanism, which was applied in poplar particleboard. Both optimum conditions and curing mechanism of OL/PEI adhesive were well investigated. The mechanical properties, water wettability, heating activity, and surface properties of the obtained poplar particleboard were assessed. Briefly stated, the resultant OL/PEI wood adhesive exhibited higher mechanical properties and waterproof qualities in poplar particleboard compared to that without adhesive, enabling the requirement of formaldehyde-free wood bonding.

EXPERIMENTAL

Materials

Wheat straw soda lignin was kindly provided by Shandong New Tranlin Holdings Company Ltd., China. Poplar shavings were purchased from Dongying Sanlai Wood Industry Company Ltd., China. Sodium periodate and polyethylenimine (PEI) (Mw: 1800 g/mole) was purchased from Shanghai Aladdin Bio-Chem Technology Company Ltd., China. Sodium hydroxide and hydrochloric acid were purchased from Sinopharm Chemical Reagent Company Ltd., China. All chemicals and reagents were used without further purification.

Pretreatment of Wheat Straw Soda Lignin

To remove the sugar and ash in the lignin, the lignin was washed with distilled water several times. Wheat straw soda lignin (500 g dry content) was added into 5 L of distilled water, and the pH was adjusted to 2 using 10% (v/v) aqueous HCl. The lignin slurries were vigorously stirred using magnetic stirring for 1 h and then incubated at room temperature for one day. The lignin sediments were collected by utilizing vacuum filtration to remove the supernatant, followed by washing with distilled water once more. The obtained lignin sediments were air dried and stored at 4 °C. Its composition was as follows: 84.5% total lignin, 5.6% ash, and 4.8% carbohydrates.

Oxidation of Wheat Straw Soda Lignin and Preparation of OL/PEI Adhesive

The wheat straw soda lignin of 30 g dry content was added into the beaker with 300 mL distilled water. Next it was dissolved completely by adding 5% sodium hydroxide (based on the dry content of lignin). After that, the pH value of raw lignin solution was adjusted to 5 using aqueous solution of HCl of 10% (v/v) prior to place in a water bath at the constant temperature of 25 °C for 30 min, where the beaker filled by lignin solution was fully wrapped with aluminum foil to avoid the interfering of light oxidation. The sodium periodate (0.5:1 mass ratio of sodium periodate to lignin, 33 wt% based on the lignin content) was then added into the lignin solution, and then it was mixed using magnetic stirring for 1 h. At the end of the reaction, the pH value of the mixture was adjusted to 2.5 using 10% (v/v) aqueous solution of HCl prior to centrifugation. The

oxidized lignin (OL) was obtained by centrifugation for washing using distilled water several times and then was further dried with vacuum drying desiccator at room temperature. Subsequently, the dried OL was dissolved with 0.1M sodium hydroxide solution prior to the PEI addition according to OL/PEI weight ratio. The resulting solution was stirred for 1 h to produce the OL/PEI adhesive with solid content of 13 wt%.

Preparation of Poplar Particleboard

The poplar shavings were mixed with the OL/PEI adhesive at different proportions. The mixture was formed into a homogeneous mat of dimensions of 220 mm × 200 mm by in a forming box prior to hot-pressing (BY302X2/15, Xinxili Group Co., Ltd., Suzhou, China). The mixing mats were optimized during hot-pressing process in the temperature range of 130 to 190 °C, the range of time from 4 to 16 min, and at constant pressure of 5 MPa. The thickness of poplar particleboards was controlled by distance bars of 6 mm that were placed between the top and bottom of hot platens during hot pressing. The targeted density of particleboards was 0.7 g/cm³.

Fourier Transform Infrared (FTIR)

The dried sample (1 mg) was milled with 200 mg of potassium bromide prior to analysis, which was squashed by a Nicolet 380 FTIR spectrophotometer equipped with a DTGS detector (ThermoFisher Scientific Inc., Waltham, MA, USA). Each sample was scanned 32 times over a region of 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹. Background spectra was collected before each measurement.

Structure Characterization by ¹³C Nuclear Magnetic Resonance (¹³C-NMR)

¹³C-NMR spectra of samples were performed by using an AVANCE III HD 600 MHz NMR spectrometer (AVANCE III HD 600 MHz, Bruker, Karlsruhe, Germany) at the given test condition as follow: temperature at 300 K, sample rotation speed of 5000 Hz, observation frequency of 100 MHz, scanning width of 30 KHz, relaxation delay of 2 s, and scanning times of 3600 s. Before testing, the dried samples were ground to powders.

Mechanical Properties

The modulus of rupture (MOR), the modulus of elasticity (MOE), the internal bonding strength (IB), and the thickness swelling (TS) of wood-based panels were tested according to the China national standard GB/T 17657 (2013).

Contact Angle Measurement

The water contact angle (WCA) of wood-based panels was determined by using a JC-2000D contact angle measuring instrument (JC-2000D, Shanghai Zhongchen, China). Each sample was measured three times as parallel measurements. Five measurements of each wood-based panel at different positions were performed for calculating the final average of WCA.

Thermogravimetric Analysis

The thermal stability of wood-based panels was analyzed using a TG/DTA 6300 thermogravimeter (TG/DTA 6300, PerkinElmer, USA). Samples of 5 mg were placed on the alumina pan prior to heating. The temperature was increased from room temperature to 600 °C at an increasing rate of 20 °C·min⁻¹ under nitrogen gas.

Scanning Electron Microscopy (SEM)

SEM analysis was conducted by using a SU-8010 scanning electron microscope (SU-8010, Hitachi, Tokyo, Japan) to investigate the morphological changes of the cross-sections of the particleboard specimens. Before the cross-section analysis, the particleboard specimens were mounted on cylindrical aluminum stubs with a double-side tape, the surface of samples was then coated with a thin layer of gold by sputter coater.

RESULTS AND DISCUSSION

FT-IR Analysis

The spectra of unoxidized lignin (UL), OL, and OL/PEI adhesive was shown in Fig. 1, and its band assignments are given in Table 1 (Gosselink *et al.* 2011; Li and McDonald 2014).

