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Preparation and properties of a starch-based wood adhesive with high bonding strength and water resistance

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ABSTRACT

A Highly efficient method was developed for preparing starch-based wood adhesives with high performance, using H_2O_2, a silane coupling agent and an olefin monomer as an oxidant, cross-linking agent and comonomer, respectively. The effects of various parameters on the shear adhesive strength were investigated in the dry state (DS) and wet state (WS). The results indicated that the bonding strength of starch-based wood adhesives could reach 7.88 MPa in dry state and 4.09 MPa in wet state. The oxidation could reduce the content of the hydroxyl transforming into carboxyl and aldehyde groups, and the graft copolymerization enhanced the thermal stability, which improved the bonding strength and water resistance. The starch-based adhesive and the fractures in the bonded joints were analyzed via Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The improved properties were attributed to the modified of microstructure of the graft-copolymerized starch-based adhesive.

1. Introduction

Starch has many diverse applications in food production and other industries (Fishman, Coffin, Konstance, & Onwulata, 2000; Le Corre, Bras, & Dufresne, 2010). Chemically modified starches extend the range of physical properties available for various uses, because they exhibit excellent physicochemical properties that are markedly altered from those of their parent starches (Zdanowicz, Schmidt, & Spychaj, 2010; Zhang et al., 2007). Starches have been widely used in the adhesives industry (Kennedy, 1989), but their bonding capacity is insufficient for gluing wood. The graft copolymerization of synthetic polymers onto a starch backbone is among the best ways to improve the bonding properties of starch (Lei, Du, Wu, Xi, & Dong, 2014). Many reports describe the synthesis, characterization, and properties of starch graft copolymers (Bruyn, Sprong, Gaborieau, Rober, & Gilbert, 2007; Gong, Wang, & Tu, 2006; Lai, Don, Liu, & Chiu, 2006; Tanrattanakul & Chumeka, 2010). Nevertheless, these starch-based wood adhesives still lack the high bonding strength and water resistance. Furthermore, compared with the conventional adhesive materials, starch-based adhesives are typically too weak for practical use (Tanrattanakul & Chumeka, 2010). The molecular structure of starch adhesives must be strengthened to develop high-performance wood adhesive.

Starch oxidation is an alternative method for improving starch properties that is widely used in industry. Oxidation is a chemical modification in which carboxyl and carbonyl functional groups can be introduced into the starch chains. At a suitable temperature and pH, starch can react with several oxidizing reagents (Veelaert, de Wit, Gotlieb, & Verhé, 1997; Kuakpetoon & Wang, 2001; Wing & Willett, 1997) to form oxidized starch. Oxidized starch prepared from hydrogen peroxide has been of particular research interest (El-Sheikh, Ramadan, & El-Shafie, 2010; Zhang, Zhang, Wang, & Wang, 2009). Hydroxyl groups, primarily at the C-2, C-3, and C-6 positions, are transformed into carbonyl or carboxyl groups via oxidation (Kuakpetoon & Wang, 2006; Kurakake, Akiyama, Hagiwara, & Komaki, 2009). However, the carbonyl and carboxyl groups exhibit high-activity, easily participating in various reactions, such as cross-linking (Yanbo, Chengfei, & Meina, 2009). Hydrogen peroxide decomposes into hydrogen ions and water, making it an environmental friendly oxidizing reagent. Therefore, in this research, the hydrogen peroxide was used as the oxidizing reagent.

The oxidized starch adhesive exhibited low bonding strength and water resistance preventing its use in practical applications. Therefore, in order to improve the performance of starch adhesives, sodium dodecyl sulfate (Li et al., 2014), urea (Wang, Gu, Li, Hong, & Cheng, 2013), silane coupling agent and olefin monomer

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were added to the oxidized starch to produce a graft-copolymerized wood adhesive (Bruyn et al., 2007; Gong et al., 2006; Lai et al., 2006; Tanrattanakul & Chumeka, 2010). The bonding strength and water resistance of the adhesive have improved significantly, confirming the positive effect of adding the silane coupling agent and olefin monomer to the adhesive system. The structure of adhesive was analyzed to determine the interaction between the grafted starch and the silane coupling agent. The thermal properties of adhesive and its viscoelasticity have confirmed that the quality of the graft copolymerized starch-based wood adhesive was improved.

