MODIFIED NANOCRYSTALLINE CELLULOSE FROM TWO KINDS OF MODIFIERS USED FOR IMPROVING FORMALDEHYDE EMISSION AND BONDING STRENGTH OF UREA-FORMALDEHYDE RESIN ADHESIVE

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In this study, nanocrystalline cellulose (NCC) was used for increasing the bonding strength of urea-formaldehyde (UF) resin adhesive, with a reduction of formaldehyde (HCHO) emissions. The surface of NCC was modified by 3-aminpropyltriethoxysilane (APTES) and 3-methacryloxy-propyltrimethoxysilane (MPS) for the lack of compatibility with UF resin adhesive. The modified NCC was characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TG), and wetting property. HCHO emission and bonding strength of the UF resin adhesive with modified NCC were tested according to Chinese National Standards GB/T 17657-1999 and GB/T 9846-2004. The results of XRD, TG, and wetting property from NCC modified by APTES showed more significant improvements than that from NCC modified by MPS. The HCHO emission of UF resin adhesive with 1.5% NCC modified by APTES decreased by 53.2% and bonding strength increased by 23.6%, while the results from the NCC modified by MPS were 21.3% and 7.0%, respectively.

Keywords: Nanocrystalline cellulose; Urea-formaldehyde resin adhesive; Formaldehyde emission; Bonding strength

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INTRODUCTION

UF resin adhesive is the major adhesive of the timber industry because of its high bonding strength and low cost. With the increasing concern about environmental pollution from the HCHO of the UF resin adhesive, polymer composites fabricated from natural fibers used for reducing HCHO emission have evoked great interest. Using environmentally friendly polymers, such as modified NCC, is the most promising area in reducing the amount of HCHO (Levendis 1992).

Lots of materials have been studied in order to reduce the HCHO emission of UF resin adhesive. Amide-containing biopolymers and sludge from pulp mills were added during the synthesis of UF resin to decrease the emission of free formaldehyde (Basta et al. 2011; Migneault et al. 2011). Hydrolytic stability of modified UF resin was investigated as a way of lowering the HCHO emission of cured UF resin (Abdullah et al. 2009). Most modifiers used in the reduction of HCHO emission have been found to decrease bonding strength, and many studies concerning the enhancement of bonding strength and HCHO emission have been conducted. The effects of UF resin adhesive modified EPU, pMDI, and melamine-bridged alkyl resorcinol to the internal bonding strength and HCHO emission were studied (Zhang et al. 2011; Dziurka et al. 2010; Pan et al. 2010; Hse et al. 2010). Also, the influences of acrylamide copolymerization in HCHO emission and bonding strength of UF resin adhesive were investigated; the results showed that the HCHO emission was reduced (Abdullah et al. 2010). The mechanical properties of UF resin reinforced by pine needles and *Grewiaoptiva* fiber were investigated; the results suggested that pine needles and *Grewiaoptiva* fiber were potential candidates for use in natural fiber reinforced polymer composites (Thaku et al. 2010; Singha et al. 2009). The internal bonding strength of wood particleboard bonded with UF resin modified by fluorinated polyethers was enhanced obviously (Mansouri et al. 2007). There were relationships between UF resin ratios and physical properties of particleboard made from vine prunings (Yasar et al. 2010).

The thermal stability of modifiers affected the thermal stability of UF resin adhesive. Thermal behaviors of pure UF-resin and UF-resin modified by nano-SiO_2 and melamine were investigated with thermogravimetric analysis (Samarzija-Jovanovic et al. 2011; Siimer et al. 2010). The UF resin adhesive modified by various alcohols was detected and was improved by isopropynol as modifier (Kutra et al. 2004).

Inorganic and synthetic organic materials used for reducing the emission of HCHO led to the reduction of bonding strength and environmental pollution to a certain extent. As a kind of natural and environmental friendly polymer, NCC has attracted much attention for its renewable and environmentally benign nature and its outstanding mechanical properties (Hubbe et al. 2008). UF resin adhesive modified by NCC was able to reduce the free formaldehyde emission, as well as improve the bonding strength without pollution.