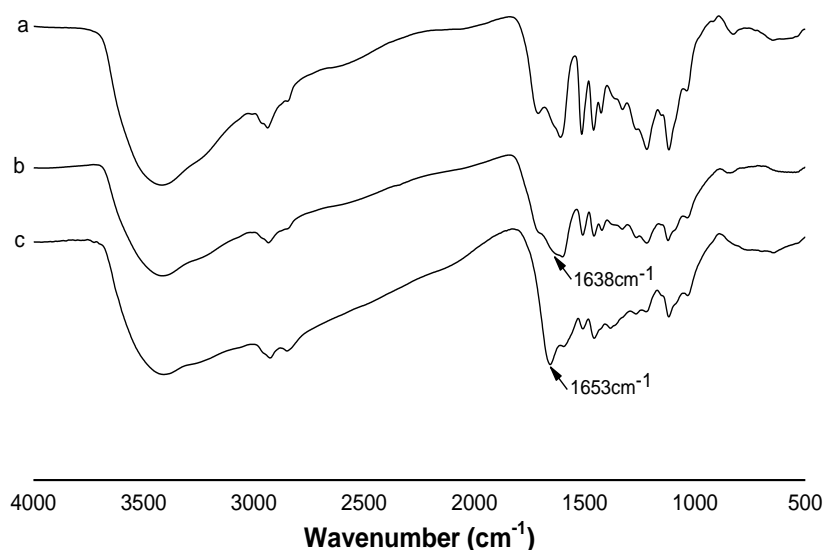


Fig. 1. FTIR spectra of UL (a), OL (b), and OL/PEI adhesive (c)

The characteristic peaks of UL were observed at 3413 cm^{-1} (O-H stretching), 2991 cm^{-1} (C-H asymmetrical stretching), 2839 cm^{-1} (C-H symmetrical stretching), 1709 cm^{-1} (C=O stretching), 1598 cm^{-1} , 1511 cm^{-1} , and 1421 cm^{-1} (aromatic skeletal vibrations), 1328 cm^{-1} (C-O of syringyl ring), 1265 cm^{-1} (C-O of guaiacyl ring), and 1151 cm^{-1} (typical for HGS lignin). Compared to the FTIR spectra of UL, OL exhibited an obvious shoulder peak at 1638 cm^{-1} , which was assigned to the characteristic peak of the C=O groups from ortho-quinone structure of lignin (Gosselink *et al.* 2011). It was indicated that the ortho-quinone was successfully introduced into the molecular structure of lignin by selective oxidation of the methoxy group of both G and S building block of lignin. It can also be seen that the intensity of absorption peak of OL from aromatic skeletal vibrations at 1510 cm^{-1} was decreased. It was speculated that the aromatic ring of lignin was transformed into the ortho-quinones, resulting in the reduction of the aromatic ring contents of lignin. In addition, the absorption peak at 1709 cm^{-1} of OL was not significantly enhanced, which was assigned to the absorption of carboxyl groups. This indication suggested that the ortho-quinones of OL were not further oxidized to muconic acid. However, the spectrum of OL/PEI adhesive

showed that the shoulder peak of ortho-quinone in OL at 1638 cm^{-1} had disappeared. In contrast, a new absorbance peak at 1653 cm^{-1} had appeared, which was assigned to N-H stretching from amide groups of PEI (McDougall *et al.* 1996). Thus, the amino groups of PEI were successfully bonded with the ortho-quinone groups of OL, resulting from the decrease of content of the ortho-quinone in OL, as supported by FTIR spectra analysis.

Table 1. Assignment of FTIR spectra of UL, OL and OL/PEI Adhesive

Wavenumber (cm^{-1})			Assignment
UL	OL	OL/PEI Adhesive	
3413	3418	3421	OH stretching
2991	2993	2991	CH asymmetric stretching
2839	2840	2840	CH symmetric stretching
1709	1712	—	C=O Stretch of unconjugated carbonyls
—	—	1653	N-H Stretch in amide
—	1638	—	C=O Stretch of ortho-quinone
1598	1596	1598	C=C Aromatic skeletal vibration
1511	1510	1511	C=C Aromatic skeletal vibration
1458	1458	1457	Asymmetric bending deformation of methyl and methylene groups
1421	1420	1418	Aromatic skeletal vibrations combined with C-H in-plane deformation
1375	1374	1375	Symmetric bending deformation of methyl group
1331	1331	1330	C-O of syringyl ring
1265	1265	1266	C-O of guaiacyl ring
1210	1209	1209	C-C plus C-O stretch
1153	1155	1153	Typical for HGS lignin, conjugated C-O in ester groups
1118	1118	1116	C-O deformation in ester bond
1033	1033	1031	Aromatic C-H in-plane deformation (G>S) plus C-O deformation in primary alcohols

CP/MAS ^{13}C -NMR Analysis

To investigate the curing mechanism of OL/PEI adhesive, the CP/MAS ^{13}C -NMR spectra of UL, OL and OL/PEI adhesive are shown in Fig. 2. The signals were assigned as listed in Table 2, based on previous studies (Lüdemann and Nimz 1973; Krohn *et al.* 1989; Ahonen *et al.* 2010; He *et al.* 2012). According to the comparison of the spectra of UL and OL, the intensity of signals No. 8 at 56 ppm was extremely decreased, which was attributed to a great decrease in methoxy groups of lignin. On the contrary, the signal No. 1 at 176.2 ppm was increased to some extent, which was assigned to the C=O of both carboxyl groups and ortho-quinone of OL. The likely main reason was that the ortho-quinone groups were generated by selective oxidation of the methoxy groups of UL under sodium periodate, resulting in the decrease of the content of methoxy groups in OL (as shown in CP/MAS ^{13}C NMR spectra). The results have been reported with a condensed tannins/PEI adhesive (Liu and Li 2006).

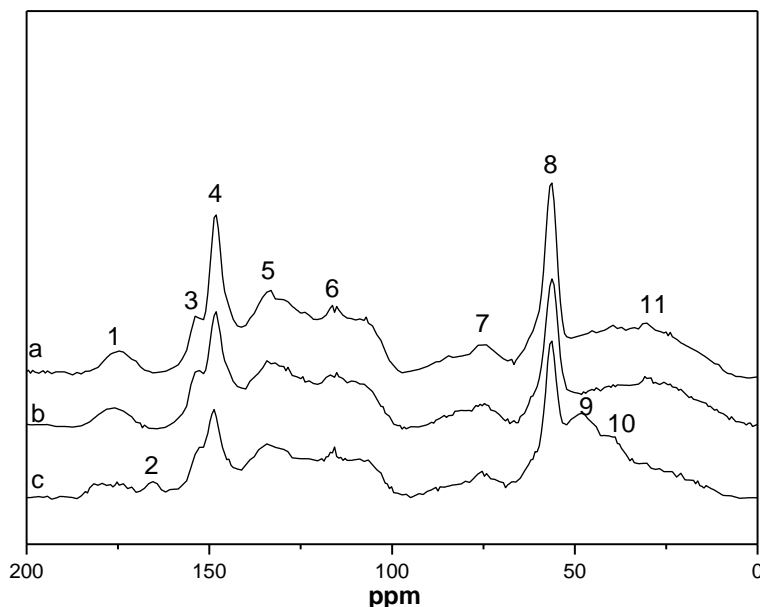


Fig. 2. CP/MAS ^{13}C -NMR spectra of UL(a), OL (b), and OL/PEI adhesive (c)

