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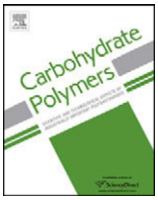

Bonding strength and water resistance of starch-based wood adhesive improved by silica nanoparticles

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ABSTRACT

Silica nanoparticles were used to improve the bonding capacity of renewable starch-based wood adhesive in this study. Compared with starch-based wood adhesive without silica nanoparticles, the bonding strength of starch-based wood adhesive with 10% of silica nanoparticles increased by 50.1% in dry state and 84.0% in wet state, while its water resistance increased by 20.2%. The improved performance of SiO_2/starch-based wood adhesive was supported by its strengthened molecular structure, enhanced thermal stability, beneficial changes in rheological properties and fracture of starch-based adhesive bonded joints from the analysis results using Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analyzer and rheometer. The improvement effect of silica nanoparticles on the structure and properties of the adhesive indicates that silica nanoparticles can be used to prepare environmentally friendly starch-based wood adhesive with high performance.

1. Introduction

With increasing of the global energy crisis, the mainly used non-renewable raw materials of wood adhesives, such as petroleum and natural gas (Imam, Gordon, Mao, & Chen, 2001), would be gradually replaced by renewable biopolymers. Starch is a relatively inexpensive and renewable product from abundant plants, and it has been extensively used as binders, sizing materials, glues and pastes (Kennedy Harry, 1989), but its bonding capacity is not strong enough to glue wood. Therefore, modified starch produced from graft polymerization with vinyl acetate and butyl acrylate has been tried to use as a wood adhesive (Yanbo, Chengfei, & Meina, 2009). Nevertheless, such kind of starch-based wood adhesive has not been sufficiently investigated, and its properties and functions have not been appropriately evaluated. Furthermore, compared with adhesives made of conventional materials, biopolymer-based adhesives are usually too weak for practical use (Bordes, Pollet, & Avérous, 2009), so the structural strength of starch-based adhesive should be strengthened to achieve high performance as a wood adhesive.

Many studies indicated that silica nanoparticles were useful performance enhancers for polymer materials because of their small size, high surface energy and unsaturated chemical bonds on the surface (Sun, Li, Zhang, Du, & Burnell-Gray, 2006; Wang et al., 2005; Yang et al., 2006; Zhang, Rong, Zhang, & Friedrich, 2003; Zhou, Wu, Sun, & Shen, 2003). Additionally, some studies found that silica nanoparticles not only showed high strength, thermal stability, and chemical stability as inorganic materials but also showed flexibility like organic materials (Chronakis, 2005; Tang, Zou, Xiong, & Tang, 2008). Therefore, silica nanoparticles likely can be used to improve the properties of starch-based wood adhesive prepared through graft polymerization of starch and vinyl monomers. However, the effect of silica nanoparticles on the performance of starch-based wood adhesive has not been investigated.

In order to improve the quality of the renewable starch-based wood adhesive, silica nanoparticles were added into vinyl acetate (VAc) grafted starch to produce SiO_2/starch-based wood adhesive in this study. Bonding strength and water resistance of the adhesive were examined to confirm the positive effect of adding silica nanoparticles into the adhesive system. Adhesive structure was analysed to show interaction between the grafted starch and silica nanoparticles, and its thermal properties, rheological properties and the fractures of wood bonded joints were determined to support the quality improvement of the starch-based wood adhesive by adding silica nanoparticles.

2. Materials and methods

2.1. Materials

Waxy corn starch was supplied by Qinhuangdao Lihua Starch Co. (China), and silica sol (Bindzil 2034DI, 33 wt.%, pH = 4.2, and particle diameter was about 20 nm) was provided by Eka Chemicals

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Co. (Sweden). VAc, ammonium persulfate (APS), sodium dodecyl sulfate (SDS), sodium bicarbonate ($NaHCO_3$), and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. (China). All the other reagents were analytical grade.