EXPERIMENTAL

Materials

Poplar panels were purchased from Hebei province, China. The original NCC was prepared by acid hydrolysis in the laboratory, which showed a length of 300 to 400 nm and a diameter of 30-50 nm. The modifiers, APTES and MPS, were analytical grade and were used as received without any further purification. UF resin adhesive was prepared by JINYUBEIMU Company in Beijing. The formaldehyde/urea molar ratio was 1.1 during the preparation of the UF resin adhesive. There was 61.2% UF resin in the adhesive and 38.8% water. And ammonium chloride was used for the curing agent of UF resin adhesive.

Methods

Modification of NCC

APTES and MPS were used to modify the original NCC, respectively. Ethanol was used as a solvent for the modifiers. Four kinds of solutions for each modifier were prepared. The concentrations of modifier in each kind of solution were 2, 4, 6, and 8% (v/v). For the hydrolysis of modifiers, the pH of the solutions was decreased to the range 3-4 using hydrochloric acid. APTES and MPS were hydrolyzed for 5 to 10 min until the solutions turned pellucid. 1 g NCC was modified by 100 ml of the ethanol and modifier solution. The modification was operated at 60 °C for 3 h.

Accession of modified NCC to UF resin adhesive

The modified NCC was added into UF resin adhesive at concentrations of 0.5, 1.0, 1.5, and 2% (w/w). The modified NCC in UF resin adhesive was dispersed by an ultrasonic probe with a power of 800 w. The ultrasonic was turned on for 10 seconds and was turned off for 5 seconds in one period; the total time of the intermittent ultrasonic was 15 min.

Preparing plywood from Poplar panels

Three pieces of *Poplar* panel were used to prepare one piece of plywood with 60 g modified UF resin adhesive and one piece of *Poplar* panel was 1.5 mm thick. Two kinds of modified NCC and four different dosages for each kind of modified NCC made up eight groups of plywood. One control group of plywood was operated with 60 g UF resin adhesive without modified NCC. The temperature of the preparation process was 120 °C, and the pressure was 1.0 MPa. The total time of the preparation for each piece of plywood was 5 min and the press time was 280 s.

Test of the plywood prepared by UF resin adhesive with modified NCC

The HCHO emissions of UF resin adhesive with modified NCC were detected by the method of Chinese National Standard GB/T 17657-1999 as follows: plywood prepared by the UF resin adhesive with modified NCC and the solution of acetylacetone and ammonium acetate were put in a hermetic container. Dimethylpyridine was generated by HCHO from UF resin adhesive and acetylacetone, and the absorbance was measured at a wavelength of 412 nm for the emission of HCHO.

The bonding strength of the UF resin adhesive was tested according to the Chinese National Standard GB/T 9846-2004 as follows: plywood prepared by the UF resin adhesive with modified NCC was put in water at the temperature of 63 °C for 3 h. The bonding strength was tested after cooling for 10 min.

RESULTS AND DISCUSSION

Characterization of Modified NCC

Thermal stability of modified NCC

Different modifications had different effects on the thermal stability of NCC (Eyholzer et al. 2010). The thermal behavior of the NCC modified by APTES and MPS was further investigated by TG. TG curves shown in Fig. 1 indicate that significant weight loss of modified NCC occurred as the temperature was increased from 280 °C to 320 °C. The loss was attributed to the thermal degradation of NCC modified by APTES and MPS. As APTES content increased, the TG peak in curves of modified NCC was raised by 12.3%, from 281.8 °C to 316.5 °C (shown in Fig. 1A). The thermal stability of NCC decreased significantly when the content of APTES was more than 4%. The TG peak in curves of NCC modified by MPS increased from 285.3 °C to 293.7 °C, which is indicated in Fig. 1B. The degradation temperature of the NCC modified by MPS was lower than that modified by APTES.