Table 2. Chemical Shifts and Assignments of Major Peaks in the CP/MAS ^{13}C NMR Spectra of UL, OL, and OL/PEI Adhesive

Peak No.	Chemical Shifts (δ , ppm)			Assignments
	UL	OL	OL/PEI adhesive	
1	174.9	176.2	—	-COO- in aliphatic esters and acetyl group, C=O of ortho-quinone
2	—	—	165.6	C in amide
3	153.9	153.2	152.4	C-3/C-4 in S etherified
4	148.3	148.2	148.8	C-3/C-4 in S, C-3/C-4 in G
5	133.4	133.8	133.9	C-1 in G, S and H
6	116.3	115.4	115.7	C-3/C-5 in H, C-6 in G
7	75.3	74.8	75.6	C- α in β -O-4
8	56.4	56.3	56.5	-OCH ₃
9	—	—	48.1	C in amino groups of PEI
10	—	—	40.9	C in amino groups of PEI
11	30.7	30.8	30.3	-CH ₃ and CH ₂ in saturated aliphatic chain

The above results displayed the generation pathway of the ortho-quinones, as shown in Fig. 3. Moreover, the differences from the spectra analysis of both UL and OL were subtle, excepting the two points above-mentioned. Sodium periodate had a high selectivity for the oxidation of lignin, and it would not lead to the opening of the aromatic ring of lignin structure under the appropriate reaction condition, which was very important for the application of oxidized lignin. In Fig. 2(b and c), the intensity of absorbance peak of OL at 176.2 ppm was greatly reduced when OL was mixed with PEI. Meanwhile, three new signals appeared in the spectra of OL/PEI adhesive as follows: 1) the signal of No. 2 at 165.6 ppm was ascribed to the carbon of amide from OL/PEI adhesive. 2) both the signal of No. 9 at 48.1 ppm and 3) signal of No. 10 at 40.1 ppm were assigned to the carbon of amino groups from PEI. The CP/MAS ^{13}C -NMR spectra of samples also further confirmed

the conjugation of between OL and PEI to some extent. In combination FTIR results with ^{13}C -NMR spectra, it can be concluded that the ortho-quinone from OL caused by selective oxidation by using sodium periodate was further reacted with amino groups from PEI to readily form the OL/PEI adhesive.

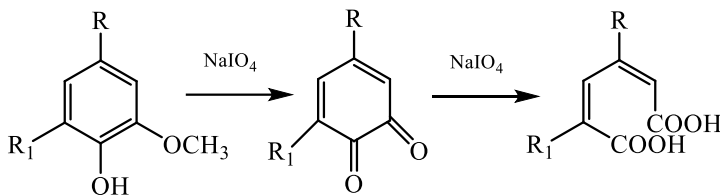


Fig. 3. Generation pathway of ortho-quinones and mucofuroic acid

Physico-mechanical Properties of Particleboard Bonded with OL/PEI Adhesive

Effects of hot-pressing temperature

In the hot-pressing process of poplar particleboard, hot pressing temperature had important influence on the MOR, MOE, IB, and TS values of the particleboard, as shown in Fig. 4, 5, and 6. The hot pressing conditions were as follows: hot-pressing time, 10 min; OL/PEI weight ratio, 2:1; OL/PEI adhesive dosage, 10%. The MOR, MOE, and IB values increased with the increasing of hot-pressing temperature from 130 to 180 °C, while the TS values decreased.

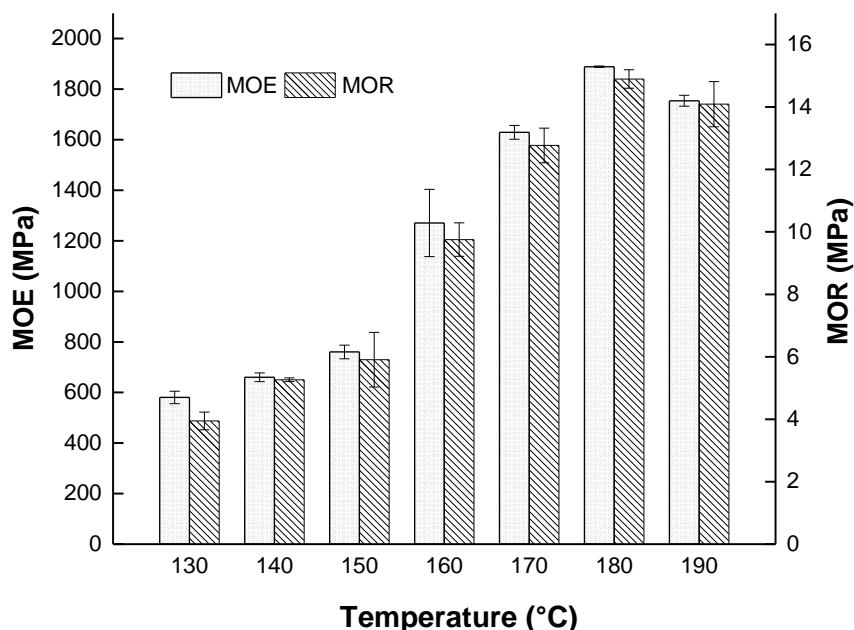


Fig. 4. Effects of hot pressing temperature on the MOR and MOE of the particleboard

