Preparation and Characterization of Waterborne Polyurethane Modified by Nanocrystalline Cellulose

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Nanocrystalline cellulose (NCC) was used as a modifier for waterborne polyurethane (WPU) to investigate the water and ethanol resistance of WPU-NCC composites. The NCC surface was modified with γ-glycidoxypropyltrimethoxysilane (GPTMS) and γ-ammnonimpropylmethyldimethoxysilane (APMDS) to improve its compatibility with waterborne polyurethane (WPU), as indicated by the contact angle (CA). The characteristic properties of WPU modified by NCC and a control group were compared by a Fourier-transform infrared spectroscope (FTIR), X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The CA between the modified NCC and WPU was decreased by 31.2% (with 8.0% APMDS (v/v)), and the NCC modified by GPTMS resulted in a 33.8% decrease of the CA. Compared to the original WPU, the crystal structure and crystallinity of the modified WPU showed a slight alteration. The SEM micrographs showed that the NCC particles modified by GPTMS were dispersed more uniformly. The FT-IR results showed that the addition of modified NCC led to the reduction of the characteristic absorption peak of the hydroxyl group. The water resistance of WPU with 1.5% NCC modified by GPTMS was increased by 47.2%, and the ethanol resistance decreased by 67.0%, while the modification from APMDS led to a 38.1% increase in water resistance and a 56.9% decrease in ethanol resistance.

Keywords: Nanocrystalline cellulose; Waterborne polyurethane; Modify; Water resistance; Ethanol resistance

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INTRODUCTION

Waterborne polyurethane (WPU) has become used to a remarkable degree as a replacement for the ordinary solvent-based polyurethane, a change that has been motivated by its environment-friendly, nontoxic, and nonflammable nature (Wegner and Jones 2006; Du *et al.* 2008; Kim *et al.* 2010). WPU is considered to be an organic material with a wide potential of applications in many fields, such as coatings, adhesives, leathers, and the textile industry (Kim and Lee 1996; Madbouly and Otaigbe 2005; Cao *et al.* 2007). However, the waterborne polyurethanes are inferior to the solvent-based polyurethane with respect to their low chemical resistance, scratch resistance, weather resistance, mechanical strength, and gloss (Rahman and Lee 2009; Zhang *et al.* 2010). Due to the hydrophilic groups from the molecular chain of WPU, the dried film of WPU shows obvious hygroscopic properties, which lead to poor water resistance, low mechanical properties, and strength decreases. (Rahman and Kim 2007; Sun *et al*. 2011)

Much attention has been given to overcoming these shortcomings and realizing the larger-scale application of WPU by the incorporation of organic and inorganic materials (Kim *et al*. 2003; Sun *et al*. 2011; Hubbe *et al.* 2008; Luo *et al*. 2009; Jackson *et al*. 2011;

Zhang *et al.* 2010). The nanosilica was added into the aqueous emulsion of polyurethane (PU) in order to improve its water and thermal resistance. The improvement could be attributed to a thermal insulation effect of nanosilica, as well as an increase of the mean free path of water molecules that pass through the matrix of the PU-nanosilica composite (Kim *et al.* 2003). Modified NCC was dropped into the waterborne polyurethane by Cao *et al*., and the results showed that Young's modulus and tensile strength had been improved. The explanation for this fact is that the synergistic effect between the NCC and the waterborne polyurethane was significantly enhanced (Cao *et al.* 2007). The addition of microcrystalline cellulose nanofibers into linear segmented polyurethanes (SPU) resulted in an increase in the Young's modulus and a decrease in the deformation at the break (Auad *et al.* 2010).

Recently, nanocrystalline cellulose (NCC) has been extensively studied because it exhibits many unique characteristics, such as high tensile strength and Young's modulus, polar groups (-OH), an enriched surface (Eyley and Thielemans 2011), and a high specific surface area (Cranston and Gray 2006; Zaman *et al.* 2012) in addition to its biodegradable and environmentally benign nature (Wegner and Jones 2006).

The thermal stability, rigidity, and hardness of the resulting composite materials were improved due to the addition of NCC (Petersson *et al.* 2007; Noorani *et al.* 2007; Habibi *et al.* 2010). The effects of the modified NCC (modified by APTES and MPS, respectively) on the HCHO emission and bonding strength of urea-formaldehyde (UF) resin adhesive were studied. The HCHO emission was decreased, which was ascribed to physical and chemi-sorption, and the bonding strength was increased (Zhang *et al.* 2011). However, there have been few reports on the preparation and characterization of the WPU modified by NCC.

