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An Eco-Friendly Wood Adhesive from Alfalfa Leaf Protein

Bengang Zhang[1,2,#], Xuedong Xi[3,#], Zhigang Wu[1,*], Hong Lei[2,*], Lifen Li[1] and Meifen Tian[1]

[1]College of Forestry, Guizhou University, Guiyang, 550025, China
[2]Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, Southwest Forestry University, Kunming, 650224, China
[3]ENSTIB-LERMAB, University of Lorraine, Epinal, 88051, France
[*]Corresponding Authors: Zhigang Wu. Email: wzhigang9@163.com; Hong Lei. Email: lfxgirl@163.com
[#]The two authors contributed equally to this work
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Abstract: According to the preparation method commonly used for soy protein-based adhesives, alfalfa leaf protein was used as the raw material to prepare alfalfa leaf protein-based wood adhesive. Differential scanning calorimetry analyzer (DSC), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize properties of the alfalfa leaf protein-based adhesive in this paper. The results revealed the following: (1) Chemical compositions and chemical structures of the alfalfa leaf protein were basically identical with those of the soy protein, both belonging to spherical proteins with the basis and potential for protein adhesives preparation, and spatial cross-linked network structures would be easily formed. (2) Alfalfa leaf protein and soy protein adhesives had the similar curing behaviors, curing temperature of alfalfa leaf protein-based adhesive was relatively lower, and the heating rate had minor influence on curing temperature of alfalfa leaf protein-based adhesive. At different heating rates, change tendencies of curing reaction degrees of both the two adhesives were not totally the same. (3) Activation energy and reaction frequency factor of the alfalfa leaf protein-based adhesive were higher than those of soy protein-based adhesive, indicating that the curing reaction of the alfalfa leaf protein adhesive was more difficult than soy protein-based adhesive, thus the dry shear strength and water resistance of alfalfa protein-based adhesive were lower than those of soy protein-based adhesive. Dynamics models of curing reactions of alfalfa leaf protein-based adhesive and soy protein-based adhesive are $d\alpha/dt = 1.06 \times 10^{13} e^{-97370/RT}(1-\alpha)^{0.938}$ and $d\alpha/dt = 1.09 \times 10^{11} e^{-84260/RT}(1-\alpha)^{0.928}$ respectively. The results of this study will expand the selection of raw materials for protein-based wood adhesives.

Keywords: Alfalfa leaf protein; wood adhesive; curing properties; thermal performance

1 Introduction

With the increasing shortage of renewable resources and continuously enhanced environmental awareness among the public, the wood adhesive industry is more and more inclined to prepare formaldehyde-free, green and environmentally friendly wood adhesives using bio-based materials. Soybean protein has attracted high attention as a raw material to prepare environmentally friendly timber adhesives by virtue of many advantages such as abundant sources, high reactivity, etc. [1–9].

Synthetic resins including acrylate, polyvinyl acetate, isocyanate, amino resins, etc., are often selected as cross-linking agents of soybean protein-based adhesive to improve its bonding strength and water resistance. Jin selected acrylate-modified soybean protein-based adhesive, study results indicated that both bonding strength and water resistance were obviously improved, and performance of plywood could satisfy type II plywood requirements [10]. Taking urea as denaturing agent of soybean protein and PVAC as the cross-linking agent, Zeng et al. [11] modified soybean protein glue, and study results indicated that when soybean protein concentration was 13%, dry shear strength and water resistance of the prepared soybean protein-based adhesive modified using 11.1% PVAC were superior. Qi et al. [12] prepared soybean protein-based adhesive used for paper and tag using PVAC. Soybean protein-based plywood prepared by Zhang et al. [13] with pMDI taken as modifying agent of soybean protein adhesive reached national type II plywood requirements of China. Zhang [14] treated soybean protein using alkali and took sealed-type pMDI as cross-linking agent for soybean protein adhesive, and the prepared plywood could satisfy national type II plywood performance requirements and the adhesive had relatively long shelf life. Zheng [15] treated degreased soybean flours using urea and anhydride and improved water resistance of soybean protein-based adhesive by taking polymethylene polyphenyl polyisocyanate as the cross-linking agent. Qiu [16] treated soybean flours using isocyanate-modified alkali, and bonding strength of the plywood reached to 1.21 MPa.

