Investigation of a Formaldehyde-free Cottonseed Flour-based Adhesive for Interior Plywood

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A new formaldehyde-free wood adhesive, primarily composed of defatted cottonseed flour (CF) and polyamine-epichlorohydrin (K736) resin, was investigated for the preparation of interior plywood. Sodium hydroxide was an essential component of the adhesive. The effects of pH values of the CF-K736 adhesive, the CF/K736 weight ratio on the pot life of the adhesive, and the water resistance of the resulting plywood panels were investigated in detail. The hot-pressing temperature and time were optimized in terms of the water resistance of the resulting plywood panels. The resulting 5-ply plywood panels met the industrial water resistance requirements for interior application under the following conditions: pH > 11, CF/K736 weight ratio in the range of 8/1 to 5/1, hot-press temperature ≥ 120 °C, and hot-pressing time > 4 min. The pot life of the adhesive was approximately 3 h when the pH was 12 and the CF/K736 weight ratio was 8/1. The curing mechanism of the adhesive is discussed.

Keywords: Cottonseed flour; Formaldehyde-free; Polyamine epichlorohydrin resin; Water resistance; Wood composites

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INTRODUCTION

Wood adhesives play a key role in the production of wood-based composite panels such as plywood, particleboard, and fiberboard. The most widely used wood adhesives are formaldehyde-based resins such as urea-formaldehyde (UF) resins, melamine-formaldehyde resins, melamine-urea-formaldehyde resins, and phenol-formaldehyde resins (Dunky 2003). The UF resins are the dominant adhesives in the production of interior wood-based composite panels, such as decorative plywood, particleboard, and medium density fiberboards, because they are low cost, have low cure temperatures and high reactivity, and the resulting panels have good properties (Conner 1996). However, carcinogenic formaldehyde is released during the production and use of the wood-based composite panels bonded with UF resins, which has prompted the development of formaldehyde-free wood adhesives (Meyer and Hermanns 1986; IARC 2004).

Extensive work has been done to develop formaldehyde-free wood adhesives from soybean proteins because soybean proteins are abundant, inexpensive, and readily available (Chen *et al.* 2019; Mousavi *et al.* 2019; Pradyawong *et al.* 2019). Two soybean flour-based, formaldehyde-free wood adhesives are currently used in the commercial production of interior plywood (Li *et al.* 2004; Li 2007; Jang *et al.* 2011; Jang and Li 2015). However, soybean flour can be used for animal feed and human consumption. It is preferable to develop formaldehyde-free wood adhesives from non-food renewable materials.

Cotton is one of the most important crops in the world for fiber production. After harvesting the fibers, a tremendous amount of cottonseed remains. The cottonseeds consist of shell, oil, and meal. After de-hulling and oil removal, the product is called cottonseed meal (CM). The CM contains a chemical called gossypol that is toxic to humans and animals, and it is thus not considered a food source for human consumption. Some cottonseeds are mixed with other animal feeds for adult ruminants, such as cattle and sheep, but the amount of cottonseeds cannot exceed the toxicity level tolerated by adult ruminants (Morgan 2017). Presently, cottonseeds and the CM are underutilized.

Some work to develop CM-based wood adhesives was conducted in the 1950s (Hogan and Arthur, Jr. 1951a,b, 1952). Due to various factors, such as low water resistance and long press time, CM-based wood adhesives have not been accepted by the forest products industry. There are several recent studies on CM-based wood adhesives (Cheng *et al.* 2013; He *et al.* 2014a,b, 2016). In these studies, two small pieces of veneers were made into a laminate with a CM-based adhesive with a bonding area of approximately 12.7 mm x 25.4 mm or 25.4 mm x 25.4 mm at the ends of the veneers. Such a laminate is too simple to be representative of plywood panels. The solids content of the CM-based adhesives in these studies was approximately 11 wt%, which is too low to be practical in commercial applications on wood composites (He *et al.* 2014a,b; Hughes 2015; He and Chiozza 2017).

