A Low-Cost, Formaldehyde-Free, and High-Performance Starch-based Wood Adhesive

Yang Jiang, Qifeng Chen, Haiyan Tan,* Jiyou Gu, and Yanhua Zhang*

An environmentally friendly starch-based wood adhesive was developed using cassava starch (CS) and polyvinyl alcohol (PVOH). A set amount of polymethylene polyphenylene isocyanate (PAPI, modified in the laboratory) was used as the cross-linking agent to improve the water resistance. To evaluate the mechanical properties of the adhesive, the shear strength was measured by a mechanical testing machine. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were used to characterize the properties of the adhesive and the curing products. The results indicated that the adhesive using PVOH with a low alcoholysis degree was better than high alcoholysis degree and adding 7 wt% PVOH (RS-1717) could obtain good mechanical properties; the dry shear strength was 7.77 MPa, reaching 1.36 MPa in the wet state. The favorable results were attributed to reactive hydrogens in the wood and CS, which can form a cross-linking network with the -NCO groups of PAPI to obtain excellent shear strength and water resistance.

Keywords: Starch adhesive; Polyvinyl alcohol; Shear strength; Stability

Contact information: Key Laboratory of Bio-Based Material Science and Technology, Northeast Forestry University, Ministry of Education, Harbin 150040, China; * Corresponding authors: zyhnefu@163.com, tanzzx168@163.com

INTRODUCTION

It is well known that China has one of the lowest amounts of forestland per head in the world. To make up for the shortage of forest resources, the wood-based panel industry is well developed, which allows the wood adhesive industry to flourish. At present, urea-formaldehyde resin, phenolic-formaldehyde resin, and melamine-formaldehyde resin adhesives are predominantly used in the wood-based composite industry. These adhesives have mature technologies. However, they depend on petroleum, natural gas, and other non-renewable resources. Moreover, during the production or use of wood composite products, these adhesives emit carcinogenic formaldehyde and volatile organic compounds into the environment, thus reducing indoor air quality and posing a health risk to humans (Jang et al. 2011; Böhm et al. 2012; He et al. 2012; Moubarik et al. 2013). Scholars have made many efforts to reduce or replace phenol and formaldehyde contents in adhesive formulations (Jin et al. 2010; Boran et al. 2011), but these methods cannot solve the fundamental problem. This has prompted scientists to look for environmentally friendly wood adhesives based on renewable resources (Kim 2010; Li et al. 2014).

Starch is one of the most abundant, renewable, biodegradable, and natural polymers, which makes it a good alternative for synthetic polymers (Le Corre et al. 2010). It has been used as an adhesive in a wide range of products; however, it also has several shortcomings, such as poor water resistance, low bonding strength, and lower stability compared to conventional adhesives. Recently, several efforts have been made to
improve the performance of starch adhesives, especially the stability behavior, to enable starch-based wood adhesives to compete with petrochemical-based wood adhesives (Imam et al. 1999, 2001; Sin et al. 2010). One of the most common methods of starch modification is gelatinization, which is a process that involves molecular events associated with the heating of starch in the presence of water. When starches are subjected to high temperatures (typically greater than 50 °C) in a sufficient amount of water, the granules absorb water, swell, and rupture because of the disruption of amylopectin double helices (hydrogen bonds dissociation), while amylase preferentially leaches out of the swollen granules. These events are accompanied by a dramatic increase in the system’s viscosity as the granule structure is progressively ruptured (García et al. 2016; Ji et al. 2017).

The cassava starch used in this study was taken from the roots of subtropical crops, where amylose accounted for 17% of the composition and amylopectin accounted for 83% (Hung et al. 2017). In recent years, with the improvement of living standards, CS has gradually displaced grain starches in various applications. CS is delicate and contains a small amount of impurities. The granules are spherical and have a diameter of 20 μm or less. The gelatinization temperature of CS is between 58 and 69 °C. When CS is gelatinized, it has a high peak viscosity and is easily gelled. However, if the gelatinization temperature is properly controlled, a transparent starch paste can be achieved, which can be used for the bonding of corrugated board, plywood, and adhesive tape.