At present, most studies showed that the bonding strength and water resistance of starch-based wood adhesive were usually too weak to practical use (Wang, Gu, Hong, Cheng, & Li, 2011; Bordes, Pollet, & Avérous, 2009). The purpose of the study was to investigate in the bonding strength and water resistance performance of starch-based wood adhesive prepared by grafting copolymerization and adding the silane coupling agent.

2. Materials and methods

2.1. Materials

Cornstarch was provided by Changchun Dacheng Corn Co. (China). The silane coupling agent (CH_2=CH—$Si(OC_2H_5)_3$,A-151) was obtained from Nanjing Forward Chemical Co. (China). The hydrogen peroxide (H_2O_2, 30%), ferrous sulfate ($FeSO_4$), butyl acrylate (CH_2=$CHCOO(CH_2)_3CH_3$, BA), vinyl acetate (CH_3COOCH=CH_2,VAc), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), polyvinyl alcohol (PVA), sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, SDS) and sodium hydroxide were purchased form Tianjin Kemiao Chemical Reagent Co. (China). All the other reagents were analytical grade.

2.2. Synthesis of graft-copolymerized starch-based wood adhesive

A graft-copolymerized starch-based wood adhesive was prepared as follows: 10 g dried corn starch and 100 mL distilled water were placed into a four-necked round-bottom flask and stirred at 80 °C for 30 min. After the starch gelatinization, the reaction temperature was cooled to 55 °C, following by the addition 0.1 g ferrous sulfate and H_2O_2. Oxidization after 1 h, the temperature was again raised to 80 °C, and 3 g PVA was dropped into the mixture four-necked round-bottom flask. Stirred after 0.5 h, the mixture was cooled to 60 °C, and 0.1 g of SDS, 0.05 g of APS and silane coupling agent were added. Grafting after 0.5 h, 0.05 g APS, BA and VAc were added dropwise over 2 h (addition at constant speed of 0.2 mL/min), and the reaction continued for 1 h. Finally, the temperature was raised to 80 °C and kept for 30 min and then cooled to room temperature.

2.3. Shear adhesive strength test

The shear adhesive strength of the adhesive samples was tested according to the industry standard HG/T2727-1995 (China, 1995). Freshly cut 25 mm × 25mm × 10 mm pieces of wood (*Betula platyphylla*, 0.62 × 103 kg/m) were glued with adhesives under a static pressure of 1 MPa at 25 °C for 24 h. The shear adhesive strength of the glued samples in the dry or wet (after immersing in water at 30 °C for 3 h) state was determined using a WDT-10 shear adhesive strength analyzer (KQL Co., China). The shear adhesive strength was calculated as follows: $\sigma M = F_{max}/A$ in which σM (MPa) is the shear adhesive strength, F_{max} (N) is the observed maximum failing load, and A (m^2) is the bonding surface of the sample. The testing speed was 5 mm/min. All the tests were replicated 10 times, and the results were presented as the averages.

2.4. Intrinsic viscosity measurement

The intrinsic viscosity was measured using an NDJ-5S rotational viscometer (Ping Xuan Shanghai Scientific Instrument Co., China) with no. 4 rotor at 30 r/min and 30 °C. An extended period was required to obtain a stable reading. All the tests were replicated 3 times, and the results presented as the averages.

2.5. Fourier transform infrared (FTIR) spectroscopy

The adhesive samples were precipitated with ethanol, washed with distilled water, and dried to obtain the adhesive solids. The solids were extracted with acetone using a Soxhlet extraction device at 70 °C for 48 h to remove the homopolymers of the VAc and BA monomers and then dried. The extracted solids were fully milled with potassium bromide and compressed for FTIR analysis on a Nexus 6700 FTIR spectrometer (Nicolet Co., USA). Each sample was scanned 32 times over the 4000–400 cm^{-1} region at a resolution of 4 cm^{-1}.