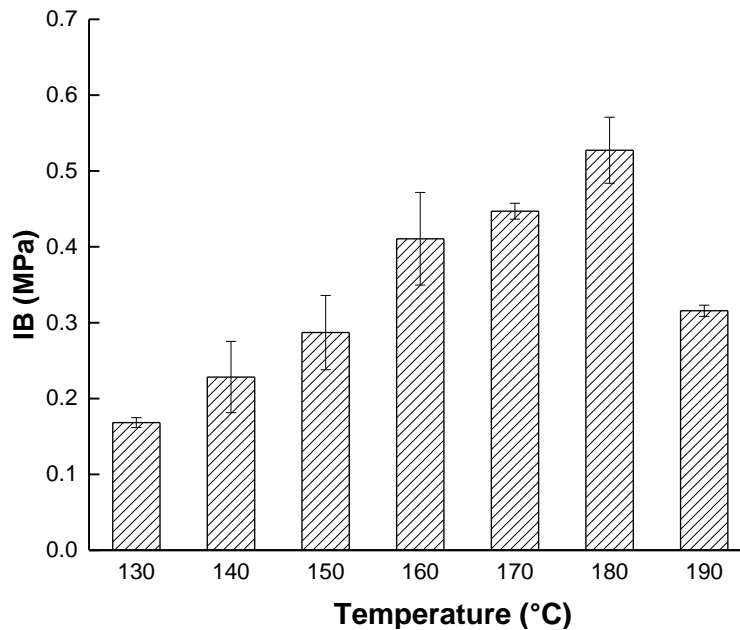


Fig. 5. Effects of hot pressing temperature on the IB of the particleboard

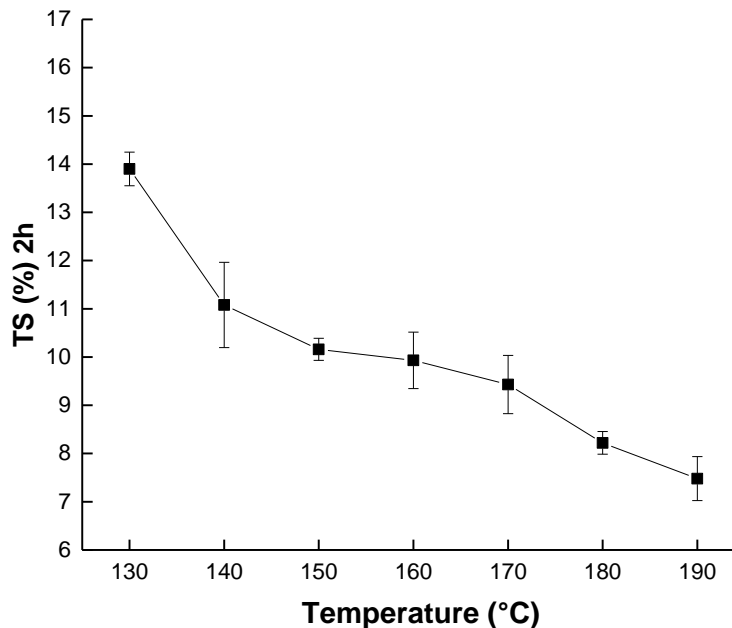


Fig. 6. Effects of hot pressing temperature on the TS of the particleboard

The mechanical strength of particleboard was enhanced with the increasing of hot-pressing temperature. It was speculated that the increase of hot-pressing temperature improved the bonding strength of the adhesive during curing process. However, the MOR, MOE, IB, and TS values were significantly decreased from 14.9 MPa, 1888.9 MPa, and 0.527 MPa to 14.09 MPa, 1753.9 MPa and 0.315 MPa, respectively, when the temperature was over 180 °C. On the one hand, the faster evaporation associated with higher temperature gave rise to rapid release of water vapor and heating in the panel compared to

the temperature of 180 °C. The internal pressure within the board was greatly increased, resulting in the formation of a large number of cracks and voids in the particleboards and the reduction of mechanical strength accordingly. It was also noted that the hot pressing temperature reached 190 °C, which might have led to degradation of the active ingredients of the adhesive. Thus, the high temperature of 190 °C would cause the weakness of bonding strength of the adhesive between particleboards, suggesting that 180 °C was the optimal hot pressing temperature for curing OL/PEI adhesive.

Effects of hot-pressing time

Figures 7, 8, and 9 show the effects of hot-pressing time on the MOR, MOE, IB, and TS of the particleboard. The hot pressing conditions were as follows: hot-pressing temperature, 180 °C; OL/PEI weight ratio, 2:1; and OL/PEI adhesive dosage, 10%. The trend of MOR, MOE, IB, and TS of the particleboard against the hot-pressing time was similar to that of hot-pressing temperature. The hot-pressing time at 13 min resulted in excellent mechanical strength of particleboards, while the MOR, MOE, and TS did not significantly change any more from the increase of 13 min to 16 min, excepting the marked decrease of IB. This was attributed to the hot-pressing time affecting the curing degree of the OL/PEI adhesive. The shorter the hot-pressing time was, the poorer bonding strength of adhesive was. However, the excess of curing time of adhesive, such as 16 min, would be a reason to explain degradation of the adhesive and shavings; thus the performance of particleboard in mechanical strength was reduced (Yuan *et al.* 2014). Therefore, the hot pressing time of 13 min was appropriate for the particleboard properties.

