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Preparation and Properties of Aldehyde Free Adhesive Based on Plant Protein

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Abstract: At present, the most used wood adhesive in China is still "formaldehyde-based adhesive", and "formaldehyde-based adhesive" will release formaldehyde in the process of production and practical application, causing damage to the environment and human body. With the continuous depletion of oil resources and people's attention to environmental protection, it is of great scientific significance and practical value to develop a new type of environmental protection adhesive with renewable biomass as the main raw material. Using plant meal as the main raw material for preparing protein adhesive can not only reduce the cost of adhesive, but also break through the supply and demand limit of soybean protein. In this study, plant meal was used as the raw material, and the raw material was used as the adhesive base material after water washing pretreatment process. The bonding properties of the prepared protein adhesive were discussed. The effects of cottonseed powder particle size and treatment temperature on the properties were analyzed. An aldehyde free adhesive with bonding strength and water resistance meeting the requirements of national standard was obtained, and the maximum water resistance adhesive strength can reach 0.98mpa, It meets the standard of national standard class II plywood, and the formaldehyde emission reaches the group standard of formaldehyde free wood-based panel, which has great market promotion potential.

Keywords: Plant Protein, Aldehyde Free, Adhesive, Properties

1. Introduction

In recent years, the wood-based panel industry has developed rapidly, with an output of 209 million cubic meters in 2019. The adhesive used is mainly UF resin, accounting for more than 90% of the total amount of wood adhesive. It is mainly used for bonding plywood, fiberboard and particleboard [1]. However, UF resin bonded wood-based panel has the problems of formaldehyde emission and poor waterproof. The California Act (CARB) implemented in 2009 imposes stricter restrictions on formaldehyde emission from wood-based panels. Reducing formaldehyde emission of wood-based panel, improving wet strength and maintaining cost advantage has always been an important direction and main goal of UF resin research. With the continuous enhancement of the public's awareness of home environmental protection, the national and industrial standards have gradually tightened the requirements on the formaldehyde emission limit of wood-based panel products. The environmental protection level of products is required to reach level E1, and some products are close to the formaldehyde limit requirements of level E_0. Because the adhesive used in wood-based panel is mainly formaldehyde thermosetting resin, its own structural characteristics determine that no matter how to improve the process technology, there is a certain formaldehyde emission in theory and practical application. Therefore, the research and development of formaldehyde free adhesive with excellent performance is the fundamental way to solve the problem of formaldehyde [2-4].

The preparation of bio based aldehyde free adhesive from plant and animal protein is a research hotspot at present, which mainly focuses on the research of soybean protein adhesive. It is usually prepared by adding crosslinking agent and additives to soybean powder or soybean protein. Through denaturation and chemical modification of soybean powder or isolated soybean protein, Soybean protein was transformed from natural polymer into a network cross-linked structure with the characteristics of synthetic resin. Soybean products can also be used as fillers or modifiers of synthetic resins to reduce the release of volatile substances such as formaldehyde, improve the content of renewable components in adhesives and reduce costs [5-7].

Soybean meal, the main raw material of soybean protein adhesive, is the plant protein raw material with the largest consumption at present. It is mainly used to produce protein feed. In 2019, the gap of protein feed raw materials in China will be about 26 million tons. It is predicted that by 2022, the gap will reach 45 million tons. Therefore, it is of great significance to develop and utilize other protein resources. From the current actual situation, soybean meal is in short supply, while the utilization rate of cotton meal is not high. In 2019, the market price of soybean meal is 2850 yuan / ton and that of cotton meal is 2600 yuan / ton. As an ideal and new raw material of protein adhesive, cotton meal has great development potential [8].