2.2. Synthesis of SiO_2/starch-based wood adhesive

SiO_2/starch-based wood adhesive was prepared as follows: 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 60 °C, followed by the addition of 0.5 g of SDS, 12.5 mL of 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 37.5 mL of VAc and 0.375 g of APS were dropped into the mixture over a period of 3 h. After 3 h of polymerization, silica nanoparticles (1–10% of the solid content of adhesive) was added, and the temperature was increased to 80 °C and kept for 30 min. Finally, $NaHCO_3$ was added to adjust the pH to 6.0–7.0 after the temperature of the mixture was cooled to room temperature.

For comparison purposes, a normal starch-based wood adhesive was prepared following the above process but without adding silica sol and increasing temperature to 80 °C.

2.3. Shear strength test

Shear strength of the adhesive samples was tested according to an industry standard of HG/T 2727-1995 (China, 1995). Freshly cut pieces of wood (Betula platyphylla, 0.62×10^3 kg/m^3) with dimensions of 25 mm × 25 mm × 10 mm were glued with adhesives under static pressures of 0.49–0.98 MPa at 25 °C for 24 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: $\sigma_M = F_{max}/A$, 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 the averages.

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

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 homopolymers of VAc monomers, and then dried. The extracted solids 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}.

2.5. Scanning electron microscopy (SEM) analysis

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. Thermogravimetric analysis (TGA)

Thermal stability of the adhesive samples was analysed using a Mettler Toledo TGA/SDTA851^e thermogravimeter (Mettler Toledo Corp., Switzerland) with a STAR^e software (version 9.01). Samples (10.0 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.

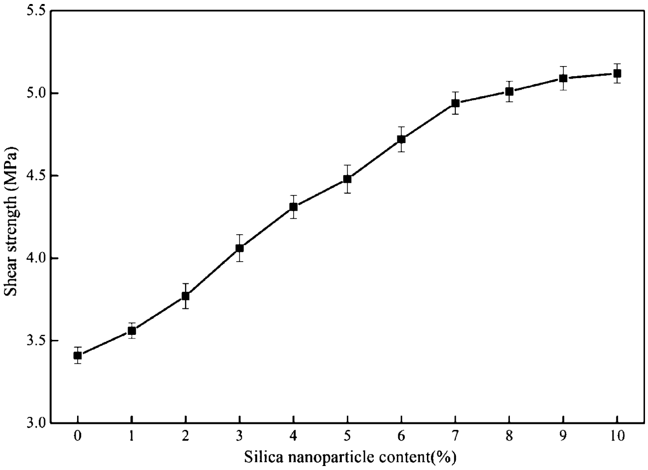

Fig. 1. Relationship between silica nanoparticle contents of starch-based wood adhesives and their shear strength in dry state.

2.7. Rheological analysis

Rheological properties of the adhesive samples under steady shear were analysed using a AR1000 rheometer (TA Corp., UK) with a parallel plate (diameter = 40 mm) at a gap of 0.5 mm from 1 to 300 s^{-1} at 25 °C, and data were fitted to power-law model as following: $\tau = K\dot{\gamma}^n$, where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is consistency index (Pa s^n), and n is flow behavior index (dimensionless).

3. Results and discussion

3.1. Improved performance of SiO_2/starch-based wood adhesive

The beneficial effect of adding silica nanoparticles to starch-based wood adhesive system was directly supported by improved bonding strength and water resistance of the SiO_2/starch-based wood adhesive.

As shown in Figs. 1 and 2, the shear strength of adhesives in both dry state and wet state increased with increasing silica nanoparti-

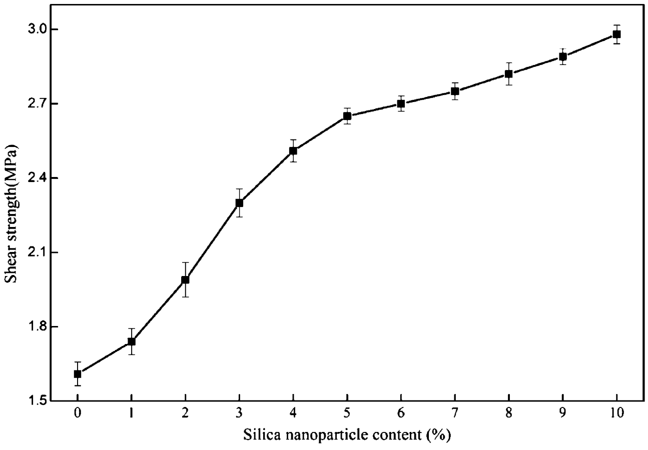

Fig. 2. Relationship between silica nanoparticle contents of starch-based wood adhesives and their shear strength in wet state.

