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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

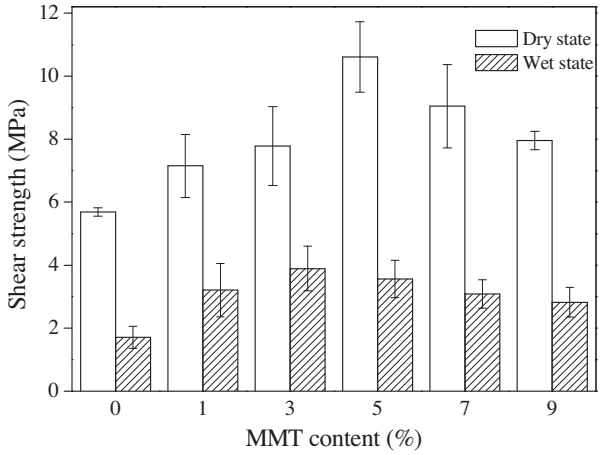

Fig. 1. Effect of MMT addition on the shear strength of starch-based wood adhesive.

(10.0 mg in an alumina pan) were heated from 50 to 500 °C at a rate of 10 °C/min under a nitrogen gas flow at 20 mL/min.

3. Results and discussion

3.1. Effects of MMT addition on the shear strengths of starch-based wood adhesive

The shear strength of starch-based wood adhesives containing 0–9% (w/w, dry starch basis) MMT are shown in Fig. 1. The addition of MMT enhanced the shear strength of the starch-based wood adhesive, in both the dry and wet states, at all contents tested. The shear strength in the dry state increased with MMT content until the MMT content reached 5%. At this optimal MMT content, the shear strength of the adhesive reached 10.6 MPa in the dry state, which was almost twice that of the adhesive without MMT (5.6 Mpa). However, at the contents above 5%, the enhancing effects of MMT on the shear strength of the adhesive began to decline.

The addition of MMT produced a greater percent increase in shear strength in the wet state than it did in the dry state, indicating that MMT addition improved the barrier properties of the starch-based wood adhesive toward water (Esposito Corcione, Mensitieri, & Maffezzoli, 2009). An approximately 90% increase in shear strength of the adhesive in the wet state was achieved by the addition of 1% MMT. At the optimal MMT content of 3%, the shear strength of the adhesive reached approximately 3.9 MPa in the wet state, which had a 1.3-fold increase over that of the adhesive without MMT. With further increases in MMT content, the shear strength of the adhesive in the wet state showed a decreasing trend. Nevertheless, when the MMT content was controlled at 5%, the shear strength of the adhesive in the wet state was approximately 1.2-fold higher than that of the adhesive without MMT, which was only 7% lower than that of the adhesive with 3% MMT. Therefore, considering the enhancements in shear strength in both the dry and wet states, starch-based wood adhesives with 5% MMT displayed the best performance in bonding wood.

In a previous study, it was showed that silica nanoparticles could also improve the shear strength of starch-based wood adhesive (Wang et al., 2011). By comparison, enhancing effects of silica nanoparticle on shear strength of the adhesive were much lower than those of MMT. Furthermore, the shear strengths of the starch-based wood adhesive with 5% MMT, in both the dry and wet states, were higher than those of other starch-based wood adhesives reported previously (Wang et al., 2011; Wang, Gu, Li, Hong, & Cheng, 2013b,c; Wang et al., 2012).

3.2. Fracture surface analysis of wood samples glued with starch-based wood adhesive

After performing the shear strength tests, SEM micrographs of the fracture surfaces of wood specimens glued with the starch-based wood adhesives were taken. These micrographs could directly assess the bonding performance of the adhesive. A cohesive failure mode was observed for the adhesive without MMT (Fig. 2A). Failure occurred primarily at the adhesive layers, suggesting that the cohesive forces were weaker than the interfacial forces. In contrast, interfacial failure was the primary failure mode for the adhesive containing 5% MMT (Fig. 2B). The severely fissured fracture surface denoted better bonding performance. These results indicated that the addition of MMT to a starch-based wood adhesive significantly reinforced its cohesive forces, which allowed the adhesive to glue wood more effectively.

