
Synthesis and Properties of Bio-based Adhesives Derived from Plant Oil Residues

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Abstract: Cottonseed oil residue (COR) is a by-product of cottonseed extracted by prepressing or direct solvent extraction. The protein content of COR can reach 50% and higher, but it has not been effectively utilized. In this study, bio-based adhesives were synthesized from COR, maleic anhydride, and urea. The obtained adhesives were then analyzed by Fourier transform infrared (FTIR) and Thermogravimetric (TG), and tested as wood composite panel binders. The results indicated that the optimal synthesis conditions of the modified COR adhesive were: the urea concentration was 2 mol/L, the maleic anhydride content was 6%, and the reaction temperature was 70°C. Infrared spectrum revealed a new characteristic peak appeared at 2216 cm⁻¹, which indicated that the protein in cottonseed reacted with maleic anhydride to form a stable structure, which improved the water resistance of the adhesive. The TG curve of maleic anhydride/urea modified COR adhesive showed that the peak value of the adhesive shifted back in the second and third stages, which indicated that the modified adhesive had better thermal stability and improved water resistance than those of unmodified ones. The study results could provide a theoretical basis and scientific guidance for the appropriate processing method and application technology development of COR.

Keywords: Bio-based Adhesive, Oil Residue, Bonding Strength, Composite Panel, Modification

1. Introduction

In recent years, wood panel industry is developing quickly in China. The annual production of wood composite panels in 2018 was 299 million cubic meters [1]. Urea-formaldehyde (UF) resin is one of the primary adhesives that are commonly used in producing wood panels, such as plywood, particleboard, and fiberboard. However, the panels bonded by UF resins have problems of formaldehyde emission and poor water resistance [2-4]. With the development of social economy and people's lives, the requirements for environmental friendly class of wood panel products are getting higher. To solve this problem, currently, two research directions have been proposed: one is to modify UF and other

formaldehyde-based resins with special materials or agents to improve water resistance and lower the amount of formaldehyde emission [5, 6]; the other direction is to replace formaldehyde-based resins with no formaldehyde-added adhesives to bond composite panel products [7-10].

Protein adhesive is one of the adhesives that have no formaldehyde addition and satisfied performance [11-13]. The primary protein adhesive is soybean adhesive which is usually made from soybean protein, crosslinking agents, and other additives. The soybean protein was usually modified into a high molecular polymer with crosslinking structure. Soybean protein powders could also be used as fillings or additives to lower the formaldehyde content of thermal setting adhesives and also lower the cost of the adhesives.

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 2018, the gap of protein feed raw material in China is about 25 million tons. It is predicted that by 2022, the gap will reach 42 million tons. Therefore, it is of great significance to develop and use other protein resources. According to the current situation, soybean meal is in short supply, while cottonseed utilization is still not very high. In 2018, the market price of soybean meal was 2767 yuan / ton, and the market price of cottonseed oil residue (COR) was only 2305 yuan / ton. COR has great potential as an ideal and new protein adhesive material.

China produces 8-10 million tons of cottonseed annually. The cottonseed contains about 50-55% cottonseed, 30-35% oil and 35-38% protein. COR is a by-product of cottonseed extracted by prepressing or direct solvent extraction. Its protein content can reach 50% and higher, but it has not been effectively utilized. The main reason is that it contains gossypol, which will affect the growth of animals after consumption. Therefore, the amount of COR added to the feed is only 3% - 4%. In many places, COR is returned to the field as fertilizer.

The objective of this study was to investigate the feasibility of using COR as adhesive for making wood composite panels. The adhesives were synthesized from cotton seed meal, maleic anhydride, and urea. The adhesives were then analyzed by Fourier transform infrared (FTIR) and Thermogravimetric (TG), and tested as plywood binders. The study results could provide a theoretical basis and scientific guidance for the appropriate processing method and application technology development of COR.

