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An environmentally-friendly soybean based resin as an alternative to formaldehyde-based counterpart for biomass composites

Hao Yin [a], Peitao Zheng [a,b], Erbing Zhang [a], Jiuping Rao [a], Qiaojia Lin [a], Mizi Fan [a,c,**], Zhiqiang Zhu [a], Maiquan Chen [a], Shengyuan Cheng [a], Qinzhi Zeng [a,***], Nairong Chen [a,*]

[a] National Forestry and Grassland Administration Key Laboratory of Plant Fiber Functional Materials, College of Materials Engineering, Fujian Agriculture and Forestry University, 350002, Fuzhou, China
[b] Department of Materials Science & Engineering, Southern University of Science and Technology, Shenzhen, 518055, China
[c] College of Engineering, Design and Physical Science, Brunel University London, UB8 3PH, Uxbridge, United Kingdom

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ABSTRACT

Wood based composites are widely used in furniture and other building construction, but the majority of which are bonded with formaldehyde-based resins that may cause serious health concern. This study presents an environmentally-friendly soybean based resin via combination of waste newspaper powder (WNP), soybean flour (DSF), and polyamidoamine-epichlorohydrin for woody composites, and its adhesion properties as investigated *via* shear strength. The results showed that the developed DSF-WNP resin (or soybean based resin) cured well at currently commercial plywood manufacture temperature (130 °C) and could be cured at a lower temperature of 85 °C for energy saving as well, through chemical cross-linking reactions between hydroxyl-azetidinium ring groups in the polyamidoamine-epichlorohydrin and hydrophilic groups, such as amido, carboxyl and hydroxyl in other components. WNP with particle sizes ranging from 120 μm to 250 μm were suitable for the resin applications. WNP resulted in poor dispersion, but lowered water absorption and increased insoluble fraction content and tensile strength in the cured resin. The wet shear strength of plywood bonded with DSF-WNP resin with a 2/5 dry weight ratio of WNP/DSF was 1.24 MPa, which met the requirements of the Chinese National Standard GB/T 9846–2015 for interior plywood. The resin characteristics including fast curing and excellent wet-cohesion performance are comparable to the mostly used urea-formaldehyde adhesives, which showed great potential in wood composites as an alternative to formaldehyde-derived adhesives.

1. Introduction

Composites, that are composed of reinforcement materials and resins have been widely used in construction, marine, aerospace and automobile industries because of their high strength, lightweight and low maintenance costs [1]. Petroleum-based resins (e.g. formaldehyde derived resins), a principal constitution of wood based composites, such as plywood, particleboard, medium density fiberboard and oriented strand board, account for more than 65% by volume of all the resins used per year in the world [2], and the utilization of these resins may lead to air pollution and health risks because of the toxic chemicals, such as formaldehyde, being released from the composites [3]. Due to ever-growing environmental concerns and reducing of petroleum reserves, researchers have been trying to replace conventional petroleum-based resins with sustainable and environmentally friendly biomass derived resins [4]. These biomasses include, but are not limited to vegetable protein [2,5–7], carbohydrate [8,9], vegetable oil [10,11], lignin [6,12] and tannin [13,14]. Among them, vegetable protein is the most widely studied because it contains a large number of functional groups such as primary amines, carboxyl and hydroxyl groups [15]. Soybeans are the main feedstock for preparing vegetable-protein-based resins owing to their high soybean protein content [16].

The wet-cohesion property is one of the most challenging criteria but a prerequisite for practical applications of soybean based resins [17].

* Corresponding author.
** Corresponding author. National Forestry and Grassland Administration Key Laboratory of Plant Fiber Functional Materials, College of Materials Engineering, Fujian Agriculture and Forestry University, 350002, Fuzhou, China.
*** Corresponding author.
E-mail addresses: mizi.fan@brunel.ac.uk (M. Fan), fajfuzqz@163.com (Q. Zeng), fafucnr@163.com (N. Chen).

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Numerous research efforts have been carried out to improve its wet-cohesion, including chemical, physical and biological treatment, and the chemical treatment appears to be an efficient approach [18], for example, polyamidoamine-epichlorohydrin (PAE) resin [19], polyethyleneimine and maleic anhydride [20], epoxy resin [21], undecylenic acid [22] and magnesium oxide [23] have been used to modify soybean protein for preparing soybean based resins with improved wet-cohesion. However, all these chemical treatments have resulted in an elevated cost, which may hinder the application of soybean based resins, even although the wet-cohesion performance may compete or even surpass those of existing petroleum-based resins. Therefore, it is imperative to develop a promising method capable of reducing cost and enhancing wet-cohesion for soybean based resins.

The global paper and pulp industries produce more than 450 million tons of paper per year [24]. For example, the newspaper circulation of the United States was around 13 billion in 2016 [25] with waste newspaper contributing around 19% of municipal solid waste [26]. Considerable efforts, such as waste paper for construction material, aerogels, fluorescent flexible film, reinforcement material of composites and bioconversion to ethanol application, have been reported [27–31]. In particular, as a reinforcing material for composite applications, waste paper has received special attention due to the fact that it contains more than 50% cellulosic fiber with properties similar to natural fibers, such as bamboo, jute, kenaf, flax, sisal and hemp, the reinforced composites of which have become realistic in many engineering applications [32–34], although various coupling agents have been required to improve interaction at the fiber-matrix interface due to the incompatibility between the hydrophilic fibers and the hydrophobic resins [35,36]. Waste newspaper shows good mechanical strength and water resistance, and there are a large number of functional groups, such as carboxyl and hydroxyl groups on the fibers after a series of production processes. These functional groups are similar to that of DSF, readily participating in various nucleophilic reactions, such as cross-linking. These characteristics would endow waste newspaper powder (WNP) reinforced soybean-based adhesives with excellent mechanical properties and make it a potential wood adhesive.