China's annual output of cottonseed is more than 10 million tons. Cottonseed contains about 54% cotton kernel, 34% oil and 40% protein. Cottonseed meal is a by-product of cottonseed oil extracted by preloading extraction or direct solvent extraction. The protein content can reach more than 55%, but it has not been effectively utilized. The main reason is that it contains gossypol, which will affect animal growth after eating [9]. Therefore, the addition of cottonseed meal in feed is less than 5%, and cottonseed meal is returned to the field as fertilizer in many places. Cottonseed can directly produce dephenolized cottonseed protein through dephenolization technology as high-quality protein feed, but as a raw material for wood adhesive synthesis, cottonseed meal can be directly used without dephenolization process. In this paper, the preparation method and basic properties of cottonseed protein adhesive were discussed, the effects of cottonseed powder particle size and treatment temperature on the properties were analyzed, and the possibility of cottonseed protein as wood-based panel adhesive was evaluated [10-12].

2. Materials and Methods

2.1. Materials

Cotton meal, industrial grade, Hebei Jiahui Feed Co., Ltd; Urea, 99%, Tianjin Zhiyuan Chemical Reagent Co., Ltd; Hydrochloric acid, analytical purity, Tianjin Zhiyuan Chemical Reagent Co., Ltd; Ammonia, analytical purity, Tianjin Zhiyuan Chemical Reagent Co., Ltd; Gelatin, analytical pure, Tianjin Zhiyuan Chemical Reagent Co., Ltd. Eucalyptus veneer: moisture content 12%, thickness 1.7mm, provided by plywood enterprises.

2.2. Instrument

BYK Gardner bubble viscometer, BYK additives & instruments, Germany; Hannahi9124 pH tester, Hanna instruments, Italy; BY302 × 2 / 15 universal test press, Suzhou XINXIELI Machine Manufacturing Co., Ltd; Cmt4104 microcomputer controlled electronic universal mechanical testing machine, Meister industrial system (China) Co., Ltd.

2.3. Synthesis of Polyol

The epoxidized vegetable oil is formed by reacting vegetable oil with peroxy acid in solvent for 3 hours at 70°C. The epoxidized vegetable oil is reacted with alcohol, deionized water and catalyst under boiling for 1.5 hours. The product is neutralized with weak alkaline substance to obtain vegetable oil-based polyol; The viscosity of the vegetable oil-based polyol is 5000-6000 mPa·s and the hydroxyl value is 200-250 mgKOH / g.

2.4. Synthesis of Adhesives

Dry the cotton meal after oil extraction and grind it to 100 mesh with a grinder to obtain the ground cotton meal powder. Add deionized water, ground cottonseed meal powder and ammonia into the reactor, stir for 1 hour, centrifuge for 20 minutes, take the supernatant, add hydrochloric acid, stir for 30 minutes and centrifuge for 20 minutes to obtain cottonseed protein curd. Add deionized water, natural modifier and urea into the reactor, raise the temperature to 50oc, add the cottonseed protein curd, stir to completely dissolve it, add clear rubber powder, and dissolve after stirring to prepare the main agent. Mix the main agent, crosslinking enhancer and filler evenly to aldehyde free protein adhesive A.

Dry the cotton meal after oil extraction and grind it to 100 mesh with a grinder to obtain the ground cotton meal powder. Deionized water, ground cottonseed meal powder and ammonia are added to the reactor, stirred for 1 hour, centrifuged for 20 minutes, the supernatant is added with hydrochloric acid, stirred for 30 minutes and centrifuged for 20 minutes to obtain cottonseed protein curd. Add deionized water, natural modifier and urea into the reactor, raise the temperature to 70°C, add the cottonseed protein curd, stir to completely dissolve it, add clear rubber powder, and dissolve after stirring to prepare the main agent. Mix the main agent, crosslinking enhancer and filler evenly to aldehyde free protein adhesive B.

Dry the cotton meal after oil extraction and grind it to 200 mesh with a grinder to obtain the ground cotton meal powder. Deionized water, ground cottonseed meal powder and ammonia are added to the reactor, stirred for 1 hour, centrifuged for 20 minutes, the supernatant is added with hydrochloric acid, stirred for 30 minutes and centrifuged for 20 minutes to obtain cottonseed protein curd. Add deionized water, natural modifier and urea into the reactor, raise the temperature to 50°C, add the cottonseed protein curd, stir to completely dissolve it, add clear rubber powder, and dissolve after stirring to prepare the main agent. Mix the main agent, crosslinking enhancer and filler evenly to aldehyde free protein adhesive C.