2. Materials and Methods

2.1. Preparation of COR Adhesive

COR was obtained from a local farm. The contents of protein, acid detergent fiber, acid detergent lignin, and neutral detergent fiber in COR are 71.8%, 10.1%, 8.9%, and 0.8% of dry matter, respectively. The viscosity of COR with 15% solid content was 25 mPa·s. The COR was stored in a sealed glass container at room temperature (22°C) before use. Maleic anhydride, urea, and sodium hydroxide were obtained from Sinopharm Group Co. Ltd, Beijing.

The synthesis procedure of COR adhesive was as following: The COR and appropriate amount of water were added into a three-neck flask. Sodium hydroxide solution of 30% concentration was used to adjust the pH of the mixture to 11. The reaction mixture was stirred at 80°C for 20 min. Then, the urea solution with different concentrations (1mol/L, 2mol/L, and 3mol/L) was added. The pH of the reaction mixture was adjusted to 11 and the reaction mixture was stirred at 80°C for 20 min. The maleic anhydride with different contents (3%, 6%, and 9%) was then added. The pH of the reaction mixture was adjusted to 11 and the reaction mixture was stirred at different temperatures (50°C, 60°C,

and 70°C) for 60 min. After that, the pH of the reaction mixture was adjusted to 7-8 and the obtained COR adhesive was stored in a container at room temperature.

Orthogonal experimental design was used to perform the study. Three experimental factors are urea concentration, maleic anhydride content, and reaction temperature (Table 1). Urea concentration has three levels: 1mol/L, 2mol/L, and 3mol/L; maleic anhydride content has three levels: 3%, 6%, and 9%; reaction temperature has also three levels: 50°C, 60°C, and 70°C. Therefore, to simplify the experiment, the total number of experiment is nine.

Table 1. Experimental factors of adhesive.

Urea concentration	1mol/L, 2mol/L, 3mol/L
Maleic anhydride content	3%, 6%, 9%
Reaction temperature	50°C, 60°C, 70°C

2.2. Adhesive Properties Evaluation

2.2.1. General Properties

Viscosities of the adhesives were measured at 25°C in accordance with Chinese National Standard GB/T 14074-2017 with a rotational Brookfield DVS+ viscometer (Brookfield Engineering Laboratories, Inc., MA). Three replicas were performed for each test.

Solid content of the adhesives was measured in accordance with Chinese National Standard GB/T 14074-2017. Three replicas were performed for each test.

Gel time of the adhesives was also measured in accordance with Chinese National Standard GB/T 14074-2017. Three replicas were performed for each test.

2.2.2. Fourier Transform Infrared Spectroscopy

FTIR analysis was conducted using a Bruker Tensor II spectrophotometer (Bruker Optik GmbH, Ettlingen). The liquid samples of the COR adhesives were located on the stage of the spectrophotometer. FTIR spectra of a total of 32 scans for each sample from 4000 to 600 cm⁻¹ wavenumber were recorded.

2.2.3. Thermogravimetric Analysis

TG analysis was carried out with a TA Q50 analyzer (TA Instruments, DE). All the adhesive samples were cured at 120°C in a convective drying oven until the weights were constant. Specimens were placed in alumina crucibles, with an empty alumina crucible used as a reference. Specimens were heated from room temperature to 600°C at a heating rate of 10°C/min. The flow rate of nitrogen purge gas was 20 mL/min.

2.3. Panel Manufacturing

Plywood manufacturing parameters were shown in Table 2. Poplar veneers with moisture content of 8-10% and thickness of 1.6-1.7 mm were cut for plywood manufacturing. The plywood with dimensions of 250 mm × 250 mm was manufactured using a laboratory hot press. The adhesive application rate was 300 g/m² (double glue line). The adhesives were applied uniformly on both sides of the middle

veneer. The hot press time, temperature, and pressure were 5.5 minutes, 125 °C, and 1.0-1.1 MPa, respectively. Two panels were made for each adhesive formulation. After pressing, the plywood panels were conditioned at room temperature and 60 percent relative humidity for 5 days.

Table 2. Plywood manufacturing parameters.