The aim of this study was to generate eco-friendly soybean based resins for the production of wood based composites, with the cellulosic content coming from WNP as the raw material. The hypothesis that WNP may functionalize soybean based resins with improved wet-cohesion and reduced cost, so does its application in wood based composites, is because (i) WNP displays good wet strength or water resistance [24,37]; (ii) WNP is compatible with soybean components; (iii) functional groups such as carboxyl and hydroxyl groups in WNP may react with other soybean based resin components at high temperature; (iv) WNP is inexpensive. An eco-friendly soybean based resin composed of WNP, defatted soybean flour (DSF) and polyamidoamine-epichlorohydrin (PAE) was developed with large portions of raw material (DSF), replaced by WNP flour, with the effect of WNP flour on resin performance characterized.

2. Material and methods

2.1. Materials

Defatted soybean flour (DSF) (53.4% of crude protein, 36.3% of carbohydrate and 7.5% of moisture) was purchased from the Shandong Wonderful Industrial Group Co., Ltd. (Shandong, China). Polyamidoamine-epichlorohydrin (PAE) (solid content 12.5%) was purchased from Qingzhou Jinhao Industry & Trade Co., Ltd. (Shandong, China). Waste newspaper with 4.5% moisture content was obtained from the People's Daily Press (Beijing, China). *Pinus massoniana* veneers (30 cm × 30 cm in size, 1.2–1.3 mm in thickness, and 10%–12% of moisture content) were obtained from Jianyang Luban Wood Industry Co., Ltd. (Fujian, China). The other chemical reagents, such as hydrochloric acid and sodium hydroxide, were analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China).

2.2. Pretreatment of WNP

Waste newspaper was shredded with a paper shredder (528, bonsai, China) and then placed in a drying oven at 105 °C for 1 h. After drying, the shredded waste newspaper was pulverized using a pulverizer (2500C, IZARA, China) at room temperature for 30 min to obtain the waste newspaper powder (WNP) with 4.5% moisture content.

2.3. Soybean based resin preparation

According to our previous work [38], the solid content of resins and (WNP + DSF)/PAE dry weight ratio were designed as 36% and 7/1, respectively. For the resins preparation, the dry weight ratio of WNP/DSF were 0/7, 1/6, 2/5, 3/4, 4/3 and 7/0, respectively. A representative procedure for preparation of a soybean based resin with the WNP/DSF dry weight ratio of 1/6 was as follows: Deionized water (30.81 g), DSF (28.42 g) and WNP flour (4.74 g) were added to a 200 mL three-neck flask and stirred at room temperature for 20 min. PAE resin (36 g) was then added and the mix stirred for 10 min. After that, the slurry was adjusted to pH 6.25 with 2 mol/L sodium hydroxide solution and further stirred at room temperature for 60 min, to obtain a DSF-WNP resin (soybean based resin) with 36% of solid content.

The prepared DSF-WNP resin sample was divided into two parts. One part was frozen in a refrigerator at −4 °C for 24 h, and then vacuum-dried for 48 h to obtain the uncured resin sample. The other part was completely cured at 105 °C for 24 h to obtain the cured resin sample.

2.4. Plywood preparation

The DSF-WNP resin was applied to three-ply plywood composites for assessing its performance by brushing about 170 g/m^2 of the resin on one loose-side of a *Pinus masson* pine veneer. The neighboring veneer plys were cross-laid up with the coated loose-side assembling with un-coated tight-side and then covered with an un-coated veneer. The assembled three-layered plywood mat was put on a table at ambient environment for 10 min, hot pressed at 1.0 MPa/130 °C for 3.0 min and then stored at ambient environment for 24 h before testing.

2.5. Fourier transform infrared (FTIR) spectroscopy

The uncured and cured DSF-WNP resin samples were ground into powder and scanned via a Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) at a resolution of 4 cm^{-1} for 64 scans in the spectral range of 500–4000 cm^{-1}.

2.6. Differential scanning calorimetry (DSC) analysis

DSC was performed on a NETZSCH STA449C Synchronous Thermal Analyzer (NETZSCHCo., Selb, Germany). The uncured resin powder was heated from 25 to 500 °C at a rate of 10 °C/min under nitrogen gas flow at 30 mL/min.

2.7. Rheological analysis

The rheological performance of the DSF-WNP resins were determined via a Hakke Rheometer (MARSIII, Thermo, Germany). The accessory PP35Ti parallel plate was used and the spacing between the plates was set to 0.105 mm. The DSF-WNP resin samples (4.0 g) were placed between the parallel plates, and then the shear stress and apparent viscosity under different shear rate (0-650 s^{-1}) were measured at 25 °C. All analyses were conducted in triplicate for their mean values.