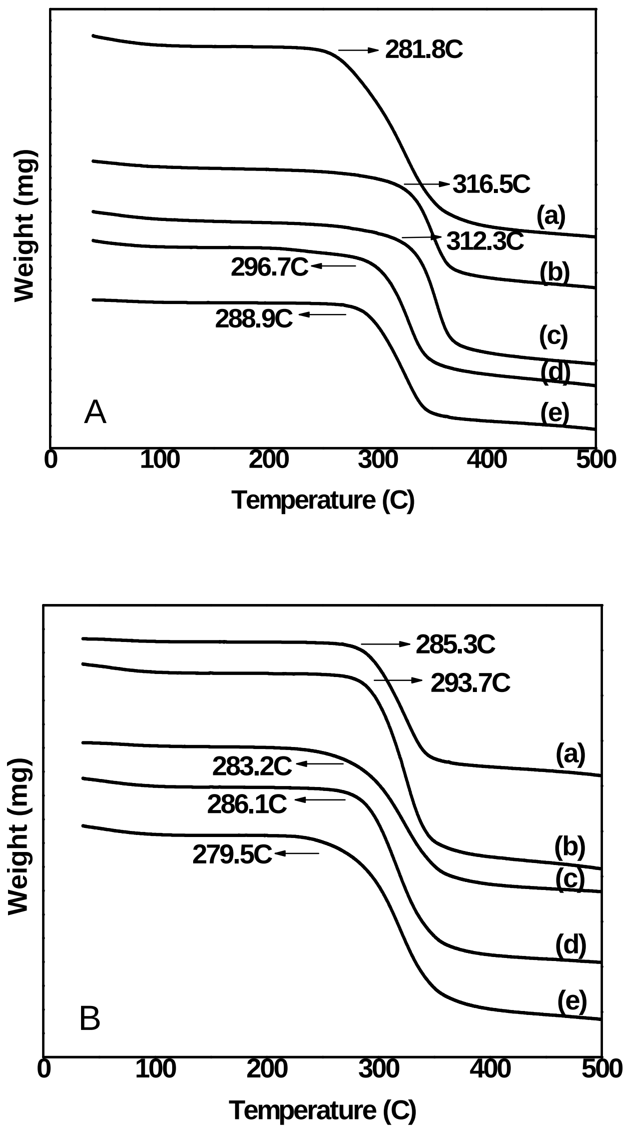

Fig. 1. Thermal stability of modified NCC: A: NCC modified by APTES: (a) original NCC; (b) 2%; (c) 4%; (d) 6%; (e) 8%; B: NCC modified by MPS: (a) original NCC; (b) 2%; (c) 4%; (d) 6%; (e) 8%

XRD patterns of modified NCC

The XRD patterns and crystallinity of the original NCC and modified NCC are shown in Fig. 2 and Table 1, respectively. The characteristic diffraction peaks at 2θ = 16.15° and 22.58° in Fig. 2 were assigned to the (101) and (002) planes of the cellulose type I. Figure 2a shows the XRD pattern of original NCC, which exhibited similar diffraction peaks with natural cellulose (Kuan-Chen et al. 2009). The diffraction pattern of cellulose was not affected by the lipophilic groups from APTES and MPS. The amorphous characteristics with peaks at 2θ = 16.15° and 22.58° were observed, as shown in Fig. 2b and c, respectively. The crystallinity of NCC showed a slight increase after the modification by APTES and MPS.

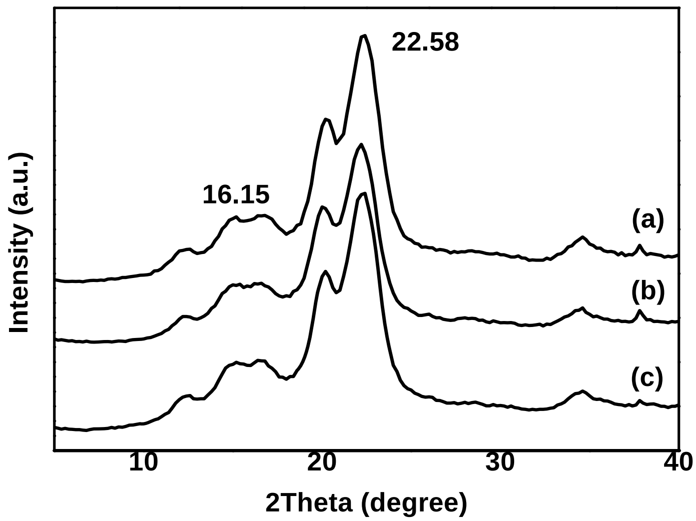

Fig. 2.XRD patterns of modified NCC: (a) original NCC, (b) NCC modified by MPS and (c) NCC modified by APTES

Table 1. Crystallinity of Modified NCC

Sample	a	b	c
Crystallinity (%)	46.9	49.0	48.5

Wetting property of modified NCC

Wetting properties of NCC can change as a consequence of chemical treatment. The wetting properties between modified NCC and UF resin adhesive were indicated by the contact angle (CA) in this study. The NCC structure of a surface affects the macroscopic properties of the surface, such as wetting property (Barba et al. 2010). Contact angle determination is a simple technique for examining the immediate surface of solids, such as natural synthetic polymers. The hydroxyl groups of original NCC were replaced by lipophilic groups from APTES and MPS.