Water-washed CM-based adhesives with high solid contents of 49% were explored for furniture and small utensil bonding (He and Cheng 2017; He and Cheng 2019). Cottonseed protein isolate treated by H_3PO_4 was reported as an adhesive to make 3-ply 30 cm × 30 cm plywood that could pass the requirements for interior applications (Li *et al.* 2019). But the hot press conditions in these studies are not suitable for the typical commercial production of plywood panels (He and Cheng 2017; He and Cheng 2019; US EPA 1995). It has also been reported that the water-washed CM could partially replace UF resins for the production of wood composites (Liu *et al.* 2018). However, the replacement cannot resolve the formaldehyde emission issue.

Soybean flour and CM have comparable protein content, but have different amino acid profiles, and different contents and compositions of carbohydrates (He *et al.* 2015). In a previous study, polyamine-epichlorohydrin (K736), an inexpensive and environmentally friendly paper wet-strength agent, was found to be a good curing agent for soybean flour (Chen *et al.* 2019). In this study, K736 was investigated to see if it could effectively crosslink the CM for the production of water-resistant plywood panels.

EXPERIMENTAL

Materials

Dehulled cottonseed flour (5.0% moisture content, MC) was provided by Cotton Inc. (Cary, NC, USA). The Kymene™ 736 (K736) resin was provided by Solenis Inc. (Wilmington, DE, USA). The solids content of the K736 resin was 38 wt%. Sodium hydroxide and potassium bromide were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Yellow poplar veneers (61 cm × 61 cm in area, 5.0 to 5.1 mm in thickness, and 12% MC) were provided by Columbia Forest Products (Greensboro, NC, USA).

Methods

Preparation of dehulled, defatted cottonseed flour (CF)

Dehulled cottonseed flour (750 g) was added to hexane (1500 mL) in a 3-L resin kettle. The mixture was stirred vigorously with a mechanical stirrer (Arrow Engineering, Hillside, NJ, USA) at room temperature (RT) for 8 h, and then left without stirring overnight. The yellow solution (approximately 800 mL) above the precipitate was removed by siphoning. The remaining mixture was centrifuged at 3500 rpm for 30 min, and the resulting precipitate was separated from the supernatant and returned to the resin kettle, where fresh hexane (800 mL) was added and the mixture was stirred for 8 h. The resulting mixture was left without stirring overnight, and then it was filtered through a Whatman™ filter paper (Grade 1). The solid material on the filter paper was washed with hexane (200 mL) and then dried in a fume hood at room temperature for 24 h to generate CF (650 g, 6.0% moisture content) with the yield of 86 wt% (the yield is defined as the dry mass of the CF divided by the dry mass of dehulled cottonseed flour). All solutions and the supernatant were combined and evaporated with a rotary evaporator for recovery and reuse of the solvent.

Preparation of a CF-K736 adhesive

The typical procedure in this experiment for the preparation of a CF-K736 adhesive with a CF/K736 weight ratio of 7/1 (dry basis) and 4.7 wt% NaOH (based on the dry weight of CF and K736) is as follows: water (207 g) and NaOH (6.1 g) were added to a Kitchen Aid mixer and stirred for 10 min; K736 (42.4 g wet weight) was then added to the NaOH solution and stirred for 1 min followed by the addition of the CF (120 g) and further mixing at room temperature for 5 min. The resulting CF-K736 adhesive had 36 wt% of the total solids content.

The determination of the adhesive pot life

The CF-K736 adhesive was stored at RT and checked for its ability to spread on a veneer. The pot life is defined as the period of the time between the completion of the adhesive preparation and the time when the adhesive becomes too viscous to be readily applied onto a veneer with a hand-held rubber roller.