Soybean protein-based wood adhesives outshines other biomass adhesives, there are many researches on soybean protein-based wood adhesives, and some of them have already realized industrialized production. However, as a grain resource, soybean protein will affect grain safety of human beings when excessively applied to wood adhesives preparation, and meanwhile, this is not advocated by Food and Agriculture Organizations of the United Nations (FAO). Therefore, developing new-type protein-based wood adhesives and reducing dependence on soybean protein will be of great importance to lower the cost of protein adhesives and improving market competitiveness of protein adhesives.

Researches regarding wood adhesives preparation using non-crop proteins have began to take shape in recent years. Dianika [17], Hamarneh [18] and Chi [19] used oil cake protein from *Jatropha curcas* L. seedto preparewood adhesives. Wu used oil cake protein from *Jatropha curcas* L. seed and rubber seed to prepare plywood together with plasmas [20]. Joseph [21] and Fan [22] used spiral seaweed protein to prepare wood adhesives. These non-crop plant proteins will not consume grains with broad sources of raw materials during the adhesive preparation process. As early as 1773, Ruline extracted plant leaf protein in the squeezed green leaf juice using heating fractional distillation method. At the beginning of World Wall II namely 1939, UK started producing leaf proteins from immature stems in a large scale in order to provide food, so green plants were the enormous resource treasury for leaf proteins. Green leaf is one of the cheapest paths to obtain proteins, and protein content is extremely abundant in plant leaves. Studies indicate that plant families rich in proteins including Moraceae, Asteraceae, Leguminosae, etc., protein contents of those are generally within 10–30%, and some can reach as high as above 50% [23–25].

Alfalfa is a Leguminosae herbal plant with leaf protein content reaching 67.6%, which is the new-type plant protein resource with the greatest potential, and the researches regarding it have attracted extensive attention. Alfalfa leaf protein was taken as the raw material in this paper to prepare alfalfa leaf protein-based adhesive and its related properties were analyzed in this work. On the one hand, this can extend the choices of protein-based wood adhesives, and on the other hand, it can provide a new path for comprehensive utilization of alfalfa—a kind of abundant plant resources.

2 Materials and Methods

2.1 Materials

The alfalfa leaf power with protein content of 55.0% and soy flour with protein content of 53.4% was from Yuxin Soybean Protein Co., Ltd., China. Other chemical reagents used in this work were all in analysis grade. Poplar veneer with a thickness of 1.5 mm and moisture content 8–10% were purchased for the preparation of plywood.

2.2 Preparation of Protein-Based Adhesive

In order to decrease viscosity of the protein adhesives, and open up the proteins structure so that to expose more reactive functional groups, the protein-based adhesives was prepared according to a method already reported work [26]: In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with 320 parts water. 80 parts soy flour or alfalfa leaf power was then charged to the rapidly stirring solution. The mixture was heated to 45°C and 21.3 parts 30% sodium hydroxide solution was added. After stirring for 30 min, 20 parts 40% urea solution was added and was stirred for 20 min. The mixture was cooled to room temperature in an ice bath. Protein-based adhesive with the content of 24 ± 1% were gotten.

Alfalfa leaf protein-based adhesive or soy protein-based adhesive was mixed well with modifier agent just before the preparation of three-layer plywood.

2.3 Preparation of Plywood with Protein-Based Adhesives and the Test of Shear Strength

The protein-based adhesives were used for the preparation of three-layer plywood with a dimension of 400 mm × 400 mm × 4 mm. During the preparation of plywood, the poplar veneers with double sides adhesive loading was 300 g/m^2 rested at room temperature for 15–20 min. The assembled veneers were then sent into a XLB type single-layer hot press from Shanghai Rubber Machinery Plant and pressed under a pressure of 1.0 MPa at 130°C for 4 min to get a plywood sample.

Before being cut into shear specimens with dimension of 100 mm × 25 mm, the plywood panel was conditioned at (20 ± 2)°C and with relative humidity (65 ± 5)% in the laboratory for 1 day. The bonded area of each specimen was 25 mm × 25 mm. A WDS-50KN mechanical testing machine was used to test dry shear strength of the plywood specimens making reference of Chinese national standard GB/T 9846.3–2004. The dry shear strength was from the mean result of 8–10 specimens.

2.4 Fourier Transform Infrared Spectroscopy (FT-IR)

0.001 g of alfalfa leaf power or soy flour was mixed well with 1 g KBr to prepare a pill. And then the pill was tested in a Varian 1000 infrared spectrophotometer USA within the range of 400–4000 cm^{-1} with a 4 cm^{-1} resolution using 32 scans.

2.5 Differential Scanning Calorimetry (DSC)

(1) Calculation of curing degree

Integration processing of curing peak on DSC curve is implemented, and curing time taken as X-coordinate and integral area as Y-coordinate, curing degree curve chart of the protein adhesive under different heating rates can be obtained (Fig. 1).

