Preparation and Properties of Cassava Starch-based Wood Adhesives

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A biodegradable, environmentally friendly starch-based wood adhesive with cassava starch as a raw material and butyl acrylate (BA) as a co-monomer was synthesized. Results revealed that this cassava starch-based wood adhesive (SWA) was more stable than corn starch-based wood adhesive, and its bonding performance was close to that of commercial PVAc emulsion, even after 90 days of storage. Further analysis found that the improved stability of the adhesive could be attributed to its low minimum film forming temperature (MFFT) and glass transition temperature (T_g) of cassava starch. Moreover, the amount of total volatile organic compounds (TVOCs) emitted by the cassava starch-based wood adhesive were much lower than the Chinese national standard control criteria. Therefore, cassava SWA might be a potential alternative to traditional petrochemical-based wood adhesives.

Keywords: Cassava starch; Corn starch; Wood adhesive; Vinyl acetate; Butyl acrylate; Total volatile organic compounds

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INTRODUCTION

Wood adhesives play an essential role in the furniture, construction, and building industries. In 2014, the global consumption of wood adhesives in woodworking, including furniture, building products and other applications, was about 1.95 million metric tons (European Coatings 2014). However, most wood adhesives used in the wood products industry are based on non-renewable petrochemical resources, such as phenol/formaldehyde and polyurethane. Adhesives also contain volatile organic compounds (VOCs) and residual toxic chemicals, such as formaldehyde (Haag *et al.* 2004, 2006). As such, this heavy dependence on petroleum and the harmful effects of emissive pollutants on human health have created an urgent need for environmentally friendly wood adhesives based on renewable resources.

Starch is a relatively inexpensive and renewable product obtained from various plant sources; this product has been extensively used as a wet-end additive, coating binder, sizing agent, and adhesive (BeMiller and Whistler 2009). Several researchers have evaluated the potential utilization of starch (Imam *et al.* 1999, 2001), starch/tannin (Moubarik *et al.* 2009, 2010, 2011), and starch/isocyanates (Tan *et al.* 2011) as starch-based wood adhesive (SWA). SWA can be prepared by grafting an olefin monomer (VAc or VAc + BA) onto starch granules; the monomer then reacts with the OH group of the glucose unit to produce an ether linkage (Wang *et al.* 2012, 2015; Zhang *et al.* 2015). Emulsifiers (Wang *et al.* 2013a; Li *et al.* 2014), urea (Wang *et al.* 2013b), and nanomaterials (Wang *et al.* 2011; Li *et al.* 2015) have been used to improve the properties of SWA. Nevertheless, studies have mostly used normal or waxy corn starch as a raw material to prepare SWA; other kinds of starch have not yet to be fully explored. Moreover, the properties and functions of SWA with other kinds of starch have not yet to be appropriately evaluated.

Cassava is often considered as a low-quality raw material that can be processed to produce dried cassava chips, cassava starch, ethanol, liquid sugar, sorbitol, monosodium glutamate, and modified cassava flour because this raw material contains low amounts of proteins, minerals, and vitamins (Hillocks and Thresh 2002). Among various types of starches, cassava starch is advantageous because of its paste clarity, low gelatinization temperature, good gel stability, and good fil m-forming properties (Mali *et al.* 2006). Films produced by cassava starch are more flexible than those formed by other starches (Parra *et al.* 2004). The bond strength of SWA, which is a non-reactive adhesive, is largely dependent on the interaction (weak secondary forces) with wood and adhesive polymers. Therefore, SWA films may play a significant role in adhesion (Qiao and Easteal 2001). Considering this property, we used cassava starch as an alternative material for preparing SWAs.

This study aimed to produce a renewable SWA that can be used at room temperature. Cassava starch was used as a raw material. Normal corn starch was also prepared for comparison. Butyl acrylate (BA) was added as an assistant monomer to enhance the performance of the synthesized SWA.