The addition of the modified NCC was used as an effective strategy to alter and enhance the properties of the WPU. The resulting materials were prepared by casting the suspensions of NCC and WPU in various weight ratios. The morphology, structure, and performance of the resulting nanocomposite films were investigated by the wetting property, XRD, SEM, FT-IR, water resistance, and ethanol resistance of WPU.

EXPERIMENTAL

Materials

All of the experiments were conducted under an air atmosphere. Poplar pulp (α-cellulose content 87.23%, with a 1288 degree of polymerization) was obtained from Russia. The waterborne polyurethane was prepared by Leyi Co., Ltd., Beijing, China. The original NCC was prepared by acid hydrolysis in the laboratory. The modifiers for NCC, GPTMS, and APMDS, were purchased from Mingyang chemical industry Co., Ltd., Shandong, China. All chemicals were of an analytical grade and were used as they were received without any further purification.

Methods

The preparation experiment of the original NCC was carried out as follows: Poplar pulp (16.6 g) and 35% sulphuric acid solution (100 g) were mixed homogeneously and heated at 65 °C for 6 h under continuous stirring. Subsequently, the resultant suspension, which had a weight concentration of about 1.5%, was neutralized with distilled water and subjected to 10 min of an ultrasonic treatment. Then it was freeze-dried to obtain NCC powder.

GPTMS and APMDS were each used to modify the original NCC. Ethanol was chosen as a solvent for the modifiers. Five kinds of solutions for each modifier were prepared. The concentrations of modifier in each kind of solution were 2, 4, 6, 8, and 10% (v/v). For the hydrolysis of modifiers, the pH was decreased to the range of 3 to 4 using hydrochloric acid. APTES and MPS were hydrolyzed for about 10 min until the solutions turned pellucid. NCC (1 g) was added into an ethanol solution (75 mL)/distilled water (25 mL), and the solvents were mixed. The modification was carried out at 60 °C for 3 h.

The dried NCC modified by GPTMS or APMDS was dropped into the WPU at the concentrations of 0, 0.5, 1.0, 1.5, and 2.0% (w/w). After mixing, the resulting mixtures were dispersed by an ultrasonic probe with a power of 800 W and stirred on a rotavapor under vacuum for 30 min to remove the remaining air.

The above obtained mixtures were cast in polystyrene square dishes and dried at 80 °C for 48 h. A series of nanocomposite films with a thickness of around 0.3 mm were conditioned at room temperature in desiccators.

CHARACTERIZATION

Contact Angle Measurements

The contact angle for modified NCC was determined by using a video optical contact angle measuring device (OCAH200, Dataphysics, Germany). WPU suspension was used as the contact liquid. A WPU droplet was deposited on the NCC sample surface, and the droplet shape was recorded. A CCD video camera and image analysis software were used to determine the contact angle evolution. The experimental results were the average values of at least five measurements made on different areas of the film surface.

X-ray Diffraction (XRD) Analysis

The crystallinity of the NCC-WPU composites was evaluated by XRD, using a Shimadzu diffractometer (XRD 6000). The measurement conditions were: Cu Kα radiation with graphite monochromator, 30 kV voltage, and 40 mA electric current. The patterns were obtained within a 4 to 40° 2θ angular interval with 0.05° step and scan speed of $2°\bullet\text{min}^{-1}$. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions.

SEM Analysis

A S-570 scanning electron microscope (SEM) (Hitachi, Japan) was used to observe both elemental analysis and morphology of the NCC-WPU composites. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold, and observed in the SEM using a voltage of 15 kV.

FT-IR Analysis

The NCC-WPU composites specimens of 120 mesh size were used in the FT-IR spectroscopy measurement. The dried specimens were embedded in potassium bromide (KBr) pellets and analyzed by using a Tensor 27 (Bruker, Germany) spectrometer. They were recorded in the absorption mode in the range of 4000 to 400 cm^{-1} with an accumulation of 64 scans at a resolution of 4 cm^{-1}.