(2) Calculation of apparent activation energy, reaction order and reaction frequency factor

Kissinger equation [27]:

$$-ln\left(\beta/T_P{}^2\right) = E/RT_P - lnAR/E \tag{1}$$

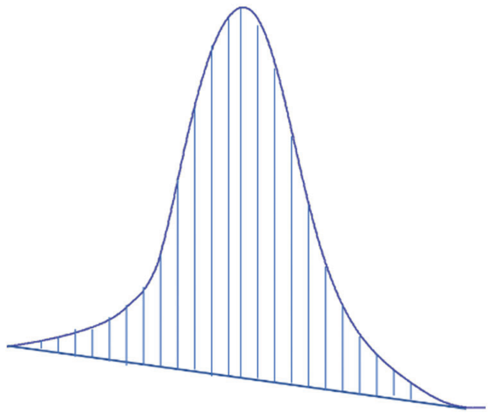

Figure 1: The curve of DSC integration

where: β—heating rate, K·min^{-1}; T_P—peak curing temperature, K; E—apparent activation energy, J·mol^{-1}; A—pre-exponential factor, s^{-1}; R—perfect gas constant, being 8.314J·min^{-1}·K^{-1}.

According to Kissinger equation, relations of curing apparent activation energy with peak temperature and enhancing rate on the thermal analysis curve can be expressed as $\frac{dln(\beta/T_P^2)}{d(Tp-1)} = -\frac{E}{R}$; under different heating rates β (5, 10, 15 and 20 K/min), a straight line is drawn using $ln(\beta/T_P^2)$ for $1/T_P$, and the fitted straight slope is used to calculate apaprent activation energy E of curing reaction:

$$E = -KR \tag{2}$$

Reaction frequency factor A is solved according to approximation formula of Kissinger equation:

$$A \approx \frac{\beta E exp(\frac{E}{RT_P})}{RT_P^2} \tag{3}$$

Crane equation [28]:

$$d(ln\beta)/d(T_P{}^{-1}) = -E/nR - 2T_P \tag{4}$$

where n—reaction order, and other are dittoed.

According to Crane equation, relations of curing reaction order with peak temperature and heating rate of the thermal analysis curve can be expressed as $\frac{d(ln\beta)}{d(Tp-1)} = -\frac{E}{nR} + 2Tp$; when $\frac{E}{nR}$ is far greater than $2T_P$, $2T_p$ can be neglected, and then: $\frac{d(ln\beta)}{d(Tp-1)} = -\frac{E}{nR}$. A straight line is drawn using $ln\beta$ for $1/T_P$, and the fitted straight slope is used to calculate curing reaction order n:

$$n = -E/(KR) \tag{5}$$

Curing dynamics model:

$$d\alpha/dt = Aexp(-E/RT)(1-\alpha)^n \tag{6}$$

2.6 X-Ray Diffraction (XRD)

The crystalline structures of alfalfa leaf protein-based adhesive and alfalfa protein-based adhesive were analyzed using an X-ray diffraction spectrometer (Hitachi, Ltd., Tokyo, Japan) with Cu Kα radiation (Cu Kα, λ = 1.5406 Å) at the range of 5~80°with a scanning speed of 6° min^{-1}.

3 Results and Discussion

3.1 Compositions and Structures Analysis of Protein

Protein molecules can be divided into spherical protein and linear protein from structural scale, the former can form spatial cross-linked network structures more easily, so d using spherical protein to prepare wood adhesives can have favorable bonding effect. FT-IR spectrograms of soybean protein and alfalfa leaf protein are shown in Fig. 2. Most of natural protein molecules are spherical structures, and soybean protein is typical spherical protein [29,30]. It can be known from Fig. 2 that FT-IR spectrograms of alfalfa leaf protein and soybean protein are basically identical, indicating that alfalfa leaf protein is also belong to spherical protein. Asymmetric stretching vibration absorption peak of methylene $-CH_2$ appears at 2,925.9 cm^{-1}, stretching vibration absorption peak of amide I band -C=O appears at 1,648.6 cm^{-1}, in-plane flexural vibration absorption peak (stretching vibration of C–N bond is approximate to flexural vibration frequency of N–H bond, and coupling vibration occurs) of amide II band-N-H appears at 1,549.4 cm^{-1}, at 1,243.9 cm^{-1} is stretching vibration peak of amide III band C-N, at 1,401.9 cm^{-1} is symmetric flexural vibration peak of –C–H bond, and at 1,049.8 cm^{-1} is stretching vibration peak of C–O and C-O-C.FT-IR test indicates that soybean protein and alfalfa leaf protein have significant $-NH_2$ and -COOH groups.