2.6. Scanning electron microscopy (SEM)

The surfaces of cast films of the adhesive samples and the fractured surface of the sample under dry conditions and the fractured surface were coated with gold under vacuum. Then, all samples were observed under a scanning electron microscope (Quanta-200, Holland).

2.7. Thermogravimetric analysis (TGA)

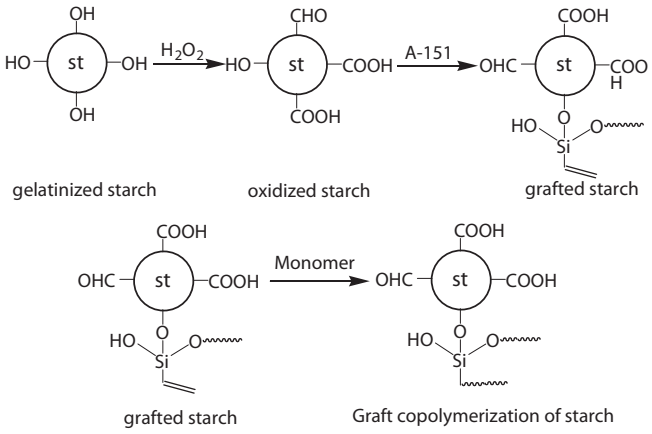
The solid adhesive samples were extracted with acetone using a Soxhlet extraction device at 70 °C for 48 h to remove the homopolymers of the VAc and BA monomers and then was dried. The thermal stability of the solid samples was analyzed using a NETZSCH TGA209 thermogravimeter (NETZSCH Co., Germany). The samples (5 mg in a 70 μL alumina pan) were heated from 25 to 600 °C at a rate of 10 °C/min under a 30 mL/min nitrogen gas flow.

3. Results and discussion

Given the vast hydroxyl structure of the native starch, oxidized starch is hydrophilic and therefore cannot be used as a wood adhesive without modification. Consequently, the water resistance of starch adhesives must be improved. In this paper, a silane coupling agent and an olefin monomer were added to oxidize starch to produce a starch-based wood adhesive. The synthesis process is provided in Scheme 1. All oxidized starches were prepared after gelatinization, and then, the effects of the oxidant, catalyst, and monomer contents and the mole ratio of the monomer and coupling agent on the shear adhesive strength in the dry (DS) and wet states (WS) were investigated in detail.

3.1. Effect of oxidant content on shear adhesive strength

The native starch was oxidized using hydrogen peroxide; some of the hydroxyl groups in the starch were transformed to carbonyl or carboxyl groups via oxidation (Sangseethong, Termvejsayanon, & Sriroth, 2010), significantly improved the water resistance of the starch adhesive. Fig. 1a depicted the effect of the oxidant content on the shear adhesive strength. When the oxidant content was increased from 0 to 3.0 (by weight based on the solid content of adhesive), the shear strength in the DS increased from 3.28 to 7.30 MPa, and the shear strength WS increased from 1.40



Scheme 1. The synthesis of starch-based wood adhesive.

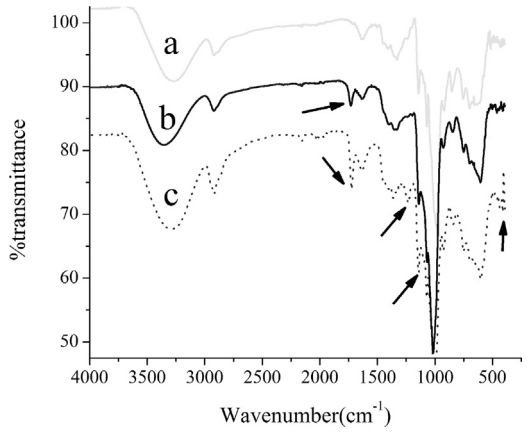


Fig. 2. Infrared spectrograms of (a) native starch, (b) oxidized starch and (c) starch adhesive.

