



Preparation, characterization and properties of starch-based wood adhesive

Zhenjiong Wang, Zhaofeng Li, Zhengbiao Gu*, Yan Hong, Li Cheng

State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, People's Republic of China

ARTICLE INFO

Article history:

Received 3 November 2011

Received in revised form 6 January 2012

Accepted 6 January 2012

Available online 13 January 2012

Keywords:

Waxy cornstarch

Wood adhesive

Graft polymerization

Vinyl acetate

ABSTRACT

A new biodegradable, renewable, environmentally friendly starch-based wood adhesive that can be used at room temperature was synthesized by the graft polymerization of vinyl acetate monomer onto waxy corn starch. Compared with the blend of commercial PVAc/gelatinized starch, the shear strength of grafted starch adhesive increased by 59.4% in dry state and 321% in wet state, while its water resistance increased by 61.1%. The improved performance of the grafted starch-based wood adhesive was supported by its strengthened compatibility with polyvinyl acetate and starch, based on the results of Fourier-transform infrared, ^1H nuclear magnetic resonance, thermogravimetry, and scanning electron microscopy analyses. The most economic monomer feeding ratio was also evaluated using bond characteristics and grafting parameters. A starch/monomer ratio of 1:1.2 (w/w) was considered as the best ratio in terms of economy.

Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Polyvinyl acetate (PVAc) emulsion is an odorless and non-flammable adhesive, which is commonly used in furniture and other wood product manufacture at room or low temperatures (Kim & Kim, 2006; Qiao & Easteal, 2001). However, the raw materials of PVAc adhesives completely rely on nonrenewable resources such as petroleum and natural gas. With the worsening global energy crisis, the mainly used raw materials of wood adhesives is being replaced by renewable biopolymers, such as soybean protein (Ciannanea, Stefani, & Ruseckaite, 2010; Li et al., 2009; Liu et al., 2010), natural tannin (Kim, 2009) and starch (Imam, Gordon, Mao, & Chen, 2001).

Starch is a kind of renewable, biodegradable, inexpensive, and readily available biopolymer extensively used as binders, sizing materials, glues, and pastes (Kennedy Harry, 1989). However, its bonding capacity is not strong enough to glue wood (Imam et al., 2001; Imam, Mao, Chen, & Greene, 1999). To solve this problem, physical or chemical modifications of starch molecules such as blending have been considered. Recent studies have focused on formaldehyde-free wood adhesives, which are obtained by the reaction between a cross-linker and the blend of starch or other polymers, such as starch/PVOH (Imam et al., 2001) and starch/tannin (Moubarik, Charrier, Allal, Charrier, & Pizzi, 2010) blends. However, the curing temperature of such wood adhesives is usually over 100 °C. Therefore, a new kind of starch-based wood

adhesive that can be used at room temperature needs to be synthesized.

Grafting is an important technique for modifying the physical and chemical properties of polymers. The graft copolymerization of synthetic polymers onto a starch backbone is one of the best ways of improving the bonding properties of starch. There are many reports on the synthesis, characterization, and properties of starch graft copolymers (Athawale & Lele, 2000; Bruyn, Sprong, Gaborieau, Rober, & Gilbert, 2007; Gong, Wang, & Tu, 2006; Lai, Don, Liu, & Chiu, 2006; Samaha, Nasr, & Hebeish, 2005; Tanrattanakul & Chumeka, 2010), but less is paid to the grafting of VAc onto starch as a kind of wood adhesive. Consequently, the properties and functions of such an adhesive have not yet been appropriately evaluated.

In the present study, a renewable starch-based wood adhesive that can be used at room temperature was prepared by the grafting of VAc onto starch using ammonium persulfate (APS) as the initiator. The bonding strength and water resistance of the adhesive were examined to evaluate the effect of the grafting reaction on the adhesive system. The starch/monomer ratio was varied to evaluate the bonding properties. Fourier-transform infrared (FTIR), ^1H nuclear magnetic resonance (NMR), and thermogravimetry (TG) techniques were used to obtain information on the chemical structure of the grafted starch copolymer. The morphology of the adhesive films and the fractography morphology of wood-bonded joints were used to confirm the positive effect of the grafting reaction.

2. Materials and methods

2.1. Materials

Waxy corn starch was supplied by Qinhuangdao Lihua Starch Co. (China). Commercial PVAc emulsion (33% wt) was bought from

* Corresponding author. Tel.: +86 510 85329237; fax: +86 510 85329237.

E-mail addresses: wangzhenjiong@gmail.com (Z. Wang), zhengbiaogu@yahoo.com.cn (Z. Gu).

Jiangsu Qiye Emulsion Co. (China). VAc, ammonium persulfate (APS), sodium bicarbonate (NaHCO_3), sodium dodecyl sulfate (SDS), acetone and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. (China). All other reagents were of analytical grade.

2.2. Synthesis of the starch-based wood adhesive

All reactions were carried out in a four-necked round-bottom flask with a mechanical stirrer, constant pressure funnel, nitrogen gas inlet and reflux condenser. The nitrogen atmosphere was maintained in the reactor by purging the nitrogen gas in the reactor.

2.2.1. Preparation of gelatinized starch

About 50 g of dried waxy corn starch and 100 mL of hydrochloric acid (0.5 M) were put into a four-necked round-bottom flask and stirred at 60 °C for 30 min. The pH of the mixture was adjusted to 6.0 and the temperature was increased to 95 °C. After 30 min of starch gelatinization, the reaction temperature was cooled to room temperature.