Dry the cotton meal after oil extraction and grind it to 200 mesh with a grinder to obtain the ground cotton meal powder. Deionized water, ground cottonseed meal powder and ammonia are added to the reactor, stirred for 1 hour, centrifuged for 20 minutes, the supernatant is added with hydrochloric acid, stirred for 30 minutes and centrifuged for 20 minutes to obtain cottonseed protein curd. Add deionized water, natural modifier and urea into the reactor, raise the temperature to 70°C, add the cottonseed protein curd, stir to completely dissolve it, add clear rubber powder, and dissolve after stirring to prepare the main agent. Mix the main agent, crosslinking enhancer and filler evenly to aldehyde free protein adhesive D.

2.5. Performance Test and Characterization

Free formaldehyde content, solid content and curing time shall be determined according to GB/T14074-2006. Viscosity: measured by BYK bubble viscometer. Storage period: store the resin at 25°C, measure the viscosity with BYK bubble viscometer every day, and characterize the storage period of the resin when the resin viscosity increases to P-Q.

Take out a small amount of adhesive liquid sample into aluminum foil container, place the container in an oven at 120±2°C until it reaches constant weight, grind it into powder, and pass through 200 mesh screen. Q50 thermogravimetric analyzer (TGA) was used to test the stability of the cured adhesive. Weigh about 5mg of grinding powder and put it into a platinum cup. Fill in high-purity nitrogen (99.999%) as protective gas at the flow rate of 60ml/min. scan and heat it from room temperature to 650°C at the heating rate of 10°C /min.

2.6. Plywood Preparation

Eucalyptus veneer: moisture content 12%, thickness 1.7mm; The gluing amount is 350g/m^3 (double-sided); Hot pressing temperature: 135°C, pressure 1.2 MPa, press time: 5 min and 6 min.

2.7. Determination of Bonding Strength and Formaldehyde Emission

According to the Chinese national standard GB/T9846-2015, the microcomputer controlled wood-based panel universal mechanical testing machine is used to measure the dry bonding strength and wet bonding strength. The wet bonding strength is in accordance with the test standard of class II plywood: place the sawn plywood sample in 63±3°C water for 3 h, take it out and air it at room temperature for 10 min for wet bonding strength test. During the test of sample bonding strength, clamp both ends of the test piece in two movable clamps to keep it in a straight line, and the center of the test piece passes through the axis of the movable clamp of the testing machine. The distance between the clamping part and the test piece groove shall be within 5 mm. Load the specimen to failure at a uniform speed, with the loading speed of 5.0 mm / min, and record the maximum load. Formaldehyde emission shall be determined according to the dryer method in GB/T17657-2013.

3. Results and Discussion

3.1. Basic Properties of Adhesives Under Different Synthetic Processes

The basic properties of adhesive are shown in Table 1. The four protein adhesives were brown liquid in the final stage of their synthesis. After cooling to room temperature, the color of adhesives A and C was light brown, and the color of adhesives B and D was dark brown.

Table 1. *Basic properties of adhesives with different synthetic processes.*

Adhesive	Appearance	Solid content (%)	Viscosity (mPa·s)	Gel time (s)	Free F content (%)	Storage time (d)
A	Light brown	35.1	P-Q	125	0	36
B	Dark brown	36.1	P-Q	133	0	39
C	Light brown	35.4	P-Q	117	0	40
D	Dark brown	36.4	P-Q	105	0	40

The formula of each adhesive is similar, and the difference of solid content is small and in the normal range. The solid content of adhesive C and D is slightly higher than that of adhesive A and B. Because the bubble viscometer is used to accurately control the viscosity of the resin in the polycondensation stage, the viscosity of each adhesive is in the P-Q range.

The curing time of each resin varies greatly. The curing time of adhesive A is the shortest, and the curing time of adhesive B, C and D is significantly prolonged. If this kind of resin is applied to the production practice of wood-based panel, it is recommended to increase the hot pressing temperature or prolong the hot pressing time, so as to improve the curing speed, promote the complete curing of adhesive and ensure a certain production efficiency [13].

