The Effect of Carboxymethyl Cellulose Addition on the Properties of Starch-based Wood Adhesive

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Starch adhesive was prepared utilizing corn starch, polyvinyl alcohol, and borax as raw materials. A certain amount of water-soluble carboxymethyl cellulose (CMC) was added in the preparation process, and a certain percentage of polymethylene polyphenylene isocyanate pre-polymer as cross-linking agent was used to improve its water resistance. To evaluate the water resistance, three-layer plywood was fabricated by hot pressing, and bonding strength was measured using a mechanical testing machine according to the National Standard of the People's Republic of China GB/T 17657-2013. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) were used to characterize curing of the adhesion. The results showed that the initial viscosity, solids content, and bonding strength of the starch adhesive, as well as the interface compatibility between starch adhesive and pre-polymer, were all improved. The curing temperature of the adhesive decreased, and the optimal addition of CMC was 0.375%.

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INTRODUCTION

Adhesives based on urea-formaldehyde (UF), phenol-formaldehyde (PF), and melamine-formaldehyde (MF) have relatively high bonding strength and are commonly used in the plywood industry, but they are very sensitive to hydrolysis and produce health hazards because of the volatile organic compounds they release (Imam *et al*. 2001; Desai *et al.* 2003). To overcome these shortcomings, researchers are trying to find low toxic or non-toxic adhesives. With UF resin, for example, reducing the molar ratio of formaldehyde to urea (F/U) and adding formaldehyde scavenger in the synthesis process are the main measures adopted by the adhesives industry to reduce formaldehyde emissions (Que *et al.* 2007; Guo *et al.* 2010). However, these measures cannot fundamentally solve the problem. With increasing consumption of fossil resources, the contradiction between energy supply and demand is becoming more and more prominent. The raw materials of wood adhesive may gradually need to be replaced by renewable bio-based polymers, such as soy protein, natural tannins, and starch (Moubarik *et al.* 2009; Gao *et al.* 2011; Wang *et al.* 2012).

Starch is an inexpensive, renewable, and biodegradable product that is abundant in plants. It has been extensively used in clothing, paper, printing, adhesives, and other products (Xu and Dai 2001; Lu *et al.* 2006; Wu *et al.* 2013). However, starch adhesive prepared with untreated starch has poor water resistance, mobility, and bonding strength,

affecting its application in wood-based panel industry. Therefore, it is necessary to modify starch to some degree (Li *et al.* 2007; Gong *et al.* 2009; Kaur *et al.* 2012). Isocyanate has excellent bonding strength and water resistance (Tan *et al.* 2011), contains a isocyanate group which is reactive with active hydrogen-containing substances, and can be used to improve the water resistance of starch adhesive. On the other hand, the amount of isocyanate added cannot be too high due to its prohibitive cost.

Starch is a hydrophilic material containing a large number of hydroxyl groups in its molecular chain; hence it easily combines with water molecules to form hydrogen bonds (Dai and Zhao 2011). Polymethylene polyphenylene isocyanate (PAPI) is a mixture containing different functional isocyanates. It is water-insoluble and can be dissolved in organic solvents such as benzene, toluene, and acetone (Liu 2013). Reaction with hydroxyl-containing compounds (polyether polyol, polyester polyol, other polyol and active hydrogen-containing oligomers) is often used to improve its compatibility with aqueous materials.

Despite the introduction of the hydrophilic hydroxyl functional groups in its molecular chains, the compatibility with aqueous materials is not very good. Cellulose is an important renewable natural resource, from which carboxymethyl cellulose (CMC) is obtained after some modification. Carboxymethyl cellulose has been extensively used in many fields (Liu 2002; Li *et al.* 2010). Water-soluble carboxymethyl cellulose with high molecular weight and thickening ability can be used in the adhesive industry to improve the interfacial characteristics (Cao *et al.* 2001). However, little research has been performed on the application of CMC in starch adhesives.

In this paper, native starch was modified by acid-thinning, oxidizing, and cross-linking, and CMC was added in the preparation process to obtain a starch adhesive. Given the poor water resistance of pure starch adhesive, a synthetic pre-polymer was introduced to improve its adhesion, without adding hexamethoxymethylmelamine (Cymel 323) crosslinker, which may be harmful or act as an irritant (Imam *et al.* 1999; Basta *et al.* 2013), and also avoiding the need for acid to be added as catalyst prior to application. The effect of CMC addition on the physical and chemical properties of the starch adhesive and the interface compatibility between the starch and pre-polymer were investigated.

EXPERIMENTAL

Materials

Native starch (NS) (industrial grade, moisture content 10 to 12%) was purchased from Dacheng Corn Starch Co., Ltd. (Changchun, China). Polyvinyl alcohol (1788, the alcoholysis degree ranged from 86 to 88%) was supplied by Xinxiang Chemical Trading Company (Guangdong, China). Ammonium persulfate (APS), sodium hydroxide, hydrochloric acid, borax, and carboxymethyl cellulose (CMC) were bought from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Polymethylene polyphenylene isocyanate (PAPI) pre-polymer (P-P) was obtained according to the methods of Zhang *et al.* (2012) with some modifications. Peeling poplar veneers (size of 300 mm × 300 mm × 1.7 mm) with 8 to 10% moisture content were purchased from Jinhai Wood Co., Ltd. (Dunhua, China). Unless stated otherwise, the materials or reagents were analytical grade.

