

Optical and Mechanical Properties of Polyurethane/Surface-modified Nanocrystalline Cellulose Composites^{*}

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Abstract In order to improve the optical and mechanical performances of waterborne polyurethane (WPU), nanocrystalline cellulose (NCC)/WPU composites were synthesized in this study. NCC (prepared by acid hydrolysis of cotton fiber) was modified by (3-aminopropyl)triethoxysilane (APTES) to enhance its compatibility with WPU, and the surface-modified NCC was characterized by grafting ratio, crystallinity and contact angle (CA). NCC/WPU composites were examined by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and thermogravimetric analysis (TG). The anti-yellowing property, specular gloss, pencil hardness, and abrasion resistance of NCC/WPU composites were investigated by the methods of Chinese National Standards GB/T 23999-2009, GB/T 9754-2007, GB/T 6739-2006 and GB/T 1768-2006, respectively. The results showed that the grafting ratio of NCC modified by 6% APTES was 36.01% and the crystallinity of modified NCC was decreased with the enhancement of APTES. CA of the modified NCC was decreased by 28.8% and the nanoparticles were homogeneously dispersed in the WPU matrix. The XRD patterns of the NCC/WPU composites were relatively steady, while the thermal stability of the composites was enhanced by 6.7% with 1.0 wt% modified NCC. Modified NCC affected the specular gloss of NCC/WPU composites more obviously than the anti-yellowing property. The pencil hardness of NCC/WPU composites was increased from 2H to 4H by addition of NCC and the abrasion resistance of the composites was enhanced significantly. In general, NCC/WPU composites showed significant improvements in the optical and mechanical performances.

Keywords: Nanocrystalline cellulose; Waterborne polyurethane; Cotton; Optical and mechanical properties; Nanocomposites.

INTRODUCTION

Waterborne polyurethane (WPU) is considered to be an organic material with a wide potential of applications in many fields, such as adhesives and coatings^[1]. Non-toxic and environmental friendly natures are some of the major advantages of WPU, while the optical and mechanical properties of WPU limit its applications significantly^[2]. Lots of approaches, such as the preparation of composites synthesized with WPU and fillers, have been studied to improve the shortcomings of original WPU.

Composites synthesized with WPU and inorganic fillers have shown significant improvements in thermal and physical properties. Silane coupling agent functionalized nanosilica was used to reinforce the thermal stability of original WPU^[3–5]. The tensile properties of WPU were enhanced by the silica treated with allyl isocyanate^[6]. And the derivatives of silica have been highlighted because of the unique characteristics. For example, the mixture of chitosan and nanosilica was able to influence the mechanical properties of WPU

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composites^[7]. As the common inorganic materials, CaCO_3 , carbon black particles and clay were used to improve the tensile strength of WPU matrix^[8–10]. The glass transition temperature and storage modulus of WPU composites were enhanced by the addition of antimony doped tin oxide and organically modified montmorillonite^[11, 12].

The WPU composites consisting of organic fillers have many advantages over the composites containing inorganic fillers, such as biocompatibility and biodegradability. The composite synthesized with WPU and bis(3-(1-methoxy-2-hydroxypropoxy)propyl) terminated polysiloxane indicated reinforcement effects^[13]. The surface resistances of original WPU were improved by the addition of microcrystalline cellulose, bisphenol A and polyurethane acrylate^[14–16]. The modified silicone was used to develop the mechanical properties of WPU composites^[17].

As a kind of natural and environmentally friendly polymer, nanocrystalline cellulose (NCC) is emerging as an attractive material for the specific crystal structure and superior properties^[18–20]. Nanocomposites synthesized with NCC and WPU have attracted much attention on account of the improvements in tensile strength and Young's modulus^[21–23]. The effects of NCC on the anti-yellowing property, specular gloss, pencil hardness and abrasion resistance of NCC/WPU composites were investigated in this study.

EXPERIMENTAL

Materials

The NCC raw material was obtained from cotton pulpboard. The one-component aromatic WPU purchased from LEYI Co. Ltd. (Beijing, China) was a thermosetting resin of linear polyether type. The number-average molecular weight of the WPU latex was 75000 and the solid content was 56.5%. The (3-aminopropyl)triethoxysilane (APTES) was treated as the surface modifier of NCC, and was used as received without any further purification. All the chemicals were of commercially analytical grade and experiments were conducted in air.