Polyvinyl alcohol (PVOH) is produced through the hydrolysis of polyvinyl acetate. It has many useful properties, such as excellent water solubility, chemical resistance, and optical properties, as well as good biocompatibility. PVOH is one of the most common synthetic water polymers produced in the world (Sridach et al. 2013). For common applications, PVOH is dissolved in water to be used as an adhesive or a sizing and coating agent, as well as tissue scaffolding materials for biomedical applications (Ramaraj 2007; Kaboorani and Riedl 2011). It also plays an important role in adhesives that can be used as a protective colloid. Both PVOH and starch are polar substances, which have hydroxyl groups (-OH) in their chemical structures. These highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds, which improve the integrity of PVOH-starch blends (Tang and Alavi 2011). However, to the authors’ knowledge, the effects of PVOH on the performance of CS-based wood adhesives have not been investigated to a great extent.

Therefore, the aim of this study was to improve the mobility and storage stability of a cassava starch-based wood adhesive with the use of PVOH.

**EXPERIMENTAL**

**Materials**

Cassava starch (CS) was supplied by Beidahuang Co. (Harbin, China). Sodium hydroxide (NaOH) was purchased from Liaoning Quanrui Chemical Reagent Co., Ltd. (Liaoning, China). Ammonium persulfate ((NH₄)₂S₂O₈, APS) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). PVOH was purchased from Kurary Co. (Tokyo, Japan), the alcoholysis of PVOH₁ is 92% to 94% and the alcoholysis of PVOH₂ is 97.5% to 99%. Polymethylene polyphenylene isocyanate (PAPI, industrial
grade) was purchased from Bayer Company (Shanghai, China), and birch block (Betula platyphylla hardwood) was purchased from Jinhai Wood Co. Ltd. (Dunhua, China).

**Methods**

*Preparation of PVOH solution*

A total of 10 g of PVOH powder and 90 mL of distilled water was slowly added to a 500-mL four-necked round-bottom flask and constantly stirred at room temperature for 10 min to 15 min. This mixture was heated until completely dissolved and kept at 90 °C for 1 h to obtain a homogeneous PVOH solution with a final concentration of 10 wt%.

*Synthesis of starch-based wood adhesive*

A set amount of PVOH solution was dropped into the 500-mL four-necked round-bottomed flask equipped with a thermometer (Fangjun instrument factory, Shanghai, China), mechanical stirrer (Renhe instrument factory, Changzhou, China), and a reflux condenser (Tianbo instrument factory, Tianjin, China), and the temperature was increased to 50 °C. Then, 0.14 g (based on dry starch) ammonium persulfate was added (at a concentration of 10 wt%) and reacted for 30 min. Then, 70 g CS slurry was added to the 140 g water system and the temperature was increased to 61 °C. Finally, sodium hydroxide (concentration of 10 wt%) was added to adjust the pH of system to make the CS slurry gelatinize, and the reaction continued for 50 min to obtain the starch-based wood adhesive. Polyisocyanate was added at 24 g (based on pure starch-based wood adhesive) to the previously weighed wood adhesive to prepare the polyisocyanate starch adhesive.

*Shear strength test*

The shear strength of the adhesive was determined using a mechanical testing machine (CMT5504, SANS, Shenzhen, China) according to the industry standard HG/T2727-2010 (2010). Freshly cut 30×25×10 mm pieces of wood (Betula platyphylla, 0.62×103 kg/m) were polished using 180-mesh abrasive paper to eliminate the oxidized layer. A single-lap specimen (Fig. 1) was prepared using a coated adhesive between two parallel birch blocks. Starch adhesive was smeared on double-side birch blocks and the mass of adhesive used on each side of the wood was about 0.18 to 0.2 g, then the blocks were pressed at 1 MPa for 24 h (25 °C). After removing the pressure, the specimens were stored at room temperature for 48 h before testing the dry shear strength. Some specimens were soaked at 30 ± 1 °C for 3 h to test the wet shear strength. The shear strength was calculated using Eq. 1. All tests were repeated ten times, and average values were calculated according to Eq. 2,

\[
\tau = \frac{F}{A} \quad (1)
\]

where \( \tau \) is the shear strength (MPa), \( F \) is the shear force (N), and \( A \) is the shear area (mm²),

\[
X = \frac{\sum_{i=1}^{n} X_i}{n} \quad (2)
\]
where $X$ is the average value, $X_i$ is the result for each sample, and $n$ is the number of samples in each group.