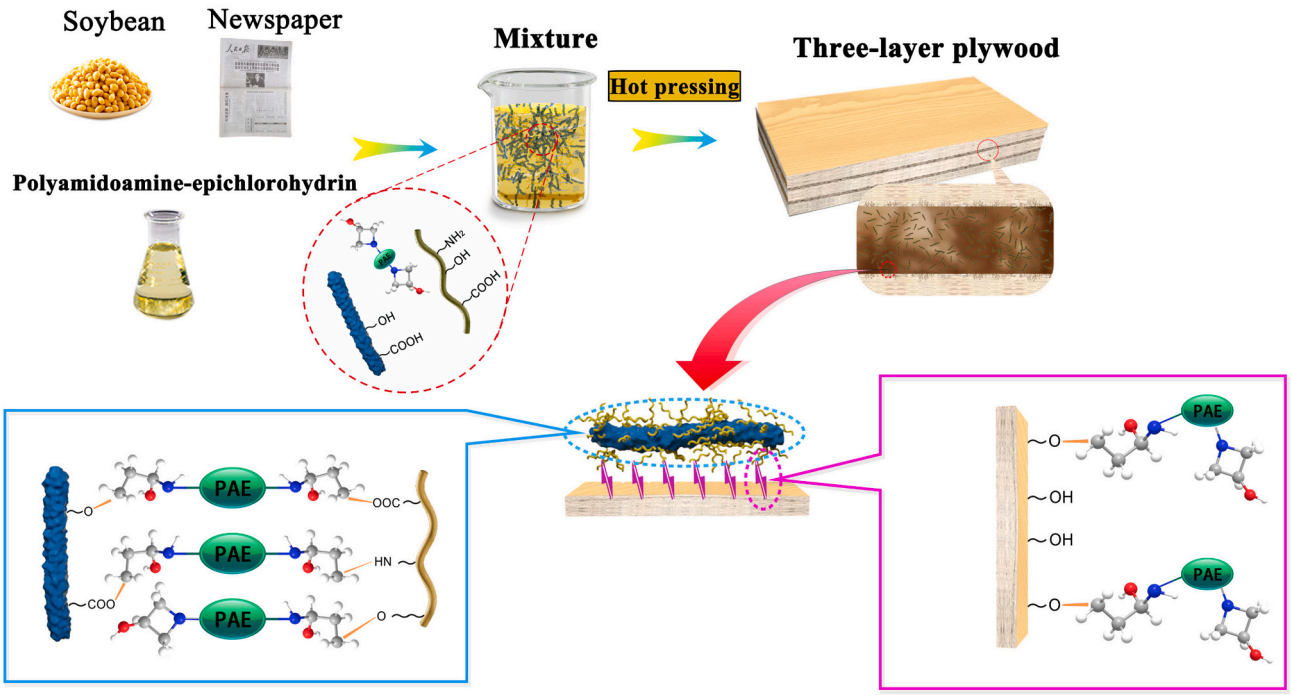

Fig. 1. Schematic of possible reactions occurred in DSF-WNP resin (soybean based resin) during curing process. DSF, defatted soybean flour. WNP, waste newspaper.

2.8. Water absorption

The water absorption of the cured resin samples were investigated according to ASTM Standard D 570 [39] with minor modifications. The pre weighed (m_1) cured resin was immersed in distilled water at a ratio of 1:20 (e.g. the cured resin 1 g and distilled water 20 g) in a glass bottle and kept in a controlled environment of 25 °C for 24 h. After removal from the water, the cured resin samples were transferred into two pieces of paper towel to remove extra moisture on the surface of the samples, and then were weighed again (m_2). The water absorption of the cured resin samples was calculated as shown in equation (1):

$$\text{Water absorption} = (m_2 - m_1)/m_1 \times 100\% \quad (1)$$

The results are presented as the mean of three replicates.

2.9. Sol-gel test

The cured DSF-WNP resin samples were pulverized and sieved, and a 250–420 μm granulometric sieve fraction was collected. After storage at 20 ± 1 °C and 70% RH for 24 h, 1 g (m_1) of cured resin sample was placed in a glass bottle containing 100 g of deionized water, and the bottle was screwed tightly and placed into a boiling water bath for 3 h. The treated adhesive sample was filtered through a weighed G3 sintered glass filter (m_2) and washed with 100 g deionized water. The G3 sintered glass filter with sample was then placed in a drying oven at 105 °C for 24 h and the weight (m_3) was noted. The insoluble fractions in cured resin were calculated by the following equation (2):

$$\text{Insol fraction} = (m_3 - m_2)/m_1 \times 100\% \quad (2)$$

All measurements were performed three replicates for their average values.

2.10. Tensile strength

The tensile strength of cured DSF-WNP resin samples were determined in accordance with the ASTM D638-14. The specimens (dog-bone shape) were tested for tensile strength using a tensile testing machine (MTS, Shenzhen, China) with a crosshead speed of 5.0 mm/min. Three specimens were tested for the tensile properties of each soybean based resin. The fractured specimens of the cured resins were sputter coated with gold under vacuum to get a good conductivity, and were further observed under a Nova NanoSEM 230 (Fei Czech Republic S.R.O., CS) to assess differences infracture surface morphology with the various resin samples.

2.11. Adhesiveness

The wet shear strength of the plywood was determined using the conditions and methods described by the Chinese National Standards GB/T 9846–2015 to evaluate the adhesiveness of DSF-WNP resin. A piece of plywood was cut into ten 10.0 cm × 2.5 cm specimens, which were soaked in 63 °C water for 3.0 h and then dried at room temperature for 10 min. After that, the specimens were tested in a tensile testing machine (MTS, Shenzhen, China) with a crosshead speed of 5.0 mm/min. Two replicates were used for each DSF-WNP resin.