2.2.2. Preparation of the PVAc/starch blend

About 50 g of dried waxy 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 30 min. The pH of the mixture was adjusted to 6.0 and the temperature was increased to 95 °C. After 30 min of starch gelatinization, the reaction temperature was cooled to 60 °C, followed by the addition of 150 mL PVAc emulsion (about 33% wt). After 30 min stirring, the pH of mixture was adjusted to 6.0 after it was cooled to room temperature.

2.2.3. Preparation of the grafted starch-based wood adhesive

The grafted starch-based wood adhesive was synthesized as follows: about 50 g of dried waxy 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 30 min. The pH of the mixture was adjusted to 6.0, and the temperature was increased to 95 °C. After 30 min of starch gelatinization, the reaction temperature was cooled to 60 °C, followed by the addition of 0.5 g SDS, 12.5 g VAc and 0.125 g of APS under nitrogen protection. After 30 min of pre-polymerization, the reaction temperature was increased to 70 °C, and residual VAc (17.5, 27.5, 37.5, 47.5, 57.5 and 67.5 g, respectively) and 0.375 g of APS were dropped into the mixture over a period of 3 h. After 3 h of polymerization, the temperature was increased to 80 °C and kept for 30 min. Finally, NaHCO_3 was added to adjust the pH to 6.0 after the temperature of the mixture was cooled to room temperature.

2.2.4. Preparation of copolymer and determination of grafting parameter

To determine the grafting parameters of the copolymer, the grafted starch samples were prepared following the above process. 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 homopolymers of VAc monomers. The final product was dried under a vacuum until a constant weight was achieved (Goñi, Gurruchaga, Valero, & Guzman, 1983; Gurruchaga, Goñi, Valero, & Guzmán, 1984).

The percentage of grafting (G) and grafting efficiency (GE) were calculated with the following equation (Gurruchaga, Goñi, Valero, & Guzmán, 1992):

$$\%G = \frac{\text{Grafted vinyl acetate polymer weight}}{\text{Grafted carbohydrate weight}} \times 100$$

$$\%GE = \frac{\text{Graft copolymer weight}}{\text{Total product weight}} \times 100$$

Results are presented as the means of three replicates.

2.3. Structural characteristics

2.3.1. Fourier transform-infrared spectroscopy (FT-IR) analysis

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

2.3.2. ^1H -NMR spectroscopy analysis

^1H -NMR spectra were obtained using a Bruker AV 400 MHz NMR system (Bruker, Rheinstetten, Germany). Samples were dissolved in dimethyl sulfoxide- d_6 using tetramethylsilane as an internal standard.

2.3.3. Thermogravimetric analysis (TGA)

Thermal stability of the adhesive samples was analyzed using a Mettler Toledo TGA/SDTA851^e thermogravimeter (Mettler Toledo Corp., Switzerland) with a STAR^e software (version 9.01). Samples (5.0 mg in a 70 μL of alumina pan) were heated from 25 to 600 °C at a rate of 10 °C/min under nitrogen gas flowing at 30 mL/min.

2.4. Shear strength test

Shear strength of the adhesive samples was tested according to a Chinese industry standard of HG/T 2727-1995 (China, 1995). Freshly cut pieces of wood (*Betula platyphylla*, 13.5% water content, 620 kg/m^3) with dimensions of 25 mm \times 25 mm \times 10 mm were glued with adhesives under static pressures of 0.49–0.98 MPa at 25 °C for 24 h (Scheme 1). Before shear strength test, the glued specimens were stored in the laboratory at 23 \pm 2 °C and 50 \pm 5% humidity for 48 h. The shear strength of the glued samples in dry or wet (after immersing in water at 23 °C for 3 h) state was determined using a WDT-10 shear strength analyzer (KQL Corp., China). The shear strength was calculated as following: $\sigma_M = F_{\text{max}}/A$, 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 is 2 mm/min. All the tests were replicated 10 times, and the results were presented as averages.

2.5. Scanning electron microscopy (SEM) analysis

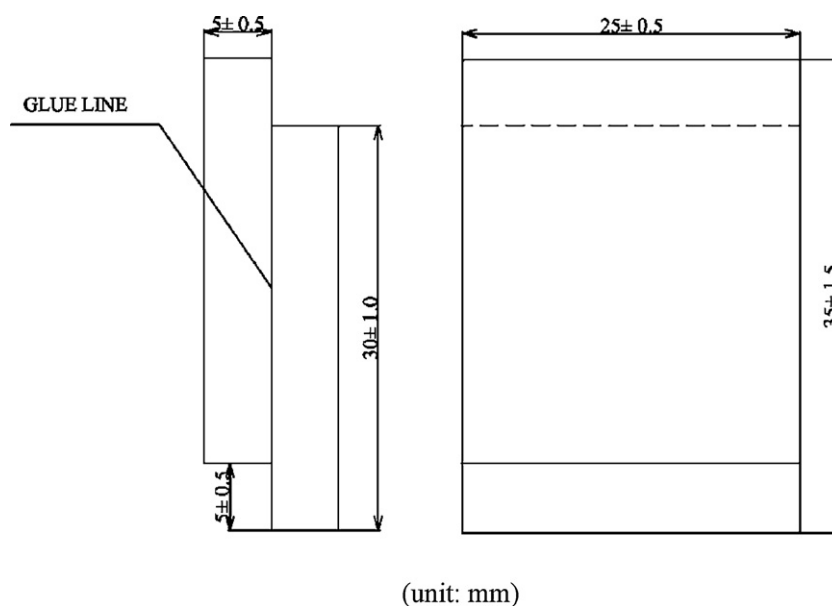
Cast films were made by casting the adhesive on a Teflon board, gently evaporating the water on a hot plate at 40 °C, and vacuum drying until a constant weight was achieved. Surfaces of cast films of the adhesive samples and the fracture surface of specimens in dry condition after shear strength test were coated with gold under vacuum. Then all specimens were observed using a scanning electron microscope (Quanta-200, Holland).

