

## Modification of NCC for Improving the Wetting Property with Polyurethane

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**Keywords:** NCC; modification; wetting property; contact angle

**Abstract.** In this study, different lipophilic groups from 3-aminopropyltriethoxysilane (APTES) and 3-glycidoxypentyltrimethoxysilane (GPTMS) were used to alter the surface structure of nanocrystalline cellulose (NCC). The diversifications of NCC surface resulted from modifiers improved the wetting property between NCC and polyurethane significantly. The modified NCC was characterized by X-ray powder diffraction (XRD). And the wetting property was indicated by contact angle (CA). Epoxy groups from 6% GPTMS led to a 47.6% decline of CA, while the improvement of wetting property from APTES was inconspicuous.

### Introduction

Polyurethane has been employed in most of the industrial applications and lots of studies are operated for improving the properties of polyurethane. Poly (2, 4-diethyl-1, 5-pentamethylene adipate) glycol (PDPAD) was synthesized and used to improve the hydrolytic stability of waterborne polyurethane [1]. The electrolytic stability of aqueous polyurethane was affected by dimethylolpropionic acid [2]. Glossiness and hardness are the main limitations of polyurethane. Large numbers of attempts have been carried out in recent years, such as SiO<sub>2</sub> [3, 4].

As a kind of promising material, the compact crystal region of NCC was useful for the glossiness and hardness of polyurethane. The reunion of NCC resulted from surface hydroxyl groups limited the applications in polyurethane. Modifications of NCC by surface active agents improved the wetting property between NCC and polyurethane [5, 6]. The wetting property of NCC modified by coupling agents, which led to a steady dispersion of the NCC particles in polyurethane, was studied in this research.

### Experimental

**Materials.** The NCC particles prepared by acid hydrolysis in laboratory showed a length of 200 to 300 nm and a diameter of 30-50 nm. Polyurethane was purchased from LEYI Co. Ltd. (China). All the chemicals were of commercially analytical grade and were used without further purification. All experiments were conducted under air atmosphere.

**Methods.** Ethanol was used as a solvent for the modifiers. Four kinds of solutions for each modifier were prepared and the concentrations of each modifier were 2, 4, 6, and 8% (v/v). The pH value of the solutions varied in the range 3–4 using hydrochloric acid for the hydrolysis of modifiers.

APTES and GPTMS were hydrolyzed for 5 to 10 min at 25 °C until the solutions turned pellucid. 1 g NCC was modified by 100 ml solution of the ethanol and modifier. The modification was operated at 60 °C for 3 h.

## Results and Discussion

**X-ray powder diffraction characterization.** The XRD patterns of original NCC and modified NCC are shown in Figure 1. The characteristic diffraction peaks at  $2\theta = 16.15^\circ$  and  $22.58^\circ$  are assigned to the (101) and (002) planes of cellulose type I. Figure 1c shows the XRD pattern of original NCC, which exhibited similar diffraction peaks with natural cellulose. The diffraction pattern of NCC was not affected by the lipophilic groups from APTES and GPTMS significantly (shown in Figure 1a and b). The crystal region of NCC showed little difference after the modifications.

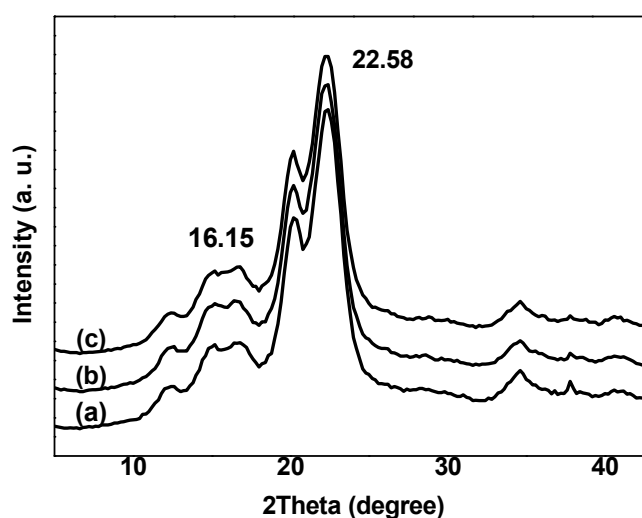


Fig. 1 XRD patterns of modified NCC: (a) NCC modified by APTES; (b) NCC modified by GPTMS; (c) original NCC

Modifications from APTES and GPTMS affected the wetting property of NCC. The wetting property between modified NCC and polyurethane was indicated by CA.