to 4.22 MPa. The shear adhesive strength in both the DS and WS increased rapidly when oxidant was only 1.0%. These results confirmed that oxidation can effectively enhance the bonding strength and water resistance of a starch adhesive. However, when the content of oxidant was increased from 3.0 to 5.0%, the shear strength (DS) dropped from 7.30 to 6.60 MPa, and the shear strength (WS) dropped slightly, which can be explained as follows: At constant starch content (concentration of starch), when the oxidant was added into the reaction system, the hydroxyl groups in the starch were effectively transformed into carbonyl or carboxyl groups. However, when the content of starch further increased, the macromolecular structure of the starch was destroyed due to the degree of oxidation increased, and created an undesirable micromolecule. The network structure of the starch adhesive was simultaneously and inevitably weakened, and its shear adhesive strength decreased. These results indicated that an appropriate oxidant content was 3.0%.

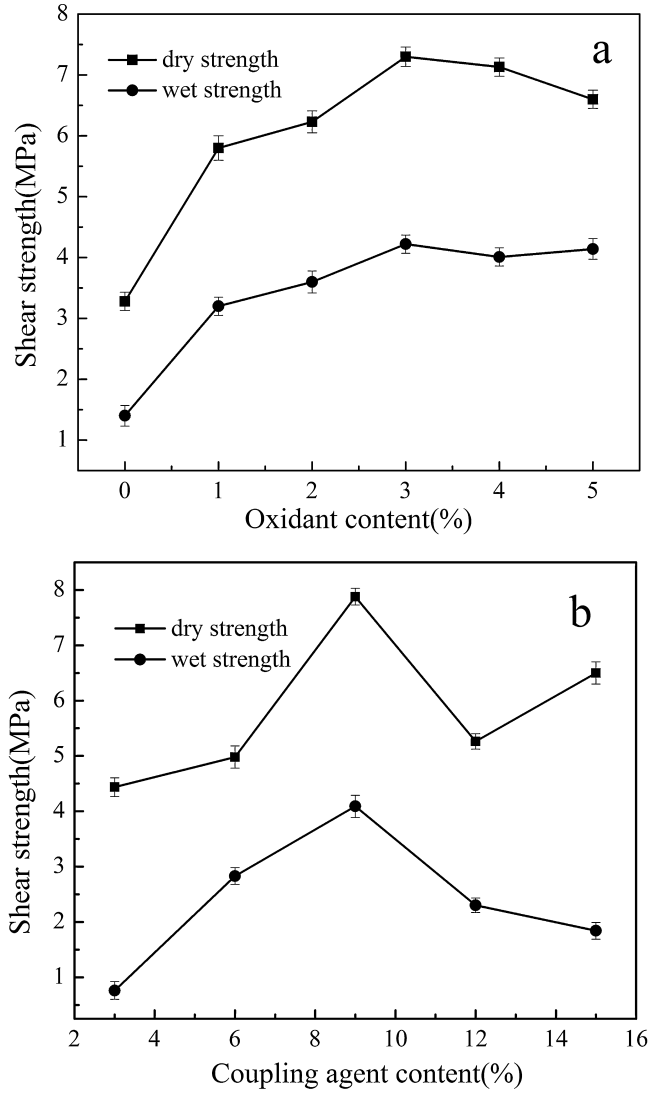


Fig. 1. Effect of oxidant and coupling agent content on DS and WS.

3.2. Effect of coupling agent content on shear strength

The starch was grafted using a silane coupling agent after oxidation and copolymerization with an olefin monomer (Chang & Kiho, 2002). The effect of content of the coupling agent on the shear adhesive strength was depicted in Fig. 2b. The bonding strength and water resistance of starch adhesive increased significantly when Si—O was introduced into the starch structure.

When the content of silane coupling agent was increased from 3.0 to 9.0% (by weight, based on the solid adhesive content), the shear adhesive strength of the adhesive increased from 4.43 to 7.88 MPa in the dry state and from 0.76 to 4.09 MPa in the wet state. Because the bonding nature of the adhesive were used to assess the shear adhesive strength, the changes suggested that the addition of 9.0% silane coupling agent significantly increased the dry bonding strength of the adhesive by 77.8% and the wet bonding strength by 4.4 times over adhesives with 3.0% silane coupling agent.

