Effect of Adhesive Content and Modification Method on Physical and Mechanical Properties of Eucalyptus Veneer–Poly-β-Hydroxybutyrate Film Composites

Zhenghao Chen Cuicui Wang Yang Cao
Shuangbao Zhang Wei Song

Abstract

Formaldehyde-based resin and petroleum-based plastic are often used as an adhesive in plywood manufacturing, which has an adverse effect on people's health and the global environment. We have investigated the plywoodlike composite with wood veneer (WV) and poly-β-hydroxybutyrate film (PHBF) as a novel formaldehyde-free and environmentally friendly composite (WV-PHBF). The composite was prepared with three veneers, and the PHBF placed between adjacent veneers varied from 22.5 to 112.5 g/m^2. The composite was hot pressed at 170°C for 70 s/mm under a pressure of 1.0 MPa. Furthermore, the WV-PHBF with an adhesive dosage at 67.5 g/m^2 was modified with three modification methods: silane coupling agent (KH-550), alkaline solution (NaOH), and polydiphenylmethane diisocyanate (p-MDI). Results showed the following: (1) under the untreated condition, a composite with more than 67.5 g/m^2 adhesive will meet the Chinese National Standard (GB/T) 9846-2015 of bonding and bending strength requirements, and 90.0 g/m^2 was the best; (2) the KH-550 and p-MDI treatment had a positive effect on WV-PHBF, but NaOH mainly had an adverse effect; (3) the physical–mechanical properties of the composite with 67.5 g/m^2 adhesive content being processed by 1 percent by weight (wt%) KH-550 or 2 wt% p-MDI was better than WV-PHBF with 90 g/m^2 adhesive content, especially in bonding strength; (4) statistical analysis shows that 1.0 wt% KH-550 significantly improved the bonding strength properties of WV-PHBF, and water-resistance properties were significantly improved by 2.0 wt% of p-MDI also; and (5) morphological observation shows that KH-550 and p-MDI treatments increase the interfacial compatibility between WV and PHBF of the composites.

With people's awareness of environmental protection, the impact of the living environment on health status is gaining increasing attention. Plywood, as a main product of China's wood-based panel industry (Wang et al. 2016b), is widely prepared for interior decoration material, and involves formaldehyde-based resin as an adhesive, especially melamine-modified urea-formaldehyde resin and phenol-formaldehyde resin (Ji-You 2017). China has become the largest producer and consumer of various wood-based panels, of which about 50 percent is plywood (Fang 2014). However, plywood with formaldehyde-based adhesive will inevitably cause formaldehyde pollution of the environment, endangering human health (Luo et al. 2017). To completely solve the problem of formaldehyde pollution during the use of plywood, the plywood processing process should be completed using a series of nonformaldehyde adhesives, such as soybean protein adhesive (Yuan et al. 2017) and isocyanate (Cheng et al. 2017), which belong to the thermosetting resins. What's more, polyethylene (PE; Fang 2014), polypropylene (PP; Li et al. 2015), and polyvinyl chloride (Wang et al. 2016a), which belong to the petroleum-based thermoplastic resins called plastics, have different properties from the thermosetting resins.

The authors are, respectively, Engineer, Engineer, and Engineer, Beijing Key Lab. of Wood Sci. and Engineering, Beijing Forestry Univ., Beijing, China (zhenghao.chen@qq.com, 1009987749@qq.com, 897237104@qq.com); and Professor and Engineer, Beijing Key Lab. of Wood Sci. and Engineering and MOE Key Lab. of Wooden Material Sci. and Application, Beijing Forestry Univ., Beijing, China (shuangbaozhangj5@163.com [corresponding author], j5international@163.com [corresponding author]). This paper was received for publication in August 2017. Article no. 17-00046.

Forest Prod. J. 68(4):419–429.
doi:10.13073/FPJ-D-17-00046

Plywood products made of the thermoplastic resins have better water resistance (Cui et al. 2010) and recyclable properties (Kamel 2010), which are mainly attributable to the hydrophobicity of thermoplastic resins and their characteristics of being recyclable after melting. Moreover, plastic can be made of film as adhesive in the production of plywood, which is convenient for sizing, and reduces air pollution during the process (Song et al. 2016). However, with the growing shortage of oil resources, substituting petroleum-based plastics with bio-based plastics has become a hot topic in applied research in related fields, which can reduce the oil resources used for chemical production resources. Bioplastics, such as polyhydroxyalkanoate (PHA) and polylactic acid (PLA), with similar mechanical properties as PP and PE as well as having environmental friendly characteristics, have now become the focus of applied research. According to the reports, bioplastics can be used as the matrix (Valente and Quitadamo 2017) or adhesive (Effah et al. 2016) for fiber–bioplastic composites on the basis of different processes. The typical methods of preparing fiber–bioplastic composites in the study were manufactured under an extrusion process (Wang et al. 2017) or an injection molding process (Farsi 2010). However, the preparation of bioplastic film-bonded plywoodlike composites (wood veneer [WV]–bioplastic film composites) using the hot–cold pressing method has rarely been reported, especially about PHAs. Poly-β-hydroxybutyrate (PHB), which is a widely used plastic in the PHA field, can be an adhesive of the wood–bioplastic composites (Ren et al. 2014). What is more, fast-growing eucalyptus veneer is meaningful and feasible for making veneer–plastic composites according to the report (Song et al. 2016), and also serves as an essential plantation tree species in Australia and has been widely cultivated in almost 100 countries and regions (McGavin et al. 2015a).

According to previous studies, with different usages of thermosetting adhesive in the plywood process, two problems must be considered when preparing WV–bioplastic film composites. First, interface compatibility between hydrophobic plastic film and WV may result in relatively poor physical–mechanical properties of the composites. Second, the adhesive dosage (between adjacent WVs) and sizing process can differ from conventional plywood. In previous studies, the dosage of WV-petroleum–based plastic composites was almost over 100 g/m^2 (Li et al. 2015, Song et al. 2016, Wang et al. 2016a), which is considered difficult for bioplastic applications for cost reasons. However, the low sizing amount of adhesive may easily reduce the physical properties of plywood, especially in WV–plastic film composites.

In recent studies, there are many interface modifiers such as acid (Yu et al. 2012), alkali (Cao et al. 2017), silane (Song et al. 2015), isocyanate (Xue et al. 2015), and maleic anhydride–grafted polyolefin (Kusumoto et al. 2016), which can be used to treat hydrophilic wood fiber. These modifiers can enhance the interface compatibility between fiber and plastic by creating an interface that contributes to better compatibility between veneer and plastic both physically (increasing the gap after alkali etching) and chemically (functional group grafting copolymerization). Inspired by the effect of modifiers, the low-cost adhesive of WV–PHB film (PHBF) composites (WV-PHBF) may be feasible.

This article investigates the first effort to develop and evaluate composites on the basis of plantation eucalyptus veneers and PHBFs. (1) The desirable adhesive content was studied through single-factor experiments. (2) The effect of different modifiers based on a desirable adhesive dosage was investigated through single-factor experiments. (3) The interaction between adhesive dosage and WV-PHBF properties, modifiers, and WV-PHBF were evaluated using analysis of variance (ANOVA) with Fisher's least significant difference (LSD) test. (4) The effects of modification of WV-PHBF were tested by mechanical testing, scanning electron microscopy (SEM), and attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectroscopy.

Materials and Methods

Material preparation

Eucalyptus veneers that were the hybrid of *Eucalyptus grandis* and *Eucalyptus urophylla* were purchased from a plantation in the Guangxi region of China, with dimensions of 400 by 400 by 1.5 mm and moisture content of 9 to 12 percent by weight (wt%).

