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

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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 SiO₂/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.

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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 SiO₂/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.
Co. (Sweden). VAc, ammonium persulfate (APS), sodium dodecyl sulfate (SDS), sodium bicarbonate (NaHCO₃), and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. (China). All the other reagents were analytical grade.

2.2. Synthesis of SiO₂/starch-based wood adhesive

SiO₂/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, NaHCO₃ 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 × 10³ kg/m³) 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: σ_M = F_max / A, where σ_M (MPa) is the shear strength, F_max (N) is the observed maximum failing load, and A (mm²) 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/SDT A851® thermogravimeter (Mettler Toledo Corp., Switzerland) with a STAR® 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.

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: τ = K·γⁿ, where τ is shear stress (Pa), γ is shear rate (s⁻¹), K is consistency index (Pa·sⁿ), and n is flow behavior index (dimensionless).

3. Results and discussion

3.1. Improved performance of SiO₂/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 SiO₂/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-