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Effects of montmorillonite addition on the performance of starch-based wood adhesive

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ABSTRACT

Effects of montmorillonite (MMT) addition on the performance of corn starch-based wood adhesive were investigated. It was found that MMT addition could enhance the shear strength of the starch-based wood adhesive. The shear strength of the adhesive with 5% (w/w, dry starch basis) MMT reached 10.6 MPa in the dry state, which was almost twice that of the same adhesive without MMT. Addition of 5% MMT also produced an approximately 1.2-fold increase in the shear strength in the wet state. Although this addition caused an increase in the viscosity, the resulting adhesive retained both good mobility and viscosity stability during storage. MMT also enhanced the shear-thinning and solid-like behaviors of the adhesive, compared with the adhesive without MMT. Finally, MMT addition improved the thermal stability of the adhesive. In conclusion, addition of MMT to starch-based wood adhesives can improve their overall performance, enhancing their value as alternatives for traditional petrochemical-based wood adhesives.

1. Introduction

Wood adhesives play an essential role in the production of wood-based composites, which offer a sustainable resource for the furniture, construction, and building industries (Haag, Geesey, & Mittleman, 2006). However, most wood adhesives are petrochemical-based and nonrenewable; many contain residual toxic components, such as formaldehyde, and volatile organic compounds (Haag et al., 2006; Imam, Mao, Chen, & Greene, 1999; Jang, Huang, & Li, 2011b; Moubarik et al., 2013). This heavy dependence on petroleum and the harm of emissive pollutants to human health have created an urgent need for environmentally friendly wood adhesives based on renewable resources (Kim, 2010; Li et al., 2014).

Starch is an abundant, renewable, biodegradable and relatively inexpensive natural polymer, which makes it an attractive alternative for synthetic polymers (Imam, Gordon, Mao, & Chen, 2001; Ma, Yu, & Wang, 2007). It is widely known that starch can be used as an adhesive in a wide range of products, including binders, glues, pastes, and sizing material (Jarowenko, 1977). Recently, several efforts have been made to improve the performance of starch adhesives for bonding wood, to enable starch-based wood adhesives to compete with petrochemical-based wood adhesives (Imam et al., 2001; Moubarik, Charrier, Allal, Charrier, & Pizzi, 2010a; Moubarik et al., 2010b; Nwokocha, 2011; Sridach, Jonjankiat, & Wittaya, 2013; Wang, Li, Gu, Hong, & Cheng, 2012). We recently described the development of a starch-based wood adhesive in which vinyl acetate was grafted to corn starch; the addition of sodium dodecyl sulfate improved the mobility and storage stability of this adhesive (Li et al., 2014). However, because the addition of sodium dodecyl sulfate decreased the shear strength of the adhesive, it is needed to further enhance its bonding performance.

Montmorillonite (MMT), a type of nano-layered silicate, is the most common member of the smectite clay family (Calvert, 1996; Chang, Shih, Yang, & Hsiao, 2007; Ye, Zhong, Chen, & Yang, 2005). It is also referred to as 'nano-clay'. MMT consists of a three-layered structure in which a layer of aluminum is sandwiched between two layers of silicon. This structure has the ability to swell markedly when it absorbs water (Chang et al., 2007). Nano-layered silicates have been shown to improve the performance of adhesives because of their small size, their high surface energy, and the presence of unsaturated chemical bonds on their surfaces (Choudalakis & Gotsis, 2009; Dorigato, Morandi, & Pegoretti, 2012; Jang et al.,

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2011a; Kaboorani & Riedl, 2011; Wang, Yuan, Fan, Sahoo, & He, 2013a). However, the effect of MMT addition on the performance of starch-based wood adhesives has not been investigated. In the present study, MMT was used to improve the performance of a starch-based wood adhesive.

2. Materials and methods

2.1. Materials

Normal corn starch [moisture content, 12.9%; amylose content, 26.5% (w/w, dry basis); protein content, 0.42% (w/w, dry basis); purity, >99%] was supplied by Zhucheng Xingmao Corn Development Co., Ltd (Shandong, China). Vinyl acetate, ammonium persulfate, sodium dodecyl sulfate, and poly(vinyl alcohol) (PVA) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Montmorillonite (sodium salt; purity, 98%; lamellar thickness, <20 nm; cation exchange capacity, 90 mmol/100 g) was purchased from Zhejiang Fenghong New Material Co., Ltd (Zhejiang, China). All other reagents were of analytical grade.

2.2. Preparation of PVA solution with MMT

PVA powder was fully dispersed in deionized water to a final concentration of 10% (w/w). This mixture was heated and kept at 95 °C for 0.5 h. Different amounts of MMT were slowly added to the PVA solution with continuous stirring, and then the mixture was kept at 95 °C for an additional 2 h.

