Synthesis and Characterization of Starch-based Aqueous Polymer Isocyanate Wood Adhesive

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Modified starch was prepared in this work by acid-thinning and oxidizing corn starch with ammonium persulfate. Also, starch-based aqueous polymer isocyanate (API) wood adhesive was prepared. The effect of the added amount of modified starch, styrene butadiene rubber (SBR), polymeric diphenylmethane diisocyanate (P-MDI), and the mass concentration of polyvinyl alcohol (PVOH) on the bonding strength of starch-based API adhesives were determined by orthogonal testing. The starch-based API adhesive performance was found to be the best when the addition of modified starch (mass concentration 35%) was 45 g, the amount of SBR was 3%, the PVOH mass concentration was 10%, and the amount of P-MDI was 18%. The compression shearing of glulam produced by starch-based API adhesive reached bonding performance indicators of I type adhesive. A scanning electron microscope (SEM) was used to analyze the changes in micro-morphology of the starch surface during each stage. Fourier transform infrared spectroscopy (FT-IR) was used to study the changes in absorption peaks and functional groups from starch to starch-based API adhesives. The results showed that during starch-based API adhesive synthesis, corn starch surface was differently changed and it gradually reacted with other materials.

Keywords: Starch-based API adhesive; Orthogonal test; Compression shearing strength; SEM; FT-IR

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INTRODUCTION

Starch is a renewable and environmentally friendly polymer material, an extensive source of raw materials, non-toxic, and readily biodegradable. Starch can be acid-thinned and oxidized with ammonium persulfate, which causes most of the hydroxyl groups to be converted to carbonyl and carboxyl groups, breaking a portion of the glycosidic bonds of long chains, decreasing the molecular weight, and significantly increasing the reactivity (Heikka *et al*. 1997). Polyhydroxy substances with glucose and ethylene glycol glycoside side-chains can be obtained by oxidizing starch with ethanediol under acid catalysis and heating (Lee *et al*. 2010). Polyhydroxy substances with high chemical reactivity can react with polyhydric acid (anhydride), producing a new type of polyester-based starch adhesive; then, the isocyanate group (–NCO) with high reactivity can be introduced. In this manner a starch-based aqueous polymer isocyanate (referred to as starch-based API) wood adhesive has been prepared (Gao *et al*. 2011a).

In this study, modified starch was prepared by acid-thinning and oxidizing the starch; then, the main agent of the starch-based API was prepared by adding polyvinyl alcohol (PVOH) and emulsifiers. Its performance indices were tested. Finally, the starch-based API adhesive was synthesized by adding isocyanate (Ling *et al*. 2008). Glulam was

pressed, and compression shearing strength was tested. The synthesis scheme of the starch-based API wood adhesive was optimized. By orthogonal testing, the best synthesis scheme for the starch-based API adhesive was determined. The synthesis process of modified starch and starch-based API adhesive were characterized by SEM and FT-IR.

The starch-based API adhesives studied were found to have good bonding properties to wood and can be used for different wood products, such as solid wood flooring, furniture parts, plywood, and finger-jointed wood. Following the introduction of the starch, the cost of the starch-based API was reduced, while meeting the requirements for starch-based API adhesive performance. So application amount of starch-based API adhesive increased gradually.

EXPERIMENTAL

Materials

Corn starch was provided by Changchun Dacheng Starch Ltd. (China). PVOH used in this experiment was 88+% hydrolyzed, and its molecular weight was in the range of 80,000 to 90,000. It was gradually added to water and stirred at 90 °C for 1 h to obtain a solution, and subsequently was stored at room temperature. The styrene butadiene rubber (SBR) employed had a solid content of 50%, viscosity of 180 mPa·s (at 25 °C), pH of 10, and styrene/butadiene ratio of 50/50 (by weight). Polymeric diphenylmethane diisocyanate (P-MDI) used in this experiment had a viscosity of 163 mPa·s (at 25 °C), an isocyanate molar concentration of 7.27 mmol/g and a specific gravity of 1.23 (at 25 °C). The moisture content of birch was 6% to 12% and its dimensions were 30 mm×25 mm×10 mm.

Preparation of Modified Starch

First, 100 g of corn starch and 3 g of ammonium persulfate were mixed with water (50% with respect to dry starch). Acid-thinned starch was thus prepared and placed in a blast drying oven at 75 °C. Grinding followed by drying for 2 h at 100 °C afforded the acid-thinned starch, which was then cooled to room temperature until ready to use.

Acid-thinned corn starch and ethylene glycol were added in a reaction device at a proportion of 2 (by weight). The temperature of ethylene glycol was kept at 70 °C for 1 h, after which the reactor was cooled down.

The hydroxyl groups content of the reaction product was measured, then maleic anhydride was added to adjust the same molar ration of carboxyl groups and hydroxyl groups in the reaction system. The stirring was continued at 70 °C. When the viscosity of the acid and oxidation starch reached 270 mPa.s at 25 °C, the system reaction stopped and was cooled to 40 °C. The resulting product was the modified starch. Its mass concentration was 35%.