Methods

Synthesis of starch-based adhesive and test

30% starch slurry (300 g) was prepared and transferred into a 500-mL three-necked round-bottom flask equipped with a rotating paddle and thermometer. The temperature was increased to the range 40 to 50 °C. The pH value was adjusted to 8 to 9 and stirred for 30 min. Then, the pH value of reaction system was adjusted to between 2 and 3 with 0.6 mL 36.5% (mass fraction) of hydrochloric acid. Next, 8% (the ratio of PVA to dry basis starch) polyvinyl alcohol was placed in the flask, and a total of 1.5% ammonium persulfate solution (10%, mass fraction) was added dropwise and stirred for 1 h. The temperature was increased to 60 to 70 °C, and a total of 0.2% borax was added. After 30 min of stirring, a certain amount of CMC (0%, 0.25%, 0.375%, 0.5%, and 0.75%, with respect to the solution mass) was added and stirred. The mixture was cooled to room temperature to obtain adhesive A.

The pre-polymer was added in the required amount to the previously weighed adhesive A (12:100, mass ratio). The mixture was thoroughly stirred with a glass rod for several minutes to obtain adhesive B.

The viscosity of adhesive was measured with a rotating viscometer (NDJ-5S, Yueping; Shanghai, China). The spinning rate was 30 rpm at 20 ℃.

The pH value and solids content of adhesive were determined according to the National Standard of the People's Republic of China GB/T 14074 (2006). Because of the high viscosity of adhesive B, the viscosity and pH value of adhesive B were not measured adequately.

Plywood preparation

Three-layer plywood panels were fabricated by applying adhesive A and adhesive B to the surface (double sides) of poplar veneer at a spread rate of 300 g/m^2. The stacked veneers were pre-pressed before being hot-pressed, and the parameters of hot-pressing were as follows: pressure, 3 MPa; temperature, 110 ℃, and time, 3 min 50 s.

Bonding strength of plywood

The bonding strength of plywood was determined by mechanical testing machine (CMT5504, SANS; Shenzhen, China) in accordance with the National Standard of China GB/T 17657 (2013) for Type II plywood. That is, six plywood panels specimens with dimensions of 100 mm × 25 mm were soaked in water at 63 ± 2 ℃ for 3 h and then dried at room temperature for 10 min before the bonding strength test was performed. The bonding strength was calculated according to Eq. (1), and the results of each panel were averaged from six specimens.

$$\text{Bonding strength(MPa)} = \frac{\text{Tensive force(N)}}{\text{Gluing area(mm}^2)} \tag{1}$$

Differential scanning calorimetry (DSC)

The curing temperature of the adhesive was characterized by differential scanning calorimetry (D204, NETZSCH; Germany). High purity indium was used to calibrate the calorimeter, and an empty high-pressure crucible was used as the reference. Adhesive samples were quickly sealed in a high-pressure crucible and heated from room temperature to 180 ℃ at a rate of 5 ℃/min under a nitrogen atmosphere (flow rate 30

mL/min). The cure temperature was calculated by NETZSCH DSC software. All measurements were repeated two or three times.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out to determine the thermal stability of the adhesives. The adhesive was dried at 120 ℃ for 3 h, milled into a homogenous powder, and loaded into an 85 μL aluminum oxide pan. The pan was heated from room temperature to 600 ℃ at a rate of 10 ℃/min under an argon atmosphere (flow 40 mL/min). The sample weight was plotted as a function of temperature for all samples, and its first derivative was used for the analysis.

Scanning electron microscopy (SEM)

Plywood samples with adhesive A (dry basis) and adhesive B (dry basis) after dry bonding strength testing were characterized with a FEI Quanta 200 (Phillips, Netherlands). The SEM was operated at an accelerating voltage of 20 kV. Samples were coated with gold under a vacuum before testing.

Statistical analysis

The data were evaluated with Minitab 16 and reported as the mean value ± standard deviation of the replication. A single factor variance analysis was carried out to differentiate significant differences among mean values of the data according to the least significant difference criteria with a 95% confidence level ($P<0.05$).

RESULTS AND DISCUSSION

Effect of CMC Addition on the Physicochemical Properties of Adhesive A

Pure starch adhesive had a low viscosity and solids content (as shown in Table 1), which had a negative effect on the plywood fabrication. The CMC was added in the preparation process to obtain adhesive A. The influence of CMC was investigated, and the results are shown in Figs. 1 and 2.

Table 1. Physical and Chemical Properties of Pure Starch Adhesive

Color	pH	Solids content (%)	Viscosity (mPa·s)
Milky	3.70±0.12	25.79±0.06	31.55±0.25

Data in the table are means ± standard deviation.
Average of duplicate measurements, n=3.

The viscosity of adhesive A increased with an increase in CMC, as shown in Fig. 1. When the CMC addition was less than 0.4%, the viscosity increased very slowly. The viscosity showed the same trend, but it rapidly increased as the CMC addition exceeded 0.4%.