EXPERIMENTAL

Materials

Normal corn starch was supplied by Shandong Shouguang Golden Juneng Corn Co. (Shandong, China). Cassava starch was obtained from the Guangxi Academy of Agricultural Sciences (China). Poly(vinyl alcohol) (PVA, the average degree of polymerization was 1750 ± 50) was purchased from Sinopec Shanghai Petrochemical Co. (Shanghai, China). Vinyl acetate (VAc), ammonium persulfate (APS), ethanol, acetone, and hydrochloric acid were procured from Sinopharm Chemical Reagent Co. (Shanghai, China). Butyl acrylate (BA) was obtained from Aladdin Chemical Reagent Co. (Shanghai, China). Glyceryl monostearate was supplied by KeLong Chemical Reagent Co. (Chengdu, China). All other reagents were of analytical grade.

Preparation

SWA1 and SWA2 were synthesized as follows. Approximately 50 g of dried normal corn starch and 100 mL of hydrochloric acid (0.5 M) were mixed in a four-necked round-bottom flask and stirred at 60 °C for 90 min. The pH of the mixture was adjusted to 4.0. Glyceryl monostearate (2% of dry starch) and APS (0.3 g) were then added under nitrogen protection. After 30 min, the reaction temperature was increased to 70 °C. Subsequently, 50 mL of olefin monomer (pure VAc (named SWA1), or a mixture of VAc and BA, with a ratio of 40:10 (named SWA2)) and 0.2 g of APS were dropped into the mixture for 2 h. After polymerization was completed, the PVA solution (1.2% of the SWA) was added. Afterward, the temperature of the reaction mixture was increased to 85 °C and maintained for 30 min. The mixture was cooled to room temperature, and its pH was adjusted to 6.0 by adding $NaHCO_3$.

For comparison, SWA3 and SWA4 were prepared following the same process, but cassava starch was used as the main raw material to replace normal corn starch.

The copolymer was obtained by preparing the grafted starch samples in accordance with the procedure described above before the PVA solution was added. The products were precipitated with ethanol, washed with distilled water, and dried in a vacuum to obtain a solid mixture. The solids were extracted with acetone using a Soxhlet extraction device at 70 °C for 48 h to remove VAc homopolymers or VAc/BA monomers. The final product was dried in a vacuum until a constant weight was obtained (Goñi *et al.* 1983).

Bonding test

The samples were stored at 23 ± 2 °C for 0, 30, 60, or 90 days. Afterward, the SWA samples were used to glue wood samples. Then, the shear strengths of the glued samples were evaluated in accordance with the Chinese industry standard HG/T 2727-2010 (2010). Freshly cut pieces of wood (Manchurian ash, approximately 0.81×10^3 kg/m^3) with dimensions of 25 mm × 25 mm × 10 mm were glued with adhesives at a static pressure of 0.5 to 1.0 MPa at 25 °C for 24 h (Fig. 1). Before the shear strength tests were performed, the glued specimens were stored in a laboratory at 23 ± 2 °C and 50 ± 5% humidity for 48 h. The shear strength of the dry glued samples was determined using a WDT-10 shear strength analyzer (KQL Corp., China). The shear strength was calculated as follows,

$$\sigma_{\mathrm{M}} = F_{\max}/A \qquad (1)$$

where σ_{M} (MPa) is the shear strength, $F_{\max}$ (N) is the observed maximum failing load, and A (mm^2) is the bonding surface of the sample. The testing speed was 2 mm/min. All tests were replicated six times, and the results are presented as averages.

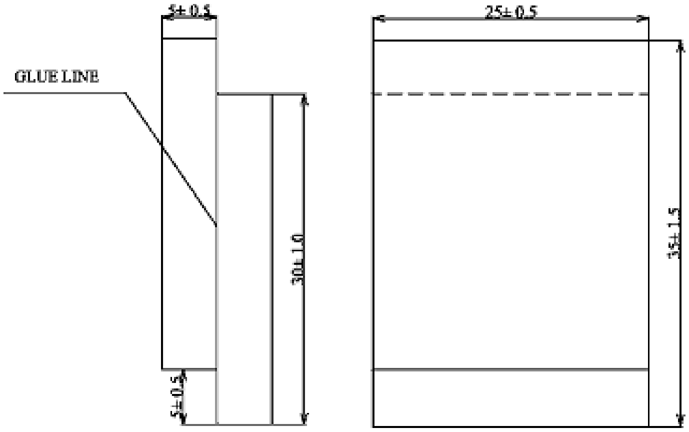

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Fig. 1. Schematic of the shape and dimension of the shear test specimen (HG/T 2727-2010)