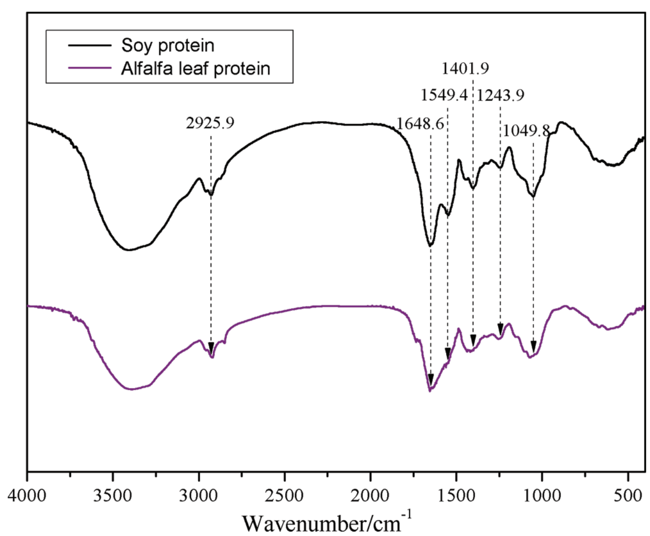

Figure 2: FT-IR spectra of alfalfa leaf protein and soy protein

Alfalfa protein and soybean protein contain nearly over 20 amino acids, and there are some active groups (like -COOH and $-NH_2$) at branches of amino acids or molecular chain ends, which can go through multiple chemical reactions. Hydrogen of amino can be replaced by alkyl and be alkylated, and carboxyl can conduct acylation and esterification reactions. In addition, carboxyl can also react with many metallic ions to form water-insoluble chelates (like Mg^{2+} and Ca^{2+}), so adding whitewash into protein adhesives can enhance water resistance of adhesives [31–33].

Besides the poor water resistance, protein adhesives also have high viscosity problem, thus most of protein-based adhesives are only applicable to plywood manufacturing. Spherical protein molecules can be further modified only after being degraded into chains to expose hydrophobic groups and active groups and generate active sites. Spherical protein molecules can be degraded and relaxed in an alkaline solution, thus making it possible for the follow-up modification and increasing the opportunity to form intermolecular bonding in the drying process [34–36]. Therefore, active groups of the protein exposed after degradation may have a certain influence on bonding performance.

Tab. 1 shows amino acid compositions of alfalfa leaf protein and soybean protein. According to Tab. 1, amino acid composition of alfalfa leaf protein is basically identical with that of soybean protein, but alfalfa leaf protein contains cystine and methionine (both contents are not high) which soybean protein does not contain. Lots of studies indicates that in order to ensure a certain strength of the soybean protein-based adhesive, a secondary structure of a certain degree must be retained. In addition, when applied to bonding of wood, protein adhesives realize bonding mainly by depending on hydrogen-bond interaction between protein molecules, and that between protein molecules and wood surface but not chemical bonding. Hence the realization of bonding performance has not much correlation with a single protein molecular structure [37–40]. Therefore, minor difference of amino acids will not exert much influence on bonding performance of the alfalfa leaf protein adhesive from a theoretical scale.

Table 1: Amino acids composition of *Alfalfa* leaf protein and soy protein

Amino acid	Content of amino acid	
	Alfalfa leaf protein (%)	Soy protein (%)
Threonine	5.01	3.66
Serine	4.26	5.43
Glutamic acid	11.44	20.25
Proline	5.45	5.24
Glycine	5.60	3.95
Alanine	7.09	3.85
Cystine	2.47	–
Valine	6.41	4.74
Methionine	1.40	–
Isoleucine	5.44	4.84
Leucine	10.39	7.61
Tyrosine	4.28	3.66
Phenylalanine	6.38	5.34
Lysine	5.56	6.03
Histidine	2.58	2.47
Arginine	6.45	7.71
Tryptophan	–	1.38
Aspartic acid	9.80	11.76
Methionine	–	1.09
Cysteine	–	0.99

3.2 Curing Characteristic Analysis

DSC measures relations with temperature and heat flux related to thermal transformation in the material, it is usually used to study the curing behavior and curing performance of soybean protein-based adhesives, and the results are related to heating rate.