**Modification by APTES.** Wetting property of NCC modified by APTES increased significantly. A visible role of APTES in reducing the contact angles of NCC is shown in Figure 2. The CA left and CA right of NCC modified by APTES decreased from  $68.6^\circ$  and  $68.4^\circ$  to  $44.0^\circ$  and  $43.8^\circ$  when the concentration of APTES was 4%. The increase in wetting property of NCC modified by APTES was 35.8%.

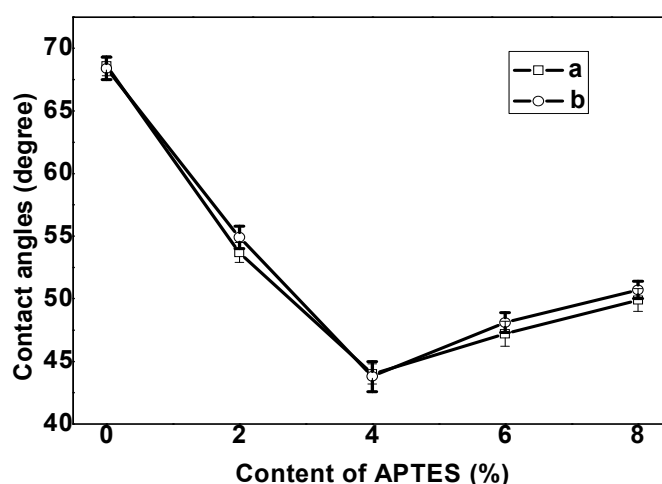


Fig. 2 CA of modified NCC: (a) CA left of NCC modified by APTES, (b) CA right of NCC modified by APTES

**Modification by GPTMS.** As shown in Figure 3, the CA left and CA right of NCC modified by GPTMS decreased from 68.6 ° and 68.4 ° to 35.9 ° and 36.1 °. The wetting property of modified NCC increased by 47.6% with 6% GPTMS. The epoxide groups of GPTMS led to an obvious steric obstruction, which was useful to improve the compatibility between NCC and polyurethane.

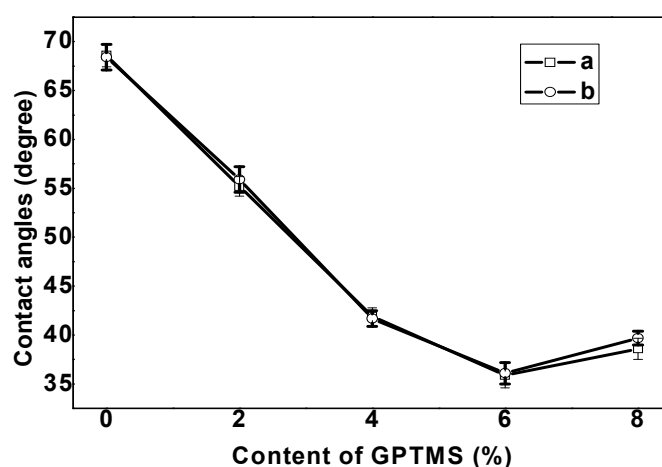


Fig. 3 CA of modified NCC: (a) CA left of NCC modified by GPTMS, (b) CA right of NCC modified by GPTMS

## Conclusions

The wetting property between NCC and polyurethane was enhanced by modifications in this study. The characteristic lipophilic groups from APTES and GPTMS led to different effects on the compatibility between NCC and polyurethane. Compared with the CA of original NCC, the epoxy groups from 6% GPTMS led to a 47.6% decline. The improvement of wetting property from APTES was inconspicuous, and the CA between this kind of modified NCC and polyurethane reduced by 35.8% (modified by 4% APTES).

## Acknowledgements

The authors are grateful for the support of the Forestry Industry Research Special Funds for Public Welfare Projects: Research and Demonstration of Fast-growing Wood Modification and Application (201204702-B2). This research was also Supported by Progress of Study on Chemical Modification and Application of Fast Growing Wood (No.YB20091002201) and Beijing Natural Science Foundation (Effects and Crosslinking Mechanism of Amino-Methyl-Urea on wood modified) (2112032).

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