Emulsion stability was analyzed by placing the adhesive samples (30 mL) in plastic containers after 0, 30, 60, or 90 days. The viscosities of SWA were determined by using a Brookfield viscometer (Model DV-II+Pro, USA) at 50 rpm with spindle number of 29 and expressed in Pa.s. The viscosity was measured in triplicate at 25 ± 1 °C.

The extracted samples were fully milled with potassium bromide and then pelletized for FT-IR spectroscopy in a Nexus 470 FT-IR spectrometer (Nicolet Corp., USA). Each sample was scanned 32 times within a region of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

The minimum film forming temperature (MFFT) of the SWA samples was determined using an MFFT-Bar 60 instrument (Rhopoint Corp., UK) within the operating range of −5 to 60 °C.

Differential scanning calorimetry (DSC) analysis was conducted in a Perkin Elmer DSC 7. Measurements were performed using 3 to 5 mg of the samples in purging nitrogen from −90 to 160 °C at a rate of 10 °C/min.

Cast films were prepared as follows. The adhesive was cast on a Teflon® board. Water was then gently evaporated on a hot plate at 50 °C. Afterward, the cast adhesive was vacuum-dried until a constant weight was achieved. All of the specimens were observed under a scanning electron microscope (FEI Quanta-200, Holland).

The total volatile organic compounds (TVOCs) of the SWA samples were analyzed in accordance with the Chinese National Standard GB 18583-2008 (2008). The amount of TVOCs was calculated as follows,

$$W_{\text{voc}}=[(W_{\text{total}} - W_{\text{water}})/(1 - W_{\text{water}})]\times\rho \qquad (2)$$

where W_{voc} (g/L) is the amount of TVOCs in SWA, W_{total} is the mass fraction of the total volatile compounds in SWA, W_{water} is the mass fraction of water in SWA, and ρ (g/L) is the density of SWA. All of the tests were replicated three times and the results are presented as averages.

Data were statistically analyzed in DPS 7.05 (Zhejiang University, Hangzhou, China). Significant differences ($p < 0.05$) between treatment means were determined *via* Duncan’s multiple range tests.

RESULTS AND DISCUSSION

Storage Stability of Starch-based Wood Adhesive at Room Temperature

Storage stability is an important property of SWAs. This property can be evaluated by observing changes in the shear strength and viscosity of adhesives during storage (Li *et al.* 2014). Apparent viscosity is an important mobility property of wood adhesives (Qi and Sun 2010). If the apparent viscosity of adhesives is too high, adhesives exhibit poor storage stability and low commercial value.

The viscosities of the SWA samples at different storage times are shown in Table 1. The apparent viscosity of the adhesive samples increased as storage time was prolonged. For example, the apparent viscosity of SWA1 on day 90 was beyond the range of the test instrument; as a result, SWA1 formed a non-flowing gel, which hardened during the prolonged storage.

In contrast, its viscosity was 4.62 Pa.s on day 0. In addition, SWA4 exhibited excellent storage stability. The apparent viscosity of SWA4 was higher than those of SWA3 and SWA2 on day 0. After 90 days of storage, the apparent viscosities of SWA2, SWA3, and SWA4 increased to 15.85, 15.21, and 11.85 Pa.s, respectively. In general, the emulsion stability of cassava SWA was superior to that of corn SWA as the storage period was extended.