At a CMC addition of 0.75%, the viscosity of adhesive A was greater than 400 mPa·s. The viscosity was so high that CMC was unevenly dispersed in the solution, resulting in application problems in the preparation of plywood. Therefore, the CMC addition should not exceed 0.75%.
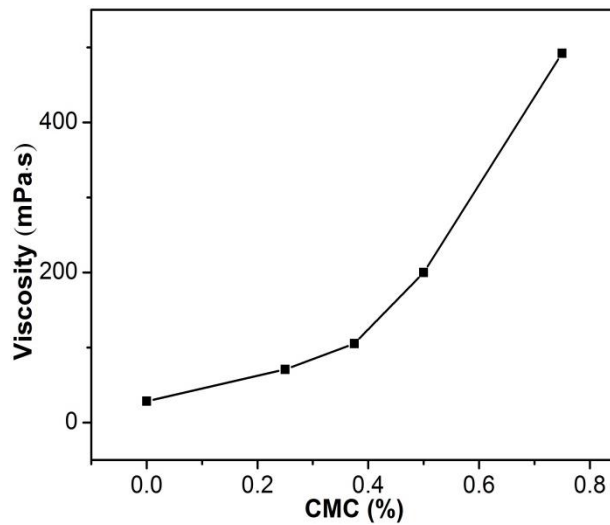
Fig. 1. The effect of CMC addition on the initial viscosity of adhesive A
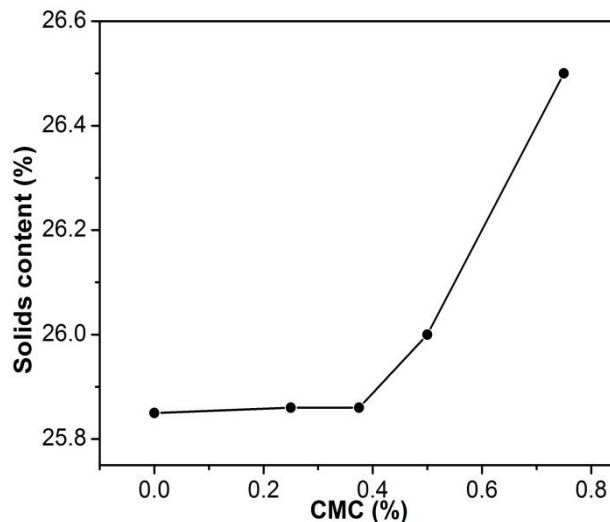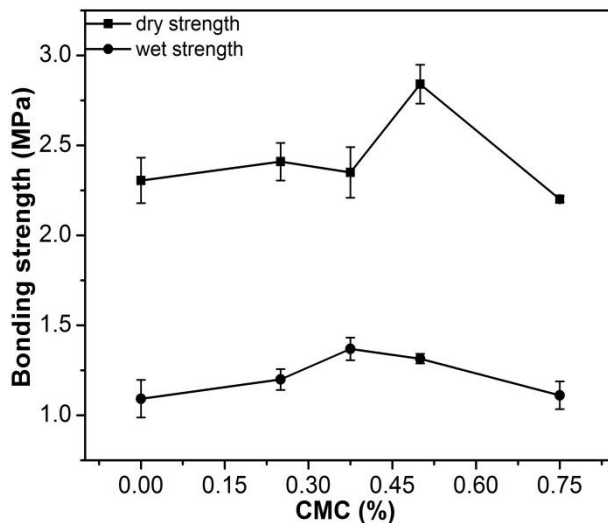

Fig. 2. The effect of CMC addition on the solids content of adhesive A

The addition of CMC also influenced the solids content of adhesive A. The solids content increased with increasing CMC addition (Fig. 2). The solids content remained almost constant when the addition was less than 0.4%. At a concentration greater than 0.4%, the solids content showed an upward tendency, but it was still less than 27%. Also, the CMC addition made the pH value (3.8 to 4.1) increase slightly and had little impact on the color (milky) of adhesive A. Given the viscosity of the adhesive, CMC addition in the range of 0.25 to 0.50% was appropriate.

Effect of CMC Addition on the Bonding Strength of Plywood
        PAPI was used to prepare pre-polymer. According to previous work by the authors, when the addition was 8%, the wet bonding strength met the GB/T 17657-2013 requirement. To avoid the influence of bonding strength caused by other factors, we did not adopt 8% addition. When the pre-polymer addition ranged from 12% to 20%, the wet

bonding strength increased slightly. Besides, PAPI is a relatively expensive chemical agent. So, we adopted 12% addition of pre-polymer. On the basis of 12% pre-polymer addition, the effect of CMC addition on the bonding strength of plywood was investigated. The results are shown in Fig. 3.

Fig. 3. The effect of CMC addition on the bonding strength of plywood (Mean ± SD)

Starch-based adhesive is an environmentally friendly adhesive compared to commercial formaldehyde-based wood adhesives. Bonding strength of starch-PVA-borax adhesive, urea-formaldehyde (UF) resin adhesive, and starch-based adhesive each must meet the same standard. Therefore, in this paper, the bonding strength of UF and starch-PVA-borax adhesives were not determined.