Preparation of plywood

The CF-K736 adhesive was applied onto one side of a yellow poplar veneer with a hand-held rubber roller with an adhesive add-on rate of 230 g/m^2 on a wet basis. A clean veneer was put on top of the adhesive layer, followed by application of the same amount (230 g/m^2) of the adhesive onto the veneer. This process was repeated until a laminate with five layers of the veneers and four layers of the adhesive was made. The grain directions of two adjacent layers of the veneers were perpendicular to each other. The laminate was placed on a table at RT for 5 min, pressed at 0.69 MPa at RT for 5 min, placed on a table at RT again for 5 min, and then hot-pressed at 1.03 MPa for a predetermined temperature and time. The resulting plywood panel was stored at RT for at least 24 h before its water resistance was evaluated. Two plywood panels were made with each adhesive formulation.

Evaluation of water resistance of the plywood panel

The evaluation was performed in accordance with the procedure shown in the Section 4.6 of the Three-Cycle soak test specified by the American National Standard for Hardwood and Decorative Plywood (ANSI/HPVA HP-1 2014). More specifically, 20 specimens (12.7 cm × 5.08 cm) were prepared from each panel, soaked in water (21.4 °C) for 4 h, and then dried in a forced air oven (50 °C) for 19 h. This soaking and drying cycle was repeated three times. A specimen was defined as “failed” if a continuous opening between two layers was longer than 50.8 mm, deeper than 6.35 mm, and wider than 0.076 mm. The plywood panel failed to meet the water resistance requirement if more than one out of 20 specimens failed after the first cycle of the soak test and more than three out of 20 specimens failed after the third cycle.

Characterization of the adhesive with Fourier transform infrared (FTIR) spectroscopy

The adhesive samples for the FTIR analysis were prepared with a predetermined CF/K736 weight ratio at pH = 12 according to the procedure in the above section ‘Preparation of a CF-K736 adhesive’. One portion of the adhesive was frozen at -20 °C, and then dried under vacuum for 24 h. The resulting freeze-dried adhesive was designated as “uncured CF-K736.” Another portion of the adhesive (21 g, wet weight) was rolled onto a Teflon film (30 cm × 30 cm) and then covered with another Teflon film. The Teflon film/adhesive/Teflon film laminate was placed onto two layers of yellow poplar veneers, and then another two layers of the veneers were put onto the laminate to form a veneer/veneer/Teflon film/adhesive/Teflon film/veneer/veneer laminate. This laminate was pressed at 120 °C for 6 min with a pressure of 1.03 MPa to obtain the cured adhesive sample. After the hot-press, the cured adhesive sample was frozen at -20 °C and then dried under a vacuum for 24 h. Each CF-based adhesive sample was ground into powder and mixed with KBr to form pellets for FTIR analysis using a Nicolet iS 50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

RESULTS

The Removal of Oil from Dehulled cottonseed flour and the Effect of the Oil on Water Resistance of the Resulting Plywood

Dehulled cottonseed flour was directly used without removing its oil for preparation of adhesives with K736. A number of adhesive formulations were prepared through changing dehulled cottonseed flour/K736 weight ratios, and the usage of sodium hydroxide and evaluated for preparation of plywood panels. Unfortunately, none of the resulting plywood panels passed the first cycle of the soak test. From the research group’s previous experience working with soybean flour and lupine flour, it was speculated that the oil in the dehulled cottonseed flour was responsible for the poor water resistance of the resulting plywood panels.

The oil in the dehulled cottonseed flour was removed through a two-step extraction process with hexane to generate CF. The yield of the CF was 86 wt%. The residual oil content of the CF was not measured because it was believed the complete removal of the oil was not necessary for this adhesive application. The research group’s experience working on soybean flour/K736 adhesive previously revealed that sodium hydroxide is an essential component of the adhesive (Chen *et al.* 2019). In the present experiment, the first aspect investigated was the effect of the NaOH in the CF-K736 adhesives on the water resistance of the resulting plywood panels.