![Fig. 1. Specimen dimensions (in mm)](image)

**Viscosity measurement**

The viscosity was measured using a NDJ-5S rotational viscometer (Ping Xuan Shanghai Scientific Instrument Co. Shanghai, China) at 25 °C with a No. 3 rotor at 30 rpm according to the standard GB/T 14074-2006 (2006).

**Solids content**

The solids content of the adhesive was determined using the oven-drying method according to the standard GB/T 14074-2006 (2006). Approximately 1.5 g to 2.0 g (weight $a$) of the adhesive was placed into an oven and the temperature was set to 120 ± 2 °C for 120 ± 2 min until a constant weight (weight $b$) was obtained. The value of the solids content was computed using Eq. 3. The average value of the solid content was calculated from five parallel samples,

$$\text{Solids content} = \frac{a}{b} \times 100\%$$

where $a$ is the quantity of adhesive (g) after drying, and $b$ is the quantity (g) before drying. The solid content had units of %.

**Scanning electron microscopy (SEM) analysis**

Birch blocks coated with starch adhesive that had undergone shear strength testing were characterized by SEM (FEI Quanta 200, Phillips, Netherlands). The SEM was operated at an accelerating voltage of 20 kV. Samples were coated with gold under a vacuum before testing.

**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis was carried out with a TG 209F3 (NETZSCH, Serb, Germany) to determine the thermal stability of the adhesives. The adhesive was ground into a homogenous powder after it was naturally dried, and 2 to 3 mg samples were loaded to uniformly cover the bottom of an 85-µL aluminum oxide crucible. The crucible was heated from room temperature to 800 °C at a rate of 10 °C/min under an argon atmosphere (flow rate: 40 mL/min).

**Fourier transform infrared (FTIR) spectroscopy**

Infrared spectra of each modified starch adhesive was measured with a Bruker OPUS 7.5 FTIR spectrophotometer (Bruker OPUS 7.5, Karlsruhe, Germany) to examine the changes in the chemical structure of the starch adhesive with modification. The specimens were naturally dried and powdered to complete the test. The spectra were recorded over a wave number range between 4000 and 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) for 32 scans.

RESULTS AND DISCUSSION

Effect of PVOH Type

The shear strength of multiple types of starch-based wood adhesives, which were obtained by changing the type of PVOH and keeping the pH similar, are shown in Fig. 2.

![Fig. 2. Shear strength of PVOH-modified starch-based wood adhesives: (a) PVOH\(_1\); (b) PVOH\(_2\)](image)

Without polyisocyanate, the shear strength of the PVOH\(_1\) (RS-1717)-modified starch adhesive was better than that using PVOH\(_2\) (RS-2117) in the dry state. Adding 12% polyisocyanate (this data was taken from previous experimental results), the shear strength of PVOH\(_2\)-modified starch adhesive was higher than that using PVOH\(_1\) in the dry state when the pH exceeded 9.00, while the shear strength of the dry state of PVOH\(_1\)-modified starch adhesive was higher than that using PVOH\(_2\) while the pH was under 8.40. However, the shear strength of the wet state of PVOH\(_2\)-modified starch adhesive was very low (about 0.2 to 0.4 MPa). Polyisocyanate improved the shear strength considerable. Thus, choosing PVOH\(_1\) as a protective colloid and adjusting the pH to 8.80 could produce good shear strength in both the dry and wet states.

The alcoholysis degree is an important indicator that measures the quantity of hydrophilic hydroxyl and hydrophobic acetyl groups in PVOH molecules. With a reduction of the alcoholysis degree, the number of hydrophilic hydroxyl groups of PVOH molecules decreases and the ability to form hydrogen bonds in PVOH molecules also decreases, while the number of hydrophobic acetyl groups increases (Minsk et al. 1941). It is known that the alcoholysis degree of PVOH\(_1\) is approximately 92.0% to 94.0%, and the alcoholysis degree of PVOH\(_2\) varies from 97.5% to 99.0% (both data got from Kurary Co.). Because the quantity of hydrophobic acetyl groups of PVOH\(_1\) was greater than that of PVOH\(_2\), the water resistance of PVOH\(_1\)-modified adhesive was superior to that of the adhesive modified by PVOH\(_2\). There are many hydroxyl groups in the PVOH and starch. The active hydrogen atoms could react with -NCO of PAPI to enhance the shear strength.
On the other hand, the water in the wood also could react with -NCO to promote the curing of the adhesive. These results suggest that the number of acetyl groups of PVOH\textsubscript{1} was greater than that of PVOH\textsubscript{2}, so the reactivity of PAPI was reduced, which made the shear strength increase by a small amount. In conclusion, the alcoholysis degree of PVOH had an important effect on the performance of the adhesive, where a higher alcoholysis degree led to poor water resistance; thus, PVOH\textsubscript{1} was selected as the protective colloid in the starch-based wood adhesives to obtain better mechanical properties.