3. Results and discussion

Soybean protein and carbohydrates are two main polymeric components in DSF. The major reactive functional groups in soybean protein include carboxylic acid groups (-COOH), amino groups (-NH_2), mercapto groups (-SH), and hydroxyl groups (-OH). Carbohydrates contain an amount of –OH groups, as well as the cellulosic fiber from WNP and wood veneer. PAE resin is a commercial paper wet-strength resin that contains hydroxyl-azetidinium ring groups [19]. During the curing process, the existing hydroxy-azetidinium groups in the PAE resin can react with the functional groups in biomass components of soybean and WNP. The reactions are expected to form three-dimensional crosslinked networks to enhance the wet-cohesion of the cured adhesive [38]. The reactions between hydroxy-azetidinium and hydroxyl groups in cellulosic fiber of wood veneer would lead to an improved shear strength of plywood composites as well. A possible pathway is shown schematically in Fig. 1.

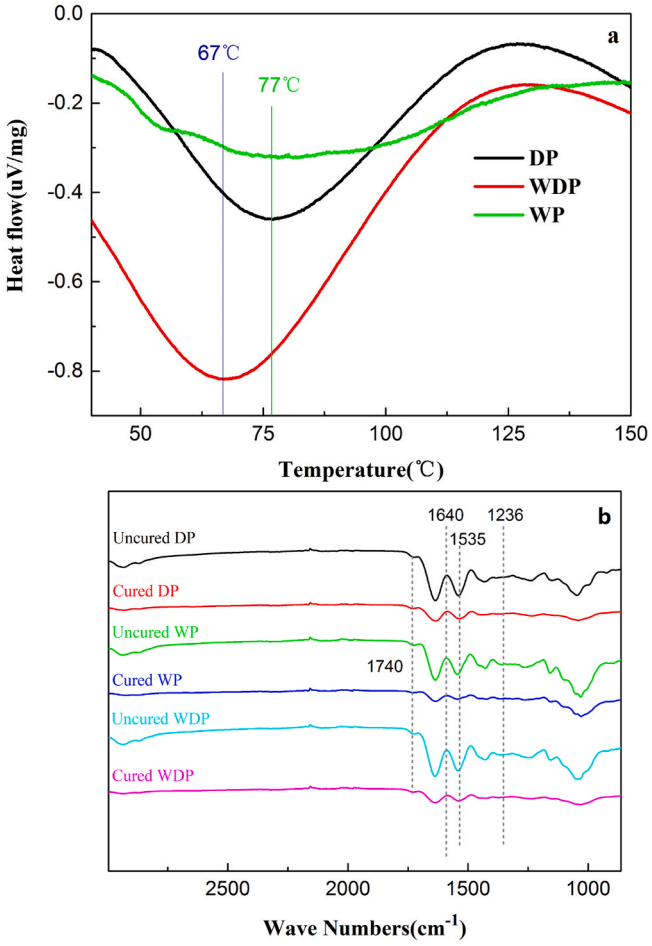

Fig. 2. DSC curves (a) and FTIR spectra (b) of the resins. DP: The adhesive sample consisted of DSF and PAE. WDP: The adhesive sample consisted of WNP, DSF, and PAE. WP: The adhesive sample consisted of WNP and PAE. WNP, waste newspaper powder. DSF, defatted soybean flour. PAE, polyamidoamine-epichlorohydrin.

3.1. Curing temperature and chemical reactions of soybean based resins

To determine if DSF-WNP resins could be processed under the temperature (e.g., 130 °C) used in commercial plywood manufacturing [40], DSC for the uncured resin samples was performed (Fig. 2i). It is apparent that all the resin samples displayed maximal rate of heat flow (T_{max}), which was lower than 80 °C. The T_{max} of DSF-WNP resin was lower than that of pure DSF resin. The heat flow temperature measured indicated that the combination of WNP with soybean resin accelerates the curing process of the DSF-WNP resin (Fig. 2i), completed at 129.7 °C. The results suggest that the curing of the DSF-WNP resin occurs under temperatures amenable to commercial plywood production, particularly since we anticipated an increase in reaction rate to promote energy savings during plywood manufacture.

FTIR was employed to analyze whether resin cure involved chemical reactions between PAE and WNP or DSF as proposed (Fig. 2ii). The absorption band at 1740 cm^{-1} due to the C═O stretching vibration of ester bonds was detected in both un-cured and cured DSF-WNP resins, but an increase of intensity was observed in the latter as a result of the formation of new ester linkages as shown in chemical bond **i** of Fig. 1. This change was also observed in ether (C–O) stretching as shown in chemical bond **ii** of Fig. 1. The common peaks at wave numbers of 1650 cm^{-1}, 1550 cm^{-1} and 1390 cm^{-1} were corresponding to amide I (C═O stretching), II (N–H bending) and III (C–N stretching), respectively. As shown in the spectrum of the cured resin without DSF, the heating process did not result in new amide (–NH–) bending at 1550 cm^{-1} due to no amide groups in WNP. While it was also hard to detect the detailed amide bending change in absorption peaks between un-cured and cured resins containing DSF because of the large amount of amide II structure in soybean protein, the increased intensity of amide II in cured resins with DSF components may be ascribed to the result of the chemical bond **iii** of Fig. 1. Even though the complicated components of the resins precludes the use of methods that would allow for better characterization of its chemical reactions during the curing process, DSC of the resins indicated that curing can be completed at 130 °C. In summary, the analysis indicates that DSF-WNP resin is efficiently cured using heat at conventional temperatures for woody composites such as plywood manufacture.