3.3. Effects of MMT addition on the viscosity of starch-based wood adhesive

Viscosity largely governs the mobility of wood adhesives (Qi & Sun, 2010). Too high viscosities lead to poor mobility, making wood adhesive more difficult to handle, spread, and penetrate into the wood surface (Li et al., 2014). After being stored for 24 h, the viscosities of the adhesives with different contents of MMT are determined and shown in Fig. 3.

The starch-based wood adhesive without MMT had a low viscosity (8.2 Pa s) and showed very good mobility. The addition of MMT resulted in an increase in viscosity, which may be caused by the absorption of water in the system by the MMT (Chang et al., 2007). Addition of 1% MMT brought about a slight increase

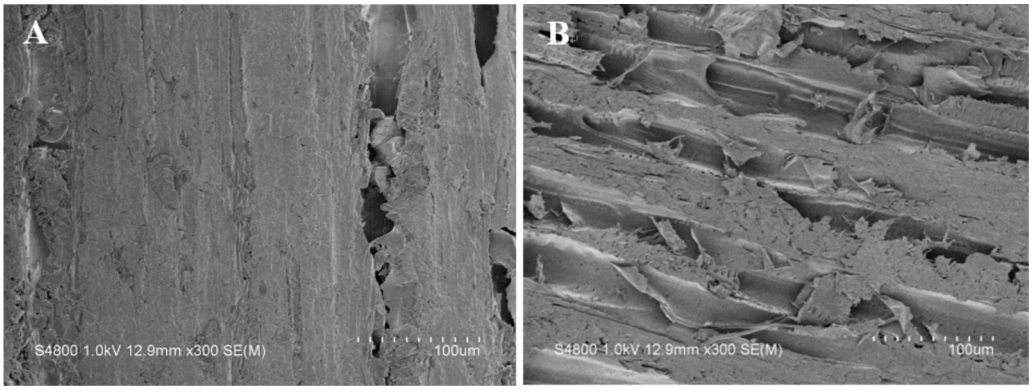

Fig. 2. SEM micrograph of the fracture surfaces of wood surfaces glued with starch-based wood adhesives with or without 5% MMT. (A) The adhesive without MMT; (B) the adhesive with 5% MMT.

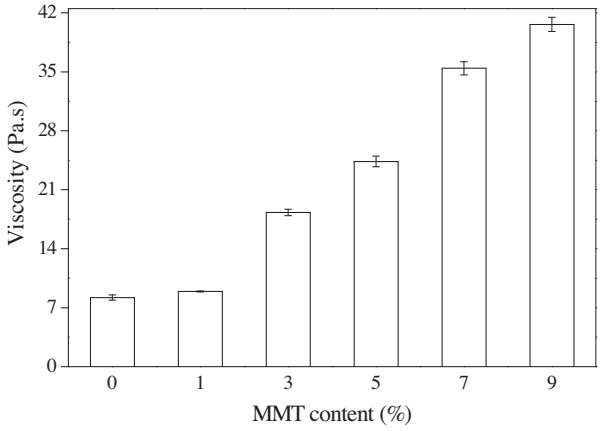

Fig. 3. Effect of MMT addition on viscosities of a starch-based wood adhesive. After being stored at 25 ± 1 °C and 70% RH for 24 h, the viscosities of starch-based wood adhesive samples were tested.