Table 1. Variation in the Apparent Viscosities of Starch-based Wood Adhesives during Storage

Sample	Viscosity (Pa.s)			
	0 days	30 days	60 days	90 days
SWA1 (corn starch + VAc)	4.62±0.23	8.80±0.42	17.95±1.08	too high
SWA2 (corn starch + VAc+BA)	6.76±0.36	9.22±0.35	13.52±0.54	15.85±1.12
SWA3 (cassava starch + VAc)	6.49±0.29	9.78±0.46	12.87±0.73	15.21±1.25
SWA4 (cassava starch + VAc+BA)	7.81±0.35	8.80±0.29	10.05±0.69	11.85±0.90

The stability of the bonding characteristics of SWA was also evaluated. Table 2 shows that the shear strength of the SWAs decreased as storage time increased: for example, the bonding strength of SWA1 after 90 days of storage was only 12.8% of the initial value. This phenomenon may have occurred because the adhesive emulsion has a high apparent viscosity that impedes the permeation of the emulsion into the wood surface (Wang *et al.* 2013b). However, the bonding stability of the adhesive was improved by adding BA: the shear strengths for SWA2 and SWA4 were 3.28 and 5.96 MPa after 90 days of storage, which were 3.38- and 1.78-fold increases compared with those without added BA (SWA1, SWA3), respectively. In particular, after 90 days of storage, the shear strength of SWA4 was still as high as 5.96 MPa, which was close to the value of a commercial PVAc emulsion (Wang *et al.* 2012). BA is a kind of a hydrophobic soft monomer, and graft copolymerization with vinyl acetate can improve the bonding strength and the emulsion stability of SWA. Furthermore, cassava SWA showed a greater bonding ability than corn SWA did after 0 or 90 days of storage: the shear strengths for SWA3 and SWA4 were 3.45- and 1.81-fold increases compared with those without added BA (SWA1, SWA2), respectively, after 90 days of storage. This may have occurred because the cassava starch formed a homogeneous, flexible film (Mali *et al.* 2006). Thus, cassava starch may be a suitable raw material for SWAs.

Table 2. Variation in the Shear Strengths of Starch-based Wood Adhesives during Storage

Sample	Shear strength (MPa)				Loss rate for 90 days of storage (%)
	0 day	30 days	60 days	90 days	
SWA1 (corn starch + VAc)	5.15 ± 0.09^{d}	3.81 ± 0.11^{d}	2.02 ± 0.19^{d}	0.97 ± 0.25^{d}	81.2%
SWA2 (corn starch + VAc/BA)	7.96 ± 0.05^{b}	6.65 ± 0.08^{b}	4.79 ± 0.13^{b}	3.28 ± 0.09^{b}	58.8%
SWA3 (cassava starch + VAc)	6.83 ± 0.08^{c}	5.57 ± 0.12^{c}	4.01 ± 0.11^{c}	3.35 ± 0.14^{b}	50.9%
SWA4 (cassava starch + VAc/BA)	10.05 ± 0.06^{a}	8.47 ± 0.09^{a}	7.11 ± 0.18^{a}	5.96± 0.16^{c}	41.2%

Mean ± SD values in the same column followed by different superscripts are significantly different ($p \leq 0.05$)

FT-IR Spectroscopy

FT-IR spectroscopy was performed to confirm the graft modification of starch and to determine the effect of graft copolymerization on the SWA structure. The results are presented in Figs. 2 and 3. Native starch showed characteristic peaks located at 3420 cm^{-1} (–OH stretching), 2930 cm^{-1} (–CH– stretching), 1630 cm^{-1} (–OH bending), 1020 cm^{-1} and 929 cm−1 (–CO stretching). Compared with the absorption bands of native starch, new absorption bands at approximately 1240 and 1740 cm^{-1} can be observed in the infrared spectra. These results indicate the existence of VAc and BA groups in the graft copolymer (Marinich *et al.* 2009). Therefore, graft copolymerization successfully occurred.