Methods

Preparation of NCC

After the treatment of the cotton pulpboard in 35% (*W/W*) sulfuric acid at a constant mixing speed of 20 r/min for 5 h at 60 °C (at a solid to liquid ratio of 1:6), the suspension was vacuum-filtered, and the cake was washed with deionized water to remove the H^+ and SO_4^{2-} . After that, the cake was dried at 105 °C for 24 h. 1 g dried cake was dispersed in 200 g deionized water and the suspension was homogenized at a pressure of 100 MPa for 10 times by a homogenizer from GEA Niro Soavi (Italy). Through the combination of acid hydrolysis and homogenization, the NCC particles showed a length of 100 nm to 200 nm and a diameter of 30–50 nm.

Pretreatment of NCC

APTES was used to modify the original NCC for improving the compatibility with WPU, and ethanol was used as a solvent for the modifier. Four different concentrations of APTES were used to modify the NCC: 2%, 4%, 6% and 8% (*V/V*). The pH of the solutions was adjusted to within the range of 3 to 4 with hydrochloric acid, and APTES was hydrolyzed until the solution turned pellucid. One gram of NCC was modified by 100 mL ethanol solution with the modifier, and the modifications were conducted at 60 °C for 3 h. The modified NCC was vacuum-dried at –50 °C for 24 h and the dried sample was used in this study.

Estimation of modified NCC

The grafting ratio (%) of the modified NCC particles was calculated by Eq. (1), where *W* represents the mass of the surface-modified NCC after the acetone extraction and *W*₀ is the mass of the original NCC

$$\text{Grafting ratio} = \left(\frac{W - W_0}{W_0} \right) \times 100 \quad (1)$$

The crystallinity of modified NCC was calculated from the XRD diffractograms, and the integral scattering intensities of the crystalline and amorphous phases were evaluated. The ratio of the crystalline phase to the real intensity was used to estimate the crystallinity. The contact angle (CA) between modified NCC and WPU was investigated with an optical contact angle-measuring instrument (Dataphysics, Germany). WPU latex was used as the contact liquid. The NCC film was prepared with 0.2 g dried NCC and pressed at 9.0 MPa. A WPU droplet was deposited on the surface of NCC film and the contact angle was measured.

Synthesis of NCC/WPU composite

The NCC/WPU composite was synthesized with WPU and surface-modified NCC. The dried surface-modified NCC was added into the latex of WPU at the concentrations of 0.5%, 1.0%, 1.5% and 2.0% (W/W). The modified NCC particles in the WPU were dispersed by an ultrasonic probe with a power of 1200 w. The ultrasonic was turned on for 10 s and was turned off for 5 s in one period. The total time of the intermittent ultrasonic was 10 min.

Characterization of NCC/WPU composites

The state of dispersion of NCC particles in the NCC/WPU composite was analyzed with a Hitachi (Japan) scanning electron microscope (SEM). Samples were mounted on conductive adhesive tape, sputter coated with gold, and observed using a voltage of 15 kV. The crystal structure of the NCC/WPU composites was examined by use of an X-ray diffractometer (XRD) from Shimadzu (Japan) with a scan speed of 2 (°)/min. The patterns were obtained within a 5° to 40° 2 θ angular interval with 0.05° step. The crystallinities of the composites were calculated as the ratio of the intensity differences at the peak positions. The thermal behavior of the NCC/WPU composite was tested with a thermogravimetric analysis (TG) device from Shimadzu (Japan) at a constant heating rate (10 K/min) in flowing air from 50 °C to 500 °C.

