Article

A Novel Environment-Friendly Adhesive Based on Recycling of *Broussonetia papyrifera* Leaf Forestry Waste Protein

Cheng Li ¹, Yang Tang ¹, Yujie Wang ¹, Xiaoyu Yuan ^{2,*} , Bengang Zhang ^{3,*}, Zhigang Wu ^{4,*} and Huafeng Tian ⁵

¹ College of Forestry, Henan Agricultural University, Zhengzhou 450002, China; licheng@henau.edu.cn (C.L.); tangy1125@163.com (Y.T.); wangyujie25141026@163.com (Y.W.)

² College of Food Science and Technology, Henan Agricultural University, Zhengzhou 450002, China

³ IUT-LERMAB, University of Lorraine, 88000 Epinal, France

⁴ College of Forestry, Guizhou University, Guiyang 550025, China

⁵ Beijing Key Laboratory of Quality Evaluation Technology for Hygiene and Safety of Plastics, College of Chemistry and Materials Engineering, Beijing Technology and Business University, Beijing 100048, China; tianhuafeng@th.btbu.edu.cn

* Correspondence: yuanxyscience@henau.edu.cn (X.Y.); zbg18082968142@163.com (B.Z.); wzhang9@163.com (Z.W.)

Abstract: Wood adhesive was prepared using *Broussonetia papyrifera* waste leaf protein as the raw material. The performance of the *B. papyrifera* leaf protein adhesive compared to soy protein was investigated using X-ray diffraction, Fourier transform infrared spectroscopy, and differential scanning calorimetry. The results indicated that both *B. papyrifera* leaf protein and soy protein were spherical proteins that could easily form three-dimensional crosslinked network structures and were of potential for protein adhesive preparation. The *B. papyrifera* leaf and soy protein-based adhesives had similar curing behaviors, but the crosslinking reaction of *B. papyrifera* leaf protein-based adhesive seems to be more complex than that of the soy protein-based adhesive. The *B. papyrifera* leaf protein-based adhesive had a lower increasing trend of particle size and crystallinity than the soy-based protein adhesive, and its water resistance and bonding strength were also weaker. The plywood with BP leaf protein adhesive had dry and wet shear strengths of 0.93 MPa and 0.59 MPa, respectively. These results are promising for future industrial production using *Broussonetia papyrifera* waste leaf protein as a new protein wood adhesive in the wood industry.

Keywords: *Broussonetia papyrifera*; leaf protein; bio-based adhesive; curing properties; bonding performance

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1. Introduction

Research into the sustainable utilization of renewable resources is important due to increasing anthropogenic activities causing global environmental changes such as climate change and pollution. In the wood industry, great focus has been put on the production and use of ecofriendly wood adhesives based on forest and agricultural resources [1–4]. Biomass materials, such as protein, starch, tannin, and lignin are commonly employed in the manufacture of wood adhesives [5–8]. The application of protein adhesives has a long history, and they are classified as animal or plant protein adhesives based on their raw material sources [9,10]. Although the latter has a late start in research, it has been studied most recently. Outshining other plant protein adhesives, partial soy protein adhesive has realized industrial production, but it is mainly applied in the preparation of plywood [11–14]. Soy protein will always belong to a grain resource. The use of agricultural raw materials in the manufacturing of wood adhesives on a large scale has a detrimental impact on food security, a practice the United Nations' Food and Agriculture Organization (FAO) opposes. As a result, conducting the study of a new type of protein-based wood adhesive based on agricultural and forestry waste material would be critical in reducing reliance on soybean protein, lowering manufacturing costs, and increasing competitiveness in the market of protein-based adhesives.