Preparation of the Main Agent for Starch-based API

A certain amount of PVOH and water were added to the three-necked flask, then the system was heated to 95 °C by means of a water bath and was kept at that temperature for 1 h. It was completely dissolved and was released after cooling down to room temperature.

According to the orthogonal test design (Table 1), a certain amount of modified starch was added to three-necked flask and heated to 45 °C. A certain mass concentration of PVOH solution (10 g) and certain mass parts of emulsifier SBR were added and kept for 30 min. The product of synthesis was namely the main agent of starch-based API adhesive.

Preparation of Starch-based API Adhesive

The main agent synthesized from the above process and the cross-linking agent p-MDI were mixed in proportion of 100 to 18 (by weight) and then stirred evenly. The starch-based API adhesive was thus prepared.

Orthogonal Test Design

On the basis of exploratory trials on starch-based API wood adhesives, various factors of important effects on the normal compression shearing strength (NCSS) and boiling repeated compression shearing strength (BRCSS) of the starch-based API wood adhesives were determined. The amount of modified starch, emulsifier SBR, and cross-linking P-MDI and mass concentrations of PVOH were chosen as variables, and compression shearing strength of laminated wood was selected as an indicator, to design an orthogonal experiment L16 (4^4) with four factors and four levels. Bit-level factors are shown in Table 1.

Table 1. Factors and Levels of Orthogonal Test

Level/factor	Modified starch (g) (MS)(A)	SBR (%) (B)	PVOH concentration (%) (C)	P-MDI (%) (D)
1	40	0	6	12
2	45	3	8	15
3	50	6	10	18
4	55	9	12	21

Characterization

Fourier transform infrared spectroscopy (FT-IR)

All infrared spectra were obtained using an FT-IR (VERTEX70) spectrometer produced by Bruker Company (Germany) using the KBr pellet method and were recorded with an average of 16 scans at a resolution of 4 cm^{-1}.

Scanning electron microscope (SEM)

All test samples were scanned by SEM (FEI Quanta 200, USA) and magnified 2000 times to observe surface changes in the starch.

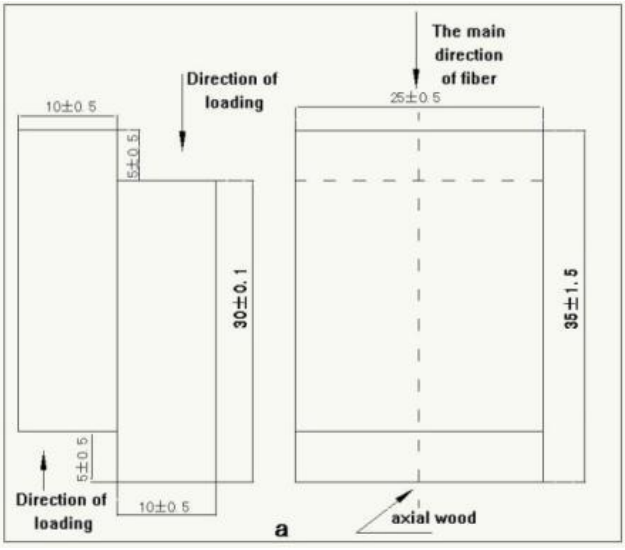

Fig. 1. Shape and dimensions of test block for compression shearing strength

Examining compression shearing strength

Specimens were prepared according to the Japanese industrial standard (JIS K-6806). The fiber direction of block was parallel to the specimen axis. The specimen dimensions were as shown in Fig. 1.

Compression shearing strength test specimens

The following method was used to test the specimen compression shearing strength. The test data are reported as the average value of 10 specimens.

Normal compression shearing strength: the specimens were placed indoors at a temperature of 23 ± 2 °C and relative humidity of 50 ± 5% for 48 h, and then tested to determine shearing strength.

Boiling repeated compression shearing strength: the specimens were placed in boiling water for 3 h. Then these specimens were immediately cooled for 10 min in room-temperature water.

Compression shearing strength test: the shear plane of the specimens was placed parallel with the load shaft, and the maximum load was recorded as illustrated in Fig. 1.

Compression shearing strength calculation: the compression shear strength of the specimens was calculated using the following formula:

$$\sigma = \frac{p}{L_a \times L_b} \quad (1)$$

In the formula, σ is the compression shearing strength (MPa), p is the maximum damage load (N), L_a is the length of the specimen adhesive (mm), and L_b is the width of the specimen adhesive (mm) (Xu *et al.* 2014).

RESULTS AND DISCUSSION

Modified Starch Physical and Chemical Properties

The physical and chemical properties of modified starch were tested. The results are shown in Table 2.

