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Study on Protein Based Adhesives Blending-Modified by Isocyanate

Jiyong Xu[1], Zhigao Luo[1], Le Luo[2, 3], Xuemei Yin[2, 3], Qi Li[2, 3, *], An Mao[2, 3, *]

[1]Department of Engineering Material, Jinshan Vocational Technical College, Yangzhong, China

[2]Suzhou Lvhao New Material Technology Co., Ltd, Zhangjiagang, China

[3]Zhenjiang Lvhuan New Material Technology Co., Ltd, Zhenjiang, China

Email address:

wonderfulliqi2364@126.com (Qi Li), dannymaoan@126.com (An Mao)

[*]Corresponding author

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Abstract: The price of cotton by-product cottonseed meal has been relatively stable and significantly lower than that of soybean meal, which has greater advantages for industrial raw materials. Cottonseed meal after cottonseed oil extraction accounts for 30% of the total content of plant meal, and the protein contained in cottonseed meal is not lower than soybean protein in terms of quality and quantity. At present, cottonseed meal, as a by-product of cottonseed oil extraction, is mainly used in animal feed, and cottonseed protein is not fully utilized. In this study, cottonseed meal was used as raw material. By studying the effects of modifier addition and reaction conditions on the bonding properties of cottonseed adhesive, the best process parameters for preparing the best cottonseed adhesive were explored, and the modification mechanism of cottonseed protein adhesive was revealed by analyzing the adhesives prepared under different conditions. The results showed that the solid content increased with the increase of isocyanate addition ratio, and the application period of the adhesive shortened with the increase of isocyanate addition ratio. When the addition amount was 40%, a large number of bubbles were produced in 30 minutes. The water resistance of blended modified cottonseed adhesive was tested. When the proportion of isocyanate was less than 10%, the water resistance bonding strength could not meet the requirements of national standard. Adding more than 10% isocyanate cottonseed protein adhesive to bond plywood can well meet the standard of class II plate, and the maximum bonding strength can reach 1.68mpa. The research results can not only provide a certain theoretical basis and practical guidance for the preparation of new low-cost green adhesive, but also open up a new way for the effective utilization of agricultural and forestry waste cottonseed meal.

Keywords: Protein Adhesive, Isocyanate, Modification, Wood Based Panel, Water Resistant Bonding Strength

1. Introduction

With the rapid development of wood processing industry, the demand for wood is increasing day by day. The national natural forest protection policy makes the supply of wood insufficient. Therefore, finding other methods to make rational and efficient use of wood resources has become an important way to solve the wood shortage. Adhesive is a kind of high molecular material which can bond two or more materials together through surface adhesion under certain conditions and has certain bonding strength after curing [1]. The emergence of wood adhesive makes full use of small-diameter grade wood, branch and stem wood, thinning wood and wood processing residues. Through bonding and composite technology, wood industries such as plywood, fiberboard and particleboard develop rapidly [2]. Adhesive plays a key role in wood-based panel industry. The preparation of wood-based panels such as plywood, particleboard, fiberboard and block board is inseparable from the participation of wood adhesive. According to the survey of the State Forestry Administration, the output of wood-based panel in 2019 was 309 million cubic meters, and the consumption of formaldehyde adhesive reached 18 million tons (solid content 100%), accounting for more than

90% of the total amount of wood adhesive [3-5].

At present, the wood adhesive widely used in the market is "trialdehyde adhesive", namely urea formaldehyde resin adhesive, phenolic resin adhesive and melamine resin adhesive. "Trialdehyde adhesive" occupies a dominant position in the wood adhesive market with its good performance and low price. However, "trialdehyde glue" takes petroleum and other nonrenewable resources as the main synthetic raw materials, and the adhesive made of formaldehyde and its derivatives will more or less release formaldehyde and other harmful substances in the application process, pollute the production and living environment and endanger human health. In October 2017, formaldehyde was included in the list of class I carcinogens in the list of carcinogens published by the international agency for research on cancer of the World Health Organization. Countries all over the world, especially developed countries, attach great importance to the formaldehyde emission of wood-based panels and their products. The international organization for Standardization (ISO), the European Union, the United States and Japan have constantly updated the formaldehyde emission limit standard of wood-based panels and their products, and put forward higher requirements for the formaldehyde emission limit [6]. In 2017, the revised gb18580-2017 standard of formaldehyde emission from wood-based panels and their products for interior decoration materials began to be implemented, which stipulates that the formaldehyde emission limit value of wood-based panels and their products for interior decoration materials is 0.124mg/m3, the limit mark is E1, and the original E2 grade plates are cancelled. More and more stringent standards have greater restrictions on the use of "trialdehyde adhesive". With the continuous improvement of people's living standards, the requirements for living environment are higher and higher [7]. Non toxic and environmental friendly bio based adhesive has attracted more and more attention. At present, starch adhesive, tannin adhesive, lignin adhesive and animal and plant protein adhesive are common in the research, among which, The research of plant protein adhesive is one of the hotspots [8-11].