The dry and wet bonding strength of pure starch adhesive were 1.7 MPa and 0 MPa, respectively (data not shown in Fig. 3). The wet bonding strength increased with CMC addition from 0 to 0.375%, and decreased with a concentration from 0.375 to 0.75%. The maximum value (~1.4 MPa) was 40% higher than that of plywood prepared under 0% CMC (~1.0 MPa). The dry shear strength showed the same trend as did the wet strength, given the overlap of standard deviation (SD) data. The maximum value was obtained with different CMC addition (0%, 0.25%, 0.375%, 0.5%, and 0.75%) compared with that of wet strength. The middle and/or surface veneer of specimens were broken rather than the failure of the adhesive layer during the course of the dry bonding strength test. Considering the above discussion, the optimal CMC addition was 0.375%.

Effect of CMC Addition on the Curing Temperature of Adhesives

The non-isothermal DSC results for adhesives with varying CMC addition are presented in Fig. 4 and Table 2.

For adhesive A (without pre-polymer), the peak temperature of the DSC curves ranged from 102.1 to 106.5 °C and decreased after adding CMC. Water, starch, PVA, and borax were components of adhesive A, and the curing behavior mostly depended on the interaction between these components.

The added CMC increased the initial viscosity of the adhesive and improved the interaction of water, starch, PVA, and borax, resulting in a decrease in the curing temperature and the evolution of a large amount of reaction heat.
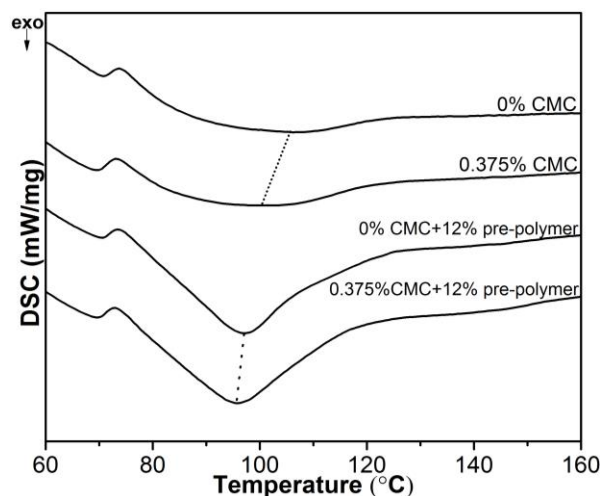
Fig. 4. DSC curves of the adhesive

Table 2. DSC Analysis Parameters

CMC (%)	Pre-polymer addition (%)	Onset temperature (ºC)	Peak temperature (ºC)	End temperature (ºC)	Reaction enthalpy (J/g)
0	—	74.5±0.2[a]	106.7±0.15[a]	122.9±0.35[a]	-24.44±0.15[a]
0	12	74.2±0.0[a]	96.7±0.0[a]	112.8±0.40[a]	-50.27±0.48[a]
0.375	—	73.7±0.05[a]	102.1±0.1[a]	121.0±0.50[a]	-25.94±0.25[a]
0.375	12	73.6±0.10[a]	95.7±0.0[a]	116.2±0.45[a]	-51.15±0.05[a]

Data in the table are means ± standard deviation.
Average of duplicate measurements,n=2.
Values in the same column with different letters are significantly different ($P<0.05$).

For adhesive B, it was interesting to note that there were slight differences in the onset temperature. For DSC analysis, the test was repeated, the results were normalized with reliable analysis software supplied by NETZSCH Company, and mathematical statistics analysis was undertaken with Minitab 16. Additionally, the DSC instrument had a resolution with 0.1 ºC. Therefore, the slight differences were attributed to the CMC addition.

The peak temperature of adhesive B became lower than that of adhesive A as the CMC was added. When the amount of CMC was 0% and 0.375%, the curing temperatures were 96.7 and 95.7 ºC, respectively. PAPI is the main ingredient of the pre-polymer, which contains many isocyanate groups (-NCO). Chemical reactions with the isocyanate group are extremely reactive, especially with the active hydrogen-containing materials. The influence of chemical reactions on the curing behavior is much stronger than that of physical force between different components. In the adhesive system, water, starch, and PVA have active hydrogen, so the curing behavior of adhesive B relies on the chemical reaction between isocyanate and active hydrogen-containing substances.

In this experiment, one kind of pre-polymer at one addition (12%) was used for a consistent degree of chemical reaction. The different curing temperature was attributed to the addition of CMC. PAPI is hydrophobic and starch is hydrophilic, so their compatibility may not be good. However, CMC can improve the interfacial properties of polymers (Cao *et al.* 2001). Therefore, the addition of CMC promoted the mixture of

PAPI pre-polymer and starch and increased the interaction between different components, leading to a lower curing temperature for adhesive B compared to adhesive A.