To further investigate the performance of the two different PVOHs, thermogravimetric analysis was used to analyze their thermal decomposition stability. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the degradation of PVOH\textsubscript{1} and PVOH\textsubscript{2} in argon are shown in Fig. 3.

![The thermal decomposition curves of PVOH\textsubscript{1} and PVOH\textsubscript{2}](image)

Fig. 3. The thermal decomposition curves of PVOH\textsubscript{1} and PVOH\textsubscript{2}

The shape of the weight loss curve is consistent with the generally accepted two-step mechanism for degradation of PVOH in an inert atmosphere and was confirmed to be a two-step process by the DTG curve (Thomas \textit{et al.} 2001). The first stage was primarily associated with the elimination of side-groups to generate water and acetic acid, followed by the breakdown of the polymer backbone at higher temperatures (Holland and Hay 2001). From the curves, it is clear that the initial decomposition temperature of PVOH\textsubscript{1} was higher than that of PVOH\textsubscript{2}. When the temperature was 309.6 °C, PVOH\textsubscript{1} had a sharp change in the rate of weight loss, indicating rapid elimination of the polymer. PVOH\textsubscript{2} had a sharp change in the rate of weight loss at 268.7 °C, which was lower than PVOH\textsubscript{1} by 40.9 °C. Therefore, PVOH\textsubscript{1} had a better thermal stability than PVOH\textsubscript{2}. This result is consistent with earlier results.

**The Dosage of Polyvinyl Alcohol**

The difference in shear strengths of multiple types of starch-based wood adhesives, which were obtained by changing the dosage of PVOH\textsubscript{1}, is shown in Fig. 4.

By increasing the amount of PVOH\textsubscript{1}, the shear strength (dry state) of starch-based wood adhesives improved gradually. The reason for this increase is that increasing the dosage of PVOH\textsubscript{1} leads to more hydroxyl groups, so the opportunity to form hydrogen bonds between starch and PVOH\textsubscript{1} increases. It is well known that hydrogen bonds are the origin of the adhesive bond, so the shear strength of the adhesive in the dry state...
increased. However, the shear strength (wet state) of the adhesive showed a tendency to increase first and then decrease with an increase in the amount of PVOH. When the amount of PVOH was 7 wt% (starch basis), the best wet shear strength was obtained, which was better than the standard of 0.7 MPa. Because there was an excess of hydroxyl groups, there was no ability for cross-linking with PAPI, which impeded the reaction of PAPI with the active hydrogen; thus, the wet shear strength was reduced. Therefore, the optimal amount of PVOH was 7 wt% (starch basis).

![Shear strength vs. PVOH content](image)

**Fig. 4.** The influence of different dosages of PVOH on shear strength of starch adhesives

The influence on the physical properties of starch-based wood adhesives, which were obtained by changing the dosage of PVOH, is shown in Fig. 5.

![Viscosity and solid content vs. PVOH content](image)

**Fig. 5.** The influence of different dosages of PVOH on viscosity and solid content of starch adhesives

The viscosity of the starch adhesives gradually increased with increasing PVOH dosage, as shown in Fig. 5 (a). When the amount of PVOH exceeded 7 wt%, the viscosity of the adhesive increased dramatically. Increasing the amount of PVOH can increase the chances that the PVOH macromolecules encounter starch macromolecules to form hydrogen bonds. Thus, the viscosity of the adhesive increased with the amount of PVOH. Considering the effect of viscosity on the sizing process which ranged from 3000 mPa•s to 5000 mPa•s to sizing easily, the amount of PVOH should be controlled to obtain a moderate viscosity. Therefore, the optimum amount of PVOH was 7% (based on dry starch), and the viscosity of the adhesive was 3200 mPa•s.
As shown in Fig. 5(b), increasing the amount of PVOH$_1$ can improve the solid content of the adhesive gradually. When the amount of PVOH$_1$ increased from 5 wt% to 9 wt%, the solid content of the adhesive was in the range of 33.1% to 33.5%, an increase of only 0.4%, which confirmed that PVOH$_1$ can produce a good network with starch. When the amount of PVOH$_1$ was greater than 9 wt%, the solid content of the adhesive increased sharply to 34.5%, indicating that the amount of PVOH$_1$ was excessive which dispersed in the starch gel and increased the solid content dramatically. Therefore, the optimum amount of PVOH was 7 wt% (starch basis), and the solid content was 33.2%.