Because water molecules can penetrate wood and act as a plasticizer for hydrophilic polymers, the bonding strength of starch-based wood adhesives decreased in a wet environment (Wang et al., 2011). As indicated in Fig. 1b, the shear adhesive strength of all starch-based wood adhesives decreased after soaking the wood samples glued using the adhesives for 3 h, but the shear adhesive strength decreased to varying degrees. The adhesive with 3.0% coupling agent lost 85.3% of its bonding strength, while that with 9.0% coupling agent lost 48.1% of its bonding strength. The 9.0% of coupling agent increased the water resistance of the adhesive by 37.2%. Therefore, a silane coupling agent could significantly increase water resistance of a starch-based wood adhesive.

However, as the content of coupling agent further increased from 9.0%, the shear adhesive strength of the adhesive in the dry and wet states dropped, which can be explained by the significant decrease in the cohesive energy of starch and polarity of the polymer. Therefore, the proper content of coupling agent was chosen to be 9.0% for a starch-based wood adhesive.

Table 1
Effect of starch/monomer ratio on the bond characteristic of the grafted starch-based wood adhesive.

Starch:monomer ratio (w/w)	Intrinsic viscosity ($\times 10^3$ mPa s)	Shear strength in dry state (MPa)	Shear strength in wet state (MPa)
1:0.5	1.46 ± 0.4^{d}	4.42 ± 0.09^{d}	0.67 ± 0.05^{e}
1:1	2.42 ± 0.2^{c}	5.45 ± 0.06^{c}	1.12 ± 0.07^{d}
1:1.5	4.08 ± 0.4^{b}	5.38 ± 0.08^{c}	2.03 ± 0.06^{c}
1:2	4.57 ± 0.3^{b}	7.88 ± 0.09^{b}	4.09 ± 0.08^{a}
1:2.5	5.81 ± 0.5^{a}	10.05 ± 0.11^{a}	2.83 ± 0.07^{b}

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

3.3. Effect of monomer content on the shear strength

The graft copolymerization of synthetic polymers onto a starch backbone is among the best method for improving the bonding properties. Many reports describe the synthesis, characterization, and properties of starch graft copolymers (Bruyn et al., 2007; Gong et al., 2006; Lai et al., 2006; Tanrattanakul & Chumeka, 2010). The shear adhesive strength of grafted starch-based wood adhesives with various monomer feeding ratios was listed shown in Table 1. Initially, the shear adhesive strength increased with increasing the monomer content. The increased monomer concentration promoted grafting along the coupling agent chains. The reaction efficiency of this grafting was attributed to the concentration of monomer molecules around the coupling agent macroradicals. Consequently, the active sites along the growing coupling agent chain increased, thereby enhancing the compatibility between the starch and the polymer and increasing shear adhesive strength.

The shear adhesive strength reached its maximum at the optimal starch/monomer ratio of 1:2 (w/w). Further increasing the monomer feeding ratio decreased the WS shear strength because homopolymerization prevailed over graft copolymerization. However, the DS shear strength continued to increase because the viscosity of the sample increased with the increased grafted monomer feeding ratio as the grafting of the macromolecular chain increased. The high-viscosity adhesive emulsion prevented the spreading and permeation of the adhesive emulsion on the wood surface. Spreading and permeation were considered important stages of the adhesion process (Wang, Li, Gu, Hong, & Cheng, 2012). Therefore, the starch/monomer feeding ratio of 1:2 (w/w) was considered optimal. With this monomer feeding ratio, the starch-based adhesive exhibited the optimal shear adhesive strengths of 7.88 MPa in the dry state and 4.09 MPa in the wet state.