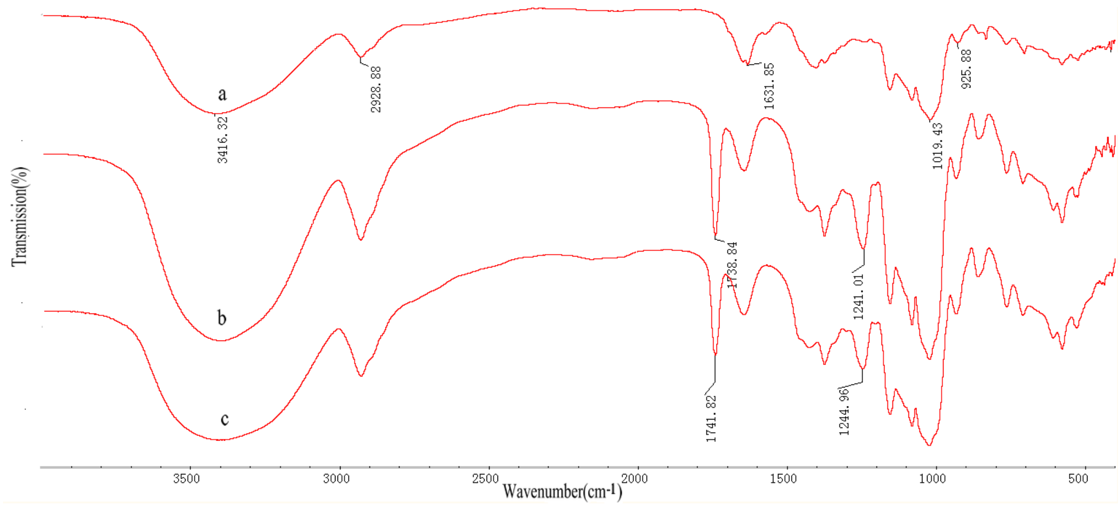

Fig. 2. Infrared spectra of (a) cassava starch, (b) cassava starch-grafted VAc copolymer, and (c) cassava starch-grafted VAc/butyl acrylate copolymer

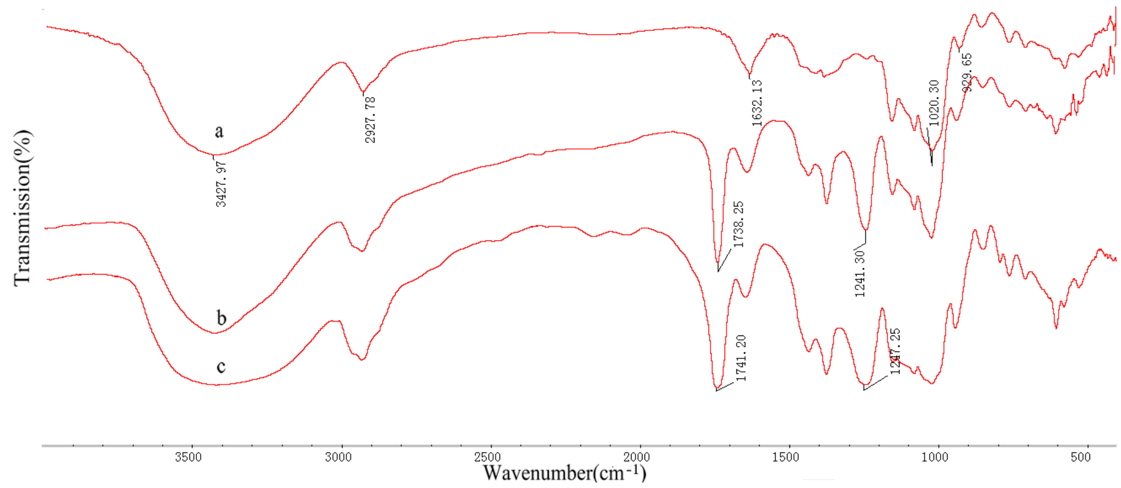

Fig. 3. Infrared spectra of (a) corn starch, (b) corn starch-grafted VAc copolymer, and (c) corn starch-grafted VAc/butyl acrylate copolymer

Minimum Film Forming Temperatures of SWAs

MFFT is an important parameter related to the film formation properties of polymer emulsions. This parameter is defined as the approximate temperature at which the forces influencing latex deformation exceed the resistance to deformation. The application temperature should be above this temperature to obtain a continuous film. Thus, the deformation and cohesion of latex particles can occur. A low MFFT is conducive to obtaining an enhanced continuous adhesive film at a set application temperature and to improve the relevant characteristics of the adhesive film (Steward *et al.* 2000). The effects of starch type and complex monomer on the MFFT of the SWA are shown in Table 3. The presence of BA in the monomer mixture reduced the MFFT of SWA, possibly because of the plasticization effect of BA on the SWA. The plasticization effect could increase the deformation rate of the adhesive; as a consequence, the MFFT of the latex decreased. In addition, the MFFTs of cassava SWAs were also lower than those of corn SWA. Therefore, the cassava SWAs could easily form a continuous adhesive film, which could help enhance the bonding ability.