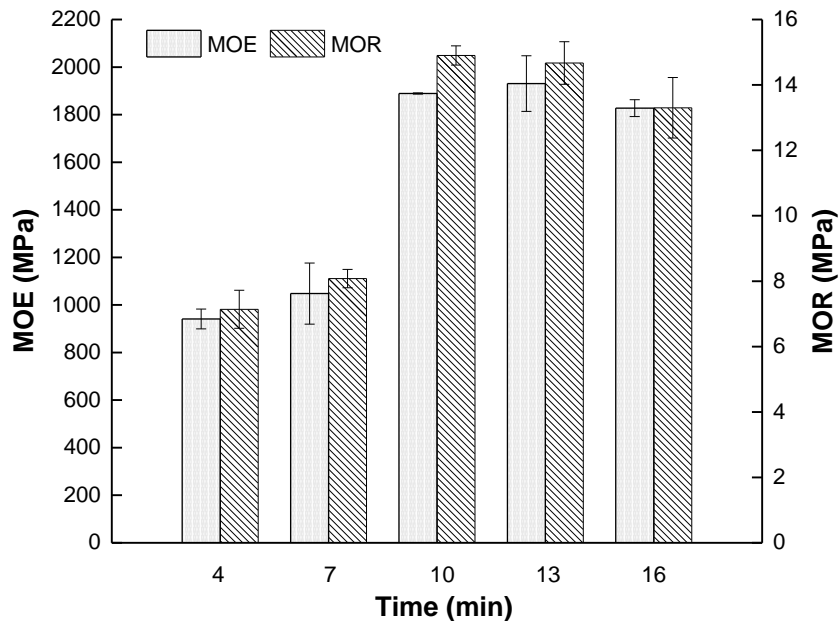


Fig. 7. Effects of hot-pressing time on the MOR and MOE of the particleboard

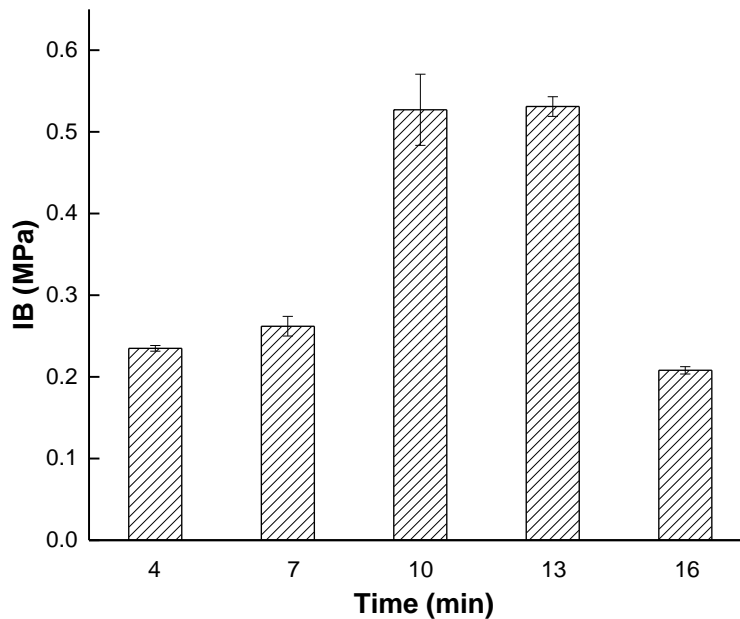


Fig. 8. Effects of hot-pressing time on the IB of the particleboard

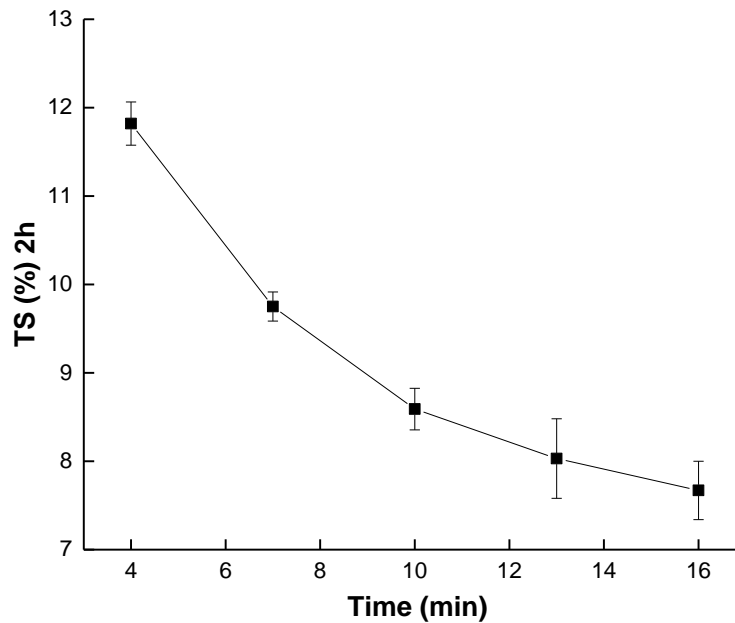


Fig. 9. Effects of hot-pressing time re on the TS of the particleboard

Effect of OL/PEI weight ratio

Figures 10, 11, and 12 shows mechanical strength of the OL/PEI with different weight ratio on MOR, MO, IB, and TS value compared to either OL or PEI alone. The hot pressing conditions were as follows: hot-pressing temperature, 180 °C; hot-pressing time, 13 min; and OL/PEI adhesive dosage, 10%. The MOR value of particleboards progressively increased to reach a maximum value of 17.0 MPa. When the weight ratio of

OL/PEI was transformed from 1:4 to 1:1, the MOE value exhibited slight changes. In contrast, both MOR and MOE values were remarkably decreased as the further increase of lignin content in OL/PEI (Fig. 11).