2.6. Determination of viscosity

The viscosities of the starch-based wood adhesive with different monomer feeding ratios were determined using a Brookfield viscometer (Model DV-II+Pro, USA) at 50 rpm using spindle number 29 and expressed in Pa s. The viscosity was measured in triplicate at 25 \pm 1 °C.

2.7. Statistical analysis

Data were statistically analyzed using DPS 7.05 (Zhengjiang University, Hangzhou, China). Significant differences ($p < 0.05$)



Scheme 1. Shape and dimension of shear test specimen (HG 2727-1995).

between treatment means were determined using Duncan's multiple range tests.

3. Results and discussion

3.1. Comparison between physical blending and copolymerization of starch and VAc

Compared with the blend of commercial PVAc/gelatinized starch, the beneficial effect of the grafting reaction on the starch-based wood adhesive system was directly supported by improved bonding strength and water resistance of the starch-based wood adhesive.

As shown in Table 1, the grafted starch-based adhesive (GSWA0, starch:VAc, 1:1) had a significantly higher shear strength than the blend of commercial PVAc/gelatinized starch and gelatinized starch. Compared with the PVAc/starch blend, the shear strength of GSWA0 was increased from 2.29 MPa to 3.65 MPa in dry state and from 0.43 MPa to 1.81 MPa in wet state. The changes of shear strength suggested that GSWA increased the bonding strength of the adhesive by 59.4% in dry condition and 321% in wet condition. Apparently, the bonding strength of the starch-based wood adhesive has been significantly improved by grafting reaction.

Since water molecules can penetrate into wood and act as a plasticizer for hydrophilic polymers, the bonding strengths of starch-based wood adhesives unavoidably decrease in a humid

environment (Qiao & Easteal, 2001). The durability of a glued timber joint after 3 h of soaking is also shown in Table 1. Wood samples glued by the PVAc/starch blend lost about 81.2% bonding strength, whereas the grafted sample only lost about 50.4% bonding strength. This result suggested that the GSWA0 increased the water resistance of the adhesive by 61.1%. Therefore, the grafting reaction can also increase the water resistance of the starch-based wood adhesive.

The performance improvement of grafting reaction on starch-based wood adhesive suggested that grafting reaction influenced on the adhesive structure, and likely affected some adhesive properties related to the bonding strength and water resistance of the adhesives. The grafted copolymer of starch-based wood adhesive system may play an important role in the performance improvement of adhesive. Therefore, the grafted starch-based wood adhesive was further analyzed to show the structural changes of adhesives, the bonding strength and water resistance of the adhesives with different monomer feeding ratios.

3.2. Effect of different feeding ratio of monomer on the bond characters and water resistance of the grafted starch-based adhesives

The viscosity profiles of the grafted starch-based wood adhesives with different monomer feeding ratio were shown in Table 2. The viscosity of the samples increased from 2.2 to 6.5 Pa s with increased monomer content. This result can be attributed to the homopolymerization and graft copolymerization under the reaction system, which led to the increased solid content of the adhesive emulsion.

Table 2 also showed the mean \pm standard deviation shear strength of the grafted starch-based adhesive with different grafting parameters. Initially, G, GE, and shear strength increased with increased monomer content. Increased monomer concentration was known to promote grafting along starch chains because of the poor mobility of starch macroradicals (Samaha et al., 2005). Therefore, the reaction efficiency of the starch grafting was attributed to the concentration of VAc molecules around starch macroradicals. Increased monomer concentration increased the chances of starch macroradicals colliding with VAc molecules. Consequently, the

Table 1
Bonding strength properties of wood joints.

Sample	Shear strength in dry state (MPa)	Shear strength in wet state (MPa)
Gelatinized starch	0.25 \pm 0.09 ^d	–
PVAc/starch blend (starch:PVAc, 1:1, w/w)	2.29 \pm 0.16 ^c	0.43 \pm 0.35 ^c
GSWA0 (starch:VAc, 1:1, w/w)	3.65 \pm 0.09 ^b	1.81 \pm 0.12 ^b
PVAc	6.10 \pm 0.07 ^a	2.32 \pm 0.29 ^a

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

Table 2
Effect of VAc monomer/starch ratio on the bond characteristic of the grafted starch-based wood adhesive.

Monomer:starch ratio (w/w)	G (%)	GE (%)	Brookfield viscosity (Pa s)	Shear strength in dry state (MPa)	Shear strength in wet state (MPa)
0.6:1	22.8 ± 1.2 ^f	42.9 ± 3.5 ^e	2.2 ± 0.2 ^f	2.63 ± 0.08 ^d	0.79 ± 0.16 ^d
0.8:1	27.3 ± 2.5 ^e	56.4 ± 3.0 ^c	2.7 ± 0.1 ^e	3.21 ± 0.06 ^c	1.16 ± 0.14 ^c
1:1	35.1 ± 2.1 ^d	62.5 ± 2.7 ^b	3.1 ± 0.2 ^d	3.65 ± 0.09 ^b	1.81 ± 0.12 ^b
1.2:1	54.5 ± 2.7 ^a	71.3 ± 3.3 ^a	3.9 ± 0.3 ^c	4.30 ± 0.07 ^a	2.17 ± 0.07 ^a
1.4:1	45.2 ± 1.9 ^b	54.3 ± 2.1 ^c	5.1 ± 0.4 ^b	4.36 ± 0.08 ^a	2.27 ± 0.12 ^a
1.6:1	39.3 ± 1.5 ^c	48.1 ± 2.9 ^d	6.5 ± 0.6 ^a	4.45 ± 0.06 ^a	2.38 ± 0.14 ^a

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

active sites along the starch-growing chain increased. The increased grafting parameters also proved that the amount of copolymer in the reaction system also increased, thereby enhancing the compatibility between the starch and the polymer, and leading to increased shear strength.