Adhesive application rate (g/m ²)	300
Moisture content of veneers (%)	8-10
Hot press temperature (°C)	125
Hot press time (min)	5.5
Hot press pressure (MPa)	1.1

2.4. Measurement of the Bonding Strength

The bonding strength was measured according to Chinese National Standard GB/T 17657-2013. Six specimens with dimensions of 100 mm by 25 mm were cut from each panel to make a total of twelve specimens for each adhesive formulation. Before the testing of the wet strength, specimens were immersed in water at 63°C for 3h and tested by lap shear strength in a CMT 4104 universal testing machine (MTS System Corporation, MN). The wood failure percentage was identified and recorded.

Table 3. General properties of adhesives.

Urea concentration (mol/L)	Maleic anhydride content (%)	Reaction temperature (°C)	Solid content (%)	Viscosity (mPa·s)	Gel time (s)
1	3	50	25.21	2543	245
1	6	60	26.11	2856	253
1	9	70	27.98	2996	198
2	3	70	33.01	3014	265
2	6	60	30.5	2754	214
2	9	50	28.97	3652	200
3	3	70	34.09	2986	199
3	6	50	31.53	3340	245
3	9	60	34.99	3860	235

The viscosities of the adhesives were in a short range, from 2543 to 3860 mPa·s. Within this range, the adhesives could be easily applied to the veneer surface and obtain a uniform glue line, which would help improve the bonding strength. The gel times of the adhesives were from 198 to 265 s. These gel times were relatively short compared with those of soybean protein adhesives reported before. Gel time is also an important property for the adhesive. Shorter gel time usually means higher hot pressing efficiency.

3.2. FTIR Analysis

Figure 1 is the infrared spectrum comparison of unmodified, urea modified and maleic anhydride/urea modified COR adhesives. The absorption peaks of 3428cm⁻¹ and 3333cm⁻¹ were N-H and O-H stretching vibration, 1674cm⁻¹ was amide I region C=O stretching vibration, 1594cm⁻¹ was amide II region N-H bending vibration, 1150cm⁻¹ was amide III region C-N stretching vibration [15]. Compared with the unmodified COR adhesive and the urea modified COR adhesive, the maleic anhydride/urea modified COR adhesive has a new small peak at 2216 cm⁻¹, which might be due to the stretching vibration caused by the reaction of cottonseed protein

3. Results and Discussion

3.1. The General Properties of COR Adhesive

The general properties of the COR adhesives were shown in Table 3. The solid content is a basic physical parameter in the performance test of adhesive. The solid content of the adhesive will affect the bonding performance. If the solid content of the adhesive is too low, it means that the water content is too high. In the process of hot pressing, the water in the adhesive will be heated to generate steam. The more water was added, the more steam would be generated and released, the bonding performance would be affected. According to the test results, the solid contents of cottonseed adhesives were still very low. When urea concentration of 1mol/ L was used, the solid contents of adhesives were even less than 30%. When the reaction temperature increased, the solid contents also increased. The higher solid content could reduce the moisture content in the adhesive. This could bring less water to the veneers which would help reduce the hot pressing time of plywood and improve the hot pressing efficiency [14].

molecules and maleic anhydride. The cottonseed protein molecules could react with maleic anhydride to form a new structure with good stability. Therefore, the adhesive prepared is conducive to the improvement of the bonding performance.

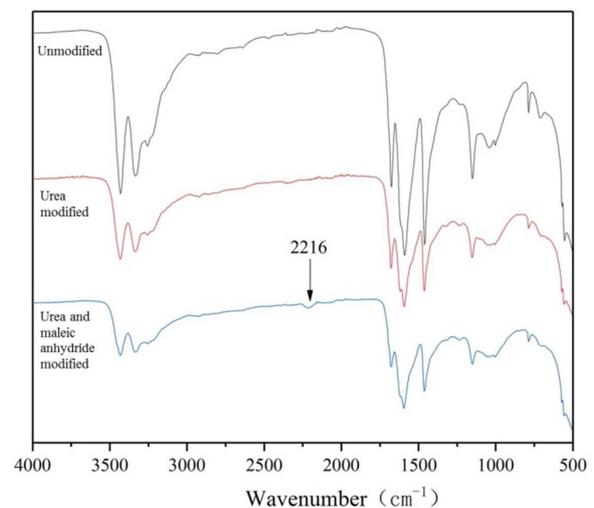


Figure 1. FTIR spectrum of COR adhesives.