Table 3. Minimum Film Forming Temperature (MFFT) of Starch-based Wood Adhesives

Sample	MFFT (°C)
SWA1 (corn starch + VAc)	30
SWA2 (corn starch + VAc/BA)	26
SWA3 (cassava starch + VAc)	25
SWA4 (cassava starch + VAc/BA)	20

Glass Transition Temperatures of SWAs

T_g is an important parameter of polymer emulsions. The T_g of an emulsion should be below room temperature to produce a continuous and flexible film at the applied temperature (Yamak and Yildirim 2013). The effects of starch type and complex monomer on the T_g of the SWA film are summarized in Table 4 and Fig. 4. Compared with the T_g of the SWA without added BA, the T_g of the SWA with BA decreased. A low T_g implies that a soft polymer film is formed. This might be due to the presence of long alkyl chains in BA, which means BA functions as a plasticizer to increase the chain mobility of SWA, resulting in reduced T_g in the SWA emulsion polymer. In addition, the T_g of the cassava SWAs are lower than those of corn SWAs. Therefore, cassava SWA can be utilized to form a continuous flexible film and to reduce the microphase separations in adhesive films.

Table 4. Glass Transition Temperature (T_g) of Starch-based Wood Adhesives

Sample	T_g (°C)
SWA1 (corn starch + VAc)	32.75
SWA2 (corn starch + VAc/BA)	29.65
SWA3 (cassava starch + VAc)	27.68
SWA4 (cassava starch + VAc/BA)	24.81