PHB (BASF SE PHB-3020MD, Dongguan Tianbang Plastic Materials Co., Ltd., China; density = 1.21 g/cm^3, melt flow index at 230°C/2.16 kg = 6.0 g/10 min, tensile resistance = 25 MPa according to the ASTM D638-14 test [ASTM International 2014], flexural modulus = 1,152 MPa according to the ASTM D790A test [ASTM International 2017], recommended processing temperature = 160°C to 170°C) was first processed into PHBFs by a single screw extruder (LABTECH LE25-30/CV Labtech Engineering Co., USA), which had a screw with a 25-mm diameter and a length/diameter ratio of 30, at a 50-rpm screw speed in the temperature range of 160°C to 170°C from feed zone to die zone. Second was the manufacture of blown film equipment, which has a 60-mm spiral die with die gap of 3 mm, at 2.5 blow-up ratio. The film thickness was controlled to be 40 μm, and the processing temperature was kept at 165°C to 170°C. The mass per unit area of PHBF was about 22.5 g/m^2.

A silane coupling agent (CHENGUANG KH-550, CHENGUANG Paint Group Co., China) was used as a surface compatibilizer; the active ingredient content was considered 97 percent.

Polydiphenylmethane diisocyanate (p-MDI; WANHUA WANNTE PM-200, Wanhua Chemical Group Co., China) was used as a surface compatibilizer; the solid content was about 100 percent.

NaOH powder (analytical reagent [AR], Beijing Chemical Works, Beijing, China) was dissolved into 2.5 wt% (as 2.5 g of NaOH powder with 97.5 g of distilled water), 5 wt%, and 7.5 wt% solutions in distilled water separately.

Anhydrous ethanol (AR, Beijing Chemical Works) was the solvent of the silane coupling agent.

Study of adhesive dosage on veneer-PHBF composite properties

The structure of WV-PHBF was assembled using three WVs, which were all dried to evaporate the solvent for about 0.5 hour at 103°C, with the grain direction of adjacent WVs perpendicular to each other. Furthermore, the PHBFs were added between adjacent WVs to serve as the adhesive. Also, one to five levels of PHBF were set with untreated WV-PHBF, with size amounts as 22.5, 45, 67.5, 90, and

112.5 g/m^2 at each level, at which three panels were prepared.

The mat was first pressed at 1.5 MPa for 4 minutes and 1 MPa for 2 minutes in a hot presser (BY302 × 2/15 150T, Xinxieli Group, Suzhou, China) with a temperature of 170°C, and then pressed at 1 MPa for 5 minutes in a cold presser (CGYJ-100 100T, Cangao Group, Shijiazhuang, China).

Study on the effect of veneer modifications

On the basis of the desirable adhesive, three methods of modifying the veneer were investigated to improve the interface compatibility between PHBF and eucalyptus veneers, levels of which are shown in Table.1. All the veneers were divided into four groups before manufacturing: control (untreated group), alkali treated, silane coupling agent treated, and p-MDI treated.

The mass fraction of alkali solution of NaOH was prepared as 2.5, 5.0, and 7.5 wt%. Silane-coupling agent KH-550 was dissolved in anhydrous ethanol (1:9 by weight), and KH-550 content was prepared as 0.5, 1, and 1.5 wt% of the ratio of resin consumption and oven-dried weight of WV-PHBF. Similarly, p-MDI was dissolved in acetone (1:10 by weight); the resin content was selected to 1, 2, and 3 wt% as calculated by the ratio of resin consumption and the oven-dried weight of WV-PHBF.

All the treatment solutions were sprayed on the surface of the veneers that were going to be sized using a spray gun at a pressure between 0.4 and 0.6 MPa. After being treated, veneers were all put into a kiln for drying to evaporate the solvent for about 0.5 hours at 103°C. The hot-pressing process was consistent with the previously described process above. For each formula, the panel was prepared three times.

Property testing

The composite properties, including bonding strength (BS), modulus of rupture (MOR), and modulus of elasticity (MOE), and water adsorption (24-h WA) were tested according to Chinese National Standard GB/T 17657-2013 (Standardization Administration of the People's Republic of China [SAC] 2013) and were evaluated according to classic II plywood in GB/T 9846-2015 (SAC 2015). The number of specimens were prepared according to GB/T 9846-2015, in which five specimens for the BS test, four specimens for the MOR-MOE test, and two specimens for the 24-hour WA test were taken from each panel. The BS property is the shear strength by tension-loading plywood-type construction. BS, MOR, and MOE were tested by a mechanical testing machine (MWW-50, Tianhua Test Device Co., Jinan, China). The 24-hour WA was tested by precision balance (JY1002, Shanghai Liang Ping Instruments Co., Ltd., China), which is accurate to 0.01 g.

Water adsorption (24-h WA)

To test 24-hour WA, the specimens were cut into 100 by 100-mm pieces according to the GB/T 17657-2013 standard; two specimens were selected from each board and immersed in water at pH = 7 and a 22°C constant temperature for 24 hours. The WA was measured by precision balance and was finished within 10 minutes. The values of 24-hour WA were calculated by Equation 1.

$$W = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where W is the WA of specimens (%), m_1 is the weight of specimens before soaking (g), and m_2 is the weight of specimens after 24 hours immersed in water (g).

Bonding strength

To test BS, four specimens were cut into 100 by 25-mm pieces according to the GB/T 9846-2015 standard and then immersed in 63°C water for 3 hours and cooled in air at room temperature for 10 minutes before testing. The load speed was about 5 mm/min, and the values of BS were calculated by Equation 2.

$$X_A = \frac{P_{\max}}{b \times l} \quad (2)$$

where X_A is bonding strength (MPa), $P_{\max}$ was the maximum force of specimen failure (N), b was the width of the specimen section (m/s), and l was the length of the specimen section.

Static bending properties (MOR, MOE)

MOR and MOE were measured in three-point bend tests. Three specimens were cut into three 150 by 50-mm individual pieces from each board. The load speed of MOR and MOE testing was about 5 mm/min and calculated by Equations 3 and 4 respectively.

$$\sigma_b = \frac{3 \times F_{\max} \times l_1}{2 \times b \times t^2} \quad (3)$$

$$E_b = \frac{l_1^3}{4 \times b \times t} \cdot \frac{\Delta F}{\Delta x} \quad (4)$$

where σ_b represents MOR (MPa), E_b represents MOE (MPa), $F_{\max}$ represents the maximum load of failure (N), b represents the width of the specimen (mm), l_1 was the length of span (mm), t was the thickness of the specimen (mm), and ΔF (N) and Δx (mm) represent the variation of load and deformation of the straight-line portion of the load-deflection curve, respectively.

Statistical analysis

The ANOVA and Fisher LSD test were used to compare the effect of adhesive dosage as well as the influence of different treatment ingredient concentrations on the physical and mechanical properties of composites. Minitab 17.1.0 software (Minitab Inc., USA) was used for the analysis with a confidence coefficient of 95 percent ($\alpha = 0.05$). $P < 0.05$ was considered a significant difference in the mass fraction of each treatment method.

Surface characteristic of modified veneers

The chemical content of the veneers' surface was qualitatively analyzed by ATR-FTIR (Nexus 870, Thermo Nicolet Corporation, USA), which provides an approximate measurement of the veneer's surface composition. Veneers being dried were then cut into 20 by 20 by 1.5-mm^3 specimens and conditioned at 18°C and 14.5 percent relative humidity before analysis. ATR-FTIR spectra were collected in the wave-number range from 4,000 to 650 cm^{-1} with resolution of 4 cm^{-1} and 32 scans per sample.

Morphological observation

SEM (ESEM; XL30 ESEM-FEG; FEI Co., USA) was used to study the interface morphology of composites by observing the section perpendicular to the adhesive layer. A small fraction of the samples was mounted on a copper stub and coated with a thin layer of gold using a high-vacuum gold sputter to avoid electrostatic charging during the examination and then analyzed in a vacuum chamber that was less than 5×10^{-5} Pa and was scanned at 7 kV.

Results and Discussion

Characterization of modified veneer by ATR-FTIR

Figure 1 shows the ATR-FTIR spectrum of modified veneer. Veneer modification with KH-550 is shown in Figure 1a, where the band intensity for Si–O at 1,233 cm^{-1}, Si–O–Si at 1,106 cm^{-1}, and Si–O–$C_{cellulose}$ at 1,033cm^{-1} became more pronounced as the mass fraction of silane increased because of the introduction and reaction of silane molecules on the surface of the veneer (Zhou et al. 2017), and the O–H (3,340 cm^{-1}) slightly decreased because of the grafting of silane molecules.