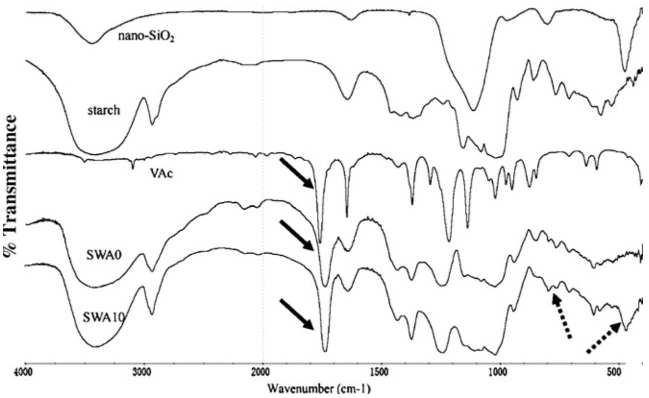

Fig. 3. Infrared spectrograms of silica nanoparticles (nano-SiO_2), waxy corn starch (starch), VAc monomer and starch-based wood adhesive without silica nanoparticles (SWA0) and with 10% of silica nanoparticles (SWA10).

cle contents of 1–10%. Compared with the adhesive without silica nanoparticles, the shear strength of the adhesive with 10% of silica nanoparticles was increased from 3.41 MPa to 5.12 MPa in dry state and increased from 1.62 MPa to 2.98 MPa in wet state. Since bonding characteristics of the adhesive is used to assess the shear strength, the shear strength changes suggest that 10% of silica nanoparticles have increased the bonding strength of the adhesive by 50.1% in dry state and 84.0% in wet state. Apparently, the bonding strength of the starch-based wood adhesive has been significantly improved by adding silica nanoparticles into the adhesive system.

Since water molecules can penetrate into wood and act as a plasticizer for hydrophilic polymers, the bonding strength of starch-based wood adhesives will unavoidably decrease in a humid environment. Comparing Fig. 2 with Fig. 1, the shear strength of all the starch-based wood adhesives with or without silica nanoparticles decreased after 3-h soak of the wood samples glued by the adhesives, but the decreasing degrees were distinctly different. The starch-based wood adhesive without silica nanoparticles lost 52.4% of bonding strength while all starch-based wood adhesives with 1–10% of silica nanoparticles lost less bonding strength. Specifically, the adhesive with 10% of silica nanoparticles lost 41.8% of bonding strength suggesting that 10% of silica nanoparticles have increased the water resistance of the adhesive by 20.2%. Therefore, silica nanoparticles also can increase water resistance of the starch-based wood adhesive.

The performance improvement of silica nanoparticles on starch-based wood adhesive suggests that silica nanoparticles have influence on the adhesive structure, and likely affect some adhesive properties related to the bonding strength and water resistance of the adhesives. Therefore, starch-based wood adhesive without silica nanoparticles (SWA0) and with 1%, 5% and 10% of silica nanoparticles (SWA1, SWA5 and SWA10) were further analysed to show the changes on structure, thermal stability and rheological properties of the adhesives.

3.2. Structural characteristics of SiO_2/starch-based wood adhesive

FT-IR was used to confirm the graft modification of starch and determine the effect of silica nanoparticles on the structure of the starch-based wood adhesive, and the results were shown in Fig. 3. Compared with the spectrum of waxy corn starch, both SWA0 and SWA10 showed the characteristic peaks of ester at 1740 cm^{-1} in the infrared spectrogram (Fig. 3, solid arrow), which indicated the existence of the VAc group in the grafted derivatives. It was also observed that the characteristic peak of ester at 1761 cm^{-1} in the infrared spectrogram of VAc monomer. The ester peak of SWA0 and SWA10 was low-frequency shifted by 21 cm^{-1} than that of VAc monomer, confirming the successful graft polymerization of waxy corn starch and the absence of unreacted VAc monomer in the samples (Kaewtatip & Tanrattanakul, 2008; Marinich, Ferrero, & Jiménez-Castellanos, 2009; Meshram, Patil, Mhaske, & Thorat, 2009). Besides, the appearance of the characteristic peaks of SiO_2 in the spectrogram of SWA10 at 474 and 802 cm^{-1} (Fig. 3b, dashed arrow) confirmed the existence of SiO_2 in the sample.