Fig. 3 shows DSC curves of alfalfa leaf protein-based adhesive and soybean protein-based adhesive under different heating rates (5 K/min, 10 K/min, 15 K/min and 20 K/min), and Tab. 2 are the result parameters of DSC. According to Fig. 3 and Tab. 2, both protein adhesive systems present similar curing characteristics in the DSC graph and exothermic peak is a single exothermic peak. As the heating rate rises, initial curing temperature (T_i), peak temperature (T_p) and termination temperature (T_f) correspondingly increase, and range of curing temperature becomes broad, namely curing time is shortened. This is because as the heating rate increases, heat effect generated within unit time is large, so is the generated temperature difference, and exothermic peak of curing reaction moves towards high temperature. As the heating rate rises, curing temperatures of the both protein-based adhesives increase, but the change of curing temperature on alfalfa protein-based adhesive is smaller than that of soybean protein-based adhesive, namely heating rate has not much influence on curing temperature of the alfalfa leaf protein-based adhesive.

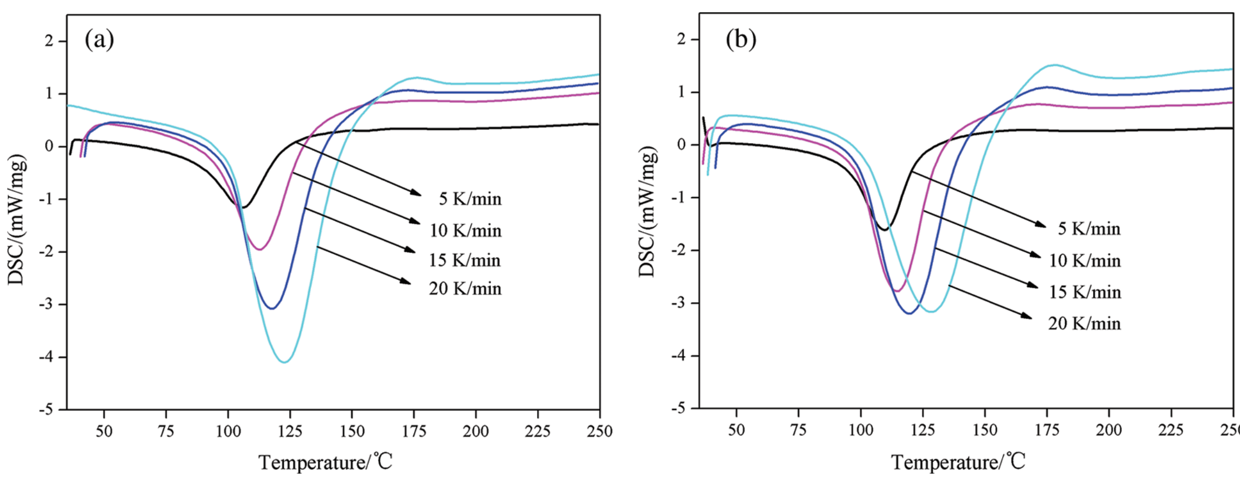

Figure 3: DSC curve under different heating rate of alfalfa leaf protein adhesive (a) and soy protein adhesive (b)

Table 2: Parameters of DSC results

Adhesives	Heating rate (K/min)	T_i (°C)	T_p (°C)	T_f (°C)
Alfalfa leaf protein adhesive	5	86.3	106.0	122.9
	10	95.1	112.6	133.5
	15	99.2	117.6	139.0
	20	100.3	122.8	145.9
Soy protein adhesive	5	94.1	109.6	124.1
	10	97.3	114.5	132.1
	15	98.3	119.5	140.5
	20	100.4	128.4	153.9

3.3 Curing Reaction Degree Analysis

Curing reaction degree is an important element used to measure cross-linking reaction. Integration processing of the DSC curing peak in 3.2 is carried out to obtain curve chart of curing and cross-linking reaction degrees of protein adhesives under heating rates 5, 10, 15 and 20 K/min as shown in Fig. 4.