Veneer modification with NaOH is shown in Figure 1b, where the band intensity for C=$O_{hemicellulose}$ at 1,737 cm^{-1}, C–O–$C_{cellulose}$ at 1,110 cm^{-1}, and C=$O_{hemicellulose}$ at 1,737 cm^{-1} significantly decreased, and the band intensity for C=C_{lignin} at 1,508 cm^{-1} slightly decreased, but the width of O–H absorption bands were not narrowed. The result implies that the relative lignin content and the proportion of free hydroxyl were increased because of the reduction of hemicellulose and cellulose under the alkaline treatment (Li et al. 2005).

Veneer modification with p-MDI is shown in Figure 1c, where the band intensity for N=C=O_{MDI} at 2,260 cm^{-1} and C=C_{MDI} at 1,520 cm^{-1} became more pronounced because of the mass fraction increase with p-MDI, and the band area for O–H at 3,700 to 3,300 cm^{-1} slightly decreased because of the reaction with the free hydroxyl group and isocyanate (Di et al. 2016). What's more, C–N at 1,321 cm^{-1}, –C–O–C at 1,105 cm^{-1}, and N–H at 808 cm^{-1} show that MDI had self polygons on the surface of the veneer.

Preliminary analysis of PHBF dosage of veneer–PHBF composites

The results of BS testing are shown in Table 2 and illustrated in Figure 2a for the different PHBF dosages.

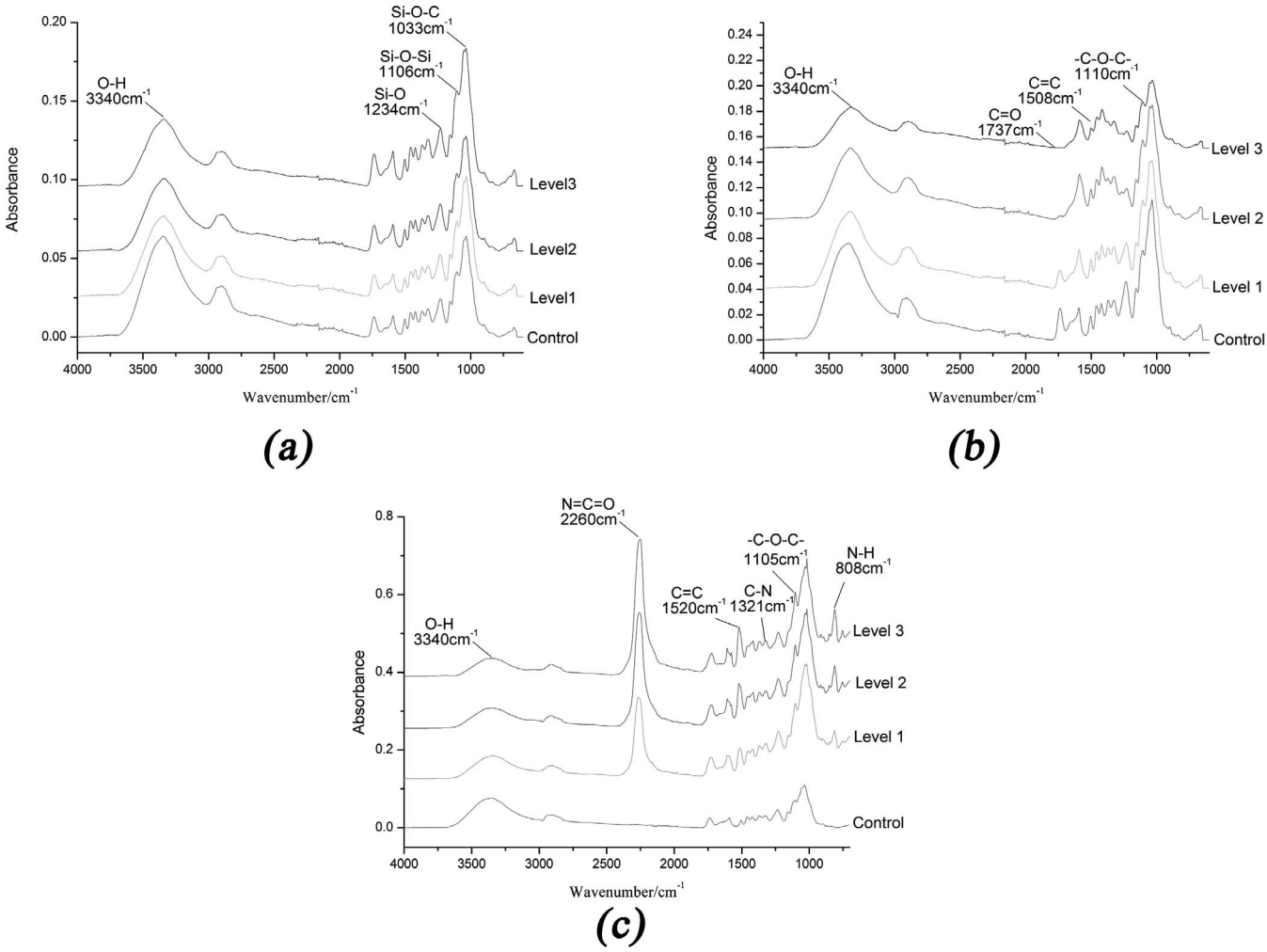

Figure 1.—Attenuated total reflection–Fourier transform infrared spectroscopy of the modified veneer surface: (a) silane (KH-550) treatment; (b) NaOH treatment; (c) polydiphenylmethane diisocyanate treatment.

Table 1.—Levels of modifiers.[a]

Level	KH-550 (wt%)	NaOH (wt%)	p-MDI (wt%)
1	0.5	2.5	1
2	1	5	2
3	1.5	7.5	3

[a] KH-550 (A-1100, USA), silane coupling agent; NaOH, alkali aqueous solution; p-MDI, polydiphenylmethane diisocyanate.

From Table 2, it can be observed that the BS value increased from 0.3 to 1.19 MPa when the dosage of PHB rose from one to four layers and then decreased to 1.06 MPa when the layers of PHBF were about five. A statistically significant difference ($P < 0.05$) was found with PHBF content; the BS of four-layer films is significantly (3.66 times) higher than one-layer film composites ($P < 0.05$). These results agree with the analysis of Chang (2014) and Song et al. (2015a), who found that the BS property between veneer and polymer was due to its mechanical adhesion, specifically in the polymer film content. What is more, because of the high density of PHB, the penetration ability of PHB for veneers was enhanced under hot-pressing conditions as the dosage of PHBF increased. However, the excess of PHBFs caused the average BS to decrease, but the difference was not statistically significant ($P = 0.11$). It might be because the slight excess of PHBFs could produce a thick bond line between the adjacent two veneers, thus weakening the shear strength of the composites (Song et al. 2017).

In this experiment, the BS of composites was greater than or equal to three-layer PHBF content, which met the BS requirements specified in GB/T 9846-2015. However, the PHBF content of one- or two-layer boards failed. Moreover, composites of three layers of film that met the BS

Table 2.—Adhesive dosage of composites manufactured in this research.[a]

Layers	Density (g/cm^3)	BS (MPa)	MOR (MPa)	MOE (MPa)	24-h WA (%)
1	0.583 (0.48)	0.30 A (13.47)	55.8 A (13.04)	5,659 A (10.58)	82.4 A (4.15)
2	0.569 (5.01)	0.55 A (7.78)	62.5 A (6.89)	6,463 A (4.68)	67.9 B (8.22)
3	0.561 (1.66)	0.72 B (14.39)	62.4 A (10.76)	6,320 AB (12.41)	65.9 B (5.25)
4	0.510 (5.27)	1.19 BC (14.94)	58.3 B (14.31)	6,001 AB (12.65)	64.8 B (12.59)
5	0.607 (2.85)	1.06 C (12.84)	55.9 B (11.49)	6,052 B (14.49)	50.1 C (3.53)

[a] Numbers in parentheses denote coefficients of variation (as a percentage). Different letters in a column indicate a significant difference in the mean value at 5 percent significance level. BS = bonding strength; MOR = modulus of rupture; MOE = modulus of elasticity; WA = water adsorption.