In recent years, studies about using non-crop proteins to prepare wood adhesives have begun to take shape. The study results of Lestari et al. [15] indicated that *Jatropha curcas* L. cake protein had considerable potential in aspects of foaming and wood adhesives. Lestari et al. [15] used *Jatropha curcas* L. cake protein to prepare a wood adhesive used for plywood. Roy et al. [16] have proven that spiral seaweed protein is feasible when used to prepare wood adhesives. *B. papyrifera* from the Moraceae family has the advantages of rapid growth, wide distribution, easy proliferation, and a short rotation. The *B. papyrifera* leaf is abundant in protein, with a crude protein concentration of up to 30% [17,18]. *B. papyrifera* leaf protein was used to prepare a protein wood adhesive, and its properties were studied in this paper. This study could highlight the efficient utilization of *B. papyrifera* leaf forestry waste protein, as well as expand the application fields of *B. papyrifera* protein.

2. Materials and Methods

2.1. Materials

B. papyrifera powder (BP) and defatted soy flour (DS) with a protein content of 30% and 53.4%, respectively, were from Yuxin Soybean Protein Co., Ltd. (Bingzhou, China). All of the other chemical reagents utilized in this study were analytical reagent grade. For the manufacture of plywood, a poplar veneer of thickness 1.5 mm and moisture content between 8% and 10% was procured from Qunyou Wood Co., Ltd., Suzhou, China. A commercial epoxy resin of E-44 was used as crosslinker for preparing the protein adhesives. For the E44, the epoxide number was 0.41–0.47 and softening point was 12–20 °C.

2.2. Preparation of Protein-Based Adhesive

Protein-based adhesives were manufactured using the following procedure [3]: a three-neck round-bottom flask with a thermometer, condenser, and mechanical stirrer was filled with 320 parts water. The protein powder was then added in 80 parts to the swiftly stirring solution. Then, 21.3 parts of 30% sodium hydroxide solution were introduced after the slurry was heated to 45 °C. After 30 min of stirring, 20 parts of a 40% urea solution was introduced and stirred for another 20 min. In an ice bath, the slurry was cooled to room temperature. Protein-based adhesive with a $24 \pm 1\%$ protein content was obtained. Before the preparation of three-layer plywood, *B. papyrifera* leaf or soy protein-based adhesives were thoroughly combined with E44 epoxy resin. The pH value was 9–10 for all adhesives.

2.3. Plywood Production with Protein-Based Adhesives and the Shearing Strength Test

Three-layer plywood (400 mm × 400 mm × 4 mm) was produced using protein-based adhesives. Veneers with double-sided adhesive loading of 300 g/m² were used to prepare plywood and were allowed to rest at room temperature for 15 min to 20 min. The plywood samples were obtained by pressing the assembled veneers under 1.0 MPa at 160 °C for 6 min in an XLB-type single-layer hot press from Shanghai Rubber Machinery Plant (Shanghai, China). The plywood was conditioned in the laboratory for 1 day at 20 ± 2 °C and relative humidity of $65 \pm 5\%$ before cutting into shear specimens of 100 mm × 25 mm. The wet shear strength of the plywood was tested using the China National Standard GB/T 9846.3 [19]. Before testing, specimens were submerged in water for 3 h at 63 °C and afterward exposed to ambient conditions for 10 min. The shear strength of the plywood specimens was tested using a WDS-50 KN mechanical testing machine (Shenzhen Sansi technology Co., Ltd., Shenzhen, China). The dry and wet shear strengths were calculated using the average results of 8 to 10 specimens.

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

A pill was prepared by thoroughly mixing 0.001 g of BP or DS protein powder with 1 g KBr. A Varian 1000 infrared spectrophotometer (Varian Inc., Palo Alto, CA, USA) was used to examine the pill with a resolution of 4 cm^{−1} in the range of 400 cm^{−1} to 4000 cm^{−1} using 32 scans.

2.5. Differential Scanning Calorimetry (DSC)

Curing degree calculation: The curing peak on the DSC curve was integrated and plotted with curing time and integral area as the X- and Y-coordinates, respectively, to obtain the curing degree curve chart of the protein adhesive at various heating rates.