The Effects of pH on the Pot Life and Water Resistance of Plywood

As shown in Table 1, the pH of the CF-K736 adhesive was 5.0 without the addition of NaOH. Both plywood panels failed to pass the three-cycle soak test. One panel passed and another panel failed after the first cycle, and 12 and 11 out of 20 specimens failed after the third cycle, respectively. The addition of 3.0 wt% of NaOH raised the pH value of the adhesive to 8.5; neither panel passed the three-cycle soak test. In one of the panels, 4 out of 20 failed after the third cycle, and, in another panel, 2 out of 20 failed in the first cycle. When the usage of NaOH was increased from 3.0 to 3.6 wt%, the pH value of the adhesive rose from 8.5 to 10. However, only one of the two panels passed the three-cycle soak test. On the other panel, 4 of the 20 specimens failed after the third cycle. When the NaOH usage was further increased to 4.2 wt%, 4.7 wt%, and 5.3 wt%, the pH value of the adhesive correspondingly increased to 11, 12, and 13; all panels passed the three-cycle soak test. The pot life of the adhesives decreased from > 12 h to only 1 h as the pH increased from 5.0 to 13. The pot life of the adhesive at pH = 11 was 4 h, when both panels passed the three-cycle soak test.

Table 1. Effects of NaOH Usage on the Pot Life of CF-K736 Adhesives and Water Resistance of the Resulting Plywood Panels

NaOH (wt%)[a]	pH	Number of Failed Specimens		Pass (P) /Failure (F)[b]	Pot Life (h)
		1st Cycle	3rd Cycle		
0	5.0	2	12	F	>12
		0	11	F	
3.0	8.5	0	4	F	>12
		2	3	F	
3.6	10	0	3	P	9
		0	4	F	
4.2	11	0	1	P	4
		0	1	P	
4.7	12	0	0	P	2
		0	0	P	
5.3	13	0	0	P	1
		0	0	P	

CF/K736 resin weight ratio: 7/1; hot-pressing conditions: 1.03 MPa, 130 °C, and 6 min
[a] Based on the dry weight
[b] After the 3rd cycle

The Effects of CF/K736 Weight Ratio on the Pot Life and Water Resistance of Plywood

As shown in Table 2, when the weight ratio of CF/K736 was 13/1 or 11/1, all panels failed the three-cycle soak test. When the weight ratio was 9/1, one panel passed the three-cycle soak test and the other one failed. The weight ratios of CF/K736 in the range of 8/1 to 5/1 enabled all panels to pass the three-cycle soak test. The pot life of adhesives decreased from > 12 h to < 1 h when the weight ratio was changed from 13/1 to 5/1. The pot life was 3 h at the weight ratio of 8/1, where both plywood panels passed the three-cycle soak test.

Table 2. Effect of the CF/K736 Weight Ratio on the Pot Life of CF-K736 Adhesives and Water Resistance of Plywood Bonded with the Adhesives

CF/K736	Number of Failed Specimens		Pass (P) /Failure (F)[a]	Pot Life (h)
	1st Cycle	3rd Cycle		
13/1	20	20	F	> 12
	2	7	F	
11/1	2	10	F	7
	7	16	F	
9/1	3	8	F	5
	0	1	P	
8/1	0	0	P	3
	0	0	P	
7/1	0	0	P	2
	0	0	P	
5/1	0	0	P	< 1
	0	0	P	

The pH was maintained at 12.0 by adding 3.3 wt%, 3.5 wt%, 3.8 wt%, 4.3 wt%, 4.7 wt%, and 6.0 wt% of NaOH to the adhesives with the following CF/K736 weight ratios of 13/1, 11/1, 9/1, 8/1, 7/1, and 5/1, respectively. Hot-pressing conditions: 1.03 MPa, 130 °C and 6 min
[a] After the 3rd cycle

The Effects of Hot-pressing Temperature on the Water Resistance of Plywood

The effect of the hot-pressing temperature on the water resistance of the resulting plywood panels is shown in Table 3. At 70 °C and 90 °C, both panels failed the three-cycle soak test. When the temperature was elevated to 110 °C, one panel passed the three-cycle soak test and the other failed because of the failure after the first cycle. At the temperature of 120 °C, 130 °C, or 150 °C, all panels passed the three-cycle soak test, and there was no single specimen that failed.