Table 2. The Performance Indicators of Modified Starch

Item	Index
Appearance	Ivory-White or Light Yellow
No Volatile Matter (%)	35-45
Viscosity (mPa.s)	200-300
pH Value	7-9
Water Miscibility (times)	≥ 4
Stability (d)	90

Carbonyl and Hydroxyl Content

Carbonyl and hydroxyl contents were determined by the relevant method (Heikka *et al.* 1997). The modified starch had higher carbonyl and hydroxyl contents than unmodified starch, as can be seen in Table 3. Under the action of ammonium persulfate, the starch in the acid hydrolysis process can simultaneously be much better oxidized than unmodified corn starch.

Table 3. The Carbonyl and Hydroxyl Contents of Modified Starch

Sample	Carbonyl content (%)	Hydroxyl content (mg KOH/g)
Corn starch	0.00	75.57
Modified starch	1.85	116.16

Orthogonal Test Results

Tests were performed according to the orthogonal test design. Glulams were produced, and the compression shearing strength was detected. Results and variance analysis are shown in Tables 4, 5, and 6. Trend charts of effect analysis of test factors on compression shearing strength for glulam are shown in Fig. 1.

Table 4. Orthogonal Test Design and Test Results for Compression Shearing Strength

Number \ Factors		MS	SBR	PVOH	P-MDI	Space	Experiment index NCSS (MPa)	Experiment index RBCSS (MPa)
1		1	1	1	1	1	10.45	6.18
2		1	2	2	2	2	11.01	6.55
3		1	3	3	3	3	11.74	6.91
4		1	4	4	4	4	12.37	7.35
5		2	1	2	3	4	12.05	7.58
6		2	2	1	4	3	11.22	7.32
7		2	3	4	1	2	12.78	7.03
8		2	4	3	2	1	12.56	7.29
9		3	1	3	4	2	11.91	7.41
10		3	2	4	3	1	11.52	7.14
11		3	3	1	2	4	10.56	6.89
12		3	4	2	1	3	10.65	6.45
13		4	1	4	2	3	10.94	6.56
14		4	2	3	1	4	11.36	6.73
15		4	3	2	4	1	10.72	7.25
16		4	4	1	3	2	10.59	7.07
NCSS	$\overline{K}_{1j}$	11.393	11.277	10.705	11.268	11.413		
	$\overline{K}_{2j}$	12.153	11.337	11.107	11.310	11.573		
	$\overline{K}_{3j}$	11.160	11.450	11.893	11.475	11.337		
	$\overline{K}_{4j}$	10.902	11.543	11.922	11.585	11.585		
	R_j	1.251	0.266	1.197	0.287	0.248		
	Importance of factors	Modified starch → PVOH→ P-MDI →SBR					T=182.43 $\overline{y}=11.40$	T=108.51 $\overline{y}=6.78$
RBCSS	$\overline{K}_{1j}$	6.748	6.933	6.865	6.623	6.965		
	$\overline{K}_{2j}$	7.305	6.935	6.982	6.822	7.015		
	$\overline{K}_{3j}$	6.998	7.02	7.085	7.175	6.835		
	$\overline{K}_{4j}$	6.902	7.065	7.02	7.332	7.188		
	R_j	0.557	0.132	0.220	0.709	0.303		
	Importance of factors	P-MDI → Modified starch→ PVOH→SBR						

Table 5. Variance Analysis of Normal Compression Shearing Strength

Sources of variance	S	f	$\bar{S}$	F	Significance
MS	3.486	3	1.162	6.213	**
SBR	0.167	3	0.056	0.299	
PVOH	4.255	3	1.418	7.583	**
P-MDI	0.221	3	0.074	0.396	
Error	0.56	3	0.187		
Summation	8.69	15	0.579		

** $F_{0.01}(3,6) = 9.78$; $F_{0.05}(3,6) = 4.76$; and $F_{0.1}(3,6) = 3.29$

Table 6. Variance Analysis of Repeated Boiling Compression Shearing Strength

Sources of variance	S	f	$\bar{S}$	F	Significance
MS	0.663	3	0.221	2.326	
SBR	0.051	3	0.017	0.179	
PVOH	0.102	3	0.034	0.358	
P-MDI	1.259	3	0.420	4.421	*
Error	0.286	3	0.095		
Summation	2.361	15	0.157		

* $F_{0.01}(3,6) = 9.78$; $F_{0.05}(3,6) = 4.76$; and $F_{0.1}(3,6) = 3.29$

Analysis and Discussion of Orthogonal Test

From Table 4 it is apparent that the effects of each factor on normal compression shearing strength of glulam were as follows: modified starch → PVOH → P-MDI → SBR. The order of effect of each factor on repeated boiling compression shearing strength was P-MDI → modified starch → PVOH → SBR.