3.4. Effect of the mole ratio of monomer on shear adhesive strength

As shown in Table 2, both the shear adhesive strength (DS) and shear adhesive strength (WS) increased rapidly when VAc:BA ratio was increased from 6:2 to 6:4. The butyl the acrylate is a soft monomer, and graft copolymerization with vinyl acetate and a coupling agent can improve the flexibility of the film and the stability of the emulsion. In addition, the butyl acrylate is strongly hydrophobic; therefore, the bonding strength and water resistance of the grafted starch-based wood adhesive significantly improved when the content of butyl acrylate increased. However, when the butyl acrylate feeding ratio increased further, the shear adhesive strength (DS) and WS decreased because the reactivity ratio of the butyl acrylate exceeded that of vinyl acetate, making it difficult to form a homogeneous block copolymer structure. Thus, a large proportion of the butyl acrylate homopolymer was formed, allowing for easy demulsification. Consequently, the bonding strength and water resistance of the grafted starch-based wood adhesives decreased. In particular, when the mole ratio of the monomer reached 6:10, the graft-copolymerized starch-based wood adhesive was broken in the wet state. Thus, the graft copolymerized starch-based wood adhesive was exhibited the high bonding strength and water resistance at a 6:4 the mole ratio of the monomer.

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

VAc:BA ratio (n/n)	Shear strength in dry state (MPa)	Shear strength in wet state (MPa)
6:2	4.15 ± 0.05^{c}	1.94 ± 0.04^{b}
6:4	7.88 ± 0.09^{a}	4.09 ± 0.08^{a}
6:6	4.48 ± 0.05^{b}	1.52 ± 0.05^{c}
6:8	4.36 ± 0.07^{b}	0.58 ± 0.03^{d}
6:10	2.84 ± 0.06^{d}	Glue broke

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

3.5. Infrared spectroscopy

FT-IR was used to confirm the graft modification of the starch and determine the effect of graft copolymerization on the structure of the starch-based wood adhesive. The results are presented in Fig. 2. Compared with native starch, the oxidized starch exhibited new peaks characteristic of an ester at 1730 cm^{-1} (C═O) in the infrared spectra, which indicated that the starch was successfully oxidized (Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009). Both the stronger absorption band at 1730 cm^{-1} and a new absorption band at 1238 cm^{-1} (C—O) can be observed in spectrum b, indicating the existence of the VAc and BA groups in the graft copolymer (Marinich, Ferrero, & Jiménez-Castellanos, 2009). In addition, the appearance of the peaks of at 420 cm^{-1} characteristic SiO_2 in the spectrum of the starch adhesive (Fig. 2c, solid arrow) confirmed the presence of the coupling agent in the sample. Therefore, the graft-copolymerized starch-based wood adhesive was successfully synthesized.

3.6. Thermal stability analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the gelatinized starch, oxidized starch and starch adhesive are presented in Figs. 3 and 4. As shown in Fig. 3, all of samples exhibited the main thermogravimetric curves of weight loss at approximately 220–420 °C, which was caused by the dehydration of the polymer chains. The temperatures at which weight loss occurred in the gelatinized starch; oxidized starch and starch adhesive were 284.9, 249.4 and 277.5 °C, respectively. The initial dehydration temperatures of the oxidized starch were below those of the gelatinized starch. However, compared with the oxidized starch, the initial dehydration temperatures of the starch adhesive increased to 28.1 °C. This phenomenon is subsequently explained.

The oxidation led to the depolymerization of the molecular chains, which decreased the molecular weight. Therefore, the thermal stability decreased when starch was oxidized. However, the hydroxyl groups in the starch also decreased with oxidation, which can effectively improved the water resistance of the adhesive. However, the initial dehydration temperatures of the starch adhesive

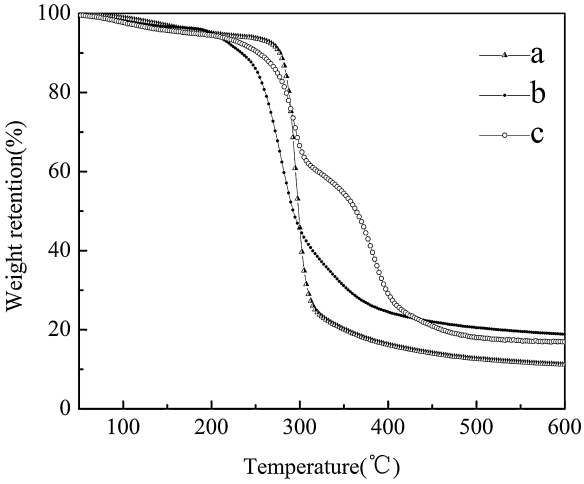


Fig. 3. TG curves of (a) gelatinized starch, (b) oxidized starch and (c) starch adhesive.