The effect of silica nanoparticles on the adhesive structure was directly shown by the SEM photographs in Fig. 4. Compared with SWA0, the cast film of SWA10 was much smoother and more compact, and no obvious microphase separation or aggregation of nanocrystals were observed on it. Obviously, silica nanoparticles dispersed evenly in the modified starch system and greatly improved the component compatibility of the starch-based wood adhesive.

Since silica nanoparticles can approach unsaturated bonds of copolymer macromolecules and interact with the electrons of the unsaturated bonds (Friedlander, 1999), the evenly dispersed silica nanoparticles in the starch-based wood adhesive likely interact with the hydroxyl groups of the grafted starch resulting in strengthened molecular interaction in the adhesive system. Starch-based wood adhesives are nonreactive when they are used, and weak secondary forces, such as hydrogen bonds and Van der Waals forces, have been found to play a significant role in the bonding between nonreactive adhesive and wood (Qiao & Easteal, 2001). Therefore, the SiO_2/starch-based wood adhesive with strengthened molecular structure will enhance the interaction between the adhesive and wood resulting in improved bonding strength and water resistance of the adhesive.

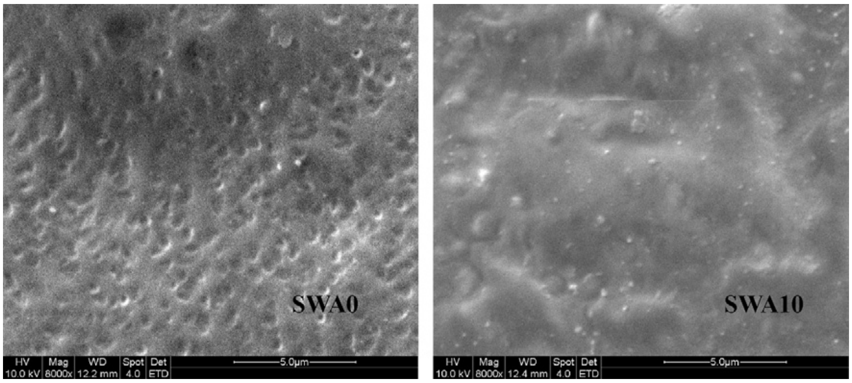

Fig. 4. SEM images of the cast films of starch-based wood adhesive without silica nanoparticles (SWA0) and with 10% of silica nanoparticles (SWA10).

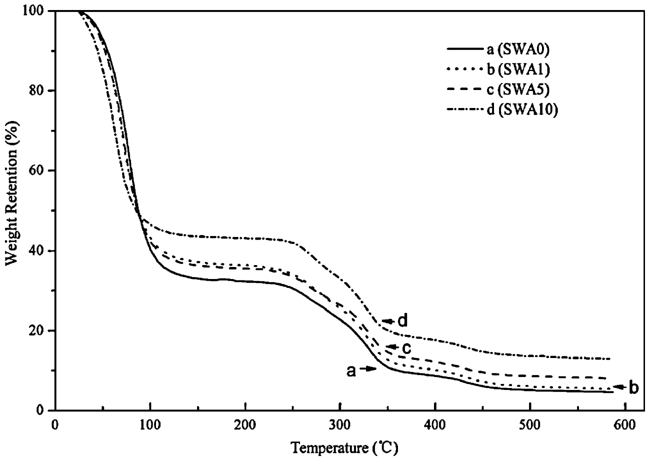

Fig. 5. Thermogravimetric curves of starch-based wood adhesives with 0% (SWA0), 1% (SWA1), 5% (SWA5) and 10% (SWA10) of silica nanoparticles.