At present, soybean protein adhesive is the most studied biomass adhesive. However, soybean is the third largest grain crop in China after wheat and corn. The relationship between supply and demand is affected by the economic situation at home and abroad, the price fluctuates greatly, and the use cost as industrial raw materials is high [12]. About 30% of the total amount of soybeans consumed in China every year are imported from the United States. The unforeseen trade disputes between China and the United States will have an important impact on the supply and demand of soybeans. For example, from 2018 to 2019, due to Sino US trade friction, the price of soybean and soybean meal in the downstream increased significantly, which also affected the production and application of soybean protein adhesive [13]. As an economic crop, cotton is not as important to the national economy as soybean, and China's cotton output is sufficient for domestic production and demand, and is little affected by the external trade environment. Therefore, the price of cotton by-product cottonseed meal has been relatively stable and significantly lower than that of soybean meal, which has greater advantages for industrial raw materials. In addition, the cottonseed meal after cottonseed oil extraction accounts for 30% of the total content of plant meal, and the protein contained in it is not lower than soybean protein in terms of quality and quantity [14]. At present, cottonseed meal, as a by-product of cottonseed oil extraction, is mainly used in animal feed, in which cottonseed protein is not fully utilized. If cottonseed meal can be used as the main raw material for preparing biomass adhesive, it can not only reduce the cost of adhesive, but also break through the supply and demand constraints of soybean protein and make high value-added use of cottonseed meal [15].

In this study, cottonseed meal was used as raw material. By studying the effects of modifier addition and reaction conditions on the bonding properties of cottonseed adhesive, the best process parameters for preparing the best cottonseed adhesive were explored, and the modification mechanism of cottonseed protein adhesive was revealed by analyzing the adhesives prepared under different conditions. The research results can not only provide some theoretical basis and practical guidance for the preparation of new low-cost green adhesive, but also open up a new way for the effective utilization of agricultural and forestry waste cottonseed meal.

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; Isocyanate, industrial grade, Yantai Wanhua Group, poplar veneer, width 300 mm × 300 mm, thickness 1.6 mm, moisture content 10%.

2.2. Instrument

Digital display rotary viscometer, bolefield, USA; Hot press, Suzhou XinXieLi company; Universal mechanical testing machine, Instron, USA.

2.3. Preparation of Protein Adhesives

The oil pressed cottonseed meal is ground into powder by a pulverizer. After passing through a 200 mesh screen, it is washed twice according to the proportion of deionized water: Cottonseed Meal=8:1. After each washing, it is centrifuged by a centrifuge at the speed of 6000r / min for 15min. The centrifuged cottonseed meal was placed in an oven and dried to constant weight at 50°C. The dried cottonseed meal powder is grinded again through a 200 mesh screen and used as an adhesive base material.

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 and filler evenly to the cottonseed protein adhesive.

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. The main agent, isocyanate with different ratios, and filler are evenly mixed to obtain cottonseed protein adhesive modified by isocyanate.

2.4. Preparation of Plywood

After the adhesive is fully stirred, it is applied to the veneer surface within 30 minutes, and the amount of glue is 150g / m^2. Hot pressing conditions: temperature 150°C, pressure 1.1 MPa, time 1.3 min / mm. After hot pressing, it is cooled to room temperature, sawed and grooved according to the specified size, and then placed in a constant temperature and humidity box with temperature of 25°C and relative humidity of 50% for 24 hours to obtain three layers of plywood.

2.5. Performance Test and Analysis

The resin viscosity shall be determined according to GB / T 14076-2004. After the hot pressed plywood is aged for 24 hours, the test specimen shall be prepared according to GB / T 9846.4-2004, and the bonding strength shall be measured according to the requirements of class II plywood in GB / T 17957-2013 and GB / T 9846-2004 standards. In the above tests, four plywood pieces are pressed in each group, six specimens are taken from each board, and the average value is taken as the result.

3. Results and Discussion

3.1. Effect of Isocyanate Content on Viscosity of Cottonseed Protein Adhesive

Isocyanate is the general name of various isocyanate esters. After blending cottonseed protein adhesive with isocyanate with different addition ratios, the basic properties of the adhesive are shown in Table 1: with the increase of isocyanate addition ratio, the viscosity and solid content of the blend modified adhesive increase, and the blend modified adhesive forms a uniform liquid after stirring for 10min.

The stirred adhesive was left to stand for a period of time and observed. It was found that there was no change after the cotton seed protein adhesive without isocyanate was placed for 120min. The adhesive with 10% - 30% isocyanate began to produce different numbers of bubbles after being placed for 60min, while the adhesive with 40% isocyanate produced a large number of bubbles within 30min, the reason should be that the isocyanate group began to react with the water in the adhesive, which affected the application period of cottonseed protein adhesive. In actual production, the application period of adhesive is generally required to be at least 60-120min to ensure the smooth progress of production. In this regard, the amount of isocyanate should not exceed 30%.