increased from 249.4 to 277.5 °C, confirming that the graft copolymerization of the oxidized starch improved the thermal stability of the adhesive. Therefore, the changes in thermal stability caused by the graft copolymerization of the oxidized starch improved the bonding strength and water resistance of the adhesive.

The maximum rate of weight loss can be obtained from the peaks in the DTG curves. As shown in Fig. 4, only one peak appeared in the DTG curves of the gelatinized and oxidized starches. However, two peaks appeared in the curve of the starch adhesive during the main decomposition stage (Fig. 4, solid arrow). The first peak (293.8 °C) confirmed the decomposition of the starch moiety, and the second (384.1 °C) represented the decomposition of the copolymer of BA and VAc (Duquesne et al., 2004), which was a graft copolymer of macromolecular chain, because the solid adhesive samples were extracted with acetone using a Soxhlet extraction device at 70 °C for 48 h to remove any homo- or copolymers of the VAc and BA monomers. Therefore, the graft copolymerization had successfully occurred.

3.7. SEM image analysis

The effect of the grafting reaction on the adhesive structure was demonstrated by the SEM photographs in Fig. 5. Compared with the gelatinized and oxidized starches (Fig. 5a and b), the cast film

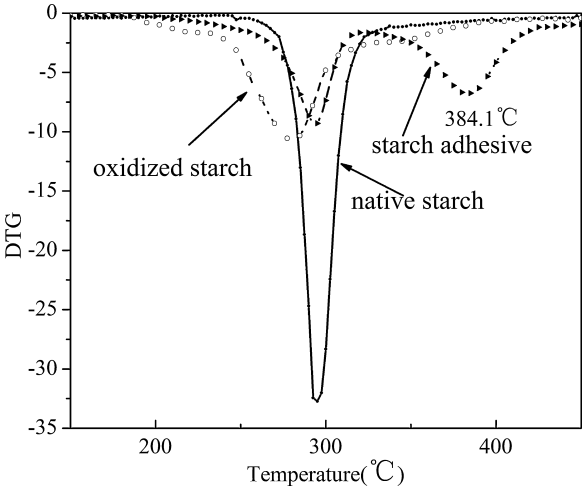


Fig. 4. DTG curves of (a) gelatinized starch, (b) oxidized starch and (c) starch adhesive.