Wetting properties of the modified NCC, affected by the lipophilic groups from APTES and MPS, increased significantly. APTES showed an obvious role in reducing the contact angles of NCC, which are indicated in Fig. 3a and 3b. The CA left and CA right of NCC modified by APTES decreased from 87.2° and 86.7° to 66.5° and 66.9° when the concentrations of APTES was 4%, respectively. The increase in wetting property of this modified NCC was 26.4% when the content of APTES was 8%. The CA left and CA right of NCC modified by MPS decreased from 87.2° and 86.7° to 71.7° and 71.2° when the concentration of modifier was 4%, respectively. The wetting properties, improved by MPS, increased 24.1% when the content of MPS was 8%. This phenomenon showed that lipophilic groups played an important role in the dispersion of NCC.

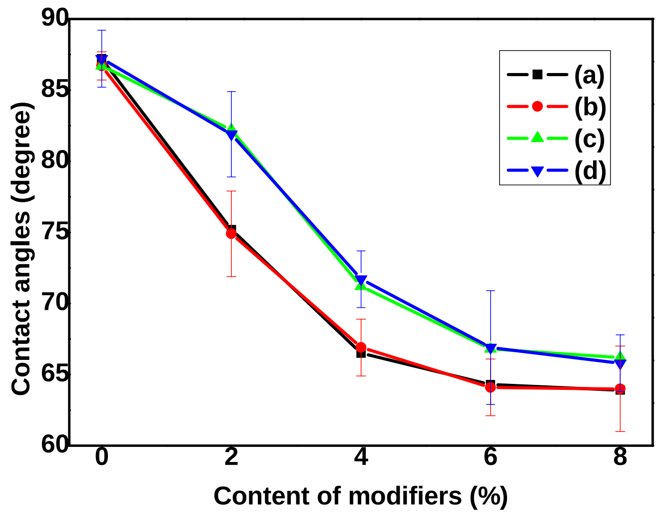

Fig. 3.CA of modified NCC: (a) CA left of NCC modified by APTES, (b) CA right of NCC modified by APTES, (c) CA left of NCC modified by MPS and (d) CA right of NCC modified by MPS

Effects of Modified NCC on UF Resin Adhesive

HCHO emission of UF resin adhesive affected by modified NCC

NCC modified by APTES and MPS resulted in different effects on HCHO emission, which are indicated in Fig. 4. The emission of HCHO from UF resin adhesive with modified NCC was reduced by physical adsorption and chemisorption without compromising internal bond strength of plywood. High ratio surface of the modified NCC was the main factor of physical adsorption which led to the decrease in HCHO. The covalent bonds and hydrogen bonds between NCC and HCHO were the main approaches of chemisorption for adsorbing the HCHO.

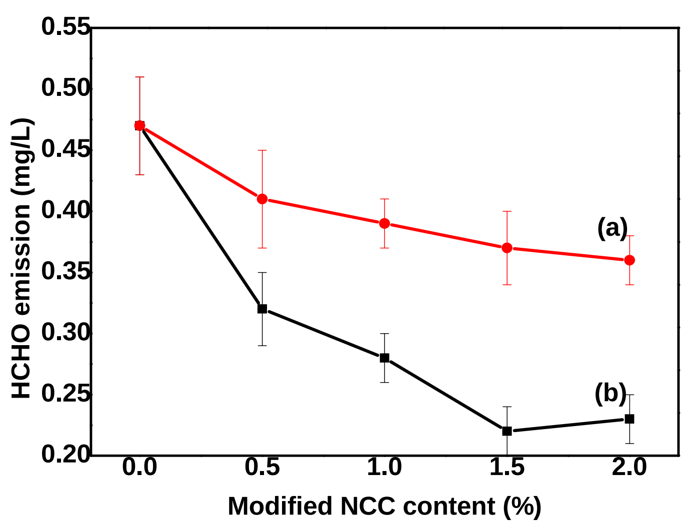

Fig. 4. HCHO emission of UF resin with modified NCC: (a) NCC modified by MPS, (b) NCC modified by APTES