When the viscosity of resin measured by BYK bubble viscometer is less than k, better atomization sizing effect can be obtained and applied to the production of particleboard and fiberboard. However, the viscosity of this experiment is large, which is P-Q, so this adhesive is only suitable for the preparation of plywood. The storage period of each adhesive can meet the requirements of production practice for the storage period of adhesive.

3.2. TG Analysis

Table 2. TG results of adhesives with different synthetic processes.

Adhesive	30-120°C	120-230°C	230-320°C	320-650°C
A	93.1	62.3	31.2	17.8
B	94.2	66.9	36.9	22.6
C	95.3	65.2	39.3	25.3
D	95.6	61.3	32.2	23.1

According to the thermogravimetric results, the first stage is 30-120°C. In this process, the weight of the adhesive is slightly lost, mainly due to the evaporation of the remaining water in the adhesive sample and the non degradation of cottonseed protein, so the weight loss rate of this part is very small. C and D adhesives have less weight loss in the first stage than A and B adhesives [14].

The second stage is 120-230°C, in which the decomposition rate of each adhesive is accelerated. At the end of the second stage, the weight loss of A and D adhesives is about 40%. In contrast to the first stage, the weight loss of C and D adhesives is the largest, with a loss of 45%.

The third stage is 230-320°C and the weight loss in this stage may be caused by the decomposition of cottonseed protein skeleton structure. At this stage, the backbone structure of cottonseed protein is completely decomposed, releasing gases such as CO, CO_2 and NH_3, resulting in weight loss. At the end of the third stage, the remaining weight of the modified adhesive was 39.3%, 36.9%, 32.2% and 31.2% from top to bottom [15].

The fourth stage is 320-650°C, and the weight loss is caused by the decomposition of the ring structure formed by the chelation reaction between cottonseed protein and zinc ion in the added zinc oxide. The addition of urea expands the structure of cottonseed protein, and the exposed active groups such as - NH_2 and - COOH react with zinc ions to form a stable ring structure and improve the water resistance of the adhesive. At the end of the fourth stage, the remaining weight of adhesive was 25.3%, 23.1%, 22.6% and 17.8% from top to bottom.

Table 3. Bonding strength and formaldehyde emission of plywood.

Adhesive	F emission (mg/L)		Dry bonding strength		Wet bonding strength	
	5min	6min	5min	6min	5min	6min
A	0.02	0.01	2.21	2.33	0.74	0.87
B	0.03	0.02	2.08	2.57	0.84	0.85
C	0.02	0.02	2.63	2.87	0.94	0.97
D	0.02	0.01	2.87	2.94	0.92	0.98

3.3. Bonding Strength of Plywood

The test results of bonding strength are shown in Table 3. The dry bonding strength is high, with an average of more than 2.0, while the wet bonding strength decreases in varying degrees after hydrothermal treatment. The test pieces are soaked in 63°C hot water for 3h without glue opening, and the strength can meet the requirements of class II plywood in the national standard GB/T9846.3-2004 (greater than 0.7MPa). The main reason should be better bonding strength. For protein adhesive, appropriately prolonging the hot pressing time is conducive to promote the curing of adhesive and improve the bonding strength, which corresponds to the determination results of curing time. These measures can improve the curing degree of adhesive, but over curing may lead to over curing of adhesive and reduce the bonding strength.

Adding some modifiers can improve the wet bonding strength of protein adhesive. For example, various thermosetting synthetic resins can effectively improve the water resistance of resin, but this part needs to be further studied to take into account the process and cost of adhesive.

3.4. Formaldehyde Emission of Plywood

The test results of formaldehyde emission are shown in Table 3. The formaldehyde emission of plywood pressed by various adhesives is very low, because there is no formaldehyde added in the preparation process of adhesives, and there is no formaldehyde produced in the reaction process. Therefore, the trace formaldehyde in plywood mainly comes from wood. Under the conditions of high temperature and humidity, hemicellulose and lignin may degrade and release trace aldehydes. Therefore, trace formaldehyde release can be detected during detection, but this formaldehyde release fully meets the group standard requirements of formaldehyde free wood-based panel (≤0.03mg/L).