Thermal Stability Analysis

The thermal stability of the adhesives and pure components were investigated in detail by TGA and derivative thermogravimetry (DTG), as shown in Figs. 5, 6, and 7. Polyvinyl alcohol, CMC, and borax are the components of adhesive A. Pre-polymer (12%) was added in the preparation process of adhesive B. The thermal stability of PAPI pre-polymer, native starch (NS), PVA, CMC, adhesive A, and adhesive B were characterized by TGA. As shown in Fig. 7, the decomposition temperature of PAPI pre-polymer, CMC, native starch, and PVA were 362, 277, 307, 284, and 423 °C, respectively. The residual masses were 35.51%, 48.70%, 21.53%, and 11.77%, respectively.
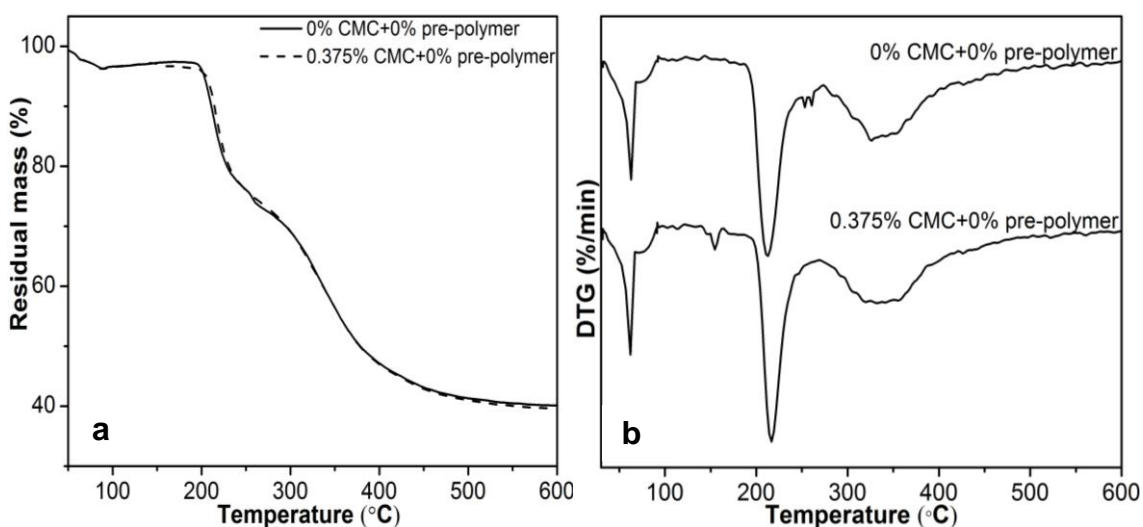

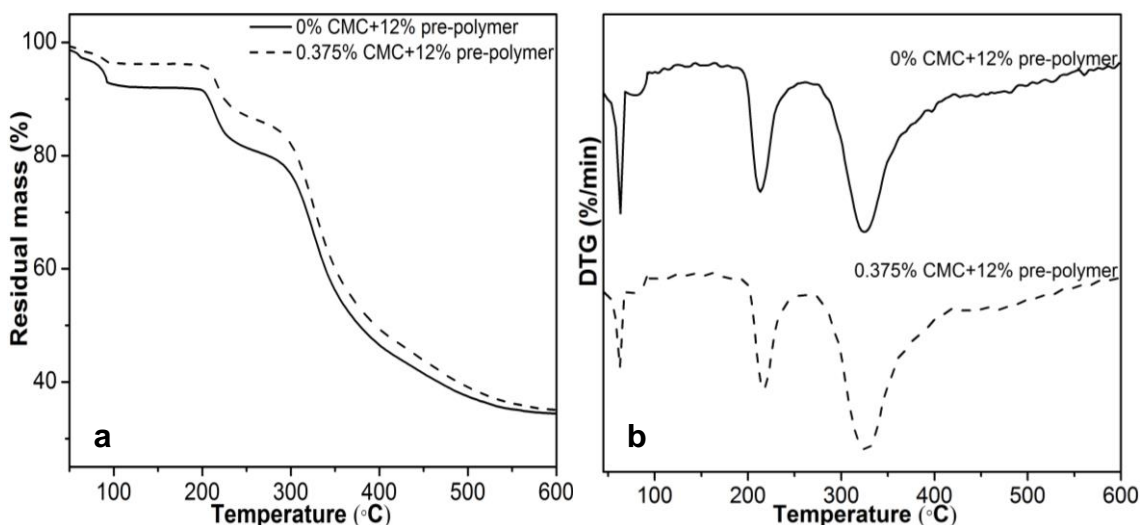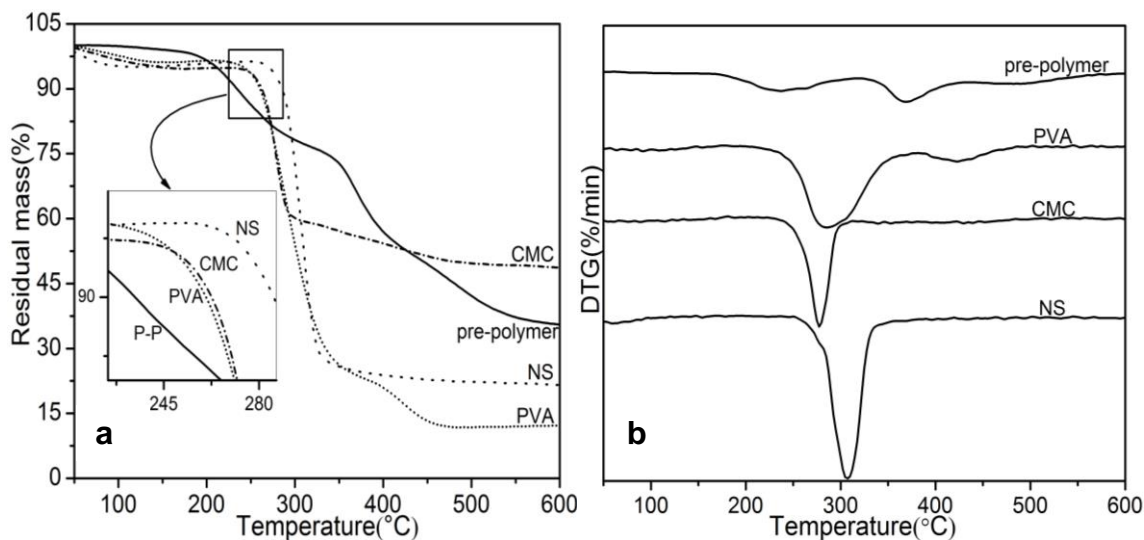**Fig. 5.** (a) TGA and (b) DTG curves of adhesive A