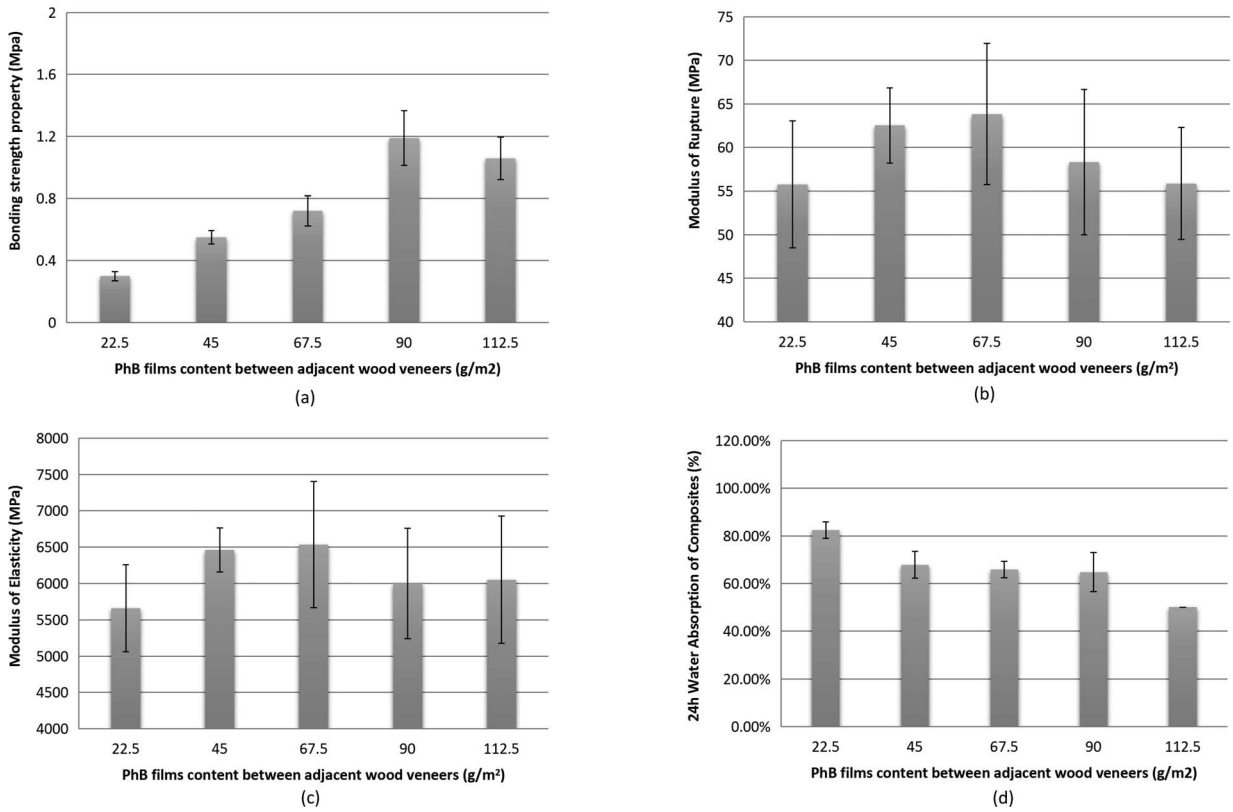

Figure 2.—Physical and mechanical properties of composites under different poly-β-hydroxybutyrate film (PHBF) content: (a) bonding strength, (b) modulus of rupture, (c) modulus of elasticity, and (d) 24-hour water adsorption. The error bar represents 1 standard deviation.

requirements of the National Standard can be considered as more cost effective and a potential choice for subsequent research, even compared with the cost of bio-based formaldehyde-free soybean protein–based plywood (Wu et al. 2016).

The results of MOR and MOE are shown in Table 2 and illustrated in Figures 2b and 2c. From Table 2 it can be observed that the average MOR of WV-PHBF significantly increased from 55.8 to 62.4 MPa ($P \leq 0.05$) when the film content increased from one to three layers and decreased from 58.3 to 55.9 MPa ($P > 0.05$) when the film content increased from four to five layers. The MOE significantly increased from 5,659 to 6,320 MPa ($P < 0.05$) when the film content increased from one to three layers, according to Table 2, and decreased from 6,001 to 5,936 MPa ($P > 0.05$) when the film content increased from four to five layers.

The strength of WV-PHBF formed mainly between PHB and the voids on the surface of the veneer according to mechanical combination theory. The improvement of MOR and MOE of WV-PHBF may be because of increased density of the adhesive layer with polymer content growth. Generally speaking, with increased polymer resin content at the same hot-pressing temperature, duration, and pressure, the PHB can enter the irregularities, pores, and grooves in the surface of the veneer after melting, which forms an excellent interface layer, and can efficiently transfer the load to enhance the bending strength of the material (D. Wang 2016, X. Z. Wang 2016). However, when the layer of PHBF was excessive, static bending properties were not increased because the roughness of the surface of the board is reduced because of it being covered with too much adhesive, which might reduce the mechanical BS of composites (D. Wang 2016). The WV-PHBF BS began to decline because the thick PHB adhesive layer has a low flexural modulus, which might easily cause damage when a load is transmitted on it. It can also be seen from the material properties of the PHB. Thus, three layers of PHBF would be considered the appropriate amount of adhesive to add with qualified quality assurance and would be recommended in processing.

The MOR and MOE of WV-PHBF were significantly improved when the content of PHBFs increased from layers one to three ($P < 0.05$). However, MOR and MOE of the composites all met the requirements for use as load-bearing plywood in dry conditions (MOR > 32 MPa, MOE > 5,500 MPa) as specified in GB/T 9846-2015.

The results of 24-hour WA are shown in Table 2 and illustrated in Figure 2d. It can be observed that the water-resistant property of composite has been enhanced with the PHBF increase. Statistical analysis indicated that PHBF content had significantly influenced the 24-hour WA of the composites when the film content increased from one to five layers ($P < 0.05$), which is reflected in the bar chart.

The water-resistant property of composites improving with PHBF content increase is mainly due to the effect of hydrophobic plastic added between adjacent veneers, which reduced the channel of water flow and enhance the water-resistance property of composites.

Study of modification of veneer–PHBF composites

The results of BS are shown in Table 3 and illustrated in Figure 3a for three methods of treatment. From Table 3, it can be observed that the average BS significantly increased from 0.72 to 1.79 MPa ($P < 0.05$) when the mass fraction of KH-550 increased from 0 to 1.0 wt%, which was higher compared with the control, and decreased from 1.79 to 1.66 MPa ($P > 0.05$) when the mass fraction of KH-550 increased from 1.0 to 1.5 wt%. Simultaneously, the average BS significantly increased from 0.72 to 1.59 MPa ($P < 0.05$) when the mass fraction of p-MDI increased from 0 to 3.0 wt%. However, the samples treated by NaOH at 5.0 and 7.5 wt% were cracked from the adhesive layer after soaking in 63°C water, but only the mass fraction of NaOH at 2.5 percent was tested, and the BS value was about 0.72 MPa, which was similar compared with the control.