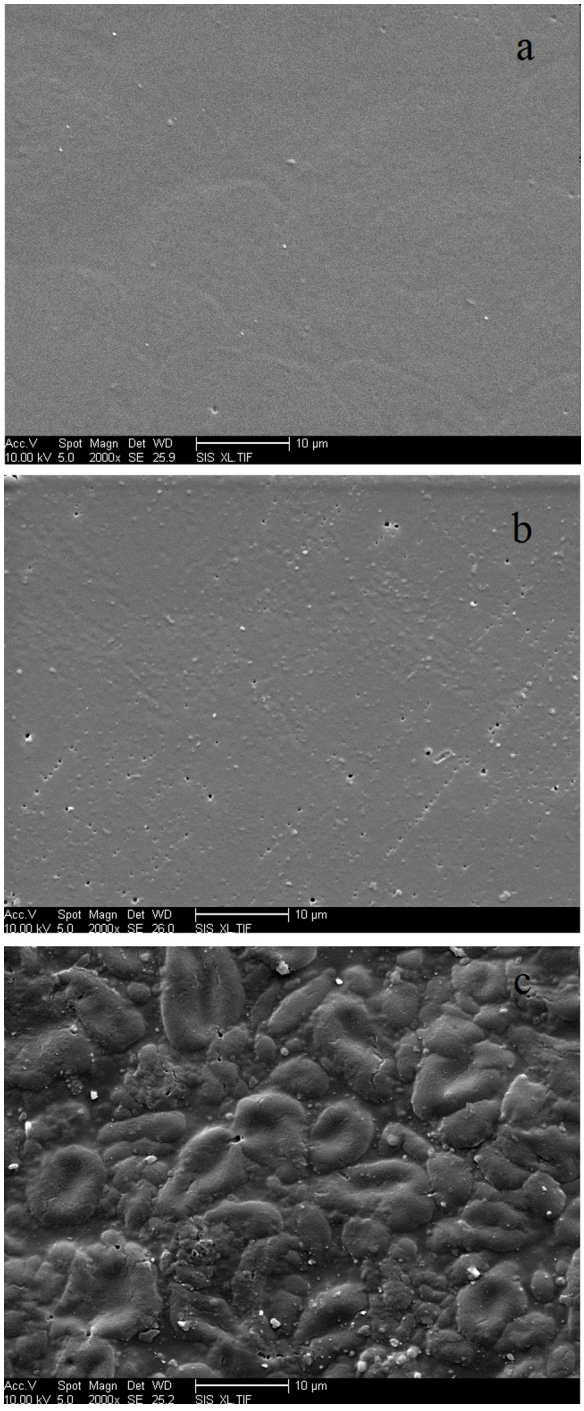


Fig. 5. SEM micrograph of the cast films of (a) gelatinized starch, (b) oxidized starch and (c) starch adhesive.

of the starch adhesive (Fig. 5c) was rougher and more compact. Many microphase separations were observed, indicating large graft copolymers around starch. The graft copolymer was evenly dispersed throughout the oxidized starch system, and improved the component compatibility of the starch-based wood adhesive.

The bonding characteristics of the starch-based wood adhesive were also directly exhibited in the SEM photographs of the fractured surface of the glued specimens after the shear adhesive strength test. Fig. 6 depicts the crack propagation in both the wood lumen and adhesive layer. The starch adhesive infiltrated the lumen of the wood sample (Fig. 6, hollowed arrow). Under lower shear stress, the fracture occurred within the adhesive layer of the

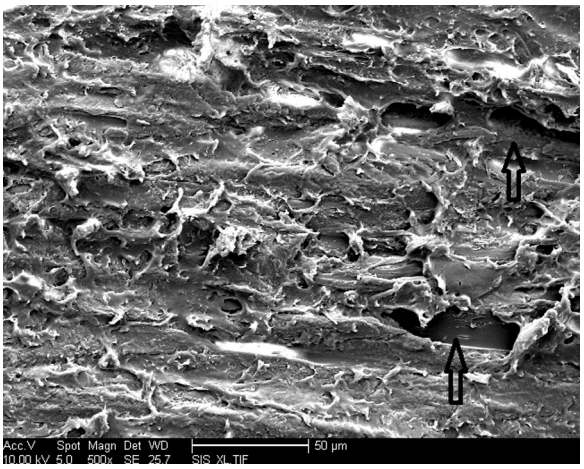


Fig. 6. SEM micrograph of fracture surface of wood surface glued with starch adhesive.

glued specimens. However, the wood lumen cell should be further damaged under higher shear stress. Therefore, strengthening the interaction between the wood cell and the adhesive, caused by graft copolymerization, could damage the surfaces of bonded joints and increase the shear strength.

4. Conclusions

A starch-based wood adhesive was synthesized via the graft copolymerization of oxidized starch with a silane coupling agent and butyl acetate and vinyl acetate monomer. The results indicated that both the bonding strength and water resistance of the starch-based wood adhesive were significantly improved. The improved performance of the graft-copolymerized starch-based wood adhesive was supported by its strengthened molecular structure enhanced thermal stability and increased bonding strength and water resistance. This study found that the bonding strength of a starch-based wood adhesive could reach 7.88 MPa in the dry state and 4.09 MPa in the wet state. Therefore, a high performance starch-based wood adhesive with high bonding strength and water resistance can be synthesized via the graft copolymerization of oxidized starch with a coupling agent and olefin monomer.

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