Effect of modified starch mass

The effect of modified starch on normal compression shearing strength of glulam was significant, while that of repeated boiling was insignificant, as can be seen from Tables 5 and 6. Figure 2 shows that normal and repeated boiling compression shearing strength first increased and then tended to decrease with increasing amounts of modified starch.

Because of the high molecular weight and containing polar functional groups such as large amounts of hydroxyl groups and small amounts of carbonyl groups of modified starch, so cohesive strength and bonding strength of the starch-based API adhesive were restricted by them. Therefore, increasing the content of the modified starch within a certain range can improve the normal and repeated boiling compression shearing strength of starch-based API. However, after modified starch in the starch-based API main agent reached a certain amount, excess modified starch was still present after the curing reaction. Because of the hydrophilic functional group in excess relative to the –NCO group, a reduction of normal and repeated boiling compression shearing strength was observed (Desai *et al*. 2003).

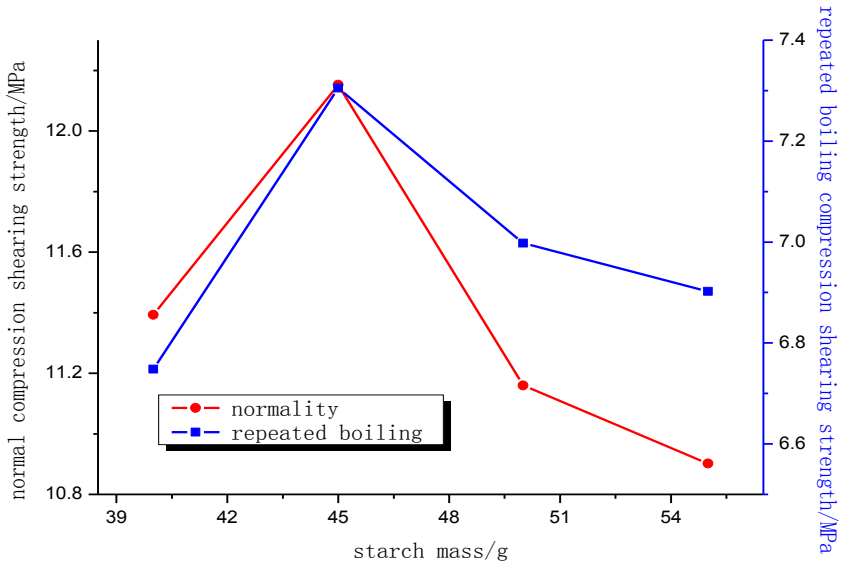

Fig. 2. The relationship between the amount of modified starch and normal and repeated boiling compression shearing strength

Effect of emulsifier mass parts

The effect of the concentration of SBR on the normal and repeated boiling compression shearing strength of glulam was evaluated in the variance analysis of compression shearing strength in Tables 5 and 6. No significant effect was found. Normal and repeated boiling compression shearing strength showed a slight tendency to increase after increasing the amount of SBR in Fig. 3.

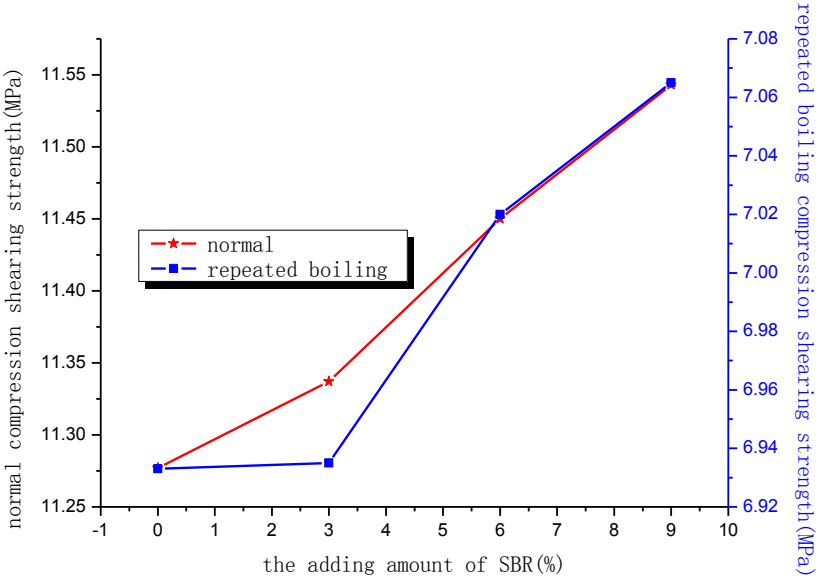

Fig. 3. The relationship between the concentration of SBR and normal and repeated boiling compression shearing strength

The different types of API adhesives have different aqueous polymers. In this experiment, SBR was used to synthesize the starch-based API adhesive. The choice of emulsion affects curing time, bonding quality, and heat and water resistance to a certain extent. SBR is an aqueous emulsion obtained by the emulsion polymerization of two vinyl monomers (Ugelstad *et al*. 1973). SBR containing reactive groups can form films with

PVOH, improving the normal compression shearing strength. SBR also reacted with P-MDI to form a water-insoluble network structure, thereby enhancing the water resistance of starch-based API (Gao *et al.* 2011b). Because of its insignificant impact on the compression shearing strength and taking account into the cost of the adhesive, the added amount of SBR was set at 3% in the starch-based API synthesized in this experiment.