The results are also reflected Figure 1. The composites of NaOH treatment reduce the lignin and hemicellulose on the surface of veneer fiber (Zhang and Hu 2014), which increases the permeability and hydrophilic property of veneer surface, but results in worse interface compatibility between hydrophobic PHBF and wood fiber. Furthermore, the composites with KH-550 treatment increased the composites' BS because of the formation of the Si–O–C bond between silane molecules and veneer surface, which

Table 3.—Properties of composites manufactured in this research.[a]

Sample	Density (g/cm^3)	BS (MPa)	MOR (MPa)	MOE (MPa)	24-h WA (%)
Control	0.583 (0.48)	0.72 E (14.39)	62.4 ABC (10.76)	6,320 AB (12.41)	65.9 ABCD (5.25)
KH-550					
0.5 wt%	0.502 (5.84)	1.00 D (11.28)	56.8 DE (7.32)	5,607 CD (7.22)	73.7 AB (1.90)
1.0 wt%	0.502 (8.23)	1.79 A (3.55)	64.1 AB (10.40)	6,627 C (8.24)	69.0 ABC (2.53)
1.5 wt%	0.520 (0.15)	1.66 AB (8.13)	60.4 BCD (7.23)	5,860 BCD (9.34)	62.6 BCD (1.52)
NaOH					
2.5 wt%	0.514 (5.50)	0.72 E (14.36)	57.6 CDE (12.38)	5,957 BCD (12.07)	60.1 BCD (2.40)
5.0 wt%	0.608 (3.35)	—	55.7 CDE (12.03)	5,840 BCD (11.63)	77.8 AB (13.48)
7.5 wt%	0.509 (3.41)	—	52.4 E (10.93)	5,551 D (4.05)	85.8 A (14.66)
p-MDI					
1.0 wt%	0.576 (7.80)	1.33 C (13.55)	61.6 ABCD (13.16)	6,062 BC (10.21)	49.9 CD (14.08)
2.0 wt%	0.551 (5.08)	1.57 B (13.61)	68.7 A (5.07)	6,361 AB (9.99)	47.9 D (7.99)
3.0 wt%	0.528 (4.32)	1.59 B (11.44)	64.2 AB (6.24)	6,261 AB (10.09)	54.7 BCD (3.56)

[a] Numbers in parentheses denote coefficients of variation (as a percentage). Different letters in a column indicate a significant difference in the mean value at 5 percent significance level. BS = bonding strength; MOR = modulus of rupture; MOE = modulus of elasticity; WA = water adsorption; KH-550 = silane coupling agent; p-MDI = polydiphenylmethane diisocyanate.

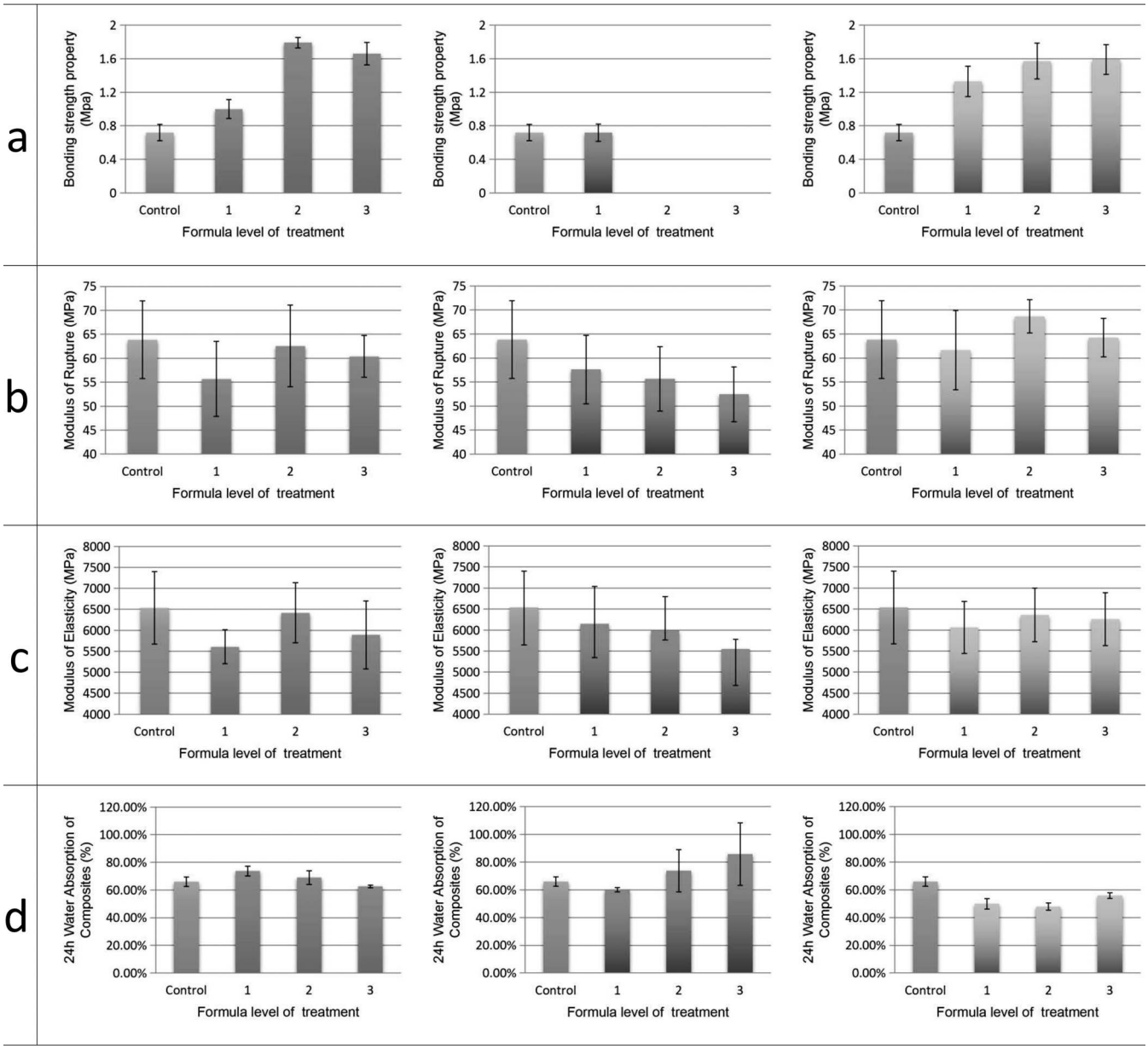

Figure 3.—Physical and mechanical properties of composites under the three modification pretreatment methods: (a) bonding strength, (b) modulus of rupture, (c) modulus of elasticity, and (d) 24-hour water adsorption. The first bar in each panel is the control, the four left-most panels are the KH-550 treatment, the four middle panels are the NaOH treatment, and the four right-most panels are the polydiphenylmethane diisocyante treatment. The error bar represents 1 standard deviation.

decreased the free hydroxyl and constructed the chemical bonding between hydrophobic and hydrophilic materials. However, the effect of KH-550 treatment was dependent on the coverage of silane molecules on the veneer surface. The insufficient mass fraction of silane, which will partially penetrate into the veneer in the presence of ethanol, will be unable to form a perfect molecular layer of compatibilizer and get a satisfactory compatibilized effect (D. Wang 2016). What's more, the excessive mass fraction of silane, which will self-cross-link on the veneer's surface, causes the uneven interface structure between PHBF and veneer plus lower BS (Fang et al. 2014). Moreover, composites treated by p-MDI show increasing BS due to the reaction between the –N=C=O groups and the veneer; plus, p-MDI treatment can reduce the water adsorption and surface polarity of the veneer, which enhances dimensional stability of composites and interface compatibility between the veneer and PHBF.

In comparison with the control, both 1.0 wt% KH-550 treatment ($P < 0.05$) and 3.0 wt% p-MDI treatment ($P < 0.05$) showed significant effects of WV-PHBF BS. However, the difference between 1.0 wt% KH-550 treatment and 3.0 wt% p-MDI treatment was not statically significant ($P > 0.05$). From the cost point of view, 1.0 wt% KH-550 treatment is the best method of BS modification.

The results of MOR and MOE are shown in Table 3 and illustrated in Figures 3b and 3c. The MOR of KH-550–treated WV-PHBF can be significantly increased from 56.78 to 64.11 MPa ($P < 0.05$), and 61.6 to 68.7 MPa for p-MDI treatment ($P < 0.05$) when the treatment level increased from level one to level two. However, the MOR of NaOH-

treated WV-PHBF decreased from 62.4 to 52.4 MPa ($P > 0.05$) with the mass fraction of NaOH increasing from 0.5 to 7.5 wt%. The MOE significantly increased from 5,607 to 6,627 MPa ($P < 0.05$) with the mass fraction of KH-550 increasing from 0 to 1.0 wt%, and decreased to 5,860 MPa ($P \leq 0.05$) when the mass fraction of KH-550 was at 1.5 percent. Similarly, the MOE of composites treated with p-MDI increased from 6,062 to 6,361 MPa ($P > 0.05$) with mass fraction of p-MDI increasing from 1.0 to 2.0 wt%, and decreased to 6,261 MPa when the mass fraction of p-MDI was at 3.0 wt%. The MOE of NaOH-treated WV-PHBF significantly decreased from 6,320 to 5,551 MPa ($P < 0.05$) with the mass fraction of NaOH increasing from 0 to 7.5 wt%.