G and GE then reached their climaxes at the optimal starch/monomer ratio of 1:1.2 (w/w). With further increased monomer feeding ratio, G and GE decreased because homopolymerization prevailed over graft copolymerization. However, the shear strength continued to rise slowly due to the increased viscosity of the sample with increased grafted monomer feeding ratio. The high-viscosity adhesive emulsion resisted the spread and permeation of the adhesive emulsion on the wood surface. The spreading and permeation process was considered as an important stage of the adhesion process.

In terms of economy, the ratio of 1:1.2 (w/w) may be considered as the best starch/monomer feeding ratio under the current conditions. With this monomer feeding ratio, the starch-based adhesive was found to have the optimal shear strengths of 4.30 MPa in the dry state and 2.17 MPa in the wet state.

3.3. Characterization of copolymer

3.3.1. FTIR analysis

FT-IR was used to confirm the graft modification of starch, and the results were shown in Fig. 1. Compared with gelatinized starch, the copolymer showed new characteristic peaks of ester at 1241 and 1740 cm^{-1} in the infrared spectrogram (Fig. 1, solid arrow), which indicated the existence of the VAc group in the grafted derivatives (Kaewtatip & Tanrattanakul, 2008; Marinich, Ferrero,

& Jiménez-Castellanos, 2009; Meshram, Patil, Mhaske, & Thorat, 2009; Samaha et al., 2005).

3.3.2. $^1\text{H-NMR}$ analysis

In order to further confirm the chemical structure of grafted starch, the structures of gelatinized starch and copolymer were evaluated by $^1\text{H-NMR}$. For $^1\text{H-NMR}$ spectrum of gelatinized starch (Fig. 2a), the proton signals were $\delta = 5.10$ ppm (H-1 of anhydroglucose unit) and 3.0–3.8 ppm (H-2 to -6 of the anhydroglucose unit of starch) were accordingly correlated to respective protons of the anhydroglucose units of starch. The characteristic signals at 4.56 ppm (OH-6) and 5.4–5.5 ppm (OH-2, 3) were assigned to the hydroxy protons of anhydroglucose unit of starch, respectively (Chi et al., 2008; De Graaf, Lammers, Janssen, & Beenackers, 1995; Wang, Yang, Wang, Zhou, & Jin, 2004). The ^1H NMR spectrum of the derivative (Fig. 2b) showed not only the characteristic proton peak of starch but also the new proton signal at 1.76, 4.78, 1.97 ppm (H_a , H_b , H_c), which were assigned to the characteristic protons of PVAc, indicating the formation of the grafted copolymers.

3.3.3. Thermal stability analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of gelatinized starch, PVAc, grafted copolymer and the blend of PVAc/starch were shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the main decomposed stage of all samples was around 220–420 $^\circ\text{C}$, which can be attributed to the dehydration of polymer chains. The initial dehydration temperatures (T_0) of the polymer chains of starch, the starch/PVAc blend, PVAc, and copolymer were 231.9, 233.2, 261.1, and 271.2 $^\circ\text{C}$, respectively.

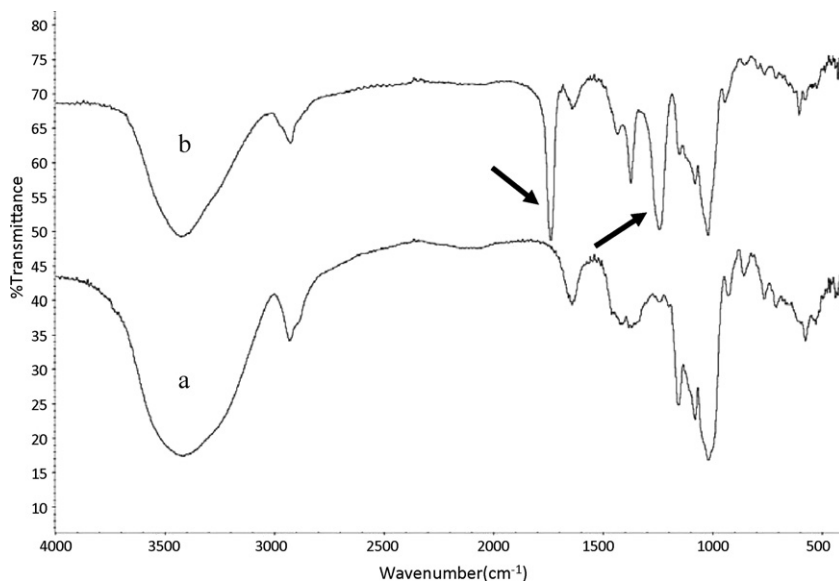


Fig. 1. Infrared spectrograms of (a) gelatinized starch and (b) grafted copolymer (VAc:starch, 1:1, w/w).