Table 1. *Effect of isocyanate content on viscosity of adhesive system.*

Addition ratio (%)		Viscosity (mPa·s)
Isocyanate	Protein adhesive	
0	100	12541
10	100	10255
20	100	9698
30	100	8123
40	100	7401

3.2. Effect of Isocyanate Content on Solid Content of Cottonseed Protein Adhesive

The addition of isocyanate has a great impact on the solid content of cottonseed protein adhesive. With the increase of the amount of isocyanate, the solid content of cottonseed protein adhesive increases rapidly, from 24.36% to 49.69%, nearly doubling. The main reason is that the solid content of unmodified cottonseed protein adhesive is low, while the solid content of isocyanate is 100%. After adding cottonseed protein adhesive, the solid content of adhesive can be increased rapidly. The solid content of adhesive generally affects the viscosity of adhesive, thus affecting the amount of glue, sizing effect and wettability, and finally affecting the bonding strength. Therefore, the appropriate solid content is very important for the preparation of wood-based panel.

Table 2. *Effect of isocyanate content on solid content of adhesive system.*

Addition ratio (%)		Solid content (%)
Isocyanate	Protein adhesive	
0	100	24.36
10	100	31.28
20	100	36.99
30	100	44.28
40	100	49.69

3.3. Effect of Isocyanate Content on Dry Bonding Strength of Cottonseed Protein Adhesive

The reaction between isocyanate and wood is very complex. Many scholars believe that in the process of bonding wood, isocyanate reacts with water in wood to form amines, and then cross-linked with excess free isocyanate group to form graphene oxide polyurea structure; At the same time, it can also self-polymerize to form dimer and trimer, and form a ring structure. These reactions make the resin obtain cohesive strength. While the resin is crosslinked and solidified, it reacts with hydroxyl groups in wood to form glue relay. Isocyanate can form a stable network crosslinking structure after curing. By measuring the bonding strength of plywood prepared with isocyanate modified cottonseed protein adhesive, it can be seen from table 3 that the dry

bonding strength of blended modified cottonseed adhesive increases with the increase of isocyanate addition ratio, reaching the maximum value of 3.89MPa at 40% isocyanate addition.

Table 3. *Effect of isocyanate content on dry bonding strength of cottonseed protein adhesive.*

Addition ratio (%)		Dry bonding strength (MPa)		Wood failure (%)
Isocyanate	Protein adhesive	Mean	Standard deviation	
0	100	1.87	0.11	90-100
10	100	2.35	0.22	100
20	100	2.69	0.19	100
30	100	3.01	0.21	100
40	100	3.89	0.27	100

3.4. Effect of Isocyanate Content on Wet Bonding Strength of Cottonseed Protein Adhesive

Table 4 shows the test results of water resistance and bonding strength of blended modified cottonseed adhesive under different isocyanate addition ratios. When the isocyanate addition ratio is 10% or less, the plywood specimens are individually opened during hot water treatment; When the addition ratio is increased to 20%, the sample is not opened after boiling, but the hot water bonding strength is only 0.99mpa; When the addition ratio reaches 30%, the boiling water bonding strength is 1.24mpa, which obviously exceeds the 0.7MPa required by the national standard class II plywood; When the addition ratio continues to increase to 40%, the water-resistant bonding strength is 1.68mpa, which can better meet the requirements of class II plates. However, it also leads to too much shortening of the application period of the adhesive, which may affect the actual production operation.

Table 4. *Effect of isocyanate content on wet bonding strength of cottonseed protein adhesive.*

Addition ratio (%)		Wet bonding strength (MPa)		Wood failure (%)
Isocyanate	Protein adhesive	Mean	Standard deviation	
0	100	0.65	0.05	50-60
10	100	0.87	0.11	80-100
20	100	0.99	0.12	100
30	100	1.24	0.23	100
40	100	1.68	0.21	100

4. Conclusions

In this study, different proportions of isocyanate were blended with cottonseed protein adhesive. The viscosity and solid content of the adhesive increased with the increase of isocyanate addition proportion, and the application period of the adhesive shortened with the increase of isocyanate addition proportion. When the addition amount was 40%, a large number of bubbles were produced in 30 minutes. The water resistance of blended modified cottonseed adhesive was tested. When the proportion of isocyanate was less than 10%, the water resistance bonding strength could not meet the requirements of national standard. Adding more than 10% isocyanate cottonseed protein adhesive to bond plywood can well meet the standard of class II plate, and the maximum bonding strength can reach 1.68mpa. However, with the increase of the amount of isocyanate, the application period of the adhesive is shortened. Therefore, the preparation process of isocyanate and cottonseed protein adhesive needs to be further studied.

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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