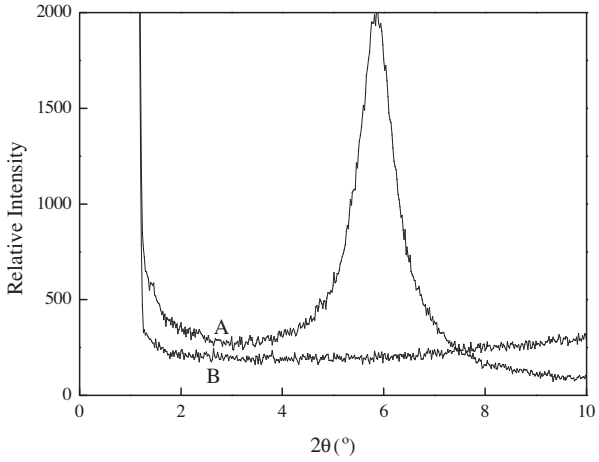

Fig. 5. X-ray diffraction patterns of MMT and the starch-based wood adhesive with 5% MMT. (A) MMT; (B) the adhesive with 5% MMT.

in the viscosity that had almost no effect on the mobility. Addition of greater contents of MMT resulted in an approximately linear increase in the viscosity of the adhesive. Although the addition of 5% MMT caused a substantial percentage increase in the viscosity (~300%), the corresponding adhesive product retained a relatively low viscosity (24.4 Pa s) that would allow easy handling, smooth spreading, and sufficient penetration of the adhesive into the wood surface. Adhesives with MMT contents of 7% or above displayed significant increases in viscosity that had an appreciably negative effect on the mobility of the adhesive.

3.4. Effect of MMT addition on viscosity stability of starch-based wood adhesive

Stability of the viscosity during storage is one of the most important properties of starch-based wood adhesives. As shown in Fig. 4, with increasing storage time, the viscosities of the starch-based wood adhesives gradually increased.

For the adhesives with or without 1% MMT, 30-day storage resulted in a very slight increase in viscosity (<10%). Adhesives containing 3% or 5% MMT displayed modest increases in viscosity over a 30-day storage period. Nevertheless, after being stored for 30 days, the adhesives with 5% MMT still showed good mobility, indicating satisfactory storage stability. However, a substantial reduction in the stability of the adhesive's viscosity was observed following addition of a higher proportion of MMT. After being stored for 30 days, the viscosities of the adhesives with 7% or 9% MMT increased by approximately 82% or 105%, respectively, compared with those stored for 24 h. Therefore, the starch-based wood adhesives with ≥7% MMT possess viscosities that, after a 30-day storage period, become too high to ensure ease of use.

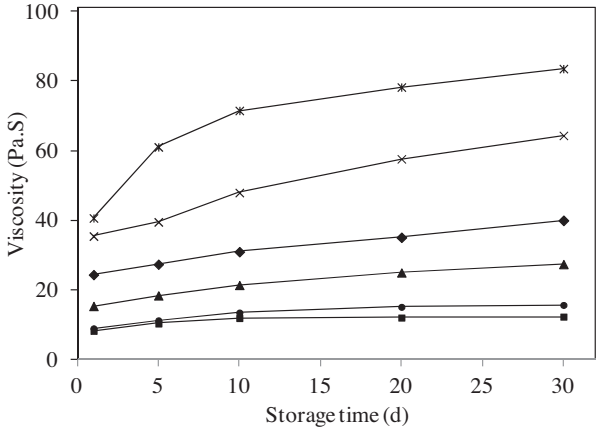

Fig. 4. Effect of MMT addition on the viscosity stability of starch-based wood adhesive. The adhesive was stored at 25 ± 1 °C and 70% RH for 30 days. The MMT content in the adhesive was 0% (■), 1% (•), 3% (▲), 5% (♦), 7% (×) and 9% (*), respectively. Each value represents the mean of three independent measurements.

3.5. The dispersion state of MMT in the starch-based wood adhesive

The X-ray diffraction patterns of MMT and the starch-based wood adhesive with 5% MMT are shown in Fig. 5. The basal spacing of the MMT was calculated from the X-ray diffraction peak position using the Bragg equation ($\lambda = 2d \sin\theta$, where λ is the wavelength, d is the basal spacing, and θ is the diffraction angle) (Ghelichi, Qazvini, Jafari, Khonakdar, & Reuter, 2012; Zhou et al., 2009). Pure MMT has one intense peak at 5.8°, meaning that the distance between MMT platelets, calculated using the Bragg equation, is 1.5 nm. In the case of the adhesive with 5% MMT, the diffraction peak disappeared from the X-ray diffraction pattern, suggesting that the layered structure of the MMT might be destroyed and exfoliated in the starch-based wood adhesive. In addition, an SEM micrograph of MMT (see Supplementary information, Fig. S1A) showed a clear layered structure, while the tensile fracture surface of the adhesive film with 5% MMT had no obvious layered MMT structure (Fig. S1B). This is also evidence of a good dispersion state for MMT in the starch-based wood adhesive.