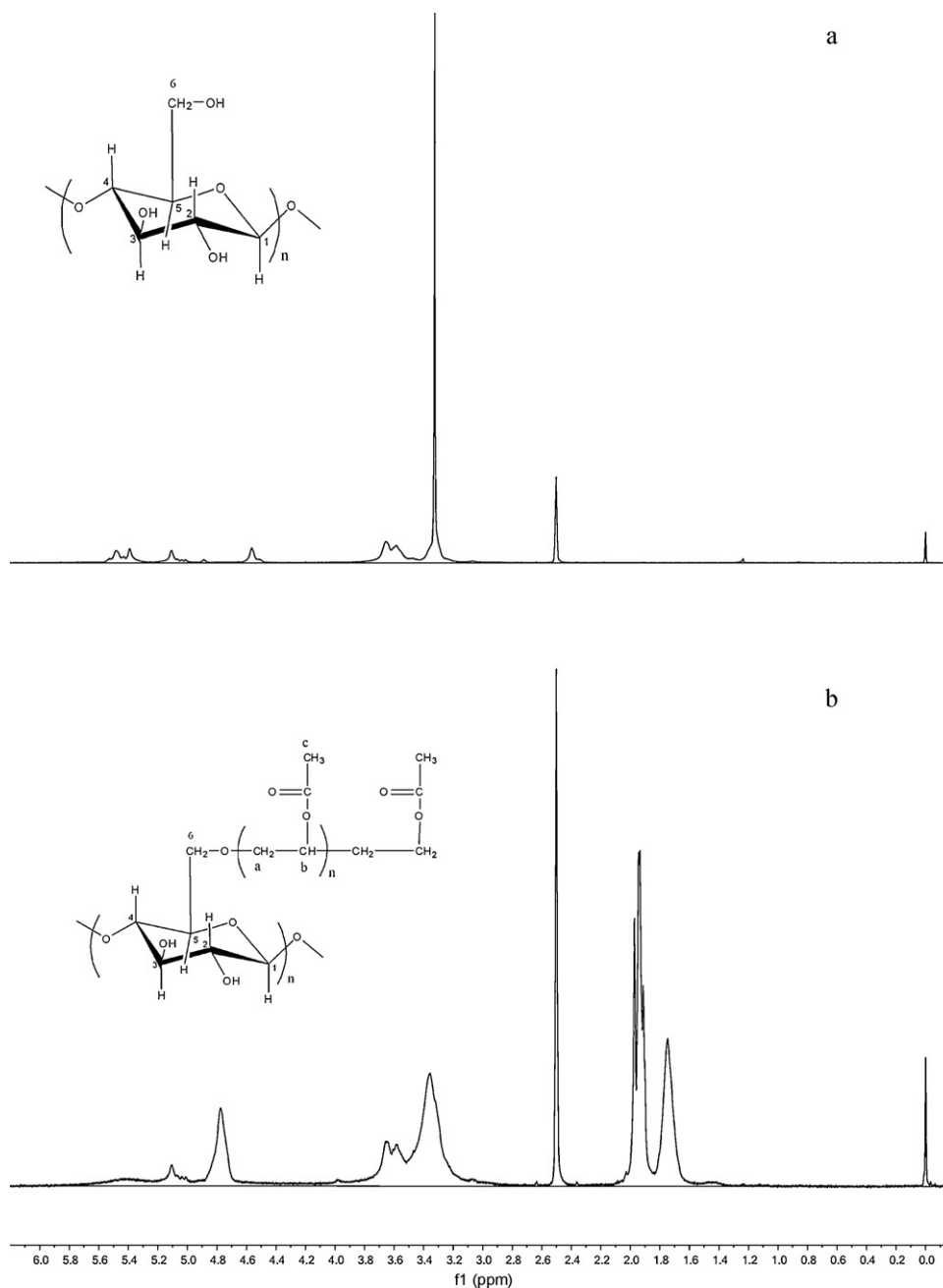


Fig. 2. ¹H NMR spectrograms of (a) gelatinized starch and (b) the grafted copolymer (VAc:starch, 1:1, w/w).

T_p is the temperature at which the maximum weight loss rate occurred, and can be obtained from the peaks in the DTG curves. As shown in Fig. 4, there was also only one peak (Fig. 4, dashed arrow) in the DTG curves of gelatinized starch, grafted copolymer, and PVAc in the main decomposition stage, and the T_p values of these samples were 304.9, 326.7, and 341.6 °C, respectively. However, there were two peaks in the curve of the starch/PVAc blend in the main decomposition stage (Fig. 4, solid arrow). The first peak (305.2 °C) was assigned to the decomposition of the starch moiety, and the second one (340.8 °C) was related to the decomposition of the PVAc moiety. These decomposition processes can be attributed to the weak interfacial combination between PVAc and starch when starch was not modified.

T_0 and T_p of the grafted copolymer were also lower (10.1 and 14.9 °C, respectively) than those of PVAc. On the other hand, compared with gelatinized starch, T_0 and T_p of the copolymer

increased to 29.2 and 21.8 °C, respectively. Due to the grafting of VAc onto starch, the interfacial combination between PVAc and starch improved, and the thermal stability of copolymer was consequently enhanced. Therefore, the thermal-stability changes caused by grafting reaction not only further confirm the strengthened molecular structure of copolymer but also support the improved bonding strength and water resistance of the adhesive from another aspect.

3.4. SEM analysis

3.4.1. Morphology of adhesive films

The effect of grafting reaction on the adhesive structure was directly shown by the SEM photographs in Fig. 5. Compared with the PVAc/starch blend (Fig. 5a), the films of the grafted starch-based adhesive (Fig. 5b and c) were much smoother and more compact.