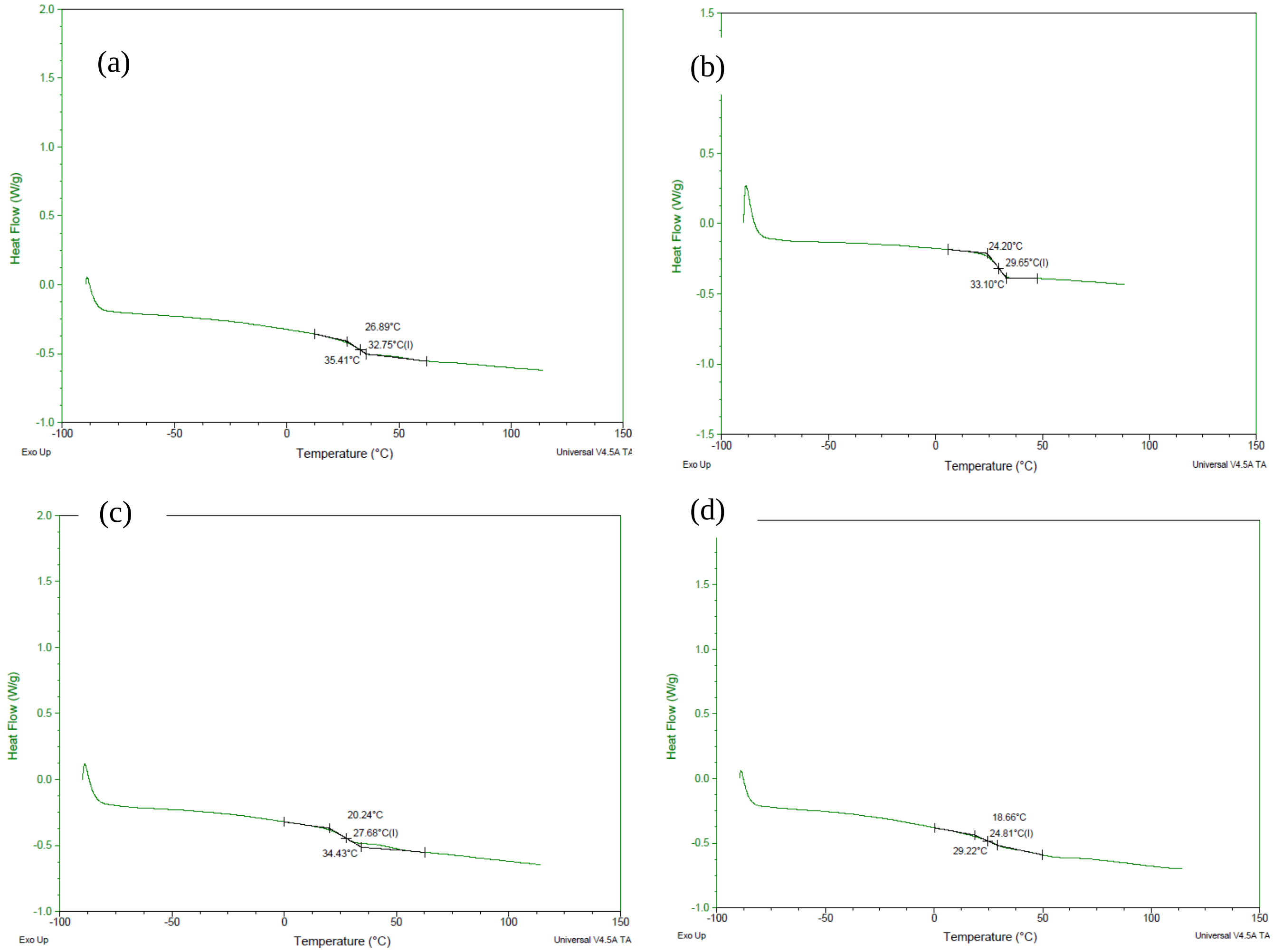

Fig 4. DSC curves of Starch-based Wood Adhesives (a) SWA1, (b) SWA2, (c) SWA3, and (d) SWA4

Morphological Characteristics of Adhesive Films

The effects of starch type and complex monomer on the adhesive structure are directly shown by scanning electron micrographs (Fig. 4). The films of the SWA with BA were smoother and more compact than those of the SWA without BA (Fig. 5a and b). Little evidence of microphase separations were observed.

The films of the cassava SWA were also smoother and more compact than those of the corn SWA. The result could be attributed to the good film-forming property of cassava starch.

As a non-reactive water-based adhesive, the SWA film may play a significant role in adhesion (Qiao and Easteal 2001). Hence, high-quality adhesive films possibly helped enhance their bonding characteristics. Thus, the MFFT, T_g, and morphological characteristics of SWA indicated that cassava could form a more continuous flexible adhesive film and be a more suitable raw material for SWA than corn starch.