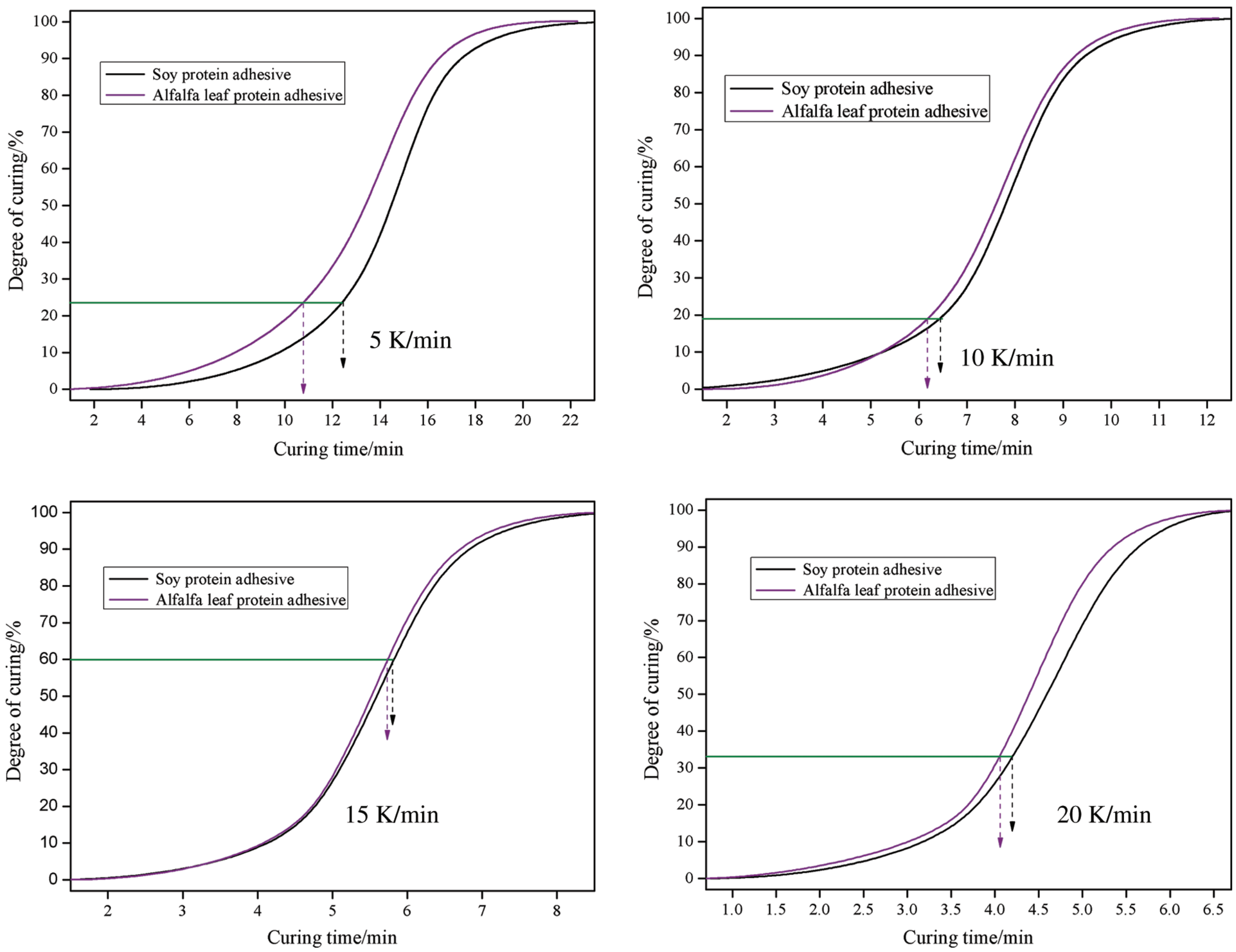

Figure 4: Curing degree of alfalfa leaf protein adhesive and soy protein adhesive

As shown in Fig. 4, time needed by complete curing reaction of the whole adhesive system is about 20 min, 11 min, 7 min and 6 min, respectively under heating rates 5, 10, 15 and 20 K/min, indicating that as the heating rate increases, the time needed to reach the same curing degree is gradually shortened, namely cross-linking reaction speed of the adhesive is accelerated.

When the heat rate is 5 K/min, curing reaction speed of the alfalfa protein-based adhesive is obviously higher than that of the soybean protein-based adhesive. At the heating rate 10 K/min, a point of intersection (degree of curing is 8%) occurs in curing reaction degree curves of both protein-based adhesives. When the heating rate is lower than 8%, curing reaction speed of the alfalfa protein adhesive is slightly lower than that of the soybean protein adhesive. When it is higher than 65%, curing reaction speed of the alfalfa leaf protein adhesive is higher than that of the soybean protein adhesive, but the reaction speed difference value is smaller than that at heating rate 5 K/min. At the heating rate 15 K/min, two curves are obviously closer with some regions overlapped. When the heating rate is 20 K/min, curing reaction speed of the alfalfa leaf protein-based adhesive is higher than that of the soybean protein-based adhesive. Under different heating rates, change tendencies of curing reaction degrees of leaf protein-based adhesive and soybean protein-based adhesive seems to be involved in protein reactivity, which related with the tertiary and quaternary protein structures destroyed during protein processing.