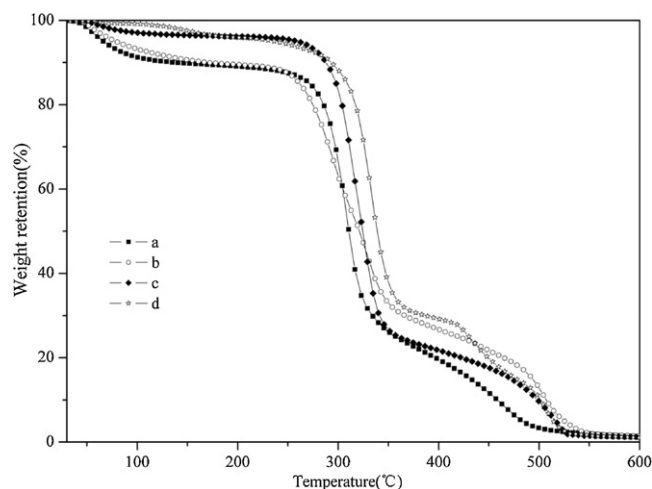


Fig. 3. TG curves of (a) gelatinized starch, (b) the starch/PVAc blend (PVAc:starch, 1:1, w/w), (c) grafted copolymer (VAc:starch, 1:1, w/w), and (d) PVAc.

Few obvious microphase separations were observed. Evidently, the grafting reaction between starch and VAc greatly improved the component compatibility of the starch-based wood adhesive as well as limited the phase separation between the starch and polymer.

3.4.2. Fractography morphology on wood glued with the starch-based wood adhesive

The bonding characteristics of starch-based wood adhesive were also directly exhibited by the SEM photographs of the fracture surface of glued specimens after shear strength test. Fig. 6a shows a thin coating of the adhesive on the surface of the glued specimens, indicating that the failure was within the adhesives. However, compared with the PVAc/starch blend (Fig. 6a), the SEM images of the grafted starch adhesives (Fig. 6b and c) show crack propagation in both the wood lumen and adhesive layer. At low shear stresses, the fracture of the glued specimens was within the adhesive layer. However, the wood lumen cell was further damaged at high shear stresses. Therefore, the interaction between the wood cell and adhesive caused by the grafting reaction led to a more obvious surface damage of the bonded joint, and to increased shear strength.

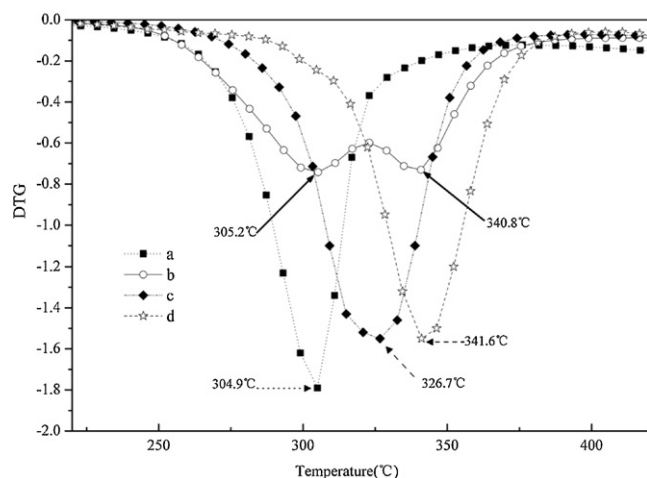


Fig. 4. DTG curves of (a) gelatinized starch, (b) the starch/PVAc blend (PVAc:starch, 1:1, w/w), (c) grafted copolymer (PVAc:starch, 1:1, w/w), and (d) PVAc.