3.2. Effect of WNP particle sizes and ink contents on soybean based resins

Fig. 3a shows that the wet shear strength of all samples increased first and then decreased as the WNP particle size decreased. In particular, the adhesive with a WNP particle size range from 120 μm to 250 μm gave a shear strength higher than 1.0 MPa, which exceeds the requirement of the Chinese National Standards GB/T 9846–2015(≥0.8 MPa). It is possible that the small particle sizes of WNP may enhance the aggregation with a huge number of hydrogen bonds, which may lead to its poor dispersion during the adhesive preparation process and hence give

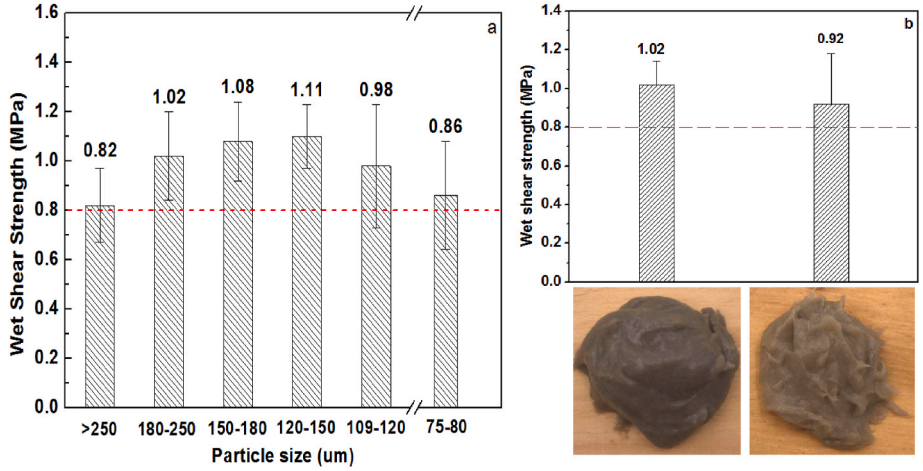

Fig. 3. Effect of particle sizes (a) and ink (b) of WNP on wet shear strength. WNP, waste newspaper. Plywood samples were hot pressed at 1.0 MPa/130 °C for 3.0 min.

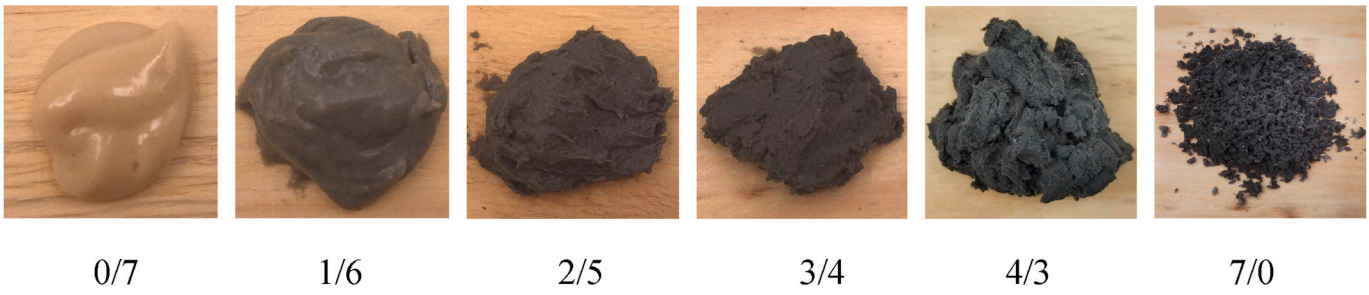

Fig. 4. Appearance of soybean based resins with different WNP/DSF dry weight ratio. DSF, defatted soybean flour. WNP, waste newspaper powder.