Effect of PVOH mass concentration

In starch-based API adhesives, PVOH plays an important role. It can participate in a cross-linking reaction with P-DMI while curing. It can also be used to adjust the viscosity and viscoelasticity of the adhesive and prevent precipitation of calcium carbonate filler. Although PVOH often is used as a thickener, other hydroxy-functional polymers such as hydroxyethyl cellulose and starch are also used as thickeners. Starch-based API adhesives contain PVOH to ensure a high degree of cross-linking reaction in the film, which can improve the water resistance of the layer. Also, the degree of hydrolysis of PVOH affects the cross-linking reaction between the emulsion polymer and the water resistance of the layer.

Tables 5 and 6 show that the impact of the mass concentration of PVOH on the normal compression shearing strength was significant, whereas repeated boiling compression shearing strength was not significant. Figure 4 shows that the normal compression shearing strength increased with increasing concentration of PVOH. However, the repeated boiling compression shearing strength first increased and then decreased.

With increasing mass concentration of PVOH, the content of free hydroxyl groups in the starch-based API was increased, and more hydrogen bond was formed between starch-based API and wood. Therefore, the bonding strength increased, namely, the normal compression shearing strength increased. However, the hydrogen bond is susceptible to desorption by a large amount of water. Therefore, with increasing PVOH content, repeated boiling compression shearing strength decreased.

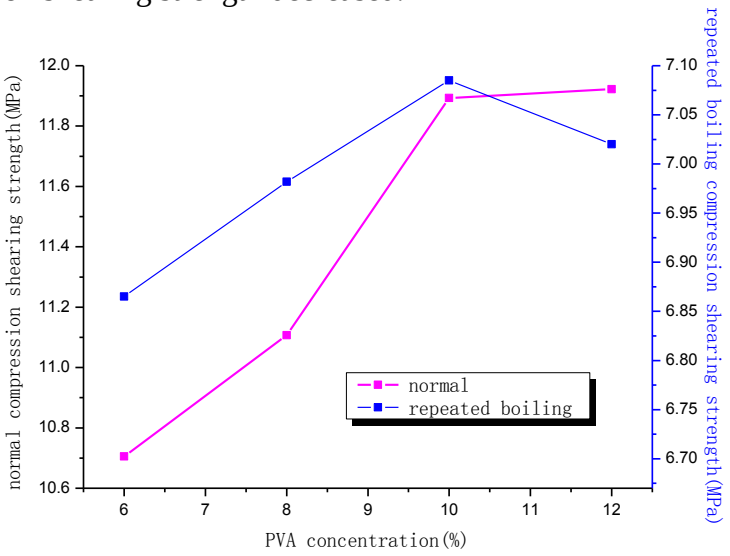

Fig. 4. The relationship between PVOH concentration and normal and repeated boiling compression shearing strength

Effect of isocyanate mass parts

P-MDI is a highly reactive substance, and the average content of -NCO groups is within the range of 30.5% to 32.5%. As a cross-linking agent, it can react with groups containing active hydrogen in the main agent of starch-based API to form a network

structure. Improving the bonding strength and water resistance of bonding products is the key factor for modification of the starch-based adhesive.

Tables 5 and 6 show that the impact of the added amount for isocyanate on normal compression shearing strength was not significant, but its effect on repeated boiling compression shearing strength was significant. Figure 5 shows that the normal and repeated boiling compression shearing strength increased with increasing isocyanate concentration, but the normal shearing strength increased by a smaller amount. Because starch-based adhesives were in the dry state, hydrogen bonds in the wood were relatively strong. Because of the presence of large number of –NCO groups, the effect on normal compression shearing strength was not evident. Repeated boiled compression shearing strength showed different results: hydrogen bonds were easily destroyed by hydrolysis, but the isocyanate still retained good strength under the action of moisture, which is the key factor to ensure the good compression shearing strength of a glulam produced by the adhesive. Therefore, the impact of the amount of isocyanate on repeated boiling compression shearing strength was very significant.