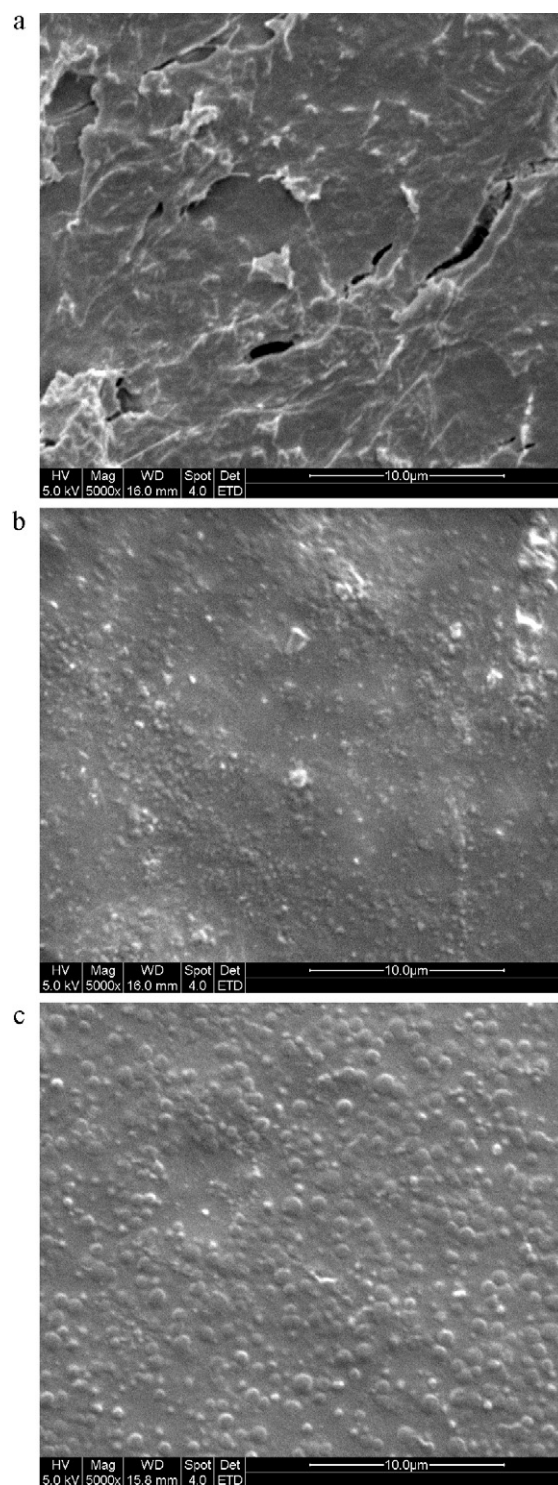


Fig. 5. SEM micrograph of the cast films of (a) the PVAc/starch blend (PVAc:starch, 1:1, w/w), (b) GSWA1 (VAc:starch, 1.2:1, w/w), and (c) GSWA2 (VAc:starch, 1.6:1, w/w).

Comparing Fig. 6b and c, there was no adhesive in the lumen of the wood sample in GSWA2 (Fig. 6c, solid arrow). This finding can be attributed to the high viscosity of GSWA2, which hindered the permeation of the adhesive emulsion on the wood surface. In contrast, GSWA1 with a lower viscosity infiltrated the lumen of the wood sample (Fig. 6b, solid arrow). This finding could explain the stagnating tendency of the shear strength when the grafted monomer feeding ratio was more than 1:1.2.

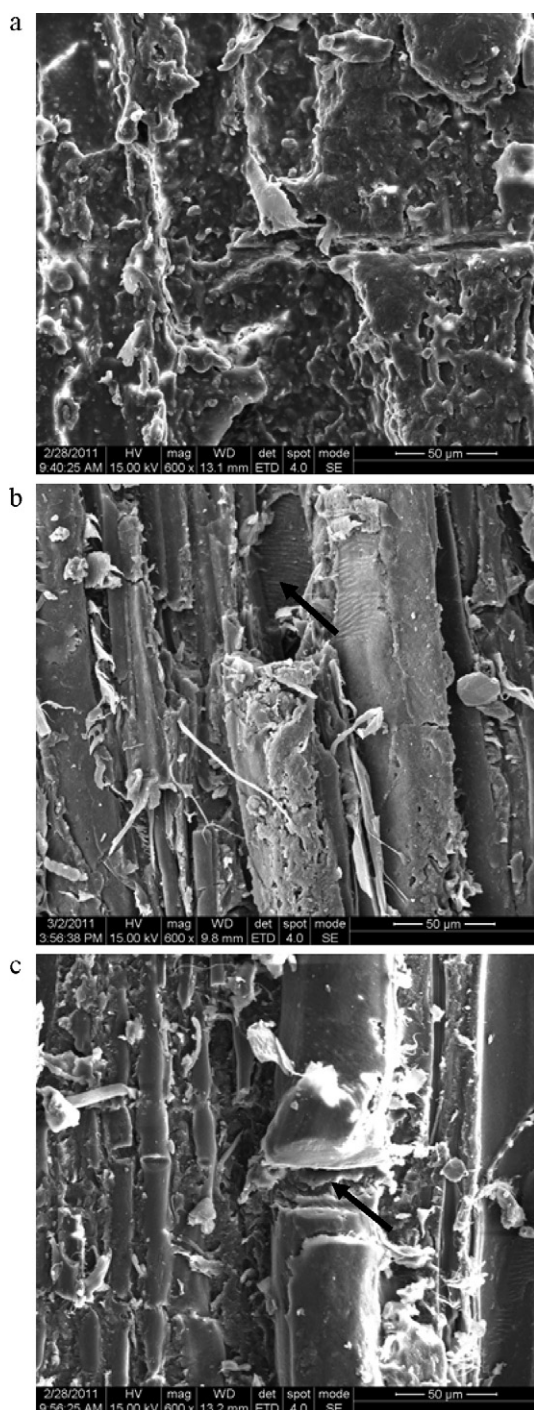


Fig. 6. SEM micrograph of fracture surface of wood surface glued with (a) the PVAc/starch blend (PVAc:starch, 1:1, w/w), (b) GSWA1 (VAc:starch, 1.2:1), and (c) GSWA2 (VAc:starch, 1.6:1).

4. Conclusions

A starch-based wood adhesive that can be used at room temperature was synthesized by graft copolymerization of starch with VAc monomer. The most economic starch/monomer ratio of 1:1.2 (w/w) was found to give the optimal shear strengths of 4.30 MPa in the dry state and 2.17 MPa in the wet state. The improved performance of grafting reaction on the starch-based wood adhesive was supported by its strengthened compatibility with PVAc and starch, based on the results of FTIR, ^1H NMR, TG, and SEM analyses.

Therefore, the grafting modification treatment of starch with VAc can be a potential alternative for manufacturing wood adhesives in lieu of less environment-friendly petroleum-based wood adhesives.

Acknowledgments

This work was financially supported by Science and Technology Support (Industry) program of Jiangsu province (BE2011015) and Transformation project for College Science and Technology Achievements (JHB2011-28).