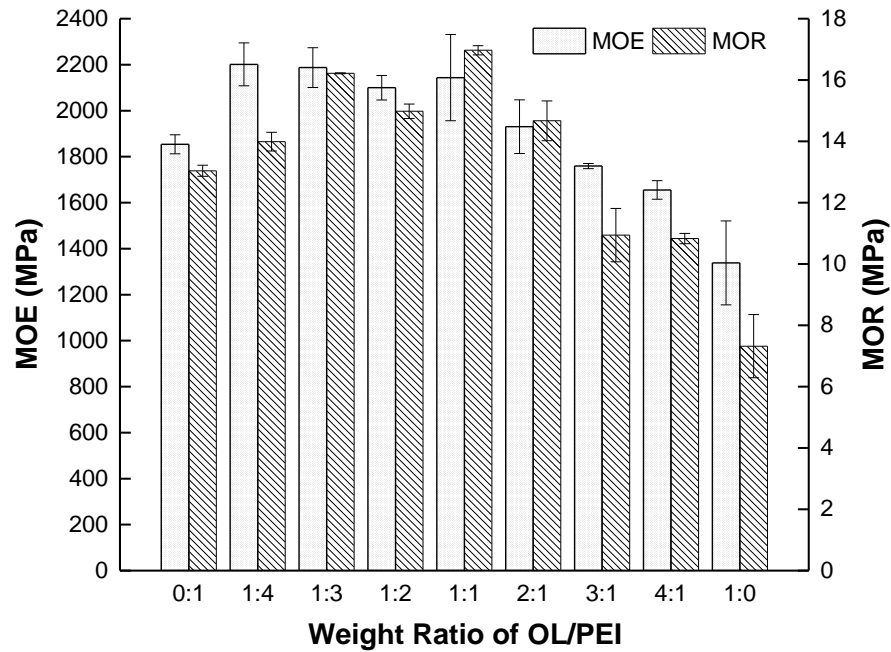


Fig. 10. Effects of OL/PEI weight ratio on the MOR and MOE of the particleboard

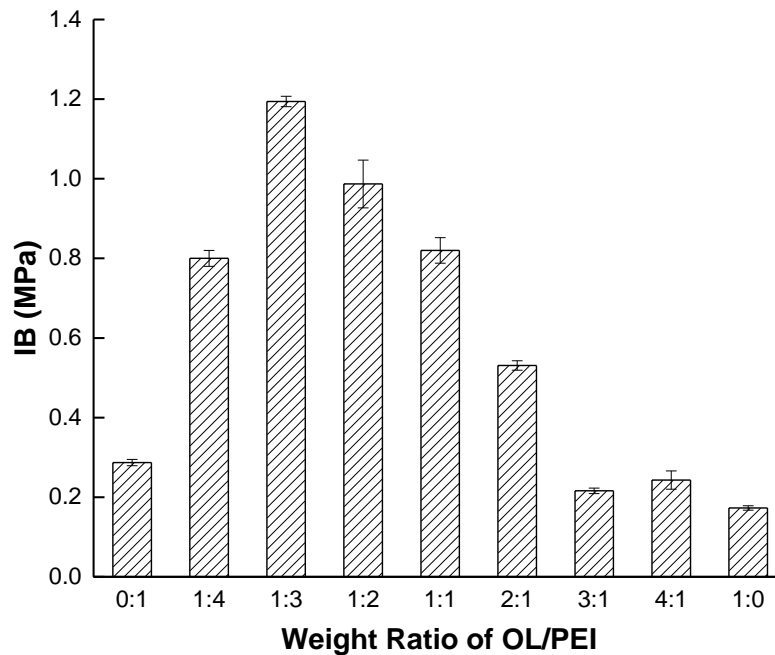


Fig. 11. Effects of OL/PEI weight ratio on the IB of the particleboard

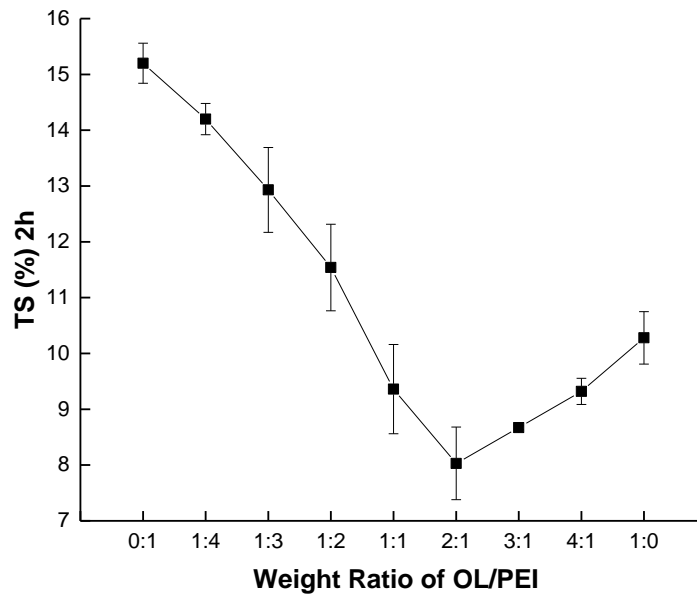


Fig. 12. Effects of OL/PEI weight ratio re on the TS of the particleboard

The IB value was able to reach the maximum value of 1.194 MPa at the OL/PEI weight ratio of 1:3, after which it markedly decreased (Fig. 12). However, the TS value was remarkably decreased up to the minimum value of 8.03% at the OL/PEI weight ratio of 1:2, after which it slowly increased. Figures 10, 11, and 12 also show that the particleboard bonded with the net OL, *i.e.*, the OL/PEI weight ratio of 1:0, exhibited lower mechanical strength compared to OL/PEI in the presence of PEI, as well as poor water resistance. In contrast, the IB of resulting particleboard was still low when the particleboard bonded with PEI, *i.e.*, the OL/PEI weight ratio=0:1. This was an indication that OL/PEI adhesive was able to create tight cross-linking between the shavings to improve the mechanical strength of the particleboards under the controlled condition, *e.g.*, the optimal hot-pressing temperature, pressure, time as well as weight ratio, owing to the formation of three-dimensional network polymer associated with physico-chemical reaction. Considering the mechanical strength and water resistance of the particleboard, the OL/PEI weight ratio was 1:1.

Effects of the OL/PEI adhesive dosage

As shown in Figs.13 and 14, the MOR, MOE, and IB values at the dosage of 10% for OL/PEI adhesive reached the maximum values of 17.0 MPa, 2140 MPa, and 0.82 MPa, respectively. The MOR and MOE value was not significantly changed at the dosage of 20% for OL/PEI adhesive; however, the IB value was decreased obviously. The TS value was decreased with the increasing of the dosage of OL/PEI adhesive, and the minimum value was 8.32% when the OL/PEI adhesive dosage was 20%, as shown in Fig. 15. In addition, the particleboard bonded without adhesive had very low strength and poor water resistance. However, the strength and water resistance of the particleboard were greatly improved after the addition of a small amount of adhesive, *e.g.*, the OL/PEI adhesive dosage of 5%. Thus, the OL/PEI adhesive had a very good bonding property, and the optimal OL/PEI adhesive dosage was 10%. The hot pressing conditions were as follows: hot-pressing temperature, 180 °C; hot-pressing time, 13 min; and OL/PEI weight ratio, 1:1.

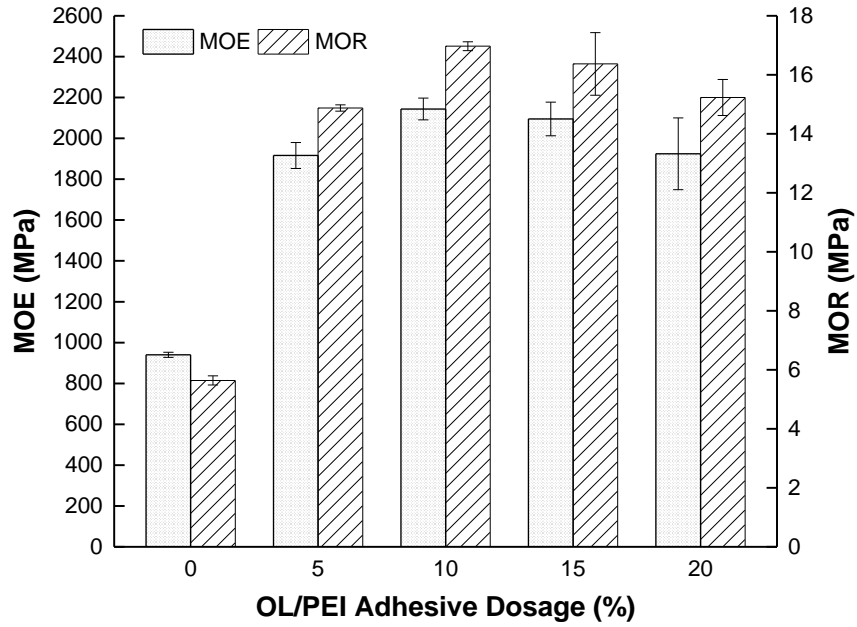


Fig. 13. Effects of OL/PEI adhesive dosage on the MOR and MOE of the particleboard