3.4 Apparent Activation Energy and Reaction Frequency Factor Analysis

Apparent activation energy can reflect apparent activation energies of two elementary reactions and can also reflect complicated apparent activation energies. Moreover, it embodies difficulty of cross-linking reaction of the system. In order to further analyze curing reactions of alfalfa leaf protein adhesive and soybean protein adhesive, a straight line is drawn using $ln(\beta/T_P^2)$ for $1/T_P$ under different heating rates β with a reference to Kissinger equation (Fig. 5). The fitted straight slope (k) is used to calculate apparent activation energy of the cross-linking reaction. Straight slopes of alfalfa leaf protein adhesive and soybean protein adhesive are −11,711 and −10,134 respectively and their corresponding apparent activation energies are 97.37 kJ/mol and 84.26 kJ/mol, respectively. Apparent activation energy of the alfalfa leaf protein adhesive is higher than that of the soybean protein adhesive, indicating that it's more difficult for the alfalfa leaf protein-based adhesive to go through reaction than the soybean protein-based adhesive.

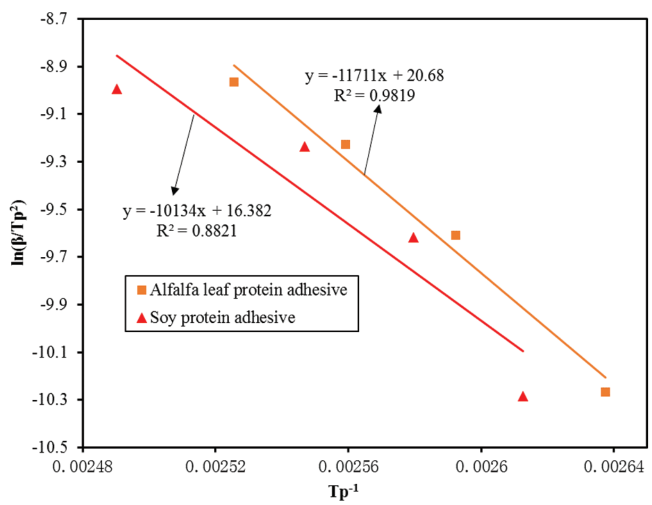

Figure 5: The relationship between $ln(\beta/T_P^2)$ and T_P^{-1} for alfalfa leaf protein adhesive and soy protein adhesive

Pre-exponential factor A represents collision frequency between reactant molecules and dependence degree of reaction rate constant on activation energy E_a, and the greater the A value, the greater the activation energy. According to Tab. 3, reaction frequency factor of the alfalfa protein-based adhesive is far higher than that of the soybean protein-based adhesive, thus further indicating that curing reaction activation energy of the alfalfa leaf protein-based adhesive is larger than that of the soybean protein-based adhesive, and it is more difficult for it to experience reaction.

Curing reaction orders (n) of alfalfa leaf protein adhesive and soybean protein adhesive are 0.938 and 0.928, respectively. Both reaction orders are non-integral, indicating that their curing reaction mechanisms are quite complicated with possible simultaneous occurrence of multiple reactions, and dynamics models of curing reaction are seen in Tab. 3.

Table 3: Curing parameters of alfalfa leaf protein adhesive and soy protein adhesive

Protein adhesives	E_a/kJ·mol^{-1}	n	A/s^{-1}	Dynamics models of curing reactions
Alfalfa leaf protein adhesive	97.37	0.938	1.06×10^{13}	$d\alpha/\mathrm{dt} = 1.06 \times 10^{13} e^{-97370/RT}(1-\alpha)^{0.938}$
Soy protein adhesive	84.26	0.928	1.09×10^{11}	$d\alpha/\mathrm{dt} = 1.09 \times 10^{11} e^{-84260/RT}(1-\alpha)^{0.928}$

3.5 XRD Analysis

After the protein goes through grafting reaction with modifying agent, degree of crystallinity increases, so do cohesion strength and cross-linking density of the protein, and thus this is finally conductive to improvement of bonding strength and water resistance of the adhesives.