The anti-yellowing property, specular gloss, pencil hardness and abrasion resistance of NCC/WPU composites were measured by the methods of Chinese National Standards GB/T 23999-2009, GB/T 9754-2007, GB/T 6739-2006 and GB/T 1768-2006, respectively. The anti-yellowing property of NCC/WPU composites was examined with a constant UV radiation (0.68 W/m²). The coatings treated with UV rays were compared with the control group, and ΔE (measured by the colorimeter) was used to indicate the yellowing of samples with different contents of surface-modified NCC. The specular gloss of NCC/WPU composites was tested with 75 μ m thick coatings. A piece of glass, the refractive index of which was 1.567, was treated as a control group. The pencil hardness test was operated with the oven-dried NCC/WPU composites. The angle between the pencil and modified WPU coatings was 45° and the load of pencil was 750 g. The abrasion resistance of NCC/WPU composites was determined using a rubber wheel and the rotation speed of the wheel was 60 r/min. And the test was operated at the temperature of (23 $\pm$ 2) °C and the relative humidity was (50 $\pm$ 5) %.

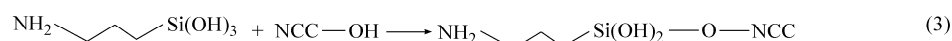
RESULTS AND DISCUSSION

Estimation of Modified NCC

Grafting ratio of modified NCC

The grafting of APTES onto the NCC particles was conducted during the process of surface modification, and the effects of APTES concentration on the grafting ratio of modified NCC are presented in Fig. 1.

The silanol groups were obtained through the hydrolyzing of alkyl-oxygen groups of APTES. The surface of original NCC was abundantly covered with hydroxyl groups. And the hydroxyl groups of NCC were substituted by the hydrolyzed APTES, with the formation of stable covalent bonds. The swelling of NCC was restrained by the hydrocarbon chains from APTES, which were presented as cross-linked networks between the WPU and surface-modified NCC particles. The grafting of APTES onto the original NCC can be illustrated according to Eqs. (2) and (3) as follows:



The weight of grafts irreversibly fixed on the NCC particles was measured and the grafting ratios are indicated in Fig. 1. When the content of APTES was 4%, the grafting ratio of the surface-modified NCC was 29.77%. The growth rate of the grafting ratio decreased as the APTES concentration increased. The grafting ratio of NCC particles modified by 6% APTES was 36.01%, which was as much as 1.2 times of that resulting from 4% APTES. The replacement of the hydroxyl groups of NCC particles was affected by the space resistance produced by the amino groups and hydrocarbon chains when the content of APTES was 8%, and the grafting of APTES onto the NCC particles was inhibited. The grafting ratio of NCC modified by 8% APTES was 35.56%.

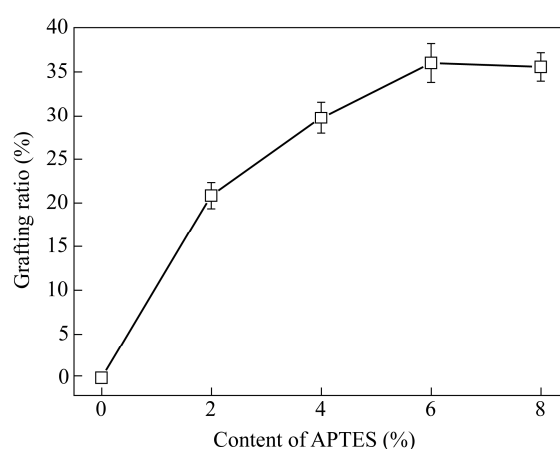


Fig. 1 Grafting ratio of modified NCC particles

Crystallinity of modified NCC

The crystal structure is the main influence factor for the crystallinity of NCC particles. The hydrolyzed APTES was grafted onto the surface of NCC and the crystalline phase of the original NCC was influenced by the surface modifier. The replacement of the hydroxyl groups by the amino groups and hydrocarbon chains of APTES resulted in the degeneration of the compact crystalline regions of NCC during the surface modification. And the slight decrease in the crystallinity of modified NCC was indicated in Table 1. The crystallinity of original NCC was 66.75%, and 4% APTES led to a 4.7% decline of the crystallinity. When the content of APTES was 8%, the crystallinity of surface-modified NCC particles was decreased to 61.57%.

Table 1. Crystallinity of the modified NCC

Content of APTES (%)	0	2	4	6	8
Crystallinity (%)	66.75	65.28	63.62	62.35	61.57

Contact angle between modified NCC and WPU

The NCC structure of a surface affects the compatibility of the surface, and CA determination is a simple technique for examining the immediate surface of solids. The compatibility of surface-modified NCC particles with WPU was indicated by CA in this study. The surface modification effects of APTES on the CA of modified NCC particles are shown in Fig. 2.