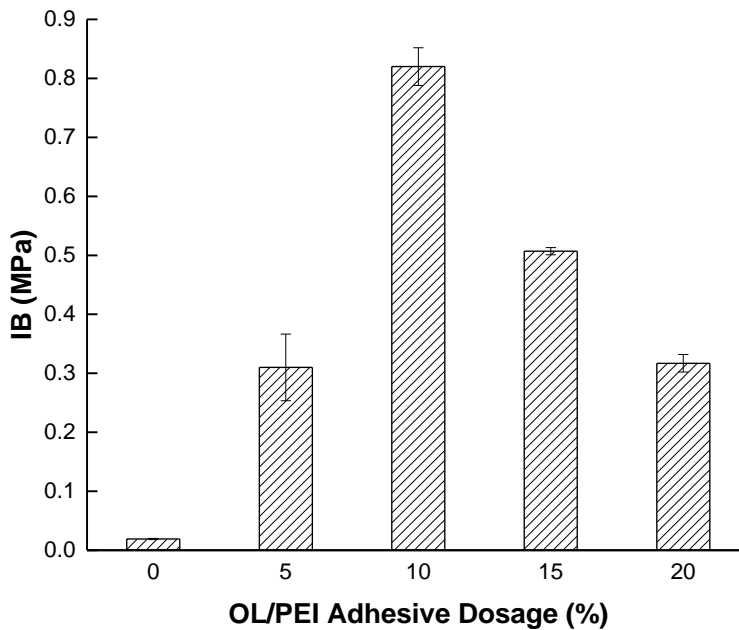


Fig. 14. Effects of OL/PEI adhesive dosage on the IB of the particleboard

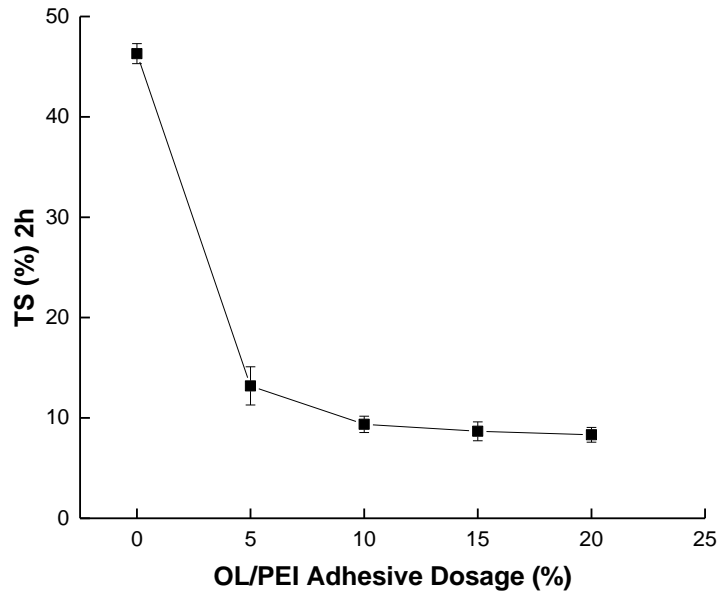


Fig. 15. Effects of OL/PEI adhesive dosage re on the TS of the particleboard

Contact Angle Analysis

Figure 16 shows that the initial contact angle of the particleboard bonded without adhesive was 78.1° , which was lower than that of the particleboard bonded with the OL/PEI adhesive (the initial contact angle of 92.5° at the OL/PEI adhesive dosage of 10%). Figure 17 shows that the contact angle curve of the particleboard was changed with the contact time between water and particleboards. It can be seen from Fig. 17 that the contact angle of the net particleboard was rapidly decreased to 0° within 10 seconds of contact time. However, the contact angle of the particleboard bonded with the OL/PEI adhesive decreased slowly with the increase of the contact time. The contact angle remained as 75.1° at 80 seconds. These results showed the shavings had strong water absorption, resulting in poor water resistance of the board. The OL/PEI adhesive could reduce the water absorption of particleboard and limit the expansion of the board, thus greatly improving the water resistance of the board. This was consistent with the results for TS value in regards of mechanical strength.

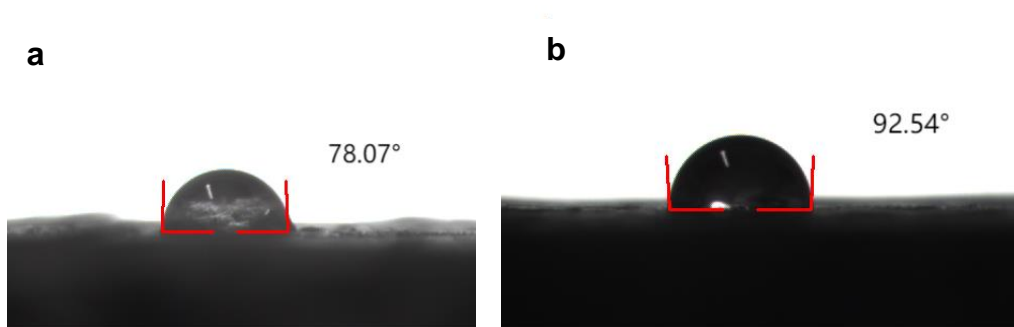


Fig. 16. Contact angle of water droplet on surface of particleboards bonded without (a) and with OL/PEI adhesive (b)

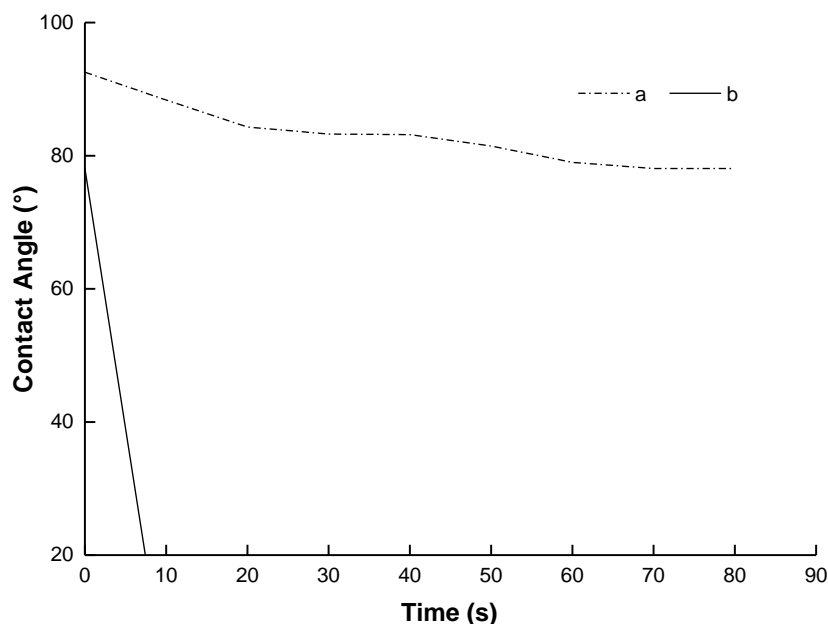


Fig. 17. Dynamic contact angle of water droplet on surface of particleboards bonded without (a) and with OL/PEI adhesive (b)

Thermogravimetric Analysis

The thermogravimetric (TG) curves of the particleboard in the absence and presence of OL/PEI adhesive are presented in Fig. 18, along with the relative derivative thermogravimetric (DTG) curves. It can be seen that the particleboard without adhesive exhibited a similar tendency of TG curves with that of particleboards with adhesive. In the initial stage of temperature below 200 °C, the mass loss of both was slightly decreased, possibly due to water volatilization (Papadopoulou and Chrissafis 2011). However, the mass loss of the particleboard bonded without adhesive was lower than that of the particleboard with adhesive when the temperature was in the range of 200 to 400 °C. This suggests that the particleboard with adhesive displayed a heating resistivity. To give a closer insight for mass loss, the DTG curves revealed the rate of mass loss for particleboards with and without adhesive (Fig. 18). The maximum mass loss of particleboards without adhesive (345 °C) was higher than that with adhesive (322 °C), resulting from degradation of the hemicellulose and cellulose fraction of the shavings (Hidayat *et al.* 2014). It is also worth noting that a small wider peak of particleboard without adhesive at the temperature of 278 °C was observed due to the decomposition of hemicellulose (Feng *et al.* 2012), while the peak disappeared for particleboards with adhesive (Fig. 18). This suggests that the OL/PEI adhesive not only prevented the hemicellulose fractions from degradation but also involved lignin with the high thermal stability to some extent (Lai *et al.* 2018). Thus, the thermal stability of the particleboard with adhesive was improved correspondingly compared to UF adhesive (Gao *et al.* 2020). More important, it was reasonable that the final mass residue of the particleboard with adhesive (29.2%) was higher than that without adhesive bonding (19.1%), as shown in Fig. 18.