Table 3. Effects of Hot-pressing Temperature on the Water Resistance of Plywood Bonded with CF-K736 Adhesives

Temp. (°C)	Number of Failed Specimens		Pass (P) /Failure (F)[a]
	1st Cycle	3rd Cycle	
70	15	19	F
	11	16	F
90	1	6	F
	2	5	F
110	0	0	P
	3	3	F
120	0	0	P
	0	0	P
130	0	0	P
	0	0	P
150	0	0	P
	0	0	P

The pH value of the adhesive was 12.0 with the NaOH usage of 4.3 wt%.
CF/K736 weight ratio was 8/1; hot-pressing: 1.03 MPa and 6 min;
[a] After the 3rd cycle

The Effects of Hot-pressing Time on Water Resistance of Plywood

As shown in Table 4, for the hot-pressing time of 2 and 3 min, all panels failed the three-cycle soak test. When the hot-pressing time was between 4 and 6 min, all plywood panels passed the three-cycle soak test. For the 6 min time, none of the specimens failed after the first and third cycles.

Table 4. Effects of Hot-pressing Time on the Water Resistance of Plywood Bonded with CF-K736 Adhesives

Time (min)	Number of Failed Specimens		Pass (P) /Failure (F)[a]
	1st Cycle	3rd Cycle	
2	11	18	F
	9	16	F
3	3	8	F
	5	9	F
4	0	0	P
	1	2	P
5	0	1	P
	0	0	P
6	0	0	P
	0	0	P

pH = 12.0 (with 4.31% NaOH); CF/K736 weight ratio of 8/1; hot-pressing: 1.03 MPa, 120 °C
[a] After the 3rd cycle

FTIR Spectroscopy of the CF-K736 Adhesives

The FTIR spectra for uncured and cured CF-K736 adhesives are shown in Fig. 1. The cured adhesive showed a new obvious peak at 1730 cm^{-1} corresponding to the stretching vibration of the C=O bonds of ester groups.

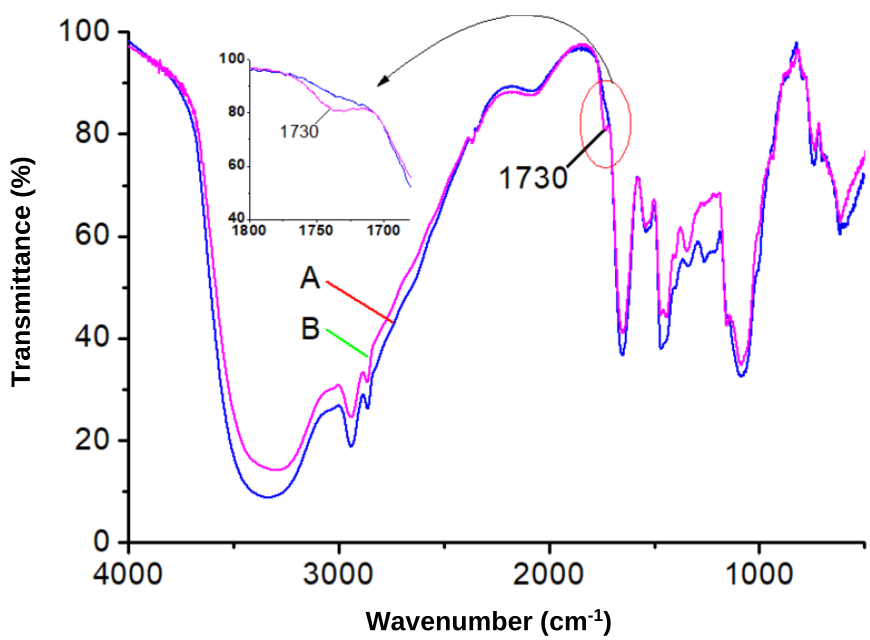

Fig. 1. The FTIR spectra of uncured (A) and cured (B) CF/K736 adhesives at pH = 12 and a CF/K736 weight ratio of 1/5