Fig. 6. (a) TGA and (b) DTG curves of adhesive B

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Fig. 7. (a) TGA and (b) DTG curves of pure components

For adhesive A, there were three weight losses, at 62, 215, and 330 °C. The first weight loss was due to the residual water being evaporated from the sample. The weight loss at 215 °C may have been the degradation of PVA due to hydrolysis in the solution. The third weight loss may be due to the decomposition of native starch, as confirmed by a comparison of Figs. 5 and 6. In the preparation process, hydrochloric acid was used to adjust the pH value. According to previous studies (Wang and Wang 2001; Lawal 2004; Sandhu *et al*. 2007; Wang *et al*. 2007; Zuo *et al*. 2014), the relative degree of crystallinity of starch granules increased after acid treatment. The increase of crystallinity is attributed to the amorphous regions being preferentially attacked and rapidly hydrolyzed below the gelatinization temperature, resulting in an increase in the decomposition temperature of native starch.

For adhesive B, three weight losses occurred (62, 217, and 325 °C). The first was attributed to the loss of moisture of the sample, and the second may correspond to the decomposition of PVA. For the third, there was an obvious difference compared to the TGA curve of adhesive A. The lower weight loss temperature was due to the interaction of starch, PVA, and pre-polymer. Starch, PVA, and water have active hydrogen atoms. Pre-polymer contains reactive isocyanate groups, which are sensitive to moisture. The isocyanate group reacts with a hydroxyl group (or H_2O) to form carbamate group, which has poor thermal stability (or gives off CO_2), resulting in the lower weight loss temperature and low residual mass (Chattopadhyay and Webster 2009; Zhao *et al.* 2011).

In addition, the change of thermal stability had little influence on the bonding strength. The relative study showed that increasing the NCO:OH ratio had an influence on side product formation. The presence of excess isocyanate in the reaction system may result in side reactions that produce allophanate and biuret.

Additionally, isocyanates may, under appropriate conditions, react with themselves to give the dimer uretidione or the trimer isocyanurates (Chattopadhyay and Webster 2009). The side product formation has a positive effect on the bonding strength improvement (Liu 2012). The finding was consistent with the results of bonding strength plywood.
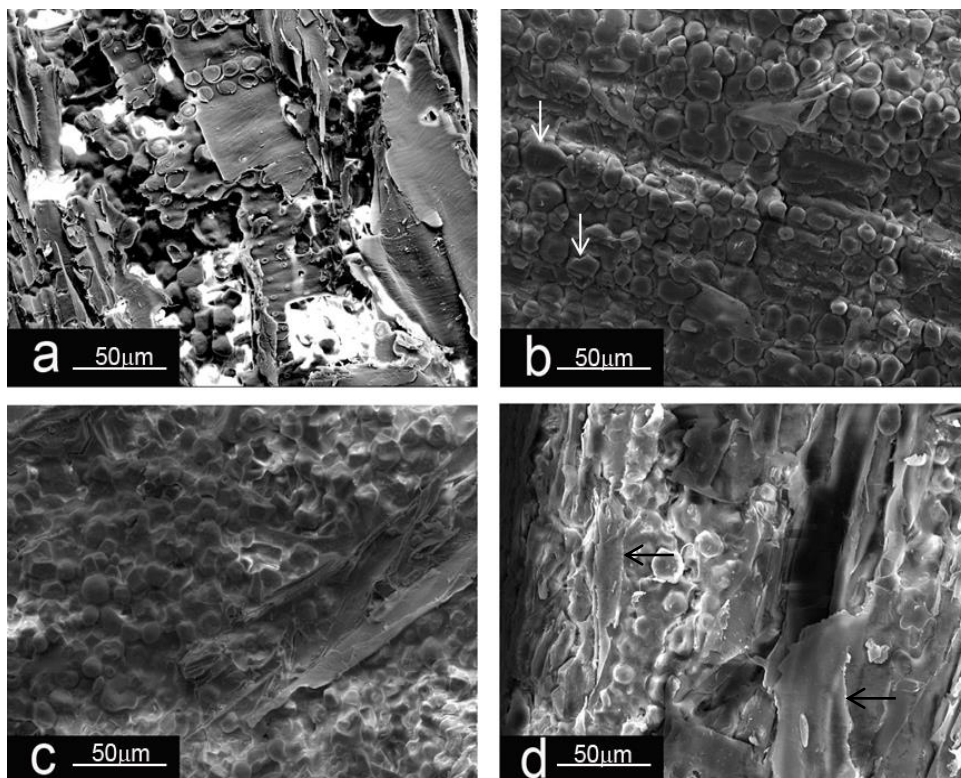
Fig. 8. Morphology of the bonding interface. (a) 0% CMC + 0% P-P, (b) 0.375% CMC + 0% P-P, (c) 0% CMC +12% P-P, and (d) 0.375% CMC + 12% P-P