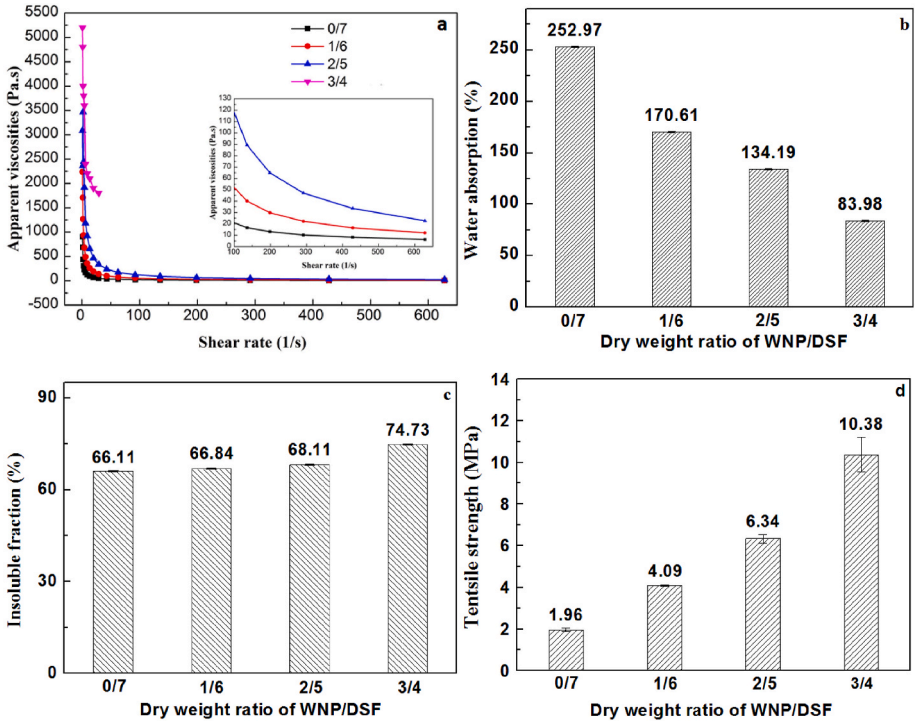

Fig. 5. Viscosity (a), water absorption (b), insoluble fraction (c), and tensile strength (d) of DSF-WNP resins. 0/7, 1/6, 2/5, or 3/4 represented dry weight ratio of WNP/DSF in different DSF-WNP resins. DSF, defatted soybean flour. WNP, waste newspaper.

rise to detrimental properties of final composites [41,42]. It is apparent that WNP with particle sizes ranging from 120 μm to 250 μm were suitable for DSF-WNP resins. A comparison of resin formulations with and without ink shows that the resins with ink displayed a better glossy surface or operability than the de-ink counterpart (Fig. 3b). A similar result was observed in adhesiveness when the resins were used in a plywood application. This means that the graphite containing ink might act as a lubricant in the resin, thus lowering its viscosity. This suggests that WNP could be used directly without pretreatment, e.g., de-ink, in DSF-WNP resins.

3.3. Effort of WNP concentration on soybean based resins

WNP and DSF were combined and subjected to varying dry weight ratios of 0/7, 1/6, 2/5, 3/4, 4/3 and 7/0. The results showed that a higher proportion of the WNP resulted in poor dispersion of the resin (Fig. 4). The combinations of 4/3 or 7/0 dry weight ratio of WNP/DSF resulted in a wet crumbly solid at room temperature that was hard to disperse evenly across the wood surface. This may be attributed to the change in the viscosity, wet-cohesion and adhesiveness of the DSF-WNP resins with different dry weight ratios of WNP/DSF lower than 3/4, which are discussed in the following sections.

3.3.1. Viscosity

The viscosity of a resin has a significant impact on its spreading, operability and penetration into the internal structure of wood. As shown in Fig. 5a, the apparent viscosity of the DSF-WNP resins sharply increase with an increase in WNP content. This may be due to the water swelling of cellulosic fibers in the WNP causing the entanglement with one another, which in turn increases their viscosity [43]. All resin samples displayed shear thinning behavior, i.e. the apparent viscosity of the resin samples decreased with the increase of the shear rate. This phenomenon will benefit the practical application of DSF-WNP resin as a wood adhesive, because the adhesives are applied by adhesive spreaders (rolls with fast rotational speed) and its low viscosity will readily penetrate into wood and facilitate the formation of cured adhesive-wood mechanical interlocking, which greatly improved mechanical properties of the final woody composites. However, the shear thinning behavior was not applicable for the resin with WNP/DSF dry weight ratio of 3/4 at a shear rate of 43 s^{-1} and beyond, because of the high viscosity, indicating that the resin should not have a WNP/DSF dry weight ratio higher than 3/4 when used as a wood adhesive. This is because the high viscosity of adhesive may restrict its practical application, due to issues relating to spreading and flowing processes.