DISCUSSION

The K736 resin is a commercial paper wet-strength resin that contains hydroxyl-azetidinium rings and chlorohydrin (Chen *et al.* 2019). The azetidinium consists of a highly strained four-member ring that can be easily opened by a nucleophile, such as carboxylate and amino groups, especially at elevated temperatures. Chlorohydrin is not expected to react with these nucleophiles as fast as azetidinium, but the presence of a strong base, such as NaOH, can accelerate the reactions by the generation of epoxy groups or azetidinium structures from chlorohydrin (Jang *et al.* 2011).

The reactive functional groups in the CF protein include the carboxylic acid groups (-COOH), amino groups (-NH_2), mercapto groups (-SH), and hydroxyl groups (-OH). Carbohydrates contain a large amount of -OH groups. All these functional groups are able to react with the azetidinium, epoxy, and chlorohydrin groups in K736 in the curing process of the adhesive. Compared to the uncured CF-K736, a new ester band at 1730 cm^{-1} in the FTIR spectrum of the cured CF-K736 provided strong evidence for the reactions between carboxylate groups of CF and K736 (Fig. 1). These reactions are expected to form three-dimensional crosslinked networks to improve the water resistance of the resulting plywood panels (Li *et al.* 2004). The proposed curing reactions of CF-K736 adhesives are shown in Fig. 2.

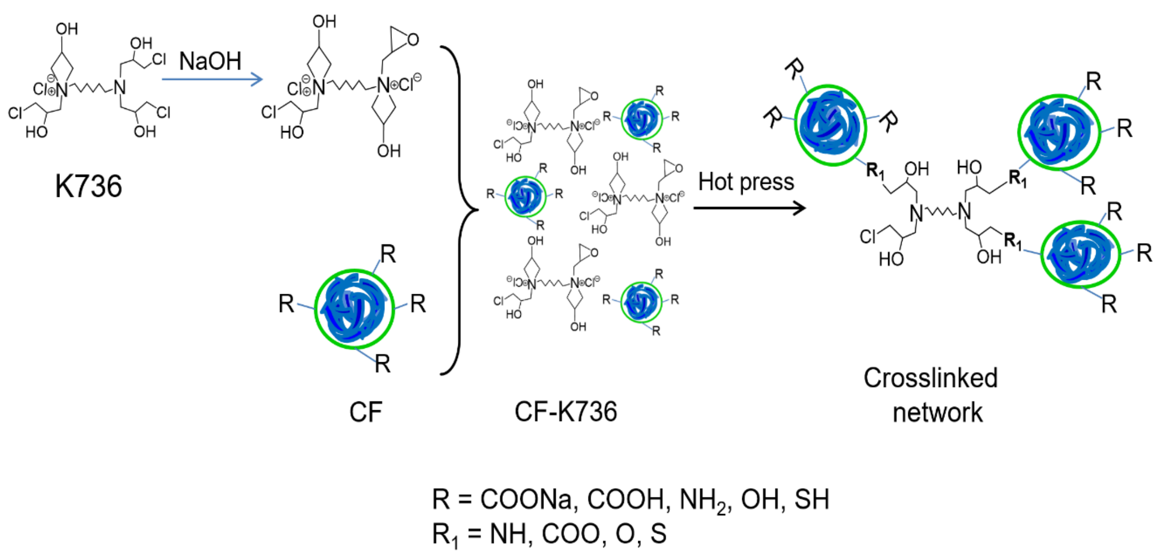

Fig. 2. Proposed curing reactions of CF-K736 adhesives

In the FTIR analysis of cured and uncured CF-K736 adhesives, the ester absorption at 1730 cm^{-1} did not appear in a FTIR spectrum of a cured adhesive until the CF/K736 weight ratio was lowered from 7/1 to 1/5, probably because the concentration of the ester groups was too low to be detected at a higher CF/K736 weight ratio. Other curing reactions with amino groups (-NH_2), mercapto groups (-SH), and hydroxyl groups (-OH) were hard to identify in the FTIR spectra due to the overlapping absorptions from the complex structures of the CF protein.