3.6. Steady shear rheological properties of the starch-based wood adhesive with MMT

The application of wood adhesive was closely related to its rheological properties. The steady shear rheological properties of the starch-based wood adhesives with or without 5% MMT are presented in Fig. 6. The adhesives exhibited shear-thinning properties, that is, their apparent viscosities decreased with increasing shear rate. At relatively low shear rates, the steady shear viscosity of the adhesive containing 5% MMT was obviously higher than that of the adhesive without MMT. At high shear rates, there was a smaller difference in steady shear viscosities between the adhesives with and without 5% MMT. Therefore, the addition of MMT enhanced the shear-thinning behavior of the starch-based wood adhesive, which would facilitate sufficient interaction between the adhesive and wood.

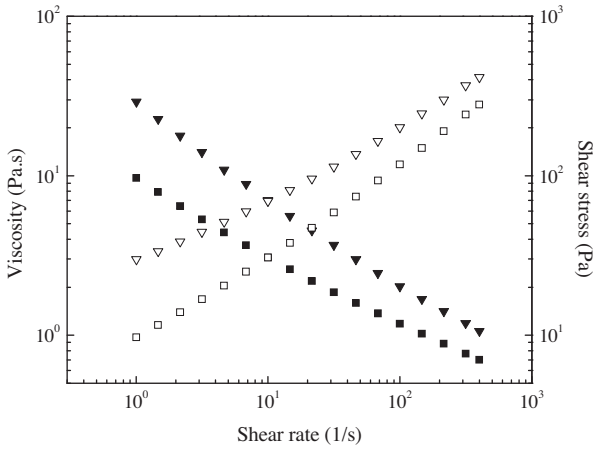

Fig. 6. Steady rheological curves of the starch-based wood adhesive with (triangle) or without (square) 5% MMT. Viscosity versus shear rate (solid); shear stress versus shear rate (open).

In addition, at the same shear rate, the shear stress for the adhesives with 5% MMT was higher than that for the adhesive without MMT (Fig. 6). The high shear stress might be the result of destroying a strong interaction between the MMT and the starch molecules. Furthermore, the shear rate versus shear stress curves were well fitted by the power-law model ($R^2 > 0.99$). The rheological parameters from the power-law model are shown in Table S1. The two adhesives exhibited pseudoplastic properties because the flow behavior index (n) was <1. Addition of 5% MMT decreased the flow behavior index (n) of the adhesive from 0.61 to 0.5, while the corresponding consistency index (K) increased from 7.23 to 21.18 Pa s^n, indicating that the adhesive with MMT was more pseudoplastic than the adhesive without MMT. The increased pseudoplasticity may be due to the orientation of silicate layers under shear stress (Giannelis, 1998; Sinha Ray & Okamoto, 2003).

3.7. Dynamic rheological properties of the starch-based wood adhesives with MMT

For adhesives with or without 5% MMT, the master curves of storage modulus (G') and loss modulus (G'') versus frequency are presented in Fig. 7A. At low frequencies (≤20 rad/s), the G' and G'' values of the adhesives displayed a slightly increasing trend. At higher frequencies, the G' value of the adhesive without MMT declined noticeably with the increase in frequency. This suggests that the adhesive without MMT might be classified rheologically as a typical weak gel structure (Santipanichwong & Suphantharika, 2009). In contrast, the G' value of the adhesive with 5% MMT keep gradually increasing at higher frequencies, suggesting that the interactions between the MMT and the starch molecules strengthen the structure of the starch-based wood adhesive. In addition, the G'' value showed a more pronounced increase with frequency than the G' value (Fig. 7A). These data were reinforced by the increasing trend in the dynamic mechanical loss tangent ($\tan\delta = G''/G'$) values of the adhesives (Fig. 7B).