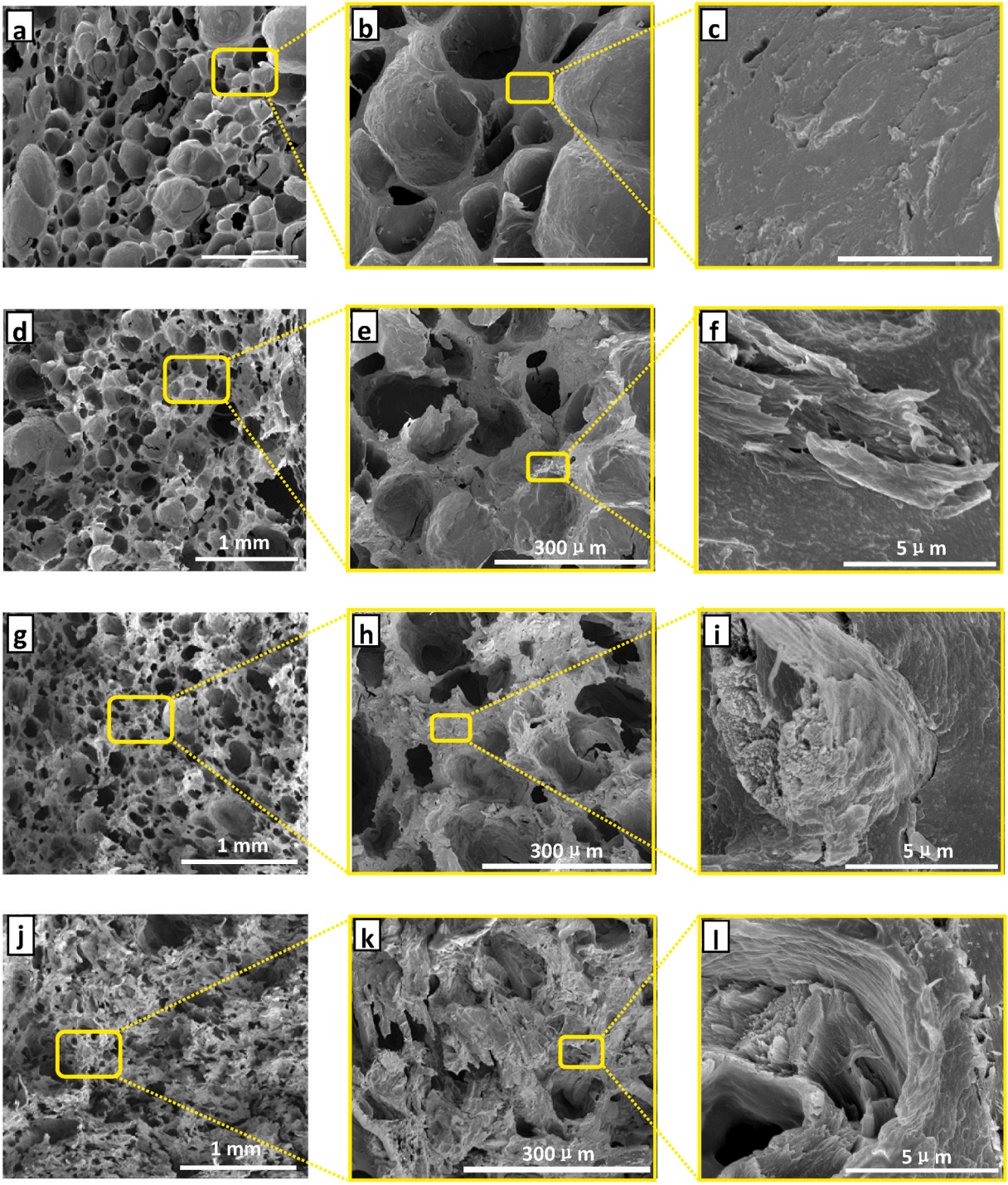

Fig. 6. SEM of cured soybean based resins with different WNP/DSF dry weight ratio. (a–c) 0/7, (d–f) 1/6, (g–i) 2/5, and (j–l) 3/4.

3.3.2. *Wet-cohesion*

It is well known that good wet-cohesion in a cured resin is a key factor in promoting excellent water resistance in a wooden composite. Generally, low water absorption can be correlated with less hydrophilic groups (e.g., –OH) in the cured resins, which can lead to an improved water resistance of resulting composites [44]. It is evident that the cured DSF-WNP resins displayed decreasing levels of water absorption as the amount of WNP was increased (Fig. 5b). This may be due to the consumption of hydrophilic groups in DSF and WNP components. For example, the hydroxyl groups in WNP and DSF could react with hydroxy-azetidinium groups in the PAE, resulting in the decreased water absorption.

The sol-gel test was carried out to determine the insoluble fraction in the cured DSF-WNP resins, because the insoluble fraction represents cross-linking or the existence of a three-dimensional (3D) structure, which is essential for the durability of the final composites [45]. The ground cured resin sample was size-fractionated to obtain sample particle sizes within a 250–420 μm range for the sol-gel test. It was found that WNP increased the insoluble fraction content of the cured DSF-WNP resins (Fig. 5c). This result indicated that WNP participated in cross-linking reactions during the resin curing process, which resulted in the formation of 3D cross-linked networks which would significantly

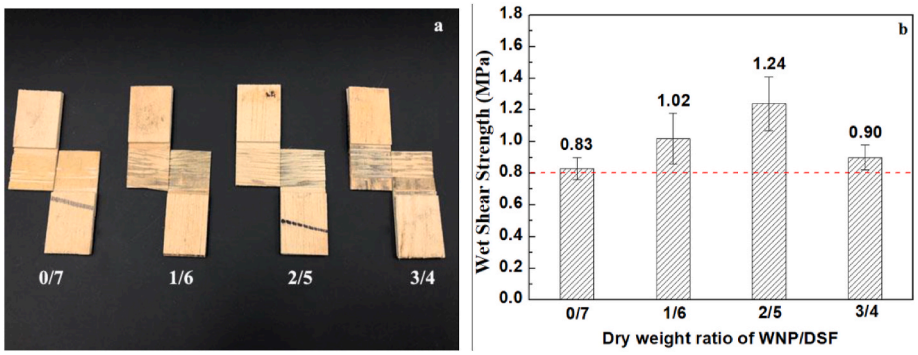

Fig. 7. Plywood samples (a) and its wet shear strength (b). 0/7, 1/6, 2/5, or 3/4 represented dry weight ratio of WNP/DSF in different DSF-WNP resins. DSF, defatted soybean flour. WNP, waste newspaper. Plywood samples were hot pressed at 1.0 MPa/130 °C for 3.0 min.

improve durability (e.g., water resistance) [45].

Further tests on the tensile strength of the cured resins by casting the adhesive samples in a dog-bone shape Teflon mold showed that the tensile strength increased from 1.96 to 10.38 MPa when the dry weight ratio of WNP/DSF in the cured DSF-WNP resins was increased from 0/7 to 3/4 (Fig. 5d). Although there is not too much of a difference in the insoluble fraction of the cured resins, there were significant decreases in water absorption and increases in tensile strength of DSF-WNP. This is ascribed to the increased WNP components, resulting in a greater crosslinking density in the cured resins. These can also be confirmed from SEM analysis on the fracture surfaces of cured resin samples after tensile strength testing (Fig. 6). It can be seen that cured resins with a high WNP content were morphologically different from those with lower WNP concentrations (Fig. 6(a, d, g, and j)). The former were comparatively rough, and displayed compact structures, while the latter were crumbly and brittle, and also showed high degrees of porosity. These results indicated that WNP facilitated the cohesion of the cured DSF-WNP resins, which can be attributed to good interfacial adhesion as a result of both WNP and DSF being cross-linked by the PAE resin (Fig. 6(f, i, and l)). The results indicate that DSF-WNP resins with high WNP contents might potentially be used as environmentally friendly resin systems for reinforced composites via a mold pressing approach; this concept will be assessed in future work.