Kissinger equation [20] for calculating apparent activation energy, reaction order, and reaction frequency factor is shown in Equation (1):

$$-\ln(\beta/T_p^2) = E_a/RT_p - \ln AR/E_a \quad (1)$$

where β is the heating rate ($\text{K} \cdot \text{min}^{-1}$), T_p is the peak curing temperature (K), E is the apparent activation energy ($\text{J} \cdot \text{mol}^{-1}$), A is the pre-exponential factor (s^{-1}), and R is the general gas constant ($8.314 \text{ J} \cdot \text{min}^{-1} \cdot \text{K}^{-1}$).

The Kissinger equation expresses the relationships of curing apparent activation energy with heating rate and peak temperature on the thermal analysis curve as $\frac{d \ln(\beta/T_p^2)}{d(T_p^{-1})} = -\frac{E}{R}$.

A straight line was plotted using $\ln(\beta/T_p^2)$ vs. $1/T_p$ at various heating rates (5, 10, 15 and 20 K/min), and the line slope was employed to compute the apparent activation energy E of the curing reaction using Equation (2):

$$E_a = -KR \quad (2)$$

2.6. Contact Angle

A clean poplar veneer was coated with a certain amount of protein-based adhesive. The microscope lens and camera (JC2000A) static drop contact angle measuring instrument (Shanghai Zhongchen Company, Shanghai, China) was used to capture a picture of a droplet. The photo was taken 1 s after the droplet dropped on the wood surface and the contact angle was obtained.

2.7. Particle Size of Adhesive

A 1 g sample of the protein adhesive was added to 60 g distilled water, and the insoluble substances were removed by centrifugation. Particle size was measured on a Zetasizer Nanoparticle size instrument (Malvern Instruments, Malvern, UK).

2.8. X-ray Diffraction (XRD)

An XRD (Hitachi, Ltd., Tokyo, Japan) with Cu K α radiation (Cu K α , $\lambda = 1.5406 \text{ \AA}$) at a scanning speed of $6^\circ/\text{min}$ and a temperature range of 5 to 80°C was used to determine the crystalline structures of the adhesives.

3. Results and Discussion

3.1. FT-IR Analysis

Spherical proteins and linear proteins are two types of protein molecules; the former can easily create special crosslinked network structures, hence spherical protein-based adhesives exhibit a high bonding performance [21,22]. Figure 1 shows the FT-IR spectra of BP leaf and DS proteins. Most natural proteins have spherical protein structures, and soy protein is typically a spherical protein [23]. Figure 1 shows that an asymmetric stretching vibration absorption peak of methylene $-\text{CH}_2$ appeared near 2926 cm^{-1} , near 1648 cm^{-1} was an amide I band $-\text{C}=\text{O}$ stretching vibration absorption peak, near 1550 cm^{-1} was an in-plane flexural vibration absorption peak of amide II band $-\text{N}-\text{H}$, near 1244 cm^{-1} was a C-N stretching vibration peak of amide III bands [24–26], near 1402 cm^{-1} was a symmetric flexural vibration peak of $-\text{C}-\text{H}$ bond, and at 1050 cm^{-1} were stretching vibration peaks of C-O and C-O-C. Several $-\text{NH}_2$ and $-\text{COOH}$ groups were found inside the protein, according to the FT-IR data. The FT-IR spectrograms of BP leaf protein and soy were almost the same, which indicated that BP leaf protein also belonged to the spherical protein group.

Figure 1. FT–IR spectra of BP protein and DS protein.

Degrading modification is a crucial step for the preparation of protein adhesives. In an alkaline solution, spherical protein molecules can be decomposed and loosened, exposing active groups and generating active sites for later crosslinking modification while increasing the possibility of forming intermolecular bonding during the adhesive curing process. Studies indicate that a specific secondary structure must be retained to ensure that soy protein adhesive has high cohesion strength [27,28]. Therefore, the degradation process not only needs to ensure that protein active groups should be effectively exposed to have high reactivity but also needs to ensure that the protein has good mobility and the major structure of the protein macromolecule will not be excessively damaged after treatment at high cohesion strength and with strong operating testing.