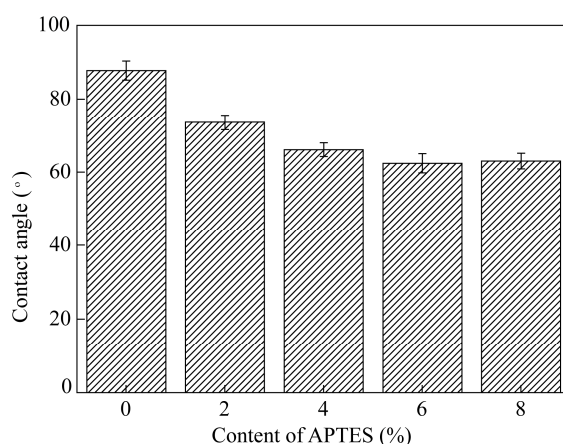


Fig. 2 CA between surface-modified NCC and WPU

As presented in Fig. 2, it can be seen that the original NCC showed significantly higher CA value as compared to that of NCC modified by APTES. The CA between original NCC and WPU was 87.8° , while the CA of NCC modified by 4% APTES was decreased by 24.6%. This phenomenon indicated that the compatibility of NCC with WPU was improved by the surface modification. The enhancement of the compatibility slowed down as the content of APTES increased and the CA of NCC modified by 6% APTES was reduced to 62.5° . The incremental contribution to the compatibility of NCC with WPU decreased when the content of APTES was 8%, and the CA between the NCC modified by 8% APTES and WPU matrix was 63.1° . The slight decline of the incremental contribution was mainly attributed to the reduction of the grafting of APTES onto the NCC particles resulting from the space resistance of the lipophilic groups from APTES.

Characterization of NCC/WPU Composites

State of dispersion of modified NCC in NCC/WPU composites

The compatibility of original NCC particles with WPU matrix was reinforced by the surface modification and the state of dispersion of the surface-modified nano particles in WPU was improved. Figure 3 shows the SEM images of composites filled with different contents of modified NCC particles in the WPU matrix.

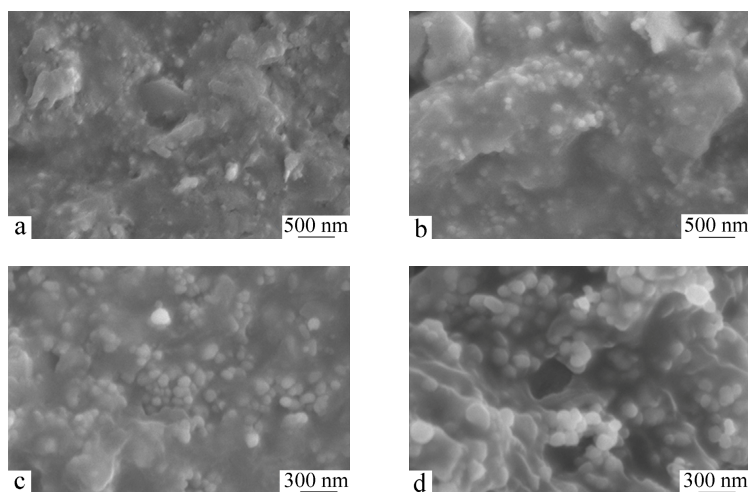


Fig. 3 SEM micrographs of the NCC/WPU composites with different contents of surface-modified NCC: (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%

The morphology of the surface-modified NCC particles (with 6% APTES) in the WPU matrix is identified as white dots (as presented in Fig. 3) and the white dots are corresponding to the nanocrystals in the perpendicular plane of the nanocomposites. The state of dispersion of NCC particles in the composite was affected by the concentrations significantly. Figures 3(a) and 3(b) present the structures of the WPU with 0.5 wt% and 1.0 wt% surface-modified NCC, respectively. And the dispersion of the nanoparticles in the NCC/WPU composites is uniform. As shown in Fig. 3(c), the homogeneous distribution of the modified nanoparticles in the NCC/WPU composite synthesized with 1.5 wt% modified NCC is observable, while the agglomeration of the surface-modified nanoparticles existed in the NCC/WPU composite when the content of modified NCC is 2.0 wt% (shown in Fig. 3d). The relatively uniform distribution of the surface-modified NCC in the WPU could play an important role in improving the optical and mechanical performances of the resulting nanocomposites.