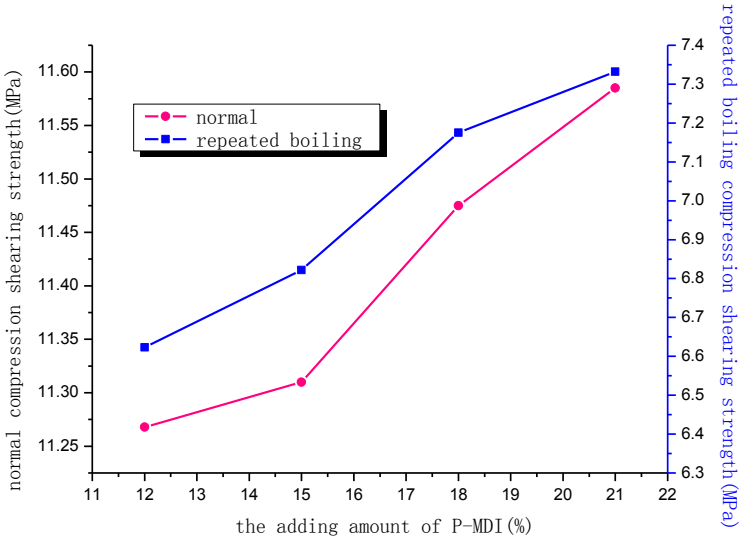

Fig. 5. The relationship between the concentration of P-MDI and normal and repeated boiling compression shearing strength

From the above tables and figures one can conclude that the best combination of various factors for the starch-based API adhesive was A2B4C4D4 on the basis of the normal compression shearing strength. However, the best combination of the starch-based API adhesive was A2B4C3D4 based on repeated boiling compression shearing strength. Considering the cost of starch-based API adhesive and compression shearing strength, the synthesis scheme of starch-based API adhesive was A2B2C3D3, namely, the added amount of modified starch (mass concentration 35%) was 45 g, the added amount of SBR was 3%, PAV concentration was 10%, and the added amount of P-MDI was 18%.

Properties of Starch-based API

Properties index of starch-based API adhesive

The main agent of starch-based API adhesive was synthesized in accordance with the best scheme determined by the orthogonal test. Its performance was tested according to the relevant standards, and the results are shown in Table 7.

Table 7. Performance Indicators of Starch-based API Adhesive

Item	Physical and chemical index	
	Main agent	Cross-linking agent
Appearance	Ivory-white or light yellow	brown homogeneous liquid
No volatile matter (%)	36-42	—
Viscosity (mPa.s)	120-250	300 ± 50
pH value	7-9	4-9
Water miscibility (times)	≥ 2.5	—
Stability (d)	≥ 60	360
Pot-life (h)	≥ 6	—

Pot-life test

The pot-life of starch-based API adhesive is directly related to its operability in practical applications. The main agent was mixed with a cross-linking agent at the mass ratio of 100:18 at room temperature. The viscosity and -NCO content were measured over time to characterize the pot-life of the starch-based API adhesives. Considering the actual application requirements, the viscosity of the starch-based API adhesives was only detected within 2.5 h; the results are shown in Fig. 6.

Using the di-n-butylamine back titration method (Lee *et al.* 2007), the -NCO mass fraction was measured at intervals of 30 min, and the results are shown in Table 8. The starch-based API adhesives developed a much longer pot-life compared to API adhesive. According to the experimental results shown in Fig. 6 and Table 8, the formulation was able to meet the application requirements.

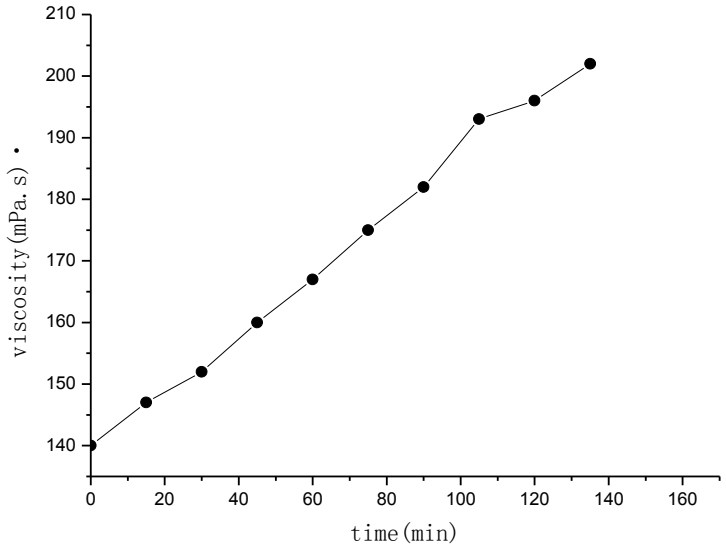

Fig. 6. Viscosity change of starch-based API adhesive with time

Table 8. Quality Percentage of -NCO of Starch-based API Adhesive at Various Times

Time (h)	-NCO (%)	Reductions of -NCO content
0	4.6024	0.0000
0.5	4.4573	0.1451
1.0	4.4046	0.1978
1.5	4.3037	0.2987
2.0	4.2296	0.3728
2.5	4.1845	0.4179

SEM Analysis

Morphology features of corn starch, modified starch, the main agent, and starch-based API were observed by SEM. All SEM pictures were magnified 2000 times.