3.3. *Thermal stability of SiO_2/starch-based wood adhesive*

The strengthened molecular structure of the SiO_2/starch-based wood adhesive was supported by the thermogravimetric analysis results as shown in Fig. 5. All the samples showed thermogravimetric curves of weight loss in three steps, and the weight loss with initial temperature around 50, 250, and 420 °C was caused by water evaporation (Lu, Duan, & Lin, 2003), dehydration of polymer chains (López, Cendoya, Torres, Tejada, & Mijangos, 2001) and complete decomposition of adhesive residue, respectively. Specially, the initial dehydration temperatures of polymer chains increased from 241.11 to 294.87 °C with increasing silica nanoparticle contents of 0, 1, 5 and 10%, while corresponding weight loss during the whole polymer chain dehydration period decreased from 24.79 to 14.03%. Apparently, the added silica nanoparticles improved the thermal stability of the starch-based adhesive. The enhanced thermal stability of the SiO_2/starch-based wood adhesive confirms its strengthened molecular structure and supports its improved bonding strength and water resistance. Additionally, higher thermal stability suggests that the SiO_2/starch-based wood adhesive can be used in a wider temperature range.

3.4. *Rheological properties of SiO_2/starch-based wood adhesive*

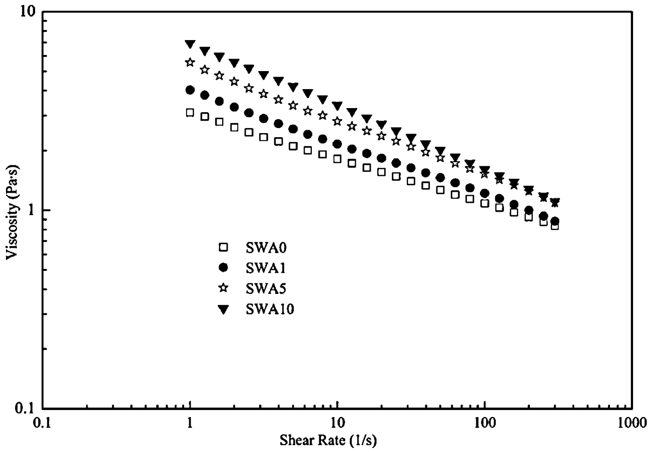

Fig. 6. Flow curves of starch-based wood adhesives with 0% (SWA0), 1% (SWA1), 5% (SWA5) and 10% (SWA10) of silica nanoparticles.

Table 1
Effect of silica nanoparticle contents on the rheological parameters of the starch-based wood adhesives.

SiO_2 content (%)	n	K (Pa s^n)
0	0.77	3.14
1	0.74	3.75
5	0.71	5.69
10	0.67	7.31

The application of adhesive was closely related to its rheological properties. The viscosity changes of the adhesives under steady shear were shown in Fig. 6, and the rheological parameters from the simple power-law model ($R^2 > 0.99$) were shown in Table 1. The flow behavior index (n) decreased from 0.77 to 0.67 with increasing silica nanoparticle contents of 0, 1, 5 and 10%, while corresponding consistency index (K) increased from 3.14 to 7.31 Pa s^n. Apparently, SiO_2/starch-based wood adhesive was more pseudoplastic and viscous. Shear thinning facilitates sufficient interaction between adhesive and wood, and higher viscosity suggests stronger interaction among the adhesive components. Therefore, the rheological property changes caused by silica nanoparticles not only further confirm the strengthened molecular structure of the SiO_2/starch-based wood adhesive but also support the improved bonding strength and water resistance of the adhesive from another aspect.