In conclusion, the final choice of the amount of PVOH$_1$ was 7 wt% because excellent mechanical and physical properties were obtained.

**The Effect of PVOH on the Storage Stability of Starch Adhesive**

From Fig. 6(a), adding 7 wt% PVOH$_1$ in the starch adhesive could reduce layering and improve the stability of starch adhesives noticeably. Starch macromolecules are composed of amylose and amylopectin. When the temperature increases, the starch granules absorb water, swell, and rupture to force the amylose and amylopectin out from the granules to form a homogeneous solution. When the temperature decreases, amylose rearranges to separate starch and water (Miles *et al.* 1985). Many polar hydroxyl groups form intermolecular and intramolecular hydrogen bonds between PVOH$_1$ and starch to prevent layering and improve the stability of starch adhesives.

![Fig. 6. The effect of PVOH on the storage stability of starch adhesive: (a) 1. without PVOH, 2. with 7 wt% PVOH; (b) viscosity stability](image)

The stability of the viscosity noticeably affects the rheological properties of starch adhesives (Wu *et al.* 2013). Figure 6(b) shows that the viscosity of the unmodified starch adhesive increased on the second day, and then decreased sharply until the fifth day of storage. However, the viscosity of the modified starch adhesive changed by only a small amount over the course of a week. Adding PVOH can effectively improve the stability of starch adhesive. Adding PVOH$_1$ improved the viscosity stability of starch adhesives because PVOH$_1$ could form hydrogen bond networks with starch and hinder the rearrangement of amylose. Therefore, the starch adhesive had a stable viscosity after modification by PVOH$_1$. The storage period of the starch based adhesive modified with PVOH is one month in the summer but two month in the winter.
Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of CS, cassava starch adhesive (CSA), modified CSA, and the main reactants and products are shown in Fig. 7. In the CSA spectrum, the 3300 cm\(^{-1}\) band is the -OH (free hydroxyl, inter-molecular association hydroxyl, and intra-molecular association hydroxyl) stretching vibration, the band at 2921 cm\(^{-1}\) is a symmetric stretching vibration of the glucose ring of C-H, and that at 1002 cm\(^{-1}\) is from the anhydroglucose ring C-O vibration peak (Han et al. 2009; Sin et al. 2010). In the PVOH spectrum, the 3300 and 2921 cm\(^{-1}\) bands are similar to those of CS, such that the band at 1714 cm\(^{-1}\) can be attributed to the carbonyl of vinyl acetate groups being partially hydrolyzed (Jayasekara et al. 2003, 2004) and this band also appeared in the CS spectrum, which indicated that there was no chemical reaction between PVOH\(_1\) and CS. At the band of 3300 cm\(^{-1}\), both CS and PVOH\(_1\) had a strong absorption peak, while the intensities of the peak visibly decreased in the CSA sample because of the polar hydroxyl groups, which tend to form intermolecular and intramolecular hydrogen bonds between PVOH\(_1\) and CS to improve the stability of CSA. The result was consistent with the above results. In the PAPI curve, the strong absorption peak at 2245 cm\(^{-1}\) is the -NCO group, and that at 1519 cm\(^{-1}\) is the N-H bending vibration (Wang et al. 2015). Comparing the curves of PAPI and CSA/PAPI, it is clear that the reactive hydrogen of the hydroxyl groups of CS reacted with the -NCO groups of PAPI to obtain an amide bond, which can improve the shear strength. There were also many reactive hydrogens in the wood, enabling the formation of a cross-linking network with the -NCO groups of PAPI and hydroxyl groups of CS to obtain good shear strength and water resistance. The schematic representation of PVOH\(_1\)-modified starch is shown in Scheme 1.