3.2. DSC Analysis

Figure 2 shows the DSC curves of BP leaf and DS protein adhesives at various heating rates. The two protein adhesives present similar curing features on the DSC curves with single exothermic peaks. The initial curing temperature (T_i), peak temperature (T_p), and termination temperature (T_f) all increased correspondingly as the heating rates increased, and the curing temperature range was widened, reducing curing time. The heat generated within unit time was largely due to the heating rate increase, resulting in a high temperature differential, as well as the exothermic peak of the curing process moving to a higher temperature. The curing temperatures of the protein-based adhesives increased with the heating rate, however, the change in the BP protein adhesive was less than the DS protein adhesive as the heating rate had a minimal effect on the BP leaf protein adhesive's curing temperature.

Curing reaction degree is an important method for measuring the curing and crosslinking reactions [29]. According to Figure 3, the times needed for the curing reaction of BP and DS protein adhesives were 20, 11.5, 8 and 6 min at heating rates of 5, 10, 15 and 20 °C/min, respectively, which indicated that the time required to obtain the same degree of curing decreased as the heating rate increased, or that the crosslinking reaction accelerated. At the heating rates of 5, 10 and 15 °C/min, the cross-linking reaction degree of the BP protein adhesive was slightly less than that of DS protein adhesive. The cross-linking reaction degree of the BP protein adhesive was clearly greater than the DS protein adhesive at the heating rate of 20 °C/min. The changing trend of crosslinking reaction degrees of the two protein adhesives at varied heating rates was related to their protein reactivity.

Figure 2. DSC curves at different heating rates of BP and DS protein adhesives.

Figure 3. Crosslinking degrees of BP and DS protein adhesives at different heating rates: (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min, and (d) 20 °C/min.

Apparent activation energy E_a , which includes apparent activation energies of two elementary reactions and complex reactions, embodies the difficulty level of the crosslinking reaction degree of this system. The E_a of the crosslinking reactions of BP leaf and DS protein adhesives were calculated based on DSC results in reference to the Kissinger equation [20], which were 115.41 and 84.26 kJ/mol, respectively (Table 1). This indicates that it was more difficult for the BP leaf protein adhesive to experience a crosslinking reaction than the DS protein adhesive.

Table 1. DSC result parameters.

Adhesives	Heating Rate (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)	E_a (kJ/mol)
BP protein adhesive	5	97.2	108.1	121.0	115.41
	10	96.9	113.5	131.2	
	15	99.2	118.3	138.7	
	20	100.1	122.3	144.1	
DS protein adhesive	5	94.1	109.6	124.1	84.26
	10	97.3	114.5	132.1	
	15	98.3	119.5	140.5	
	20	100.4	128.4	153.9	

3.3. Contact Angle Analysis

Figure 4 shows the contact angles of the BP leaf protein adhesive and the DS protein adhesive. The images in Figure 4 show that the contact angle of the un-crosslinked BP leaf protein was small, 17.3° , and it increased to 27.8° after crosslinking, an improvement of 60.7%. The contact angle of the DS protein increased from 19.0° to 42.3° , an improvement of 122.6%. Before crosslinking, the contact angles of both protein adhesives were very small, due to a great number of polar groups being generated in the post-degraded protein, which had strong compatibility with the hydroxyl groups in wood cellulose so that the contact angle was small [30,31]. The contact angles of both protein adhesives were clearly enlarged after crosslinking, which indicated that the wettability of protein adhesives after crosslinking for wood became poor, because the crosslinking agent reacted with the degraded protein, and as a result, the quantity of polar groups, such as amino acids, was reduced. The increase of the contact angle of the BP leaf protein adhesive was less than the DS protein adhesive, which further certified that the reactivity of the BP leaf protein was inferior to that of soy protein.

Figure 4. Contact angles of BP protein (a,a') and DS protein (b,b') adhesive with or without crosslinker.

The contact angles of the BP protein adhesive and the DS protein adhesive were 27.8° and 42.3° , respectively, both of them were smaller than 90° , which indicated that contact angles of both protein adhesives were enlarged after crosslinking, but they still kept strong wettability with wood. In addition, an epoxy-type crosslinker was used in this study. Residual epoxy groups in the hot-pressing process can experience chemical reactions with hydroxyls such as lignin and cellulose, and the influence of formed chemical bonds on bonding strength was greater than that on wettability. Therefore, the bonding performance of protein adhesive after crosslinking will not become poor as the wettability degrades.