4. Conclusions

In this study, the cottonseed meal was used as the main raw material. After water washing pretreatment process, the raw material was used as the base material of adhesive, and various modification reagents were added. The effects of cottonseed powder particle size and treatment temperature on the properties were discussed. An aldehyde free adhesive with bonding strength and water resistance meeting the requirements of national standard was obtained. It was pressed into three layers of plywood, and the physical and mechanical properties of plywood were tested. The maximum water-resistant bonding strength of the obtained plywood can reach 0.98MPa, which meets the standard of national standard class II plywood, and the formaldehyde emission is very low, which can reach the group standard of aldehyde free wood-based panel. Considering the huge market demand at present, this aldehyde free adhesive has great market promotion potential.

Author Contributions

The Manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of Interest

The authors declare that they have no competing interests.

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References

[1] China National Forest Products Industry Association, China Wood Based Panel Industry Report. China Forestry Publishing House, Beijing, 2019.

[2] Liu C, Zhang Y, Li X N, et al. A high-performance bio-adhesive derived from soy protein isolate and condensed tannins [J]. RSC Advances, 2017, 7 (34): 21226-21233.

[3] Shi J Y, Wen M Y, Li X Y, et al. Research progress of biomass-based formaldehyde-free adhesives [J]. Journal of Forestry Engineering, 2018, 3 (2): 1-10.

[4] Luo J. Cross-linking architecture regulation and reinforcement mechanism of soy protein-based adhesive [D]. Beijing: Beijing Forestry university, 2018.

[5] Sun E H, Wu G F, Zhang Z, et al. Performance and bonding mechanism of soy protein adhesives modified by basalt fiber [J]. Transactions of the Chinese Society of Agricultural Engineering, 2018, 34 (1): 308-314.

[6] Zhang M, Zhang Y, Chen M, et al. A high-performance and low-cost soy flour adhesive with a hydroxymethyl melamine prepolymer [J]. Polymers, 2018, 10 (8), 909-915.

[7] Lei H, Wu Z, Du G. Cross-linked soy-based wood adhesives for plywood [J]. International Journal of Adhesion & Adhesives, 2014, 50, 199-203.

[8] Zhang Y, Zhang M, Chen M, et al. Preparation and characterization of a soy protein-based high-performance adhesive with a hyperbranched cross-linked structure [J]. Chemical Engineering Journal, 2018, 354, 1032-1041.

[9] Frihart C, Satori H. Soy flour dispersibility and performance as wood adhesive [J]. Journal of Adhesion Science and Technology, 2013, 27 (18-19): 2043-2052.

[10] Li H, Li C, Gao Q, et al. Properties of soybean-flour-based adhesives enhanced by attapulgite and glycerol polyglycidyl ether [J]. Industrial Crops and Products, 2014, 59, 35-40.

[11] P. Qu, H. Huang, G. Wu, E. Sun, and Z. Chang. Effects of hydrolysis degree of soy protein isolate on the structure and performance of hydrolyzed soy protein isolate/urea/formaldehyde copolymer resin. Journal of Applied Polymer Science, 132 (7): 41469-41477, 2015.

[12] Xu F J, Dong Y, Zhang W, et al. Preparation of cross-linked soy protein isolate-based environmentally-friendly films enhanced by PTGE and PAM [J]. Industrial Crops and Products, 2015, 67, 375-40.

[13] L. C, Y. Zhang, and X. N. Li. A high-performance bio-adhesive derived from soy protein isolate and condensed tannins. RSC Advances, 7 (34): 21226-21233, 2017.

[14] Jin C, Zhang S, Pang J, et al. Plywood with soy protein-acrylate hybrid adhesive [J]. Advanced Materials Research, 2014, 884-885, 108-111.

[15] Wu Z, Lei H, Cao M, et al. Soy-based adhesive cross-linked by melamine-glyoxal and epoxy resin [J]. Journal of Adhesion Science and Technology, 2016, 30 (19): 2120-2129.