Sodium hydroxide can unfold the globular structure of the CF protein. The unfolding exposes more functional groups, such as carboxylic acid and amino groups, which can undergo reactions with K736 resin. This sequence of steps is consistent with the results, shown in Table 1, that NaOH is an essential ingredient for the CF-K736 adhesives. The minimum amount of NaOH required to produce water-resistant plywood panels was 4.2 wt% for the CF-K736 adhesive at the CF/K736 weight ratio of 7/1, whereas the minimum amount of NaOH required for the defatted soybean flour (DSF)-K736 adhesive was 5.9 wt% at the same 7/1 DSF/K736 weight ratio, with hot press conditions of 130 ºC and 6 min (Chen *et al.* 2019).

The K736 acts as a curing agent, and its usage in the adhesive formulation should be sufficiently high to provide adequate crosslinking density that forms a strong and water-resistant adhesive network (Chen *et al.* 2019). Another argument for an adequate amount of K736 is that a sufficient amount of the carboxylic acid groups in the CF must be blocked by K736 because the high content of the carboxylic acid groups causes poor water resistance (He *et al*. 2015; Ma *et al*. 2019). The K736 is much more expensive than the CF. The high usage of K736 increases the overall cost of the CF-K736 adhesive and also shortens the pot life of the adhesive, which may reduce the operational window of the commercial application of this adhesive. Therefore, the CF/K736 weight ratio should be as high as possible, as long as the adhesive still enables the resulting plywood panels to pass the three-cycle soak test. Results from this study appear to suggest that the CF/K736 ratio of 8/1 is optimal for production of water-resistant plywood panels. For the DSF-K736 adhesives, the DSF/K736 weight ratio could be as high as 11/1, which implies that the DSF-K736 adhesive could be less expensive than this CF-K736 adhesive if the sale prices of DSF and CF were the same (Chen *et al.* 2019).

Elevated temperature facilitates the reactions between K736 and protein (Fig. 2) (Gustafsson *et al.* 2016; Chen *et al.* 2019). The results in Table 3 indicate that the CF-K736 adhesive performed well in a wide hot-pressing temperature range from 120 °C to 150 °C, which is a typical hot-pressing temperature range for the commercial production of plywood. The minimum hot-press temperature required for the DSF-K736 adhesive was 110 °C, which is slightly lower than that for this CF-K736 adhesive.

For the production of plywood panels, the hot-pressing time must be long enough to ensure the complete curing of the adhesive. A higher pressing temperature typically results in a shorter hot-pressing time for plywood panels with the same number of layers and the same thickness. The results in Table 4 indicate that the hot-pressing time must be longer than 4 min to prepare water-resistant 5-ply plywood at the hot-pressing temperature of 120 °C. The minimum hot-press time for the DSF-K736 was 4 min at 130 °C (Chen *et al.* 2019).

CONCLUSIONS

1. A formaldehyde-free wood adhesive consisting of defatted cottonseed flour (CF), polyamine-epichlorohydrin resin (K736), and NaOH was successfully developed for production of interior plywood.
2. NaOH was found to be an essential component of the adhesive and had to be at least 4.2 wt%.
3. The CF/K736 weight ratio of 8/1 at pH 12 was the highest weight ratio that still enabled the production of water-resistant plywood panels.
4. The adhesive worked well at the hot-pressing temperature between 120 °C and 150 °C

and a hot-pressing time of longer than 4 min.

5. The CF-K736 adhesive has the potential of being an alternative to formaldehyde-based wood adhesives for interior plywood panels.

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