On the other hand, the addition of MMT resulted in an increase in the dynamic moduli of the adhesive and a change in the frequency dependence of the moduli. As a result, the frequency at the crossover point of G' and G'' for the adhesive with 5% MMT was higher than that for the adhesive without MMT (Fig. 7A). The tan δ value for the adhesive with 5% MMT was lower than that for the adhesive without MMT (Fig. 7B). These indicated a transition from liquid-like to solid-like behavior. This transition might be related to the formation of a combined network between the MMT and the starch molecules (Abdel-Goad & Pötschke, 2005).

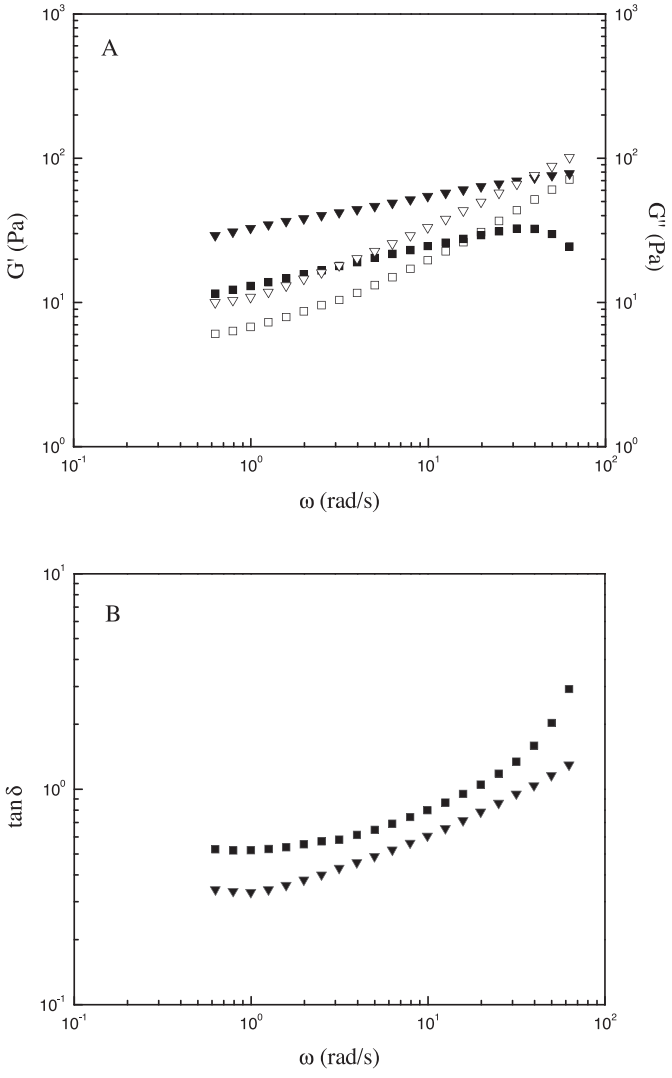

Fig. 7. Variation of G', G'', and tan δ with angular frequency for the starch-based wood adhesive with (triangle) or without (square) 5% MMT. (A) G' (solid) or G'' (open) versus angular frequency; (B) tan δ versus angular frequency.