The interfacial BS mainly depends on the bonding degree and penetration of the PHBF to the veneer (D. Wang 2016). A good bonding interface can effectively transmit the stress of the composite material (X. Z. Wang 2016). The improvement of MOR and MOE of KH-550–treated composites may be increased by forming an ether bond and a hydrogen bond between silane molecules and veneer surface (Fang et al. 2014). According to the reports, the proper amount of silane agent was the key to improve the BS of the wood–plastic composites (Chen et al. 2017). However, the mass fraction of 0.5 wt% KH-550 treatment composites was unsatisfied in static bending properties, possibly because the silane molecules were uneven in distribution on the surface of the veneer, which will easily cause stress concentration in the bending process (Zhu et al. 2015). The excess silane coupling agent of 1.5 wt% can reduce the surface activation energy of the veneer and weaken the compatibility of veneer and PHBFs (Wang et al. 2011). Moreover, the p-MDI serves as a molecular bridge between wood fiber and plastic, which can increase MOR and MOE of the composites by enhancing interface compatibility between veneer and plastic in the way of introducing the –N=C=O group on the surface of the veneer (Di et al. 2016). However, the average of MOR and MOE with 3 wt% p-MDI treatment was lower than 2 wt%, but the difference was not statistically significant. It is obvious that the excessive p-MDI does not contribute to the improvement of the bending performance, which may be because the excess p-MDI forms the cured layer after heating and hinders the penetration of PHB adhesives. What's more, with the mass fraction of alkali increased, the BS of the composite was decreased because the intracellular components decomposed (Zheng et al. 2012) and the ratio of free hydroxyl increased, which is also reflected in Figure 1.

In comparison with the control, the average MOR of 1 wt% KH-550–treated ($P > 0.05$), 2 wt% p-MDI–treated ($P > 0.05$), and 3 wt% p-MDI–treated ($P > 0.05$) composites were improved, and the average MOE of 1 wt% KH-550–treated ($P > 0.05$) and 2 wt% p-MDI–treated ($P > 0.05$) composites was better than the untreated control, but the differences were not statistically significant. Furthermore, the difference between 1 wt% KH-550, 2 wt% p-MDI, and 3 wt% p-MDI treatments of MOR ($P > 0.05$) and 1 wt% KH-550 and 2 wt% p-MDI treatments of MOE ($P > 0.05$) were not statistically significant. From the cost point of view, 1.0 wt% KH-550 treatment is the best method of bending strength modification.

The 24-hour WA results are shown in Table 3 and illustrated in Figure 3d for the three methods of treatment. Compared with the control, the 24-hour WA of composites after KH-550 treatment ($P < 0.05$) was increased first but gradually decreased as the mass fraction of KH-550 increased. It may result from the ethanol solvent penetrating into the veneer after spraying (D. Wang 2016), which can increase the permeability of the veneer surface by dissolving the extract of wood without damage to the cell structure (Jung et al. 2016). However, when the mass fraction of KH-550 increased, the water resistance of composites was enhanced by the reaction between KH-550 and free hydroxyl on the veneer, which can also be indicated by ATR-FTIR analysis. Furthermore, p-MDI will improve the water resistance of composites by reaction with the free hydrogen on the veneer surface, thus reducing the hydrophilic property of the veneer surface. However, the impact of mass fraction of p-MDI on 24-hour WA was not significant ($P = 0.05$). The reason may be that the free hydroxyl on the surface of the veneer reacted adequately with p-MDI, which can also be indicated by ATR-FTIR analysis. The NaOH treatment ($P < 0.05$) significantly affected the WA of the composites, which first decreased, and then increased as its mass fraction increased. The reason may be because the NaOH treatment of 3.5 wt% destroys the hemicellulose and the amorphous region of the cellulose on the surface of the veneer for increased water resistance of the composites (Zheng et al. 2012). However, with the mass fraction of NaOH raised more than 5.0 wt%, the interface compatibility between veneer and PHBF would be even worse as the ratio of the hydroxyl group on the veneer surface increased; simultaneously, the lignin on the veneer surface began to degrade, which mainly expanded the gap between cells and caused the WA of the composites to increase (Wei and Zhou 2012).

In short, 1.5 wt% KH-550 treatment, 2.5 wt% NaOH treatment, and 1.0 to 3.0 wt% p-MDI treatment all reduced the WA of WV-PHBF, and a statistically significant difference was found between control and 2.0 wt% p-MDI treatment ($P < 0.05$). Thus, the 2.0 wt% p-MDI treatment is the best method to water-resistance modification.

SEM analysis of composites

Figures 4 through 7 are display SEM photographs of WV-PHBF sections. Figures 4 and 5a through 5c show the poor

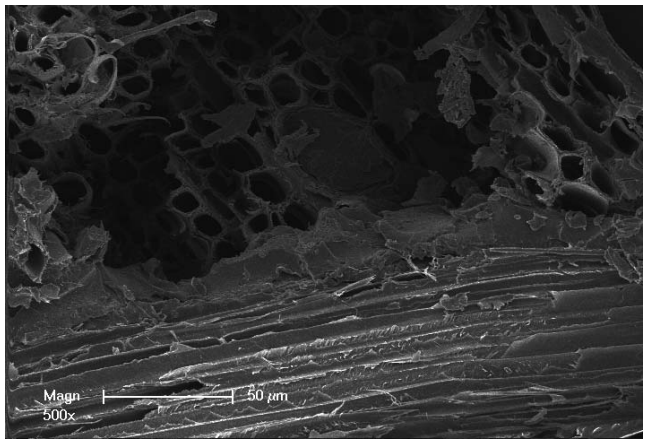

Figure 4.—Scanning electron microscope image of the untreated control.

adhesion between veneers and PHBFs. There are many cavities and voids, which were due to the low interface compatibility between hydrophobic plastic and hydrophilic veneer, especially that being treated by NaOH, even though the alkali treatment of veneer can corrode the cell wall, which forms a lot of porosity that can be filled by adhesive. During the BS and static bending test, creaks developed through the weaker interface regions, resulting in low BS, MOR, and MOE values of samples.

On the contrary, with an addition of the mass fraction of KH-550 and p-MDI, the interface compatibility of PHBFs and veneer were enhanced, which is shown in Figures 6 and 7. However, 1.5 wt% KH-550 added will lead to the formation of the weak interface, which is mainly caused by the laminated molecules of KH-550 and decreases the mechanical property of composites.

The better property of WV-PHBF discussed above can be seen in Figures 6b and 7b, in which veneers were treated by 1.0 wt% KH-550 and 2 wt% p-MDI, with better interface compatibility as well as less gap between two phases, resulting in higher adhesion between the component and better water-resistant properties.