Water Resistance and Ethanol Resistance

Water absorption was measured by emersion of film samples in water. The water absorption (%) as a function of immersion time was calculated by Eq. (1), where W_0 is the original film weight and W is the film weight after water absorption

$$\%\ \text{absorption}=\frac{W-W_0}{W_0}\times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Compatibility of NCC Modified by GPTMS and APMDS

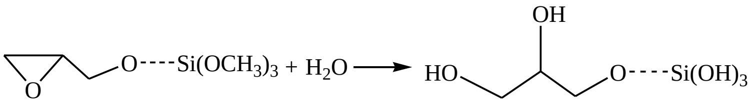
The compatibility between the WPU and the modified NCC was determined by the contact angle (CA). The modification effects of the GPTMS and the APMDS to the wetting properties of the NCC are shown in Fig. 1.

The silanol group was obtained through the hydrolyzing of alkyl-oxygen group. The surface of the original NCC was abundantly covered with hydroxyl groups; therefore it combined with water easily. The hydroxyl groups of the original NCC were replaced by alkyl-oxygen groups from the hydrolysed GPTMS and APMDS, with the formation of stable covalent bonds. The swelling of NCC fiber was restrained by the hydrocarbon chains from the modifiers, which were present as a cross-linked network structure between the WPU and modified NCC. These can be illustrated according to Eqs. (2)-(5) as follows:

$$NH_2CH_2{-}{-}{-}{-}Si(OCH_3)_3 + H_2O \longrightarrow NH_2CH_2{-}{-}{-}{-}Si(OH)_3 + 3CH_3OH \qquad (2)$$

$$NH_2CH_2{-}{-}{-}{-}Si(OH)_3 + NCC\text{-}OH \longrightarrow NH_2CH_2{-}{-}{-}Si(OH)_2\text{-}O\text{-}NCC + H_2O \qquad (3)$$

Eqs. 2 and 3. Modification of NCC with APMDS



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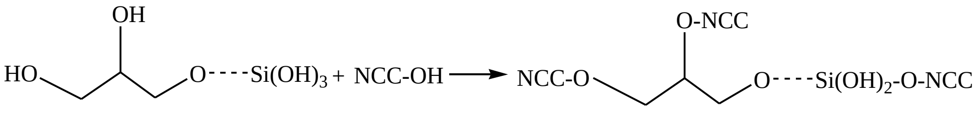

(5)

Eqs. 4 and 5. Modification of NCC with GPTMS

The CA was obtained as the average values of CA left and CA right. The CA of the original NCC were 68.5°. The wetting properties of the modified NCC increased significantly due to the lipophilic groups from the GPTMS and the APMDS. The GPTMS showed an obvious role in improving the wetting properties of the NCC, which are indicated in Figs. 1c and d. The CA of the NCC modified by GPTMS decreased to 51.5° when the concentration of GPTMS was 4%. The increase in the wetting property was 33.8% when the content of GPTMS was 8%. The CA decreased by 31.2% when the content of APMDS was 8%. The molecular structure of the GPTMS and the APMDS were filled with C-Si and C-O-Si groups, which led to the reduction of the surface energy of the NCC. The epoxy groups from the hydrolysis of the GPTMS can produce obvious space resistance due to their large size，and the –OH was broken by the C-O from the epoxy groups, which displaced the –OH further from the NCC surface. Moreover, it is known that the CA is affected by the surface roughness and the surface energy. The linkages within the composite materials affected the surface characteristics and led to a lower surface energy.

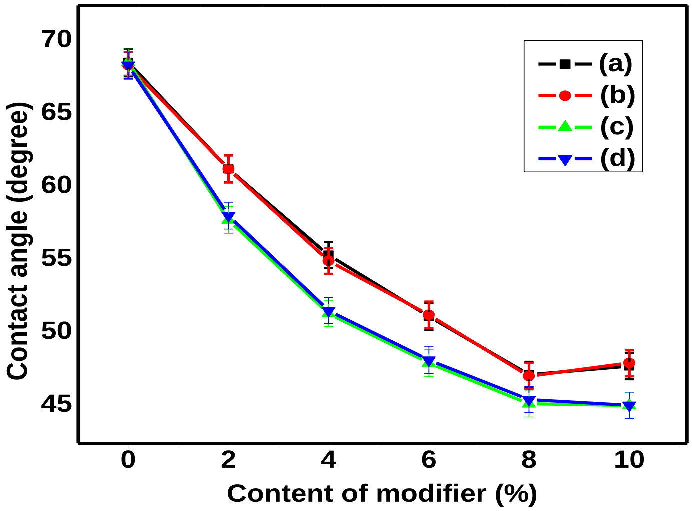

Fig. 1. Contact angle between modified NCC and WPU: (a) CA left of NCC modified by APMDS; (b) CA right of NCC modified by APMDS; (c) CA left of NCC modified by GPTMS; (d) CA right of NCC modified by GPTMS