Crystal structure of NCC/WPU composites

The surface-modified NCC affected the crystal structures of NCC/WPU composites, and the XRD patterns of the composites are presented in Fig. 4. It was shown that the XRD profiles of the original WPU exhibited typical diffraction angles (2θ) around at 27.3° , 29.1° and 35.7° . The addition of the surface-modified NCC influenced the characteristic peaks of NCC/WPU composites slightly. The diffraction intensities of original WPU at $2\theta = 27.3^\circ$ and 29.1° were increased with the addition of modified NCC, while the diffraction peaks at $2\theta = 35.7^\circ$ were affected by the NCC modified by APTES inconspicuously and the intensity was relatively steady.

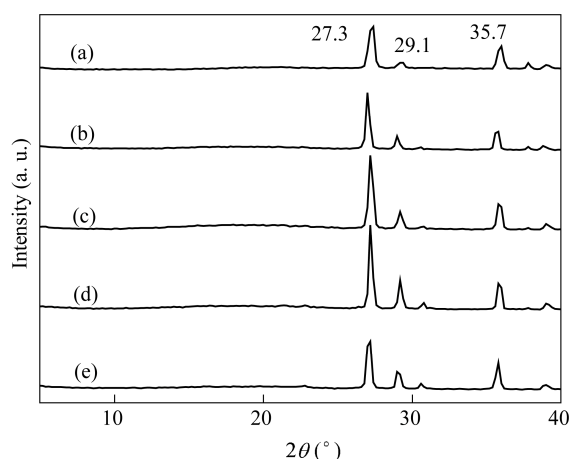


Fig. 4 XRD patterns of the NCC/WPU composites with different contents of surface-modified NCC: (a) control group, (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt% and (e) 2.0 wt%

The amorphous and crystal regions of WPU matrix were influenced by the addition of the modified NCC. The crystallinities of the NCC/WPU composites enhanced as the modified NCC concentration increased, and the values are shown in Table 2.

Table 2. Crystallinity of the NCC/WPU composites

Sample	a	b	c	d	e
Crystallinity (%)	48.56	50.32	50.77	51.45	51.68

Thermal stability of NCC/WPU composites

TG analysis was proposed to ascertain the thermal stability of NCC/WPU composites, and the thermal behavior of the composites with different contents of NCC is compared in Fig. 5.

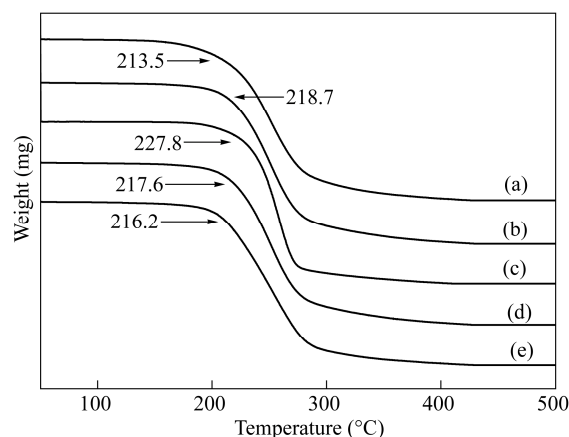


Fig. 5 TG curves of the NCC/WPU composites with different contents of surface-modified NCC: (a) control group, (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt% and (e) 2.0 wt%

The TG curves shown in Fig. 5 indicated that significant weight loss of the NCC/WPU composites occurred as the temperature was increased from 210 °C to 230 °C. The loss was likely attributed to the thermal degradation of the urethane linkages in the composites. It was found that the modification of WPU by surface-modified NCC improved the thermal stability and increased the degradation temperature. The TG peak of the composites was raised from 213.5 °C to 227.8 °C when the content of modified NCC was 1.0 wt%. The delay in degradation caused by the addition of NCC may be related to the improvements of the