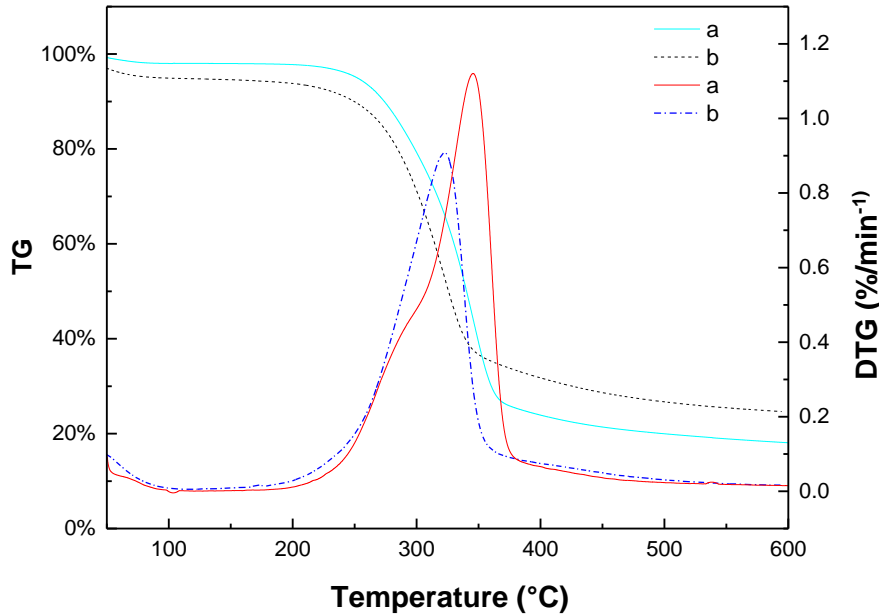


Fig. 18. TG and DTG curves of particleboards bonded without (a) and with OL/PEI adhesive (b)

SEM Analysis

The distribution and bonding of the OL/PEI adhesive in particleboard was investigated through the morphology for cross-section of the particleboard specimens with SEM analysis, as shown in Fig. 19. After hot-pressing, there were obvious voids among the shavings for the particleboard without adhesive (Fig. 19a), while a flatter cross-section was seen for the particleboards with OL/PEI adhesive (Fig. 19b). This was attributed to the ability of OL/PEI adhesive to be dispersed evenly into the voids of shaving after hot-pressing treatment, thus achieving higher mechanical strength and water resistance than the particleboards without adhesive. These findings were consistent with the results for mentioned physico-mechanical properties.

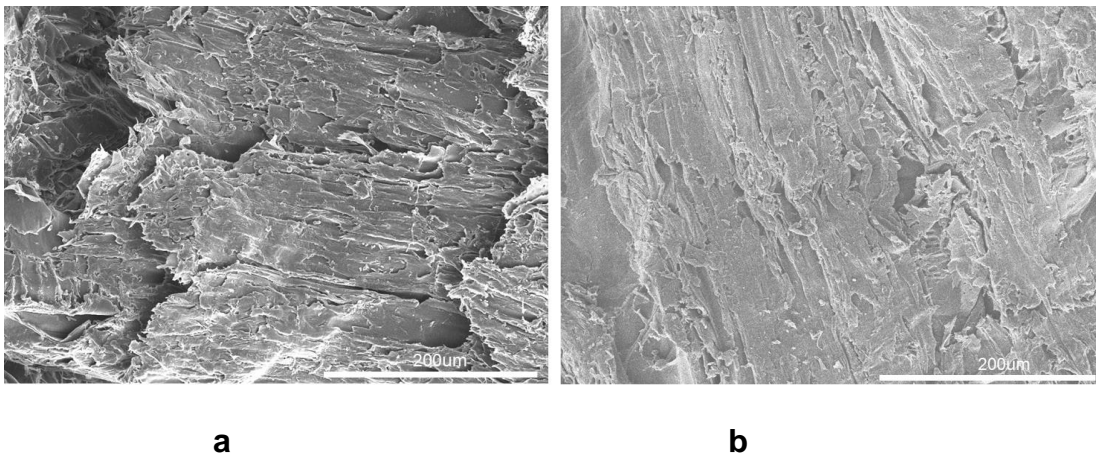


Fig. 19. SEM micrographs of cross-sections of particleboards bonded without (a) and with OL/PEI adhesive (b), with magnifications of 250 ×

CONCLUSIONS

1. The curing mechanism of oxidized lignin/poly(ethyleneimine) (OL/PEI) adhesive was that ortho-quinone groups were directly generated by selective oxidation the guaiacyl (G) and syringyl (S) building blocks of lignin under sodium periodate, which were able to further react with the amino groups of PEI molecular structure. In addition, the aromatic ring of lignin molecular structure was not involved in this reaction to ensure the unique properties from lignin, such as higher heating stability.
2. Poplar particleboards in the presence of OL/PEI adhesive were prepared using shavings and OL/PEI by hot-pressing assistance, providing a great mechanical strength and water resistance under the optimized hot-pressing condition, *i.e.*, hot pressing temperature of 180 °C, hot pressing time of 13 min, the OL/PEI weight ratio of 1:1, and the dosage of 10%. More important, the as-prepared OL/PEI adhesive was tightly bonded with the shavings to prevent the expansion of particleboards after hot-pressing and was also well dispersed into the voids of shavings by SEM analysis. The results for modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond (IB) met with the requirement of GB/T 4897.3-2003. Moreover, the thickness swelling (TS) value (9.36%) was basically consistent with the standard value (8%). In addition, the particleboard bonded with the OL/PEI adhesive had better heat resistivity due to the high thermal stability of lignin in the OL/PEI adhesive. In sum, the OL/PEI adhesive can be used as a promising wood bonding material, suggesting a greener and more sustainable way from the perspective of environmentally friendly effects and the health of human beings.

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