3.3. TG Analysis

The TG curves of unmodified, urea modified and maleic anhydride/urea modified adhesives are shown in Figure 2. It can be seen that the thermal decomposition process of the three adhesives after curing could be divided into four stages (stages I, II, III, and IV): the first stage is from 40°C to 130°C, the weight loss of the three adhesives should be the water loss in the adhesive samples, and the weight loss of the maleic anhydride/urea modified adhesive is the smallest in the first stage.

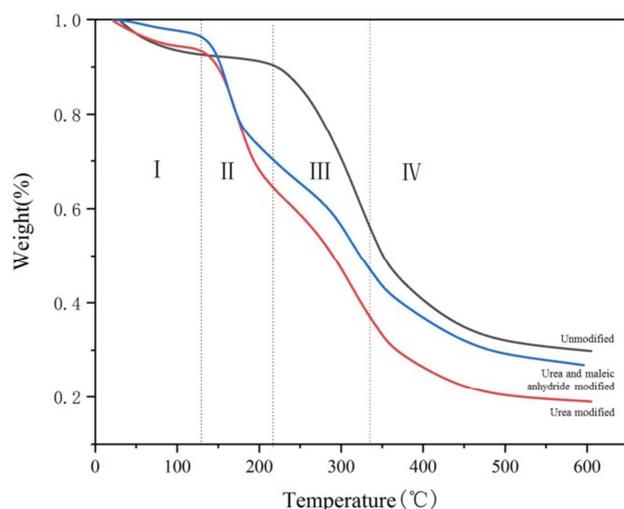


Figure 2. TG curves of COR adhesives.

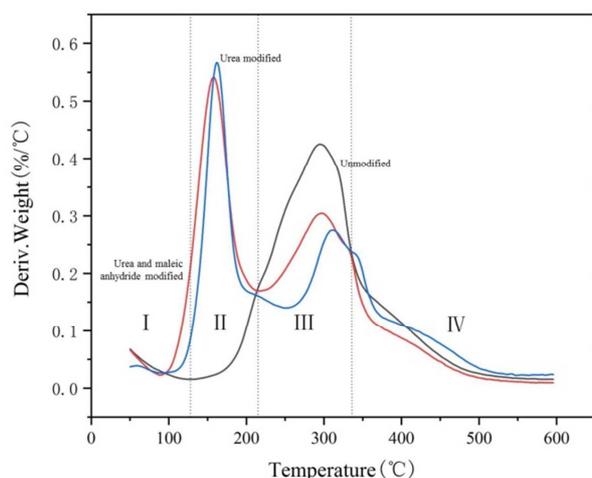


Figure 3. DTG curves of COR adhesives.

The second stage is from 130°C to 220°C, during which the weight loss of unmodified COR adhesive is the smallest. The decomposition rate of urea modified adhesive is faster than that of maleic anhydride/urea modified adhesive. At the

end of the second stage, the weight loss of urea modified adhesive is about 40%, indicating that only using urea to modify adhesive would reduce the stability and result in no improvement of water resistance. The weight loss of the two modified adhesives might be caused by the addition of urea, which could destroy the composition of cottonseed protein and break down the macromolecular protein into protein with smaller molecules. Under the condition of high temperature, the micromolecule protein was degraded. It could be seen from the DTG curves (Figure 3) that the peak temperature (162°C) of the adhesive with maleic anhydride and urea added in the second stage is higher than that of the adhesive with only urea added (159°C).

The third stage is from 220°C to 335°C. The weight loss in this stage could be caused by the breakdown of cottonseed protein skeleton structure. At this stage, the skeleton structure of cottonseed protein is completely decomposed, releasing CO, CO₂, NH₃ and other gases resulting in weight loss. The DTG curve showed that the peak value of maleic anhydride/urea modified adhesive increased significantly from 297°C to 313°C, which indicated that the thermal stability of the cross-linked modified adhesive was better than the other two adhesives.