This surface appearance may be explained by a stronger interaction between the two phases, and the morphological

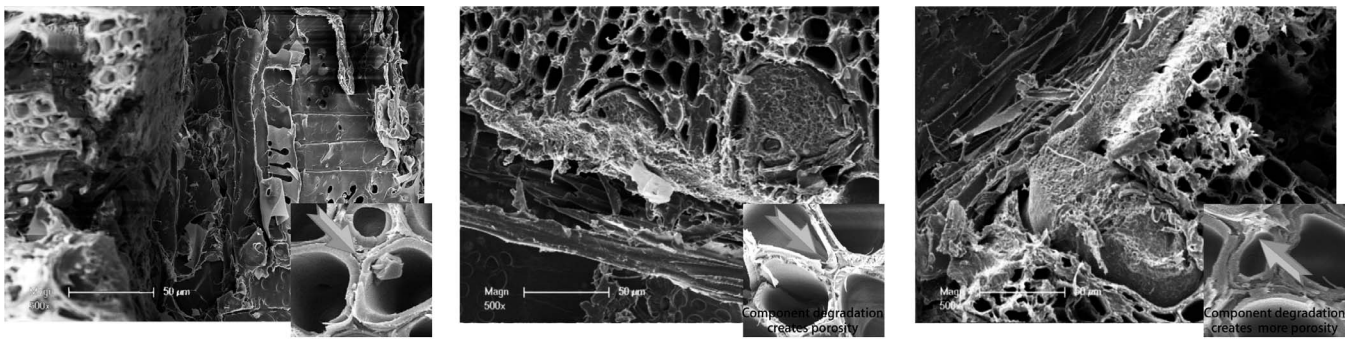

Figure 5.—Scanning electron microscope images of composites with NaOH treatments: 3.5 (a), 5.0 (b), and 7.5 (c) weight percent.

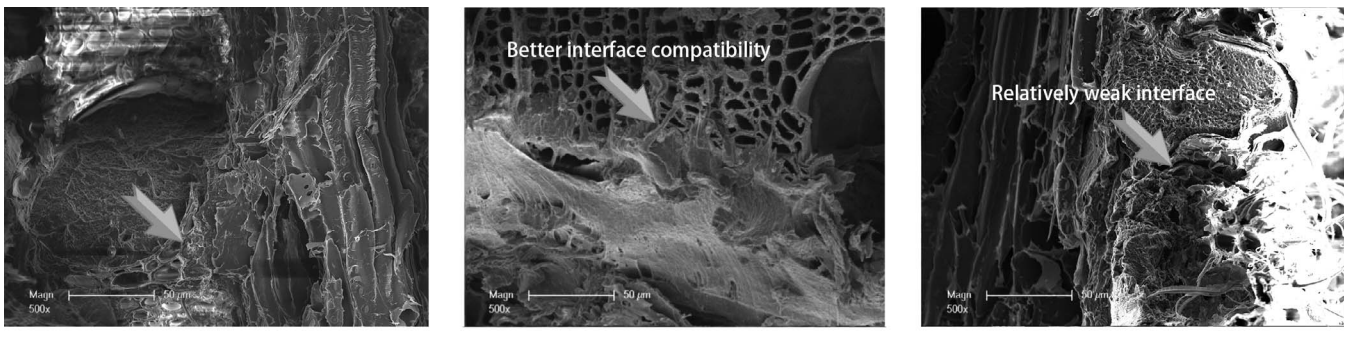

Figure 6.—Scanning electron microscope images of composites with KH-550 treatments: 0.5 (a) 1.0 (b), and 1.5 (c) weight percent.

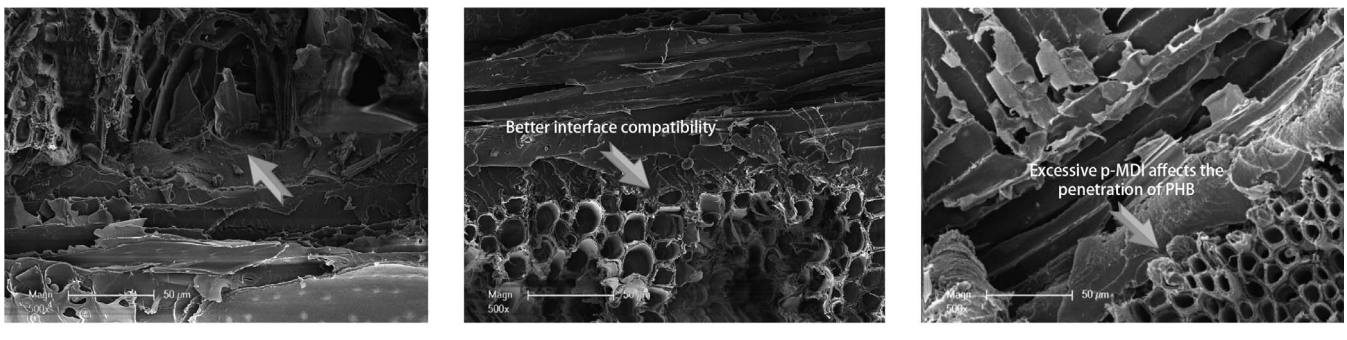

Figure 7.—Scanning electron microscope images of composites with polydiphenylmethane diisocyante treatments: 1.0 (A), 2.0 (b), and 3.0 (c) weight percent.

observation is consistent with the mechanical and dimensional stability performance of the composites.

Conclusions

1. A desirable adhesive dosage for preparing WV-PHBF composites was about 67.5 g/m^2 (three layers added). The adhesive dosage among 67.5 to 112.5 g/m^2 of veneer-PHBF composites met the mechanical requirement of GB/T 9846-2015.
2. The surface modification of KH-550 and p-MDI of the veneer could improve the interface compatibility of veneer-PHBF composites. However, the surface modification of NaOH shows an adverse effect on veneer-PHBF composites. Furthermore, the physical–mechanical properties of veneer-PHBF composites at the adhesive dosage of 67.5 g/m^2 with 1 wt% KH-550 or 2 wt% p-MDI modifier was even better than those of untreated veneer–PHB composites at the adhesive dosage of 90 g/m^2.
3. A statistical difference ($P < 0.05$) was found among the effects of KH-550, NaOH, and p-MDI treatments on the properties of composites. Where the 1.0 wt% of KH-550 treatment had a significantly higher effect than control on BS ($P < 0.05$) and had been proven to be the best method of BS modification, 2.0 wt% p-MDI treatment had a significantly lower effect than control on 24-hour WA ($P < 0.05$) and had been proven to be the best method of water-resistance modification. Furthermore, the modifier has no significant effect on the improvement of bending performance; 1.0 wt% KH-550 had been proven to be the best method of bending strength modification.
4. SEM and ATR-FTIR indicated that KH-550 and p-MDI treatments showed a positive effect on the adhesive interface. However, the NaOH treatment can increase the porosity of the veneer surface to promote the plastic glue, but severely damaged the cell wall and interface compatibility between veneer and plastic, thus resulting in poor properties of the composites after treatment.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (31670571), National Key R & D Program of China (2017YFD0600804), Beijing Natural Science Foundation (6162019), Co-built Foundation with Zhejiang Province ''R & D on Natural Fiber Composites and Environmentally Friendly Adhesives'' (CZXC201410), and Zhejiang Chengzhu Advanced Material Technology Co. Ltd.

Literature Cited

ASTM International. 2014. Standard test method for tensile properties of plastics. ASTM D638-14. ASTM International, West Conshohocken, Pennsylvania. www.astm.org.

ASTM International. 2017. Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. ASTM D790-17. ASTM International, West Conshohocken, Pennsylvania. www.astm.org.

Cao, Y., W. Song, Z. Yang, Z. Chen, and S. Zhang. 2017. The properties of particleboard made from alkaline-treated wheat straw and methylene diphenyl diisocyanate binder. *BioResources* 12(2):3265–3276.

Chang, L. 2014. Formation mechanism and interface status evaluation of high density polyethylene poplar composite plywood. PhD dissertation. Chinese Academy of Forestry, Beijing.

Chen, Z. H., L. I. Jin-Qi, L. X. Tian, W. Song, and S. B. Zhang. 2017. Current situation and prospective research of interfacial modification of straw–plastic composite (spc). *Wood Process. Machine*. 28(3):42–48.

Cheng, G., X. Bo, J. Yanli, T. Song, and Q. Wangshun. 2017. Application of MDI in wood-based panel manufacturing. *China Forest Prod. Ind*. 2017(1):38–42.

Cui, T., K. L. Song, and S. B. Zhang. 2010. Research on utilizing recycled plastic to make environment-friendly plywood. *Forest Ecosyst*. 12(4):218–222.

Di, M., L. You, T. Zhao, and J. Cui. 2016. Surface coating treatment with isocyanate and bonding for wood/polyethylene composites. *J. Build. Mater*. 19(1):94–99.