3.3.3. Adhesiveness

To investigate the adhesiveness of DSF-WNP resins as adhesives, three-ply plywood was prepared using the resins and *Pinus massoniana* veneer. The bonding strength of developed adhesives was determined by testing wet shear strength of plywood subjected to a 63 °C water soaking pretreatment. All the plywood samples showed wood failure after testing, but the plywood bonded with DSF-WNP adhesives displayed a significant increase in wood failure area (Fig. 7a), indicating that the cohesive strength of cured DSF-WNP adhesives was higher than *Pinus massoniana* wood veneer. The wet shear strength of the plywood bonded with different WNP contents all met the requirement of the Chinese National Standards GB/T 9846–2015 (Fig. 7b). Wet shear strength of plywood increased as WNP content was increased and then decreased at WNP/DSF dry weight ratio beyond 2/5. This lowered strength may be attributed to poor interlocking with the pore structure of the wood. Even though the adhesives with high WNP/DSF dry weight ratios (e.g., 3/4) had the highest cohesive strength (Fig. 5d), the viscosity was significantly increased (Fig. 5a), leading to difficulties in spreading, flow, and penetration into the pore structure of the wood to form the cured adhesive-wood mechanical interlocking [45]. Hence, the DSF-WNP resin with 2/5 of WNP/DSF dry weight ratio was suitable for in-lab wood composite processing.

3.4. Exploring energy saving approach for preparing woody composites

The DSF-WNP resin with a WNP/DSF ratio of 2/5 exhibited excellent properties, which were obtained using the adhesive curing process currently used in the industrial manufacturing of plywood. In an effort to reduce the energy input required for plywood manufacture, we next tested if our current resin curing process could be further optimized by changing pressing temperature and time to reduce energy usage. We observed that the wet shear strength of plywood still met the requirement of GB/T 9846–2015 when lowering curing temperature to 100 °C for 3.0 min or to 85 °C for 15.0 min (Fig. 8). In spite of there being a reduction in the mechanical strength of woody composites, the savings in energy obtained with decreased pressing temperature were significant. The results indicated that we can extend the pressing time with lowered temperature for production plywood composite to obtain

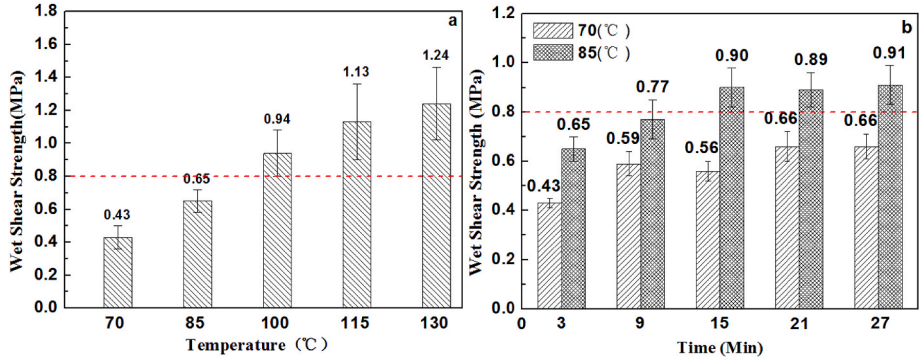

Fig. 8. Effect of pressing temperature (a, with pressure 1.0 MPa for 3.0 min) and time (b, with pressure 1.0 MPa) on wet shear strength of plywood. Soybean based resins, WNP/DSF and (WNP + DSF)/PAE dry weight ratio were of 2/5 and 7/1, respectively. WNP, waste newspaper powder. DSF, defatted soybean flour. PAE, polyamidoamine-epichlorohydrin.

excellent mechanical properties. Particularly, the resin might have the potential for use as an adhesive for thick (i.e., ≥10 cm) wood composites production, because the adhesive in the core area of a thick composite would readily reached the required curing temperature than its conventional counterpart (e.g., formaldehyde-based adhesives).

4. Conclusions

The present study has discussed a 'green' soybean based resin consisting of WNP and DSF, both of which are derived from renewable resources, crosslinked with polyamidoamine-epichlorohydrin *via* ester, ether and amide bonds. WNP with ink and particle sizes range from 120 μm to 250 μm were suitable for DSF-WNP resins. The resin with optimized 2/5 of dry weight ratio WNP/DSF exhibited excellent properties. The DSF-WNP resin could be cured at a lower temperature than those currently used in the industrial manufacturing of plywood, and displayed improved mechanical properties and higher resistance to the effects of water. Similar reactions could also be utilized to crosslink other vegetable proteins with waste newspaper products. This green, easy and low cost technology could be useful in making inexpensive bio-based resins from low content waste newspaper for potential thick woody composites or making cellulosic fiber reinforced composites with high content waste newspaper for biodegradable material applications.

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