The HCHO emission decreased from 0.47 mg/L of the original UF resin adhesive to 0.22 mg/L when the content of NCC modified by APTES was 1.5%, while the HCHO emission of the UF resin adhesive decreased 21.3% (from 0.47 mg/L to 0.37 mg/L) when the content of NCC modified by MPS was 1.5%. This phenomenon showed an excellent adsorption of HCHO, which was caused by the modification from APTES. The reunion of modified NCC destroyed the adsorption of HCHO when the content was more than 2.0% in UF resin adhesive.

Bonding strength of UF resin adhesive affected by modified NCC

Connections between modified NCC and UF resin adhesive improved the bonding strength. The modifiers APTES and MPS, which were used to modify NCC, led to two kinds of covalent bonds. The improvements of bonding strength were shown in Fig. 5.

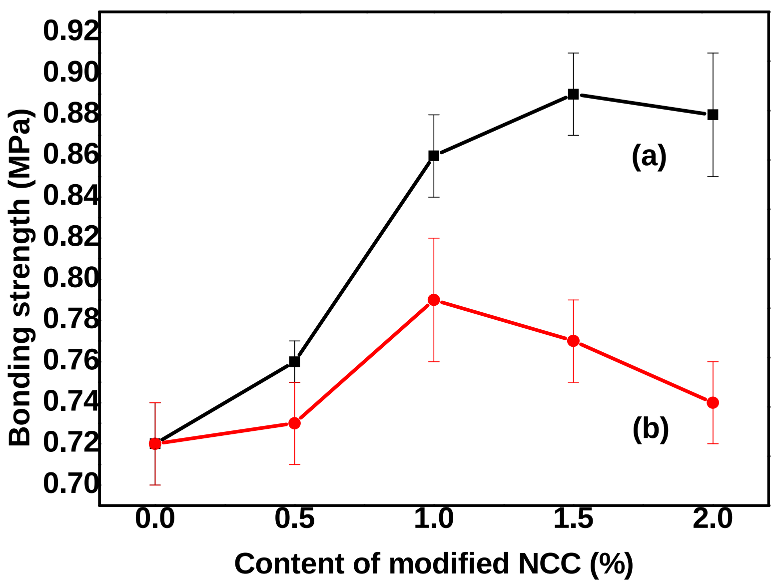

Fig. 5. Bonding strength of UF resin with modified NCC: (a) NCC modified by APTES, (b) NCC modified by MPS

The growth rate of the bonding strength slowed down as the concentration of modified NCC increased. With the presence of NCC modified by APTES, the bonding strength increased 23.6% (from 0.72 MPa of the virgin UF resin adhesive to 0.89 MPa when the content of modified NCC was 1.5%). The bonding strength of UF resin adhesive with the NCC modified by MPS increased 7.0% at a concentration of modified NCC of 1.5%. It was obvious that the contribution to bonding strength from modified NCC was reduced by its self-agglomeration, occurring when the content of NCC modified by APTES was more than 2.0% and the content of NCC modified by MPS was more than 1.5%.

CONCLUSIONS

1. Lipophilic groups from APTES and MPS led to different effects in modified NCC. The compatibility between modified and UF resin adhesive reflected by contact angles increased 26.4% after the modification from APTES, and that of the NCC modified by MPS increased 24.1%. Thermal stability of the NCC modified by APTES increased 12.3%, while the degradation temperature of modified NCC from MPS increased from 285.3 °C to 293.7 °C. The crystallinity of NCC showed a slight increase after modifications.
2. Physical adsorption and chemisorption were the main approaches for decreasing HCHO emission of UF resin adhesive. The modification from APTES and MPS affected the abilities of physical adsorption and chemisorption. 1.5% NCC modified by APTES resulted in a 53.2% decline of HCHO emission, which was as much as 2.5 times of the decrease in NCC modified by MPS.
3. Bonding strength of the UF resin adhesive with NCC modified by APTES showed a significant improvement, increasing by 23.6% when the concentration of modified NCC was 1.5%, while the modification from MPS led to the bonding strength increase by 7.0% (from 0.72 MPa to 0.77 MPa at the concentration of 1.5%).

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