Scanning Electron Microscopy

Scanning electron microscopy (SEM) is useful for studying the morphology of almost all kinds of samples (Zhang *et al.* 2013). The bonding interface plays an important role in the bonding process (Breschi *et al.* 2008). For adhesive A, CMC addition had little effect on the dispersion of adhesive on the bonding interface. As Figs. 8a (0% CMC + 0% P-P) and 8b (0.375% CMC + 0% P-P) show, there were a large number of starch granules at the interface. This was consistent with the preparation parameters for adhesive A. Starch granules were closely packed, and there were no obvious gaps between the granules. Most starch granules were round, with a diameter of approximately 10 μm. The morphology of some granules (denoted by white arrows in Fig. 8b) changed, which can be confirmed from their size and shape. Starch has a hypo-crystalline structure, composed of a crystal region and non-crystal region. The amorphous regions of starch granules were preferentially degraded in the process of acid hydrolysis, resulting in the changes to starch granules (Zhang and Yang 1997; Ma *et al.* 2004).

For adhesive B, CMC added in the preparation process improved the dispersion at the interface. As shown in Fig. 8d, the adhesive layer exhibited a continuous distribution, and only a small portion of starch granules remained unchanged. The clear difference between Fig. 8c (0% CMC + 12% P-P) and Fig. 8d (0.375% CMC + 12% P-P) confirmed that CMC addition improved the interface properties of the starch adhesive and pre-polymer as well as the dispersion of the adhesive.

CONCLUSIONS

1. The initial viscosity and solids content of pure starch were improved by adding CMC.

2. At a fixed pre-polymer concentration, the bonding strength of adhesive A and adhesive B was improved; the optimal concentration of CMC was 0.375%.

3. The curing behavior of adhesive A mostly relied on the interaction between different components, and that of adhesive B depended on the reaction of hydro-containing substances and isocyanate groups in the adhesive.

4. With the help of CMC, the viscosity of adhesive A increased and the interaction between the components was enhanced, reducing the curing temperature.

5. For adhesive B, CMC addition decreased the curing temperature and improved the interfacial properties and the compatibility between the starch adhesive and the PAPI pre-polymer.

ACKNOWLEDGMENTS

REFERENCES CITED

Basta, A. H., El-Saied, H., and Lotfy, V. F. (2013). "Performance of rice straw-based composites using environmentally friendly polyalcoholic polymers-based adhesive system," *Pigment & Resin Technology* 42(1), 24-33.

Breschi, L., Mazzoni, A., Ruggeri, A., Cadenaro, M., Lenarda, R. D., and Dorigo, E. D. S. (2008). "Dental adhesion review: Aging and stability of the bonded interface," *Dental Materials* 24(1), 90-101.

Cao, Y., Li, H. L., and Xu, X. (2001). "Influence of block structure on conformation and properties of carboxymethyl cellulose series of polymeric surfactants," *Acta Polymerica Sinica* 1(1), 3-7.

Chattopadhyay, D. K., and Webster, D. C. (2009). "Thermal stability and flame retardancy of polyurethanes," *Progress in Polymer Science* 34(10), 1068-1133.

Dai, Y. S., and Zhao, W. Y. (2011). "Composite starch adhesive research progress," *Chemistry and Adhesion* 33(5), 51-53.

Desai, S. D., Patel, J. V., and Sinha, V. K. (2003). "Polyurethane adhesive system from biomaterial-based polyol for bonding wood," *International Journal of Adhesion & Adhesives* 23(5), 393-399.

Gao, Z. H., Wang, W. B., Zhao, Z. Y., and Guo, M. R. (2011). "Novel whey protein-based aqueous polymer-isocyanate adhesive for glulam," *Journal of Applied Polymer Science* 120(1), 220-225.

GB/T 14074. (2006). "Testing methods for wood adhesives and their resins," Chinese National Standardization Management Committee, China.

GB/T 17657. (2013). "Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels," Chinese National Standardization Management Committee, China.

Gong, Y. M., Wang, H. G., Dan, W. H., Mi, Z. J., Hu, S., and Jia, S. P. (2009). "Present situation of modified starch and its development," *China Leather* 38(5), 46-49.

Guo, R. Z., Gao, Z. H., Zhang, L., and Wang, X. M. (2010). "Application and progress of biomass formaldehyde scavengers," *Adhesion in China* 40(4), 64-69.