References

- Athawale, V. D., & Lele, V. (2000). Thermal studies on granular maize starch and its graft copolymers with vinyl monomers. *Starch (Stärke)*, 52(6–7), 205–213.
- Bruyn, H. D., Sprong, E., Gaborieau, M., Rober, J. A., III, & Gilbert, R. G. (2007). Starch-graft-(synthetic copolymer) latexes initiated with Ce^{4+} and stabilized by amylopectin. *Journal of Polymer Science Part A: Polymer Chemistry*, 45(18), 4185–4192.
- Chi, H., Xu, K., Wu, X., Chen, Q., Xue, D., Song, C., et al. (2008). Effect of acetylation on the properties of corn starch. *Food Chemistry*, 106(3), 923–928.
- Ciannamea, E. M., Stefani, P. M., & Ruseckaite, R. A. (2010). Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives. *Bioresource Technology*, 101(2), 818–825.
- De Graaf, R. A., Lammers, G., Janssen, L. P. B. M., & Beenackers, A. A. C. M. (1995). Quantitative analysis of chemically modified starches by ^1H -NMR spectroscopy. *Starch (Stärke)*, 47(12), 469–475.
- Goñi, I., Gurruchaga, M., Valero, M., & Guzman, G. M. (1983). Graft polymerization of acrylic monomers onto starch fractions. I. Effect of reaction time on grafting methyl methacrylate onto amylose. *Journal of Polymer Science Part A: Polymer Chemistry*, 21(8), 2573–2580.
- Gong, Q., Wang, L.-Q., & Tu, K. (2006). In situ polymerization of starch with lactic acid in aqueous solution and the microstructure characterization. *Carbohydrate Polymers*, 64(4), 501–509.
- Gurruchaga, M., Goñi, I., Valero, M., & Guzmán, G. M. (1984). Graft polymerization of acrylic monomers onto starch fractions. II. Effect of reaction time on grafting of methyl methacrylate onto amylopectin. *Journal of Polymer Science: Polymer Letters Edition*, 22(1), 21–24.
- Gurruchaga, M., Goñi, I., Valero, M., & Guzmán, G. M. (1992). Graft copolymerization of hydroxylic methacrylates and ethyl acrylate onto amylopectin. *Polymer*, 33(13), 2860–2862.
- Imam, S. H., Gordon, S. H., Mao, L., & Chen, L. (2001). Environmentally friendly wood adhesive from a renewable plant polymer: Characteristics and optimization. *Polymer Degradation and Stability*, 73(3), 529–533.
- Imam, S. H., Mao, L., Chen, L., & Greene, R. V. (1999). Wood adhesive from crosslinked poly(vinyl alcohol) and partially gelatinized starch: Preparation and properties. *Starch (Stärke)*, 51(6), 225–229.
- Kaewtatip, K., & Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers*, 73(4), 647–655.
- Kennedy Harry, M. (1989). *Starch and dextrin based adhesives*. ACS symposium series 385. Adhesives from renewable resources (2nd ed.). Washington, DC: American Chemical Society., pp. 326–336.
- Kim, S. (2009). Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission. *Biore-source Technology*, 100(2), 744–748.
- Kim, S., & Kim, H.-J. (2006). Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on the adhesion for engineered flooring in under heating system; ONDOL. *Thermochimica Acta*, 444(2), 134–140.
- Lai, S.-M., Don, T.-M., Liu, Y.-H., & Chiu, W.-Y. (2006). Graft polymerization of vinyl acetate onto granular starch: Comparison on the potassium persulfate and ceric ammonium nitrate initiated system. *Journal of Applied Polymer Science*, 102(3), 3017–3027.
- Li, X., Li, Y., Zhong, Z., Wang, D., Ratto, J. A., Sheng, K., et al. (2009). Mechanical and water soaking properties of medium density fiberboard with wood fiber and soybean protein adhesive. *Bioresource Technology*, 100(14), 3556–3562.
- Liu, D., Chen, H., Chang, P. R., Wu, Q., Li, K., & Guan, L. (2010). Biomimetic soy protein nanocomposites with calcium carbonate crystalline arrays for use as wood adhesive. *Bioresource Technology*, 101(15), 6235–6241.
- Marinich, J. A., Ferrero, C., & Jiménez-Castellanos, M. R. (2009). Graft copolymers of ethyl methacrylate on waxy maize starch derivatives as novel excipients for matrix tablets: Physicochemical and technological characterisation. *European Journal of Pharmaceutics and Biopharmaceutics*, 72(1), 138–147.
- Meshram, M. W., Patil, V. V., Mhaske, S. T., & Thorat, B. N. (2009). Graft copolymers of starch and its application in textiles. *Carbohydrate Polymers*, 75(1), 71–78.

- Moubarik, A., Charrier, B., Allal, A., Charrier, F., & Pizzi, A. (2010). Development and optimization of a new formaldehyde-free cornstarch and tannin wood adhesive. *European Journal of Wood and Wood Products*, 68(2), 167–177.
- Qiao, L., & Easteal, A. J. (2001). Aspects of the performance of PVAc adhesives in wood joints. *Pigment and Resin Technology*, 30(2), 79–87.
- Samaha, S. H., Nasr, H. E., & Hebeish, A. (2005). Synthesis and characterization of starch-poly(vinyl acetate) graft copolymers and their saponified form. *Journal of Polymer Research*, 12(5), 343–353.
- Tanrattanakul, V., & Chumeka, W. (2010). Effect of potassium persulfate on graft copolymerization and mechanical properties of cassava starch/natural rubber foams. *Journal of Applied Polymer Science*, 116(1), 93–105.
- Wang, X.-L., Yang, K.-K., Wang, Y.-Z., Zhou, Z.-X., & Jin, Y.-D. (2004). Synthesis and nuclear magnetic resonance analysis of starch-g-poly(1,4-dioxan-2-one) copolymers. *Journal of Polymer Science Part A: Polymer Chemistry*, 42(14), 3417–3422.