XRD Patterns of Modified WPU

The XRD patterns and crystallinity of the original WPU and modified WPU are shown in Fig. 2A, Fig. 2B, and Table 1, respectively.

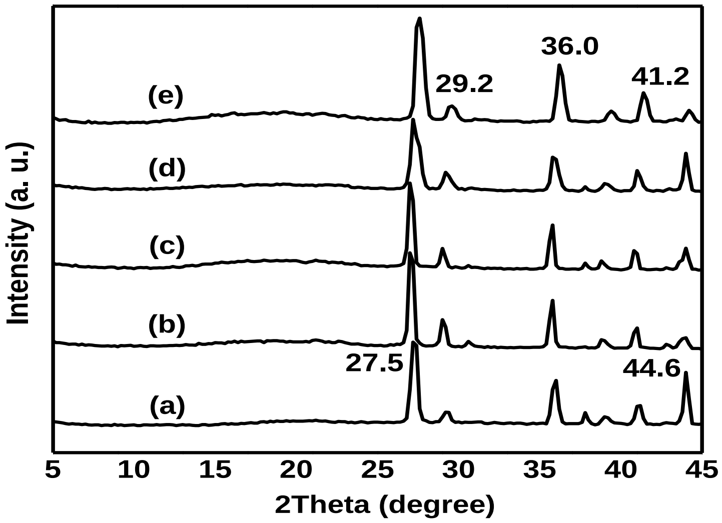

Fig. 2A. XRD patterns of (a) the original WPU; (b-e) the modified WPU with different content of APMDS-modified NCC: (b) 0.5 %; (c) 1.0 %; (d) 1.5 %; (e) 2.0 %

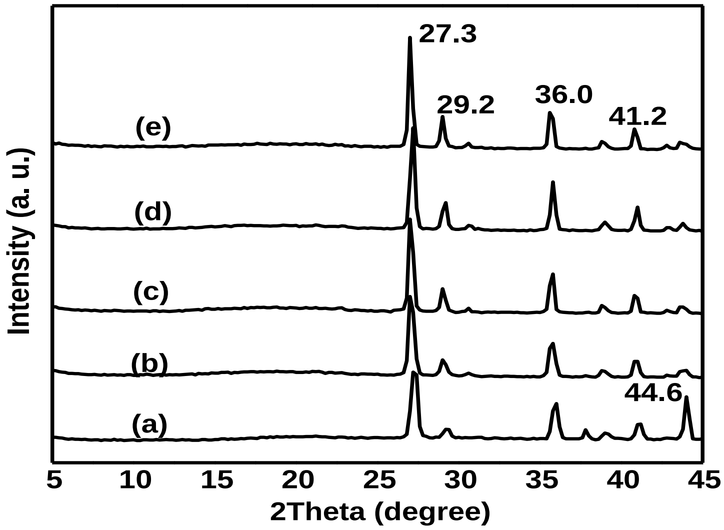

Fig. 2B. XRD patterns of (a) the original WPU; (b-e) the modified WPU with different content of GPTMS-modified NCC: (b) 0.5 %; (c) 1.0 %; (d) 1.5 %; (e) 2.0 %

The diffraction peaks of the WPU were centered at 2*θ*= 27.5° and 29.2°, as shown in Fig. 2A(a). Fig. 2A(b)-2A(e) showed the XRD patterns of the modified WPU, which exhibited similar diffraction peaks compared to Figure 2A(a). With the addition of the NCC modified by GPTMS, the intensity of the diffraction peaks at 2*θ* = 27.3°, 29.2°, and 41.2° increased insignificantly.