3.4. Particle Size Analysis

Figure 5 show particle size graphs of the BP leaf protein adhesive and the DS protein adhesive. The peaks of the particle sizes of the BP leaf protein and the DS protein before crosslinking were 452.2 nm and 463.7 nm, respectively, and the peaks after crosslinking became 889.2 nm and 1419 nm, respectively. The peaks of the particle sizes between the two adhesives before modification were not large, but they clearly increased after modification, and thus certified that molecular chains of the BP leaf protein and the DS protein were opened and extended with the help of NaOH, the crosslinker reacted with exposed polar groups, and as a result, molecular chains became long and particle size became large [32–36]. After crosslinking, the peaks of the particle sizes of the BP leaf protein adhesive were smaller than the DS protein adhesive, indicating that the BP leaf protein had a lower reactivity than the DS protein.

Figure 5. Premodification and postmodification of BP (a,a') and DS protein adhesives (b,b').

3.5. XRD Analysis

After the protein adhesives reacted with the crosslinker, the degree of crystallinity increased, as well as the cohesion strength and crosslinking density of the adhesives, which finally contributed to an improvement in the water resistance and bonding strength of the adhesives. The XRD curves of the BP leaf and DS protein adhesives are shown in Figure 6. Urea and protein have a crystalline structure; however, their reaction could cause the crystallinity to be lost partially or completely, resulting in a decrease in crystallinity and the formation of a totally different three-dimensional crosslinked network structure. According to Figure 6, the degree of crystallinity of the BP leaf protein adhesive was lower compared to the DS protein adhesive. The protein reacted with the crosslinker, increasing the hydrogen-bond interaction and acting force between the crosslinker and protein, and thus the adhesive's degree of crystallinity. The BP protein reactivity and its crystallinity improvement were lower compared to the DS protein.

Figure 6. XRD spectrum of BP and DS protein adhesives.

3.6. Shearing Strength

Figure 7 shows the results of the bonding performance of the BP leaf and soy protein adhesives. The plywood with the BP leaf and soy protein adhesives had dry shear strengths of 0.83 and 1.56 MPa, and wet shear strengths of 0.59 and 1.13 MPa, respectively. The cohesion strength and crosslinking density of the adhesives have a strong effect on their water resistance and bonding strength. Under a certain amount of crosslinker, the most likely factor that influenced the crosslinking density of adhesive was protein activity after degradation. Therefore, the poor activity of the BP leaf protein resulted in poor bonding performance. Nevertheless, this study lays a foundation for the development of novel protein-based adhesives by increasing raw material availability.

Figure 7. Bonding properties of BP protein adhesive and DS protein adhesive. Note: all dry wood failures were over 50% and those of BP protein adhesive were low. All wet wood failures were less than 30% and those of BP protein adhesive were low.

4. Conclusions

In this study, we found that both *B. papyrifera* leaf protein and soybean protein were spherical proteins that could easily form three-dimensional crosslinked network structures with the potential for protein adhesive preparation. *B. papyrifera* leaf and soy protein adhesives had comparable curing behaviors, and the heating rate influence on the curing temperature of *B. papyrifera* leaf protein adhesive was less compared to soy protein adhesive at the lower rates. The crosslinking activation energies of *B. papyrifera* leaf protein adhesive and soy protein adhesive were 115.41 and 84.26 kJ/mol, respectively, indicating that the crosslinking reactions of *B. papyrifera* leaf protein adhesive seem more complex than soy protein adhesive. After crosslinking, the contact angles of both protein adhesives were remarkably enlarged, their wettability with wood deteriorated, and the contact angle of *B. papyrifera* leaf protein adhesive improved less compared to soy protein adhesive. The *B. papyrifera* leaf protein adhesive showed good shearing strength and water resistance, which lays a solid foundation for raw material expansion for new protein-based adhesives.

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