As can be seen from Fig. 7a, the shapes of the corn starch granules were not the same; they were circular, ovoid, and polygonal, and the surface had a smooth and dense structure. Figure 7b indicates that the acid-thinned and oxidized starch remained granular, very similar to the original corn starch. However, some starch granules appeared broken, caused by acid-thinning and oxidization, showing that acid had damaging effects on the starch granules.

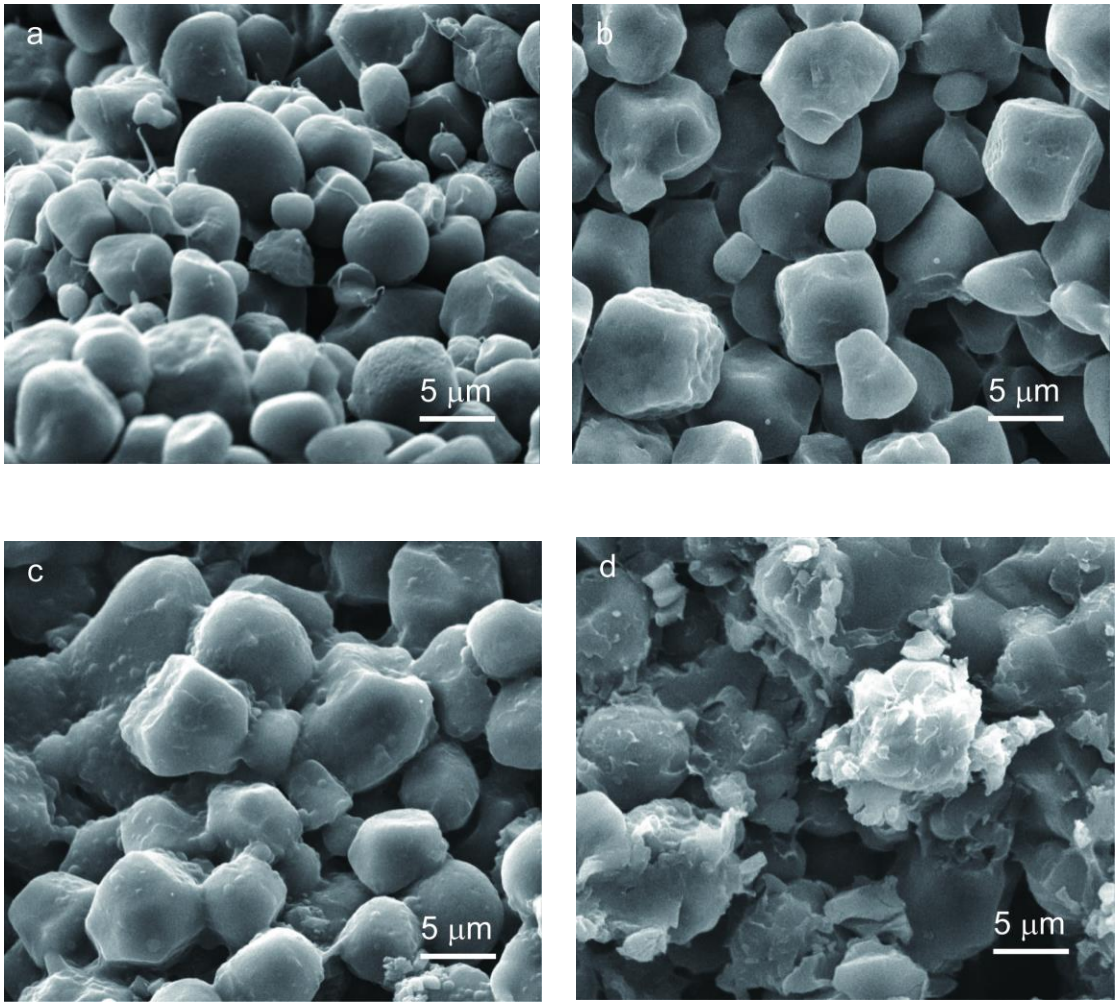

Fig. 7. SEM patterns of the starch and relevant products (scale bars 5 μm).

As shown in Fig. 7c, the starch granule shapes in the main agent were deformed, the surfaces were not smooth, and there were a number of small particles over it, which illustrated the reaction among the main agent components when attached to the starch surface. As can be seen from Fig. 7d different degrees of reaction of the starch-based API surface occurred, which indicated that isocyanate groups caused cross-linking reaction with hydroxyl groups on the starch and other reactive hydroxyl groups.

The starch shape and surface state were changed, which gave rise to more close links between starch molecules. SEM images illustrated that the entire system gradually changed from modified starch to synthesis of a starch-based API adhesive (Lou and Di 2013).

FT-IR Analysis

The infrared spectra of corn starch, modified starch, the main agent, and starch-based API are shown in Fig. 8. The spectra of corn starch and modified starch are basically the same, which showed that acid hydrolysis and oxidation only increased the reactivity of corn starch and did not change its structure.