The NCC modified by the different modifiers (GPTMS and APMDS) resulted in similar effects on the characteristic diffraction peaks of the WPU. The diffraction pattern of cellulose was not affected by the lipophilic groups from the GPTMS and APMDS.

The NCC modified by APMDS and GPTMS affected the amorphous and crystal regions of WPU. The crystallinity of the WPU showed a slight increase after the modification by modified NCC, as shown in Table 1.

Table. 1. Crystallinity of Modified WPU

Properties	Types of modified NCC	Content of Modified NCC				
		0%	0.5%	1.0%	1.5%	2.0%
Crystallinity of WPU (%)	NCC modified by GPTMS	48.87	49.18	49.84	50.54	51.52
	NCC modified by APMDS	48.87	49.19	49.93	50.33	52.40

Fracture Morphologies of Modified WPU

Figure 3 shows the SEM images of the WPU-NCC composite film (with 8% GPTMS and APMDS, respectively). The NCC particles modified by the GPTMS can be dispersed into the WPU more uniformly than the NCC particles modified with APMDS; they are compared in Figs. 3a and 3b. Figure 3c shows that particle size in the dispersion increased with the addition of NCC modified by APMDS, while the GPTMS-modified NCC dispersed more uniformly. The NCC particles modified by APMDS showed an apparent reunion, which is evident in Fig. 3c. This is mainly attributed to the fact that the lipophilic groups and the epoxide groups from the GPTMS can change the surface structure of the original WPU more obviously. The SEM images confirm the effects of the different modifiers of NCC on the increasing number and size of the NCC phase in the WPU-NCC composites.