3.5. *SEM fractography on wood glued with SiO_2/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. 7

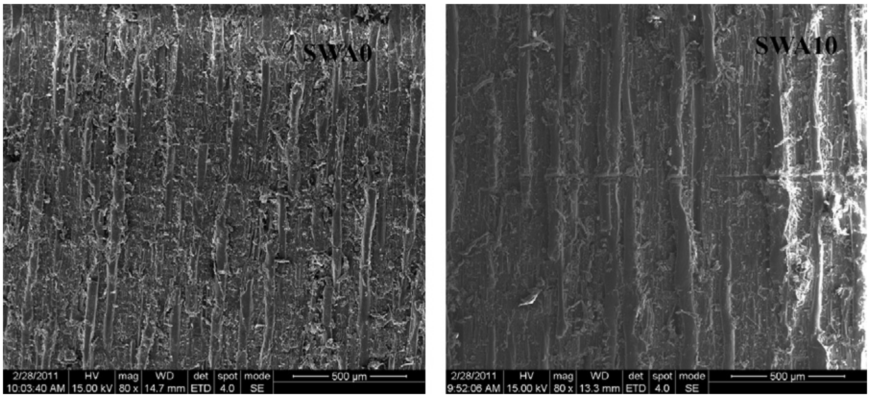

Fig. 7. SEM micrograph of fracture surface of wood surface glued with starch-based wood adhesive without silica nanoparticles (SWA0) and with 10% of silica nanoparticles (SWA10).

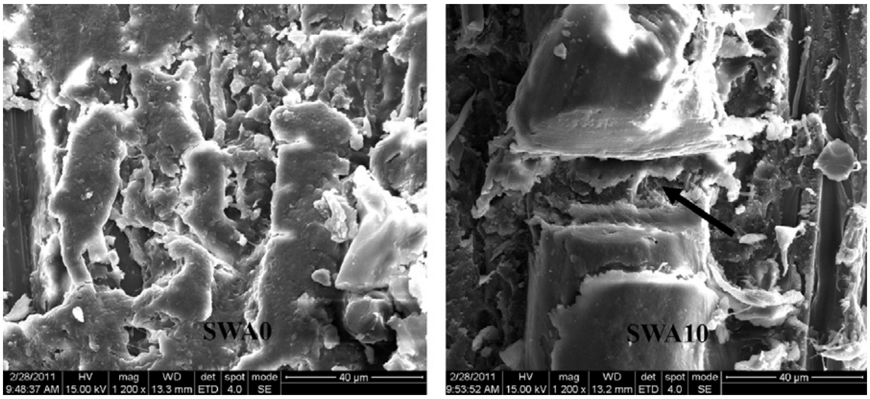

Fig. 8. SEM micrograph of fracture surface of wood surface glued with starch-based wood adhesive without silica nanoparticles (SWA0) and with 10% of silica nanoparticles (SWA10), a magnification of Fig. 7.

demonstrates the fracture surface of the glued samples of SWA0 and SWA10 at a lower magnification. Many lumens were filled with starch-based adhesive, indicated that the failure was within the adhesives. Apparently, there was a thin coating of adhesive on the surface of the glued specimens of SWA0 and SWA10. Fig. 8 shows the surface in Fig. 7 magnified showing traces of the wood cell structure. In Fig. 8, we could observe many small adhesive fragments appear on the surface of the wood lumens. The arrow indicates a possible cohesive fracture between wood and starch-based adhesive, most of surface was characterized by cohesion failure in our adhesives. Compared with SWA0, the SEM image of SWA10 showed that there was crack propagation occurred in both wood lumen and adhesive layer. At lower shear stress, the fracture of glued specimens was within the adhesive layer. However, the wood lumen cell would be further damaged at higher shear stress. Therefore, the enhancement of the interaction between wood cell and the adhesive, which caused by silica nanoparticles, would lead to more obvious surface damage of bonded joint and the increase in shear strength.

4. Conclusions

Compared with starch-based wood adhesive without silica nanoparticles, both the bonding strength and water resistance of starch-based wood adhesive with silica nanoparticles were significantly improved. The performance improvements of the SiO_2/starch-based wood adhesive were supported by its strengthened molecular structure, enhanced thermal stability and beneficial changes in rheological properties and more obvious surface damage of bonded joints. The starch-based wood adhesive with 10% silica nanoparticles (w/w) added was found to have the best shear strengths of 5.12 MPa in the dry state and 2.98 MPa in the wet state. Therefore, silica nanoparticles can be used to prepare renewable starch-based wood adhesive with high performance.

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