Imam, S. H., Gordon, S. H., Mao, L. J., and Chen, L. (2001). "Environmentally friendly wood adhesive from a renewable plant polymer: Characteristics and optimization," *Polymer Degradation and Stability* 73(3), 529-533.

Imam, S. H., Mao, L. J., Chen, L., and Greene, R. V. (1999). "Wood adhesive from crosslinked poly (vinyl alcohol) and partially gelatinized starch: preparation and properties," *Starch‑Stärke* 51(6), 225-229.

Kaur, B., Ariffin, F., Bhat, R., and Karim, A. A. (2012). "Progress in starch modification in the last decade," *Food-Hydrocolloids* 26(2), 398-404.

Lawal, O. S. (2004). "Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid-thinned new cocoyam (Xanthosoma sagittifolium) starch," *Food Chemistry* 87(2), 205-218.

Li, D. F., Li, H. L., Lin, W., and Mu, C. D. (2007). "Research and application of modified starch," *China Leather* 36(1), 32-37.

Li, J. L., Liu, Q. X., Xu, L. J, and Xu, W. C. (2010). "The application and research progress of carboxymethyl cellulose in paper printing & packing materials," *Packing Engineering* 31(17), 22-27.

Liu, G. S. (2002). "Production and application of sodium carboxymethyl cellulose," *Liaoning Chemical Industry* 31(10), 445-447.

Liu, Y. J. (2012). *Polyurethane Resin and its Application,* Chemical Industry Press, Beijing.

Liu, Y. J. (2013). *Handbook of Raw Materials and Additives for Polyurethanes*, Chemical Industry Press, Beijing.

Lu, L. M., and Zhang, L. F. (2006). "The application of starch as wood adhesive," *Jiangsu Chemical Industry* 34(17), 19-21.

Ma, X. F., and Yu, J. G. (2004). "Studies on the properties of formamide plasticized-thermoplastic starch," *Acta Polymerica Sinica* 1(2), 240-245.

Moubarik, A., Pizzi, A., Allal, A., Charrier, F., and Charrier, B. (2009). "Cornstarch and tannin in phenol-formaldehyde resins for plywood production," *Industrial Crops and Products* 30(2), 188-193.

Que, Z. L., Furuno, T., Katoh, S., and Nishino, Y. (2007). "Effects of urea-formaldehyde resin mole ration the properties of particleboard," *Building and Environment* 42(3), 1257-1263.

Sandhu, K. S., Singh, N., and Lim, S. T. (2007). "A comparison of native and acid thinned normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties," *LWT- -Food Science and Technology* 40(9), 1527-1536.

Tan, H. Y., Zhang, Y. H., and Weng, X. L. (2011). "Preparation of the plywood using starch-based adhesives modified with blocked isocyanates," *Procedia Engineering* 15, 1171-1175.

Wang, L., and Wang, Y. J. (2001). "Structures and physicochemical properties of acid‑hinned corn, potato and rice starches," *Starch-Stärke 53*(11), 570-576.

Wang, S. J., Yu, J. L., Yu, J. G., Chen, H. X, and Pang, J. P. (2007). "The effect of acid hydrolysis on morphological and crystalline properties of *Rhizoma dioscorea* starch," *Food Hydrocolloids* 21(7), 1217-1222.

Wang, Z. J., Li, Z. F., Gu, Z. B., Hong, Y., and Cheng, L. (2012). "Preparation, characterization and properties of starch-based wood adhesive," *Carbohydrate Polymers* 88(2), 699-706.

Wu, G. F., Sun, E. H., Huang, H. Y., Chang, Z. Z., and Xu, Y. D. (2013). "Preparation and properties of biodegradable planting containers made with straw and starch adhesive," *BioResources* 8(4), 5358-5368.

Xu, W. J., and Dai, H. Q. (2001). "Modified starch in paper industry," *Heilongjiang Pulp & Paper* 29(3), 24-27.

Zhang, B. S., and Yang, L. S. (1997). "Study on the crystallinity of pregelatinized corn starch," *Journal of South China University of Technology (Natural Science)* 25(2), 107-111.

Zhang, Y. H., Gu, J. Y., Tan, H. Y., Shi, J. Y., Di, M. W., Zuo, Y. F., and Qiu, S. (2013). "Preparation and characterization of film of poly vinyl acetate ethylene copolymer emulsion," *Applied Surface Science* 276, 223-228.

Zhang, Y. H., Qiu, S, Zuo, Y. F., Zhao, Z., Tan, H. Y, and Gu, J. Y. (2012). "Study on preparation of organic montmorillonite modified polyurethane adhesive by orthogonal experimental design," *Advances in Information Sciences and Service Sciences* 4(22), 533-537.

Zhao, S. F., Qiu, S. C., Zheng, Y. Y., Cheng, L., and Guo, Y. (2011). "Synthesis and characterization of kaolin with polystyrene via in-situ polymerization and their application on polypropylene," *Materials & Design* 32(2), 957-963.

Zuo, Y. F., Gu, J. Y., Tan, H. Y., Qiao, Z. B., Xie, Y. H., and Zhang, Y. H. (2014). "The characterization of granule structural changes in acid-thinning starches by new methods and its effect on other properties," *Journal of Adhesion Science and Technology* 28(5), 479-489.