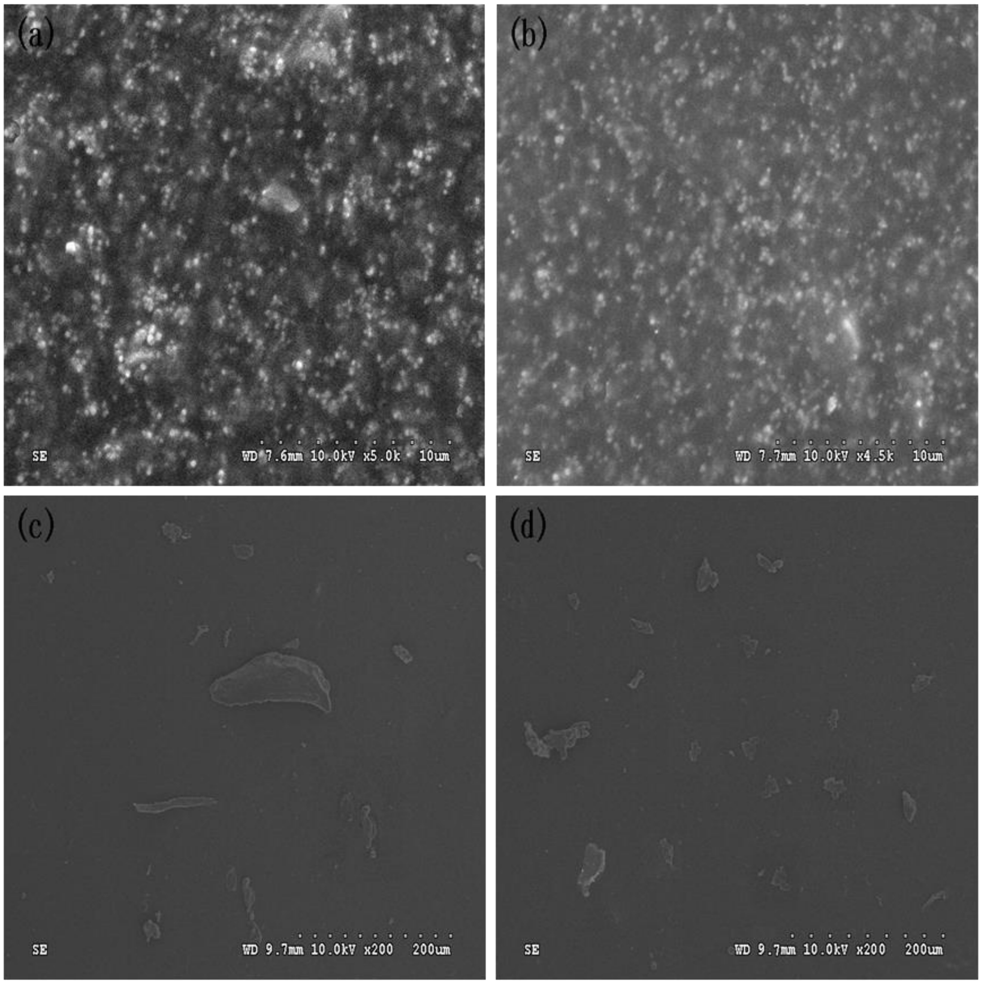

Fig. 3. SEM images of (a) WPU with APMDS-modified NCC (10 μm); (b) WPU with GPTMS-modified NCC (10 μm); (c) WPU with APMDS-modified NCC (200 μm); (d) WPU with GPTMS-modified NCC (200 μm)

FT-IR Analysis of Modified WPU

The structure of the original WPU and the WPU-NCC composite materials (modified by GPTMS and APMDS, respectively) were confirmed by FT-IR, as shown in Fig. 4. The IR spectrum of the original WPU (Fig. 4a.) shows a band at 3344 cm^{-1} corresponding to the stretching vibration modes of NH; the –CH$_2$ stretching vibration appeared at 2890-2950 cm$^{–1}$ for both the original and modified WPU, which indicated that –CH$_2$ groups were still retained in the regenerated products. The typical broad absorption peak centered at 1729 cm$^{–1}$ is attributed to the stretching vibration of the C=O. The bands at 1136 cm^{-1} and 1461 cm^{-1} are due to the stretching vibration of the C-O-C and the deformation vibration of the –CH$_2$. The regenerated WPU modified by two different kinds of modified NCC exhibited similar peaks, and the intensities of the peaks are compared in Figs. 4b and Fig. 4c. The characteristic stretching mode of NH in the original WPU was evident, which illustrated that the residual NH bond from the polyurethane chains had been incorporated in the modified NCC.

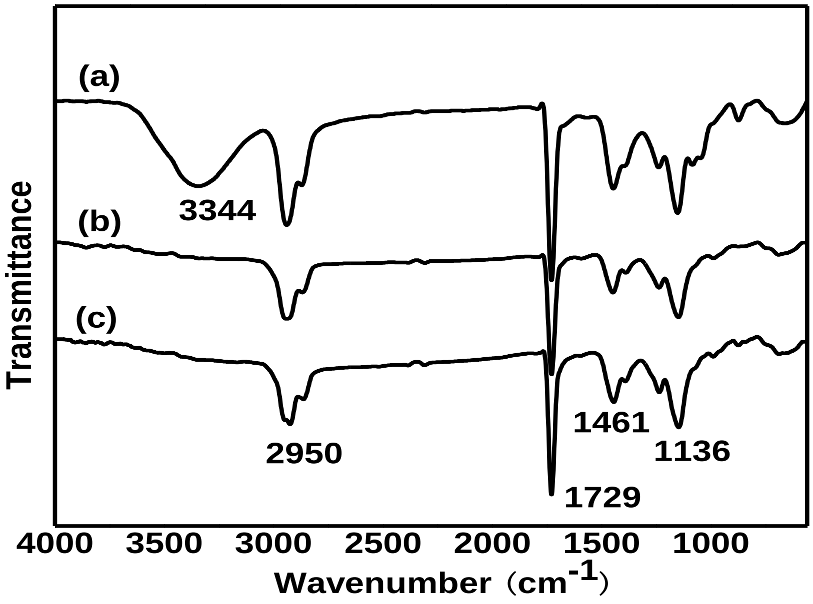

Fig. 4. The FT-IR spectra of (a) the original WPU; (b) WPU with GPTMS-modified NCC; (c) WPU with APMDS-modified NCC

Water and Ethanol Resistance of Modified WPU

The water resistance and ethanol resistance were affected by the addition of the modified NCC and the type of modifier, which are indicated in Figs. 5 and 6.

With the addition of the GPTMS-modified NCC, the water resistance increased by 47.2% (from 36.8% to 19.5% with 1.5% modified NCC), while that of the modified WPU increased by 38.1% at a concentration of 1.5% of the APMDS-modified NCC. The modified NCC resulted in the opposite effect on water resistance and ethanol resistance, respectively.