**Fig. 7.** FT-IR spectra: (a) PVOH\(_1\); (b) CSA+PAPI; (c) CS+PAPI; (d) CSA; (e) CS; (f) CS+PVOH\(_1\); (g) PVOH\(_1\)+PAPI; (h) PAPI; (i) PAPI+H\(_2\)O
Scheme 1. Schematic representation of PVOH-modified starch

Thermogravimetric Analysis (TGA)

Analyzing the TG and DTG curves of the reactants of the starch adhesives provided valuable information, as shown in Fig. 8. PVOH had a decomposition peak at 421.8 °C, which was not present in either of the curves of CS and CSA, indicating that PVOH was completely blended with CS. However, the initial decomposition temperature ($T_0$) and the peak temperature ($T_p$) of the cross-linked CSA adhesive decreased after the addition of 12% of the cross-linking agent because of the low thermal decomposition temperature of PAPI, which caused $T_p$ to shift to slightly lower temperatures. After modification, the terminal temperature ($T_f$) increased to prolong the entire degradation process and obtain a higher residue quality to improve the thermal stability of the adhesive. There are numerous active hydrogens in PVOH and CS, which could react with PAPI to form cross-linked networks to hinder the decomposition of the polymer (Chattopadhyay and Webster 2009). Thermal decomposition parameters are shown in Table 1.

Fig. 8. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of reactants
**Table 1. Thermal Decomposition Parameters**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_0$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_f$ (°C)</th>
<th>Residue quality (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH</td>
<td>285.9</td>
<td>319.0</td>
<td>364.9</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>416.1</td>
<td>421.8</td>
<td>450.9</td>
<td></td>
</tr>
<tr>
<td>PAPI</td>
<td>195.2</td>
<td>239.3</td>
<td>270.5</td>
<td>22.67</td>
</tr>
<tr>
<td></td>
<td>427.8</td>
<td>477.3</td>
<td>550.5</td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>295.6</td>
<td>312.5</td>
<td>326.6</td>
<td>12.38</td>
</tr>
<tr>
<td>CSA</td>
<td>288.8</td>
<td>306.5</td>
<td>322.5</td>
<td>7.18</td>
</tr>
<tr>
<td>CSA+12%PAPI</td>
<td>279.6</td>
<td>302.9</td>
<td>340.8</td>
<td>21.98</td>
</tr>
</tbody>
</table>

$T_0$: Initial decomposition temperature; $T_p$: Peak temperature; $T_f$: Terminal decomposition temperature.

**Scanning Electron Microscopy (SEM) Analysis**

Scanning electron micrographs revealed that the starch adhesive was distributed on the surface of the wood. The SEM images of the distribution of pure starch adhesive and starch adhesive with 12 wt% PAPI are shown in Fig. 9. The addition of PAPI improved the shear strength and the distribution of the adhesive. From the SEM images, it is clear that the starch adhesive with 12 wt% PAPI was distributed equally on the surface of wood and starch granules were encapsulated by PAPI, while pure starch adhesive was distributed unevenly on the surface of wood and some starch granules were destroyed, but part of the granules remained globular.

![Fig. 9. SEM images of distribution of adhesives: (a) pure starch adhesive; (b) starch adhesive with 12% PAPI](image)

The distribution of adhesives had noticeable differences, as shown in Fig. 9(a) and (b), which illustrates that PAPI played a role in the curing process of the adhesive, providing evidence for the improvement of water resistance (Qiao et al. 2015).

**CONCLUSIONS**

1. An environmentally friendly starch-based wood adhesive was synthesized by adding polyvinyl alcohol as a protective colloid to improve the storage stability of the starch adhesive and polymethylene polyphenylene isocyanate (PAPI) as the cross-linking...
agent was used to improve water resistance.

2. The results indicated that both shear strength and water resistances of the starch-based wood adhesive were significantly improved. When adding 7 wt% of poly-(vinyl alcohol) with a low alcoholysis degree (PVOH₃) and adjusting the pH to 8.80, the shear strength could reach 7.77 MPa in the dry state, which was improved by about 55% and 1.36 MPa, while in the wet state it was increased by 100%, and the storage stability of the adhesive improved as well. While adding poly-(vinyl alcohol) with a high alcoholysis degree (PVOH₄) to modify adhesive, the water resistance of the adhesive was very poor. PVOH₃ can effectively improve the stability of starch adhesive.

3. Adding 12 wt% PAPI resulted in good water resistance and distribution because the -NCO groups of PAPI could form a cross-linked network with the reactive hydrogen in wood and cassava starch (CS) or PVOH₃.

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