The fourth stage is from 335°C to 600°C, and the weight loss is caused by the decomposition of the structure formed by the reaction of cottonseed protein and maleic anhydride. The addition of urea expanded the structure of cottonseed protein, and the exposed -NH₂, -COOH and other active groups reacted with maleic anhydride, resulting in a stable new structure to improve the water resistance of the adhesive.

3.4. Bonding Strength Measurement

The adhesive strength is an important index to evaluate the adhesive performance. According to the national standard for class II plywood for indoor use, the wet adhesive strength after 63°C water treatment should be no less than 0.7 MPa. According to the data of wet adhesive strength in Table 4, the result of reaction temperature affected the most during the preparation of adhesive, which indicated that reaction temperature had a primary influence on wet shear strength and should be the main factor.

According to the range R: reaction temperature R3 = 0.458 > maleic anhydride content R2 = 0.281 > urea concentration R1 = 0.229, so the primary and secondary order of influence of each factor is: reaction temperature > maleic anhydride content > urea concentration. It could be seen from this result that the reaction temperature has the greatest influence on the wet shear strength of the prepared adhesive, while the urea concentration has the least.

Table 4. Bonding strength of adhesives.

Urea concentration (mol/L)	Maleic anhydride content (%)	Reaction temperature (°C)	Bonding strength (MPa)	Wood failure (%)
1	3	50	0.758	100
1	6	60	1.151	100
1	9	70	0.860	90
2	3	70	0.946	80

Urea concentration (mol/L)	Maleic anhydride content (%)	Reaction temperature (°C)	Bonding strength (MPa)	Wood failure (%)
2	6	60	0.912	100
2	9	50	0.878	90
3	3	70	1.203	100
3	6	50	0	50
3	9	60	0.763	100
T1	2.769	2.907	1.636	T=7.740
T2	2.736	2.063	2.826	
T3	2.081	2.501	3.009	
k1	0.923	0.969	0.545	
k2	0.912	0.688	0.942	
k3	0.694	0.834	1.003	
R	0.229	0.281	0.458	

Table 5. Analysis of variance.

Factors	Class III sum of square	Degree of freedom	Mean square	F	Significance
Maleic anhydride	0.156	2	0.078	0.521	0.657
Temperature	0.407	2	0.204	1.362	0.423
Urea	0.137	2	0.069	0.459	0.685
Error	0.299	2	0.150		
Total	7.166	9			

It could be seen from Table 5 that considering the wet shear strength of the prepared adhesive as the index, the best synthesis parameters were that: the urea concentration was 2 mol / L, the maleic anhydride content was 6%, and the reaction temperature was 70°C, the wet shear strength of the prepared adhesive was the highest. According to the analysis of variance, the influence of the three factors on the adhesive strength of the prepared COR adhesive was not significant.

According to the data in Table 4, the plywood bonded by adhesive prepared under the conditions of urea concentration of 3 mol / L, maleic anhydride content of 6%, and reaction temperature of 50°C, was completely failed during the 63°C water treatment. The reason might be that the chain structure of cottonseed protein was not fully developed at low temperature and the urea concentration was also too high. The excessive urea was not involved in the reaction and stayed freely in the adhesive. Therefore, the adhesive strength was reduced.

4. Conclusions

In this study, bio-based adhesives were synthesized from COR, maleic anhydride, and urea. The obtained adhesives were then analyzed by FTIR and TG, and tested as plywood binders. The results indicated that the optimal synthesis conditions of the modified COR adhesive were: the urea concentration was 2 mol/L, the maleic anhydride content was 6%, and the reaction temperature was 70°C. Infrared spectrum revealed the principle of maleic anhydride/urea modification to improve the bonding strength, that is, after adding maleic anhydride, a new characteristic peak appeared at 2216 cm⁻¹, which indicated that the protein in COR reacted with maleic anhydride to form a stable new structure, which improved the water resistance of the adhesive. The TG curve of maleic anhydride/urea modified COR adhesive showed that the peak value of the adhesive shifted back in the second and third stages, which indicated that the modified adhesive had better thermal stability and improved water resistance.

In conclusion, the study results could provide a theoretical basis and scientific guidance for the appropriate processing method and application technology development of COR.

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Conflicts of Interest

The authors declare that they have no competing interests.

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