2.3. Synthesis of starch-based wood adhesive with MMT

Approximately 50 g of dry corn starch and 100 mL of hydrochloric acid (HCl, 0.5 M) were put into a four-necked, round-bottomed flask and stirred at 60 °C for 60 min. During this period, the corn starch was partially hydrolyzed by HCl. The pH of the starch slurry was then adjusted to 4.0 with 2 M sodium hydroxide. Sodium dodecyl sulfate (1.5% of dry starch) was added into the slurry, followed by the addition of 0.4 g of ammonium persulfate as free-radical initiators under nitrogen protection. The reaction temperature was increased to 70 °C, and then vinyl acetate (43 mL) was added, dropwise, to the slurry over a period of 1.5 h. Graft copolymerization of vinyl acetate with the hydrolyzed starch was performed to synthesize grafted starch with better adhesive properties. Due to the evolution of heat by the exothermic reaction, the grafted starch was partially gelatinized. After that, the PVA solution with MMT was added. The final concentrations of PVA and MMT in the starch-based wood adhesive were 1.2% and 1–9% (w/w, dry starch basis), respectively. The temperature of the reaction mixture was increased to 85 °C and kept there for 0.5 h. Finally, after the reaction mixture was cooled to 30 °C, the pH value was adjusted to 6.0 with 1 M sodium hydroxide.

A starch-based wood adhesive without MMT was also prepared following the process described above, as a control.

2.4. Shear strength test

After being stored at 25 ± 1 °C and 70% RH for 24 h, the shear strength of starch-based wood adhesive samples were tested, as described in previous reports (Li et al., 2014; Moubarik et al., 2013; Wang, Gu, Hong, Cheng, & Li, 2011). Freshly cut pieces of wood (Betula platyphylla, 13–14% water content, approximately 750 kg/m^3) with dimensions of 25 mm × 25 mm × 10 mm were glued with the adhesives under static pressures of 0.5 to 1.0 MPa at 23 ± 2 °C and 50 ± 5% humidity for 24 h. Then, the glued specimens were stored at 23 ± 2 °C and 50 ± 5% humidity for 48 h. The shear strength in the dry state was directly determined using a WDT-10 shear strength analyzer (KQL Corp., China). After immersing in water at 23 °C for 3 h, the shear strength in the wet state was determined. All tests were repeated ten times. The results were reproducible, with standard deviations of <2.5 MPa.

2.5. Scanning electron microscopy (SEM) analysis

A film of starch-based wood adhesive with 5% MMT was 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. The MMT at the tensile fracture surface of adhesive film was observed by using a scanning electron microscope (Hitachi S4800, Tokyo, Japan).

After testing the shear strength in the dry state, the fracture surfaces of the wood specimens glued with the starch-based wood adhesives with and without 5% MMT were also observed by using a scanning electron microscope (Hitachi S4800, Tokyo, Japan).

2.6. X-ray diffraction analysis

X-ray diffraction patterns of MMT and the starch-based wood adhesive with 5% MMT were recorded on a D8 Advance X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) using Cu $K\alpha$ radiation (wavelength λ = 0.154 nm) at a generator voltage of 40 kV and current of 40 mA. The analyses were carried out with a scan rate of 1°/min and diffraction angle range of 1–10° (2θ).

2.7. Measurement of rheological properties

After being stored at 25 ± 1 °C and 70% RH for 24 h or longer, the viscosities of starch-based wood adhesive samples were determined using an NDJ-1 rotational viscometer (JK Corp., China). The adhesive samples were transferred into the holder of the viscometer, and subjected to rotation at a rotor speed of 30 rpm for 10 min. The viscosities were determined in triplicate at 25 ± 1 °C.

After being stored at 25 ± 1 °C and 70% RH for 24 h, the rheological properties of starch-based wood adhesives with and without 5% MMT were assessed using a controlled stress rheometer (AR1000, TA Instruments, Crawley, UK) with an aluminum parallel plate geometry (40 mm diameter, 1.00 mm gap). All measurements were performed at 25 °C.

The steady shear rheological measurements were performed to obtain shear rate versus viscosity or shear stress curves. The cone was programmed to ramp the shear rate from 0.1 to 300 s^{-1}, and the data were used to characterize the flow of the paste samples. The data were fitted to the power-law model: $\tau = K\dot{\gamma}^n$, where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa s^n), and n is the flow behavior index.

The dynamic viscoelasticity measurements were performed over the frequency range of 0.1–10 Hz. The strain amplitude for the frequency sweep measurements was selected as 1%. The mechanical spectra were obtained by recording the storage modulus (G'), loss modulus (G''), and loss tangent (tan $\delta = G''/G'$) as a function of angular frequency.

2.8. Thermogravimetric analysis

After being stored at 25 ± 1 °C and 70% RH for 24 h, thermogravimetric analyses of the starch-based wood adhesives with and without 5% MMT were performed by using a thermogravimetric analyzer (Model TGA/SDTA 851e; Mettler Toledo Inc., Schwarzenbach, Switzerland) running STARe software (version 9.01). Samples