Fig. 6 shows XRD curves of alfalfa leaf protein adhesive and soybean protein adhesive. Urea can present a crystalline structure and the protein has cristallinity areas as well, but if reaction between the two has occurred then the cristallinity should be partially or even totally lost hence decrease and a total different spacial structure has been formed. As shown in Fig. 6, degree of crystallinity of the alfalfa leaf protein-based adhesive is smaller than that of the soybean protein-based adhesive, protein experiences cross-linking reaction with modifying agent, and acting force and hydrogen-bond interaction between modifying agent and protein are enhanced, so degree of crystallinity of the adhesive is elevated. As the reactivity of alfalfa protein may be low, elevation amplitude of its degree of crystallinity is smaller than that of the soybean protein-based adhesive.

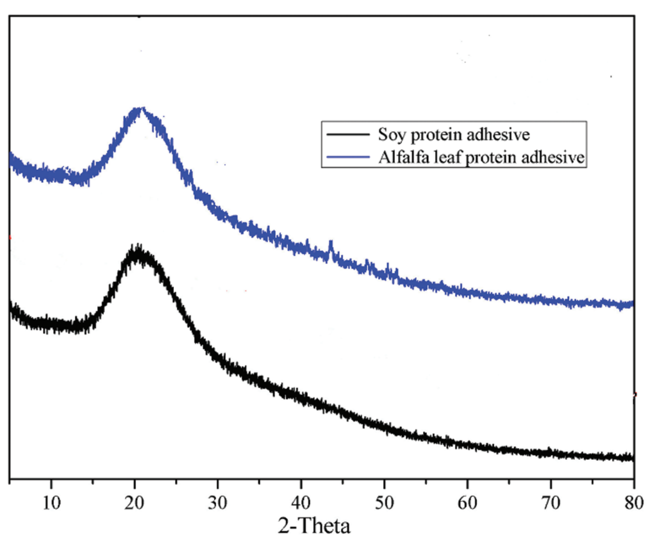

Figure 6: XRD spectrum of alfalfa leaf protein adhesive and soy protein adhesive

3.6 Bonding Performance

Performance of plywood based on alfalfa protein-based adhesive and soybean protein-based adhesive are shown in Tab. 3. According to Tab. 4, dry shear strengths of alfalfa protein-based adhesive and soybean protein-based adhesive are 0.77 MPa and 1.56 MPa, respectively, and warm water strengths are 0.56 MPa and 1.13 MPa, respectively.

Table 4: Bonding properties of alfalfa leaf protein adhesive and soy protein adhesive

Adhesives	Dry shear strength/MPa	Shear strength in warm water/MPa
Soy protein adhesive	1.56 (0.05)	1.13 (0.04)
Alfalfa leaf protein adhesive	0.77 (0.04)	0.56 (0.03)

The influence of cohesion strength on dry shear strength of the adhesive is the greatest, and it has the closest relation with protein molecular weight after degradation. Protein without degradation is of large molecular weight, high cohesion strength but poor bonding performance. Therefore, protein should be degraded firstly before chemical cross-linking reaction. Active sites can be generated only when spherical protein is degraded to expose active groups. Degradation will reduce cohesion strength of protein, but it is an essential working procedure in the follow-up cross-linking modification. Therefore, degradation of the protein should be properly controlled [41–43].

Cohesion strength especially cross-linking density has a major influence on water resistance of the protein-based adhesive. Under a certain content of cross-linking agent, what may influence cross-linking density of the protein-based adhesive most probably is protein itself activity after degradation. Dry shear strength and water resistance of the alfalfa protein-based adhesive are lower than those of the soybean protein-based adhesive, and what may be related to alfalfa protein activity.

4 Conclusions

Alfalfa leaf protein was used as the raw material to prepare a new-type protein-based wood adhesives in this paper, and it shows a satisfactory results for plywood bonding, although its performance is worse than soy protein glue. XRD and FT-IR analysis showed that the chemical compositions and chemical structures of the alfalfa leaf protein were basically identical with those of the soy protein, both belonging to spherical proteins with the basis and potential for protein adhesives preparation, and spatial cross-linked network structures would be easily formed. DSC experiment confirmed alfalfa leaf protein and soy protein adhesives had the similar curing behaviors, and curing temperature of alfalfa leaf protein-based adhesive was relatively lower than the latter. Activation energy and reaction frequency factor of the alfalfa leaf protein-based adhesive were higher than those of soy protein-based adhesive, indicating that the curing reaction of the alfalfa leaf protein adhesive was more difficult than soy protein adhesive, thus the dry shear strength and water resistance of alfalfa protein-based adhesive were lower than those of soy protein-based adhesive. Overall, the results of this study will expand the selection of raw materials for protein-based wood adhesives.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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