Effah, B., A. Van Reenen, and M. Meincken. 2016. Localisation and quantification of potential binding sites for compatibilisers on soft and hardwood in wood–plastic composite systems. *Surf. Interface Anal*. 49:527–532.

Fang, L. 2014. Interfacial modification methods and mechanism of high density polyethylene film/poplar veneer plywood. PhD dissertation. Chinese Academy of Forestry, Beijing.

Fang, L., L. Chang, W. Guo, Y. Chen, and Z. Wang. 2014. Influence of silane surface modification of veneer on interfacial adhesion of wood–plastic plywood. *Appl. Surf. Sci*. 288:682–689.

Farsi, M. 2010. Wood–plastic composites: Influence of wood flour chemical modification on the mechanical performance. *J. Reinf. Plast. Comp*. 29(24):3587–3592.

Ji-You, G. U. 2017. The development and research progress of domestic wood adhesives. *China Forest Prod. Ind*. (1):6–19.

Jung, J. Y., H. M. Park, and J. K. Yang. 2016. Optimization of ethanol extraction of antioxidative phenolic compounds from torrefied oak wood (Quercus serrata) using response surface methodology. *Wood Sci. Technol*. 50(5):1037–1055.

Kamel, E. D. 2010. Investigating the mechanical and physical properties of wood plastic composites (wpc). Master's thesis. The American University in Cairo, Cairo, Egypt.

Kusumoto, N., K. Takata, and Y. Kurimoto. 2016. Mechanical properties and dimensional stabilities of wood–polypropylene composites prepared using mechanochemically acetylated Japanese cedar (*Cryptomeria japonica*) wood meal. *BioResources* 11(2):3825–3839.

Li, B. 2016. Dyeing behavior based on dyed poplar with reactive dyes. Master's thesis. Northeast Forestry University, Harbin, China.

Li, L., Y. Hu, D. Liu, and Z. Chen. 2005. Effect of alkaline treatment of wood flour on properties of wood/plastic composites. *China Synth. Resin Plast*. 22(6):53–56.

Li, X., C. Ren, W. Wei, and S. Zhang. 2015. Pressing crafts and mechanical properties of eucalyptus veneer/polypropylene (PP) film composites. *J. NE Forestry Univ*. 43(2):87–90.

Luo, J., X. Li, R. Shi, Q. Gao, J. Li, and L. Li. 2017. Determination of formaldehyde and TVOC emission behavior from interior use plywood using various post heat treatment processes. *J. Appl. Polym. Sci*. 134(22).

McGavin, R. L., H. Bailleres, M. Hamilton, D. Blackburn, M. Vega, and B. Ozarska. 2015a. Variation in rotary veneer recovery from Australian plantation *Eucalyptus globulus* and *Eucalyptus nitens*. *BioResources* 10(1):313–329.

Ren, H., Z. Liu, H. Zhai, Y. Cao, and S. Omori. 2014. Effects of lignophenols on mechanical performance of biocomposites based on poly-β-hydroxybutyrate (phb) and polypropylene (pp) reinforced with pulp fibers. *BioResources* 10(1):432–447.

Song, W., Y. Cao, D. Wang, G. Hou, Z. Shen, and S. Zhang. 2015a. An investigation on formaldehyde emission characteristics of wood building materials in Chinese standard tests: Product emission levels, measurement uncertainties, and data correlations between various tests. *PLoS ONE* 10(12):e0144374.

Song, W., W. Wei, X. Li, and S. Zhang. 2016. Utilization of polypropylene film as an adhesive to prepare formaldehyde-free, weather-resistant plywood-like composites: Process optimization, performance evaluation, and interface modification. *BioResources* 12(1):228–254.

Song, W., W. Wei, D. Wang, and S. Zhang. 2017. Preparation and properties of new plywood composites made from surface modified veneers and polyvinyl chloride films. *BioResources* 12(4):8320–8339.

Song, W., F. Zhao, X. Yu, C. Wang, W. Wei, and S. Zhang. 2015. Interfacial characterization and optimal preparation of novel bamboo plastic composite engineering materials. *BioResources* 10(3):5049–5070.

Standardization Administration of the People's Republic of China (SAC). 2013. The methods of evaluating the properties of wood-based panels and surface decorated wood-based panels. GB/T 17657. Standards Press of China, Beijing.

Standardization Administration of the People's Republic of China (SAC). 2015. Plywood for general use. GB/T 9846. SAC, Beijing.

Valente, M. and A. Quitadamo. 2017. Polymeric matrix composites at reduced environmental impact. *Polym. Eng. Sci*. 57(7):651–656.

Wang, C., S. Wang, H. Cheng, Y. Xian, and S. Zhang. 2017. Mechanical properties and prediction for nanocalcium carbonate-treated bamboo fiber/high-density polyethylene composites. *J. Mater. Sci*. 52(19):11482–11495.

Wang, D. 2016. A study of the manufacturing and strengthening mechanism of composite materials made from eucalyptus veneer and polyvinyl chloride (PVC) film. Master's thesis. Beijing Forestry University, Beijing.

Wang, D., Y. Cao, C. Wang, W. Wei, and S. Zhang. 2016a. Manufacturing technology of eucalyptus veneer/polyvinyl chloride (PVC) film composites. *J. NE Forestry Univ*. 44(2):47–51.

Wang, R., B. Lv, Z. Tang, B. Hong, and Y. Wu. 2016b. Suggestions on the development of plywood industry in China. *China Forest Prod. Ind*. 43(1):19–22.

Wang, X. Z. 2016. Nanoscale investigation of the interfacial properties and modification mechanism of wood-adhesive interphase. Master's thesis. Nanjing Forestry University, Nanjing, China.

Wang, Y., X. U. Wei-Yue, L. Wang, and J. Z. Cao. 2011. Physical and mechanical properties of wood power/polypropylene composites modified by MAPP. *Forestry Machin. Woodw. Equip*. 39(2):21–24.

Wei, P. X. and D. G. Zhou. 2012. Surface characteristics of an alkaline degreasing treatment on *Pinus massoniana* veneer. *J. Zhejiang A&F Univ*. 29(5):778–782.

Wu, J.-R., H. Li-Chen, Y. H. Deng, X. Y. Chen, and J. Zhang. 2016. Research on *Salix discolor* plywood bonded with soybean protein adhesive. *China Forest Prod. Ind*. 43(7):19–23.

Xue, D., W. Lei, Y. Deng, L. Jing, and Q. Liu. 2015. Effect of interface modification on mechanical and thermal properties of high-density polyethylene/silvergrass composites. *J. Thermopl. Comp. Mater*. 28(1):128–141.

Yu, M., C. He, J. Liu, R. Hou, and J. Xue. 2012. Effects of different surface treatment for wheat straw on performances of wood–plastic composites. *Trans. Chin. Soc. Agric. Eng*. 28(9):171–177.

Yuan, C., M. Chen, J. Luo, X. Li, Q. Gao, and J. Li. 2017. A novel water-based process produces eco-friendly bio-adhesive made from green cross-linked soybean soluble polysaccharide and soy protein. *Carbohydr. Polym*. 169:417–425. DOI:10.1016/j.carbpol.2017.04.058

Zhang, L. and Y. Hu. 2014. Novel lignocellulosic hybrid particle board composites made from rice straws and coir fibers. *Mater. Design* 55(6):19–26.

Zheng, M. X., L. Li, M. Y. Zheng, X. Wang, H. Ma, and K. Wang. 2012. Effect of alkali pretreatment on cellulosic structural changes of corn stover. *Environ. Sci. Technol*. 44(44):432–432.

Zhou, D., X. Guo, S. Yan, and M. Di. 2017. Combined surface treatment of wood plastic composites to improve adhesion. *BioResources* 12(2):3965–3975.

Zhu, L., J. Cao, Y. Zhang, Y. Wang, and Z. Liu. 2015. Analysis of dielectric relaxation on interfacial compatibility of poplar wood flour/polypropylene composite. *Acta Mater. Comp. Sin*. 32(6):1641–1648.