Compared with the original WPU, the ethanol resistance of the WPU with 1.5% of GPTMS-modified NCC and APMDS-modified NCC increased from 6.7% to 20.3% and 15.6%, respectively. This is mainly because of the Si-OH groups obtained from condensation of the hydrolytic alkyl group and from the Si-O-Si groups, which are hydrophobic and lipophilic, which caused the water absorption to decrease. Moreover, the enhancement of water resistance was also explained as due to the increase of the mean free path of water molecules that passed through the matrix of WPU-NCC composites. However, the water absorption increased instead when the content of the modifier was 2.0%. The explanation of this fact is that not all the hydroxyl groups from NCC will participate in the reaction. When the concentration of the modifier was 2.0%, the rest of the hydroxyl groups from NCC were removed to the surface of WPU film and combined with water molecules, which led to the increase of water absorption.

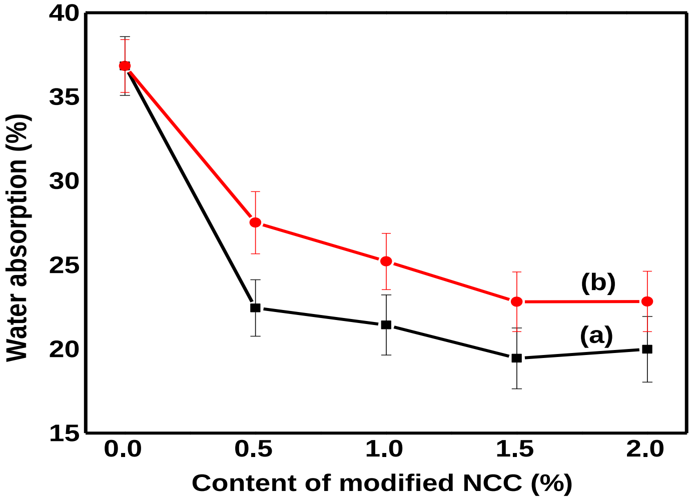

Fig. 5. Water absorption of (a) WPU with GPTMS-modified NCC; (b) WPU with APMDS-modified NCC

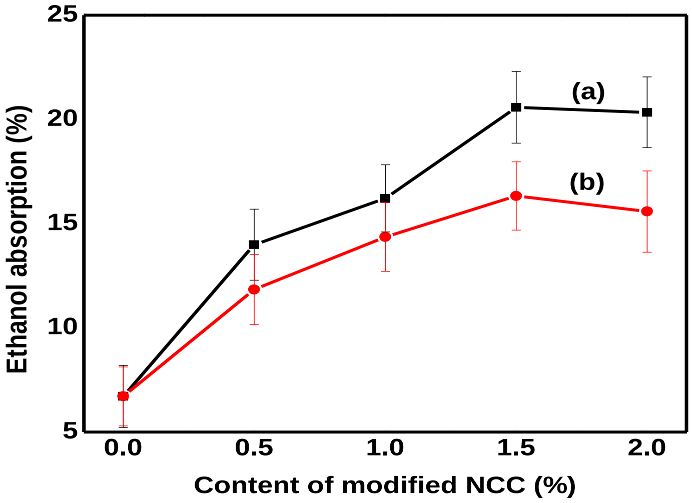

Fig. 6. Ethanol absorption of (a) WPU with GPTMS-modified NCC; (b) WPU with APMDS-modified NCC

CONCLUSIONS

1. The contact angle (CA) between the WPU and the APMDS-modified NCC decreased by 31.2%, and the modification from the GPTMS resulted in a 33.8 % decrease of the CA (when the concentration of modifier was 8%). The NCC modified by the APMDS affected the diffraction peaks of polyurethane at $2\theta = 27.5°$ and 29.2° more than that modified by GPTMS. From the FT-IR spectrum it can be concluded that the type of modifier had little effect on the structure of the WPU. The SEM results showed that the dispersal of NCC modified by GPTMS was more homogeneous in the WPU emulsion than that modified by APMDS.

2. The water resistance and ethanol resistance of the WPU were affected by the modified NCC significantly. The water resistance of the WPU with 1.5% of NCC modified by GPTMS and APMDS increased by 47.2% and 38.1%, respectively. The modification from the GPTMS and APMDS led to the ethanol resistance increase by 67.0 % and 56.9 %, respectively.

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