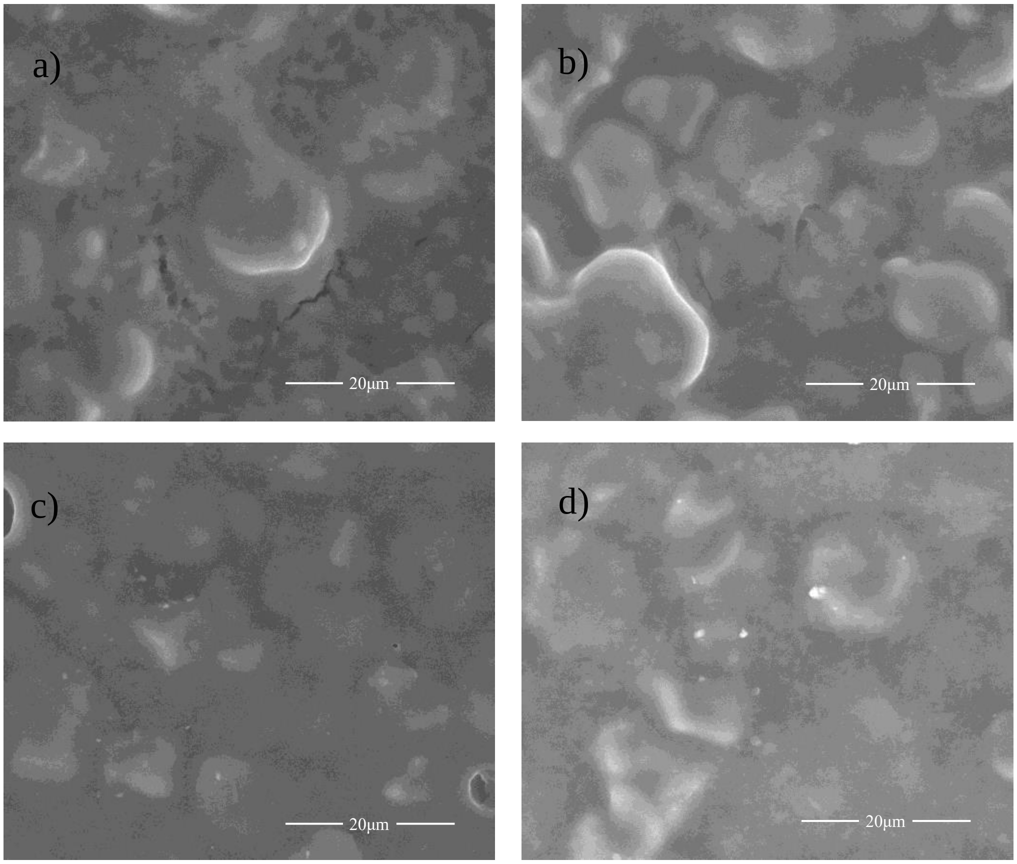

Fig. 5. Scanning electron micrograph of cast films of the starch-based wood adhesive: (a) corn starch + vinyl acetate (VAc), (b) corn starch + VAc/butyl acrylate (BA), (c) cassava starch + VAc, and (d) cassava starch + VAc/BA

TVOCs of SWAs

Studies on TVOC emissions from indoor sources have revealed that adhesives contribute to indoor air pollution (Guo *et al.* 2000). Aromatic hydrocarbons (*e.g.*, benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, styrene, and *o*-xylene) and alkanes (*e.g.*, isopentane, nonane, decane, undecane, 2-methyloctane, and 2-methylnonane), which are the target compounds of TVOCs, are emitted by wood adhesives.

Table 5. Total Volatile Organic Compounds (TVOCs) of Starch-based Wood Adhesives

Sample	TVOC (g/L)
SWA1 (corn starch + VAc)	101.3 ± 2.3^a
SWA2 (corn starch + VAc/BA)	95.1 ± 2.5^b
SWA3 (cassava starch + VAc)	89.3 ± 1.9^c
SWA4 (cassava starch + VAc/BA)	81.2 ± 2.1^d
Chinese National Standard （GB18583-2008）	≤110

Mean ± SD values in the same column followed by different superscripts are significantly different ($p \leq 0.05$).

Most of these organic compounds are potentially harmful to our health. Moreover, adhesives are used primarily in residential settings, such as carpet installed on a concrete subfloor and adhered furniture and wallpaper. Therefore, TVOCs are a relevant component of wood adhesives. We also investigated the TVOCs of our SWA (Table 5). Compared with other samples, SWA4 yielded the lowest TVOC (81.2 g/L). Furthermore, the TVOCs of our samples are below the Chinese National Standard GB18583-2008 (2008) limit (≤ 110 g/L). Thus, cassava SWA is a low-TVOC environmentally friendly wood adhesive.

CONCLUSIONS

1. A new biodegradable, starch-based wood adhesive that has a low level of total volatile organic compound emissions was prepared by utilizing cassava starch as a raw material and BA as a co-monomer.
2. Shear strength experiments demonstrated that the stability of SWA was significantly enhanced by adding BA and using cassava starch as a material; further analysis revealed that these improvements were attributed to the low minimum film forming temperature and glass transition temperature of cassava starch.
3. The amount of TVOCs emitted from cassava SWA was as low as 81.2 g/L, which was considerably lower than the Chinese National Standard control criterion. Therefore, cassava starch-based wood adhesives could be potential alternatives to traditional petrochemical-based wood adhesives.

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