3.8. Thermal stability of the starch-based wood adhesive with MMT

The thermal stabilities of the starch-based wood adhesives with or without 5% MMT were assessed using thermogravimetric analysis. As shown in Fig. 8, there were three steps in the degradation of the starch-based wood adhesives: the evaporation of water, the dehydration of polymer chains, and the decomposition of the adhesive residue. This was consistent with the previous study of wood adhesives prepared using waxy corn starch as the primary material (Wang et al., 2011). For the adhesive without MMT, the first weight loss occurred between 50 and 130 °C and accounted for approximately 68.9% of the total weight loss. The second step occurred between 270 and 363 °C and accounted for approximately 15% of the total weight loss. The final step occurred between 363 and 474 °C and accounted for approximately 3.5% of the total weight loss. For the adhesive containing 5% MMT, the first weight loss occurred between 50 and 165 °C and accounted for around 67.6% of the total weight loss. The second occurred between 270 and 363 °C and accounted for approximately 15% of the total weight loss. The third step occurred between 363 and 468 °C and accounted for approximately 3.8% of the total weight loss. Interestingly, the addition of MMT resulted in a higher end temperature (165 vs. 130 °C)

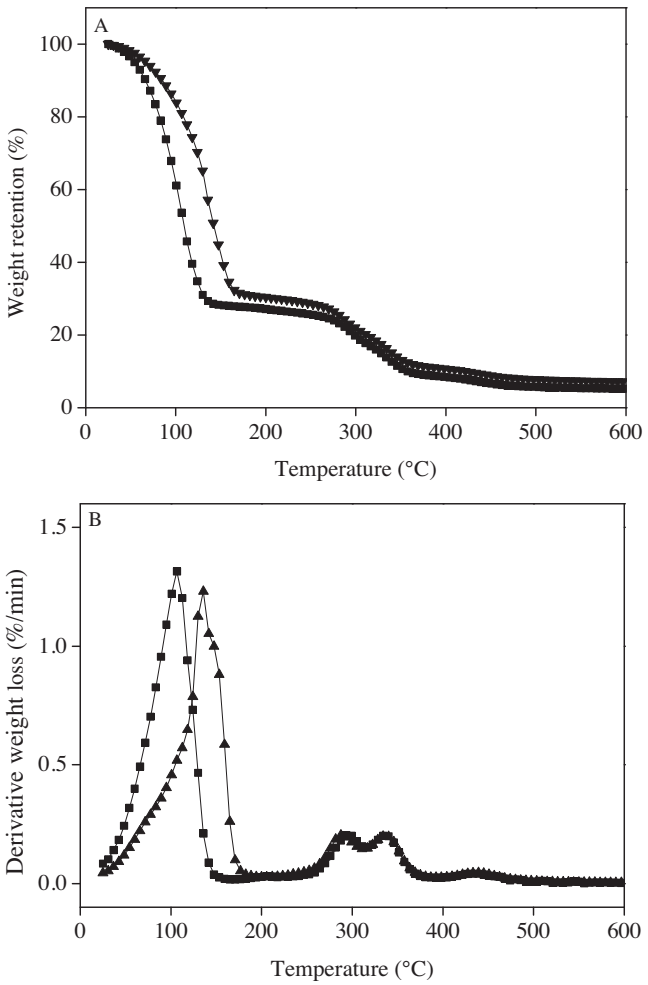

Fig. 8. Thermogravimetric curves showing weight retention (A) and derivative weight loss (B) of the starch-based wood adhesive with (triangle) or without (square) 5% MMT.

of the first weight loss, indicating that the adhesive containing 5% MMT had an enhanced thermal stability. It further confirmed that the addition of MMT strengthened the structure of the starch-based wood adhesive, which would be beneficial to the industrial application of the adhesive at a relatively high operating temperature. The addition of silica nanoparticles, in contrast, has been shown to cause an increase in the temperature of the second weight loss, but not the first (Wang et al., 2011), suggesting that silica nanoparticle and MMT might employ distinct mechanisms for enhancing the thermal stability of the adhesive.

4. Conclusion

The shear strength of starch-based wood adhesives in the dry and wet states were significantly enhanced by the addition of 5% (w/w, dry starch basis) MMT. Compared with a starch-based wood adhesive without MMT, the adhesive with MMT had the enhanced shear-thinning (pseudoplasticity) and solid-like behaviors. The addition of MMT also improved the thermal stability of the adhesive. Thus, MMT can be used to improve the performance of starch-based wood adhesives.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.106.

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