The hydrolysis reaction in corn starch in an acidic environment is represented in the following reaction scheme (Nampoothiri *et al*. 2010). A large number of glycosidic linkages in the native starch were destroyed and a large number of hydroxyl groups were generated.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{10}O_6 \quad (2)$$

From the spectra of corn starch and the main agent in Fig. 8, one can see that the OH stretching vibration absorption peak appeared at 3438 cm^{-1}, which was due to the formation of hydrogen bonds from the association of carboxyl and hydroxyl groups (-OH association state).

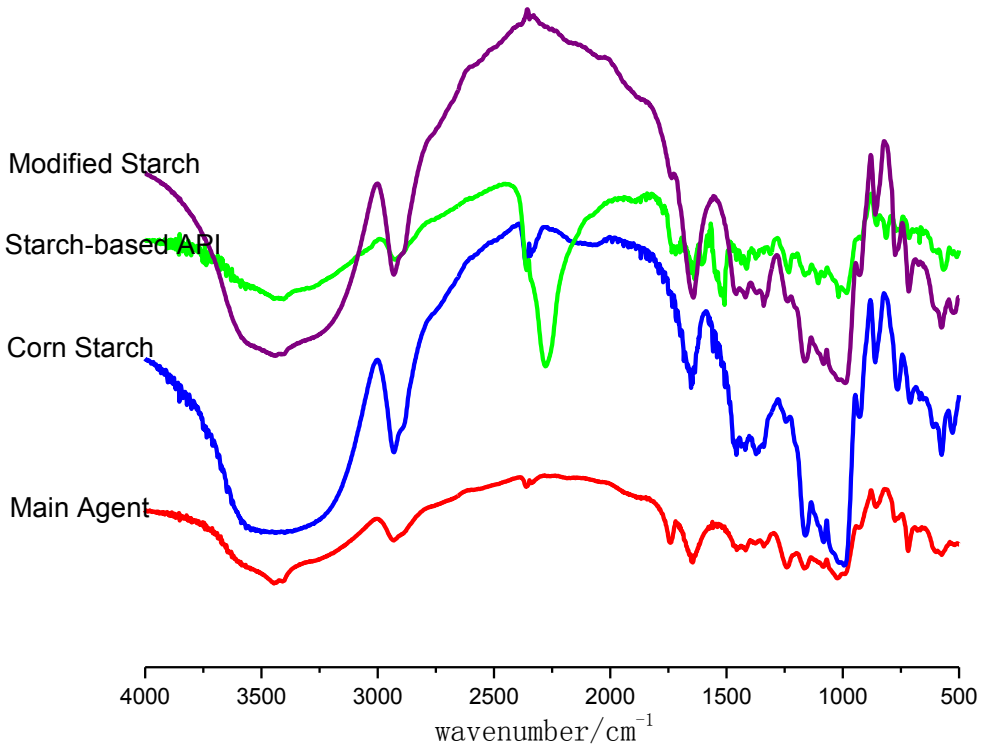

Fig. 8. The infrared spectra of starch, modified starch, main agent, and starch-based API

The characteristic absorption peaks of starch remained at 569.9 cm^{-1}, 770.1 cm^{-1}, 851.6 cm^{-1}, and 1022.8 cm^{-1}. In addition, a new absorption peak appeared at 1743.6 cm^{-1}, which showed that the chemical structure of starch glucose had fundamentally changed and a certain amount of carbonyl was introduced.

According to the infrared absorption peak of the isocyanate adhesive and spectrum of starch-based API in Fig. 8, a new absorption peak at 2278.9 cm^{-1} was present, which can be attributed to -NCO groups. Other new peaks at 1513.6, 1729.1, and 2935.2 cm^{-1} were attributed to the stretching vibrations of NH or CN, C=O, and CH. These were cross-linked product structures formed by reaction of the cross-linking agent and hydroxyl groups containing active hydrogen in the main agent.

CONCLUSIONS

1. The best synthesis scheme for the starch-based API adhesive was optimized by orthogonal testing. For the best product, the amount of modified starch (mass concentration 35%) was 45 g, the amount of SBR was 3%, PVOH mass concentration was 10%, and the amount of P-MDI was 18%. The bonding properties of laminated wood prepared with the starch-based API adhesive met national standards. Meanwhile, the cost of API adhesive was reduced because of the introduction of low-cost corn starch.
2. SEM analysis showed that the starch surface did not change during acid-thinning and oxidizing; however, the micro-morphology of the starch surface changed in the main agent and starch-based API adhesive. FT-IR showed that modified starch did not generate new functional groups, and the characteristic peaks of starch were retained. The absorption peak of the new functional group was present in the main agent and the starch-based adhesive API spectra. SEM and FT-IR analysis confirmed that reaction occurred and that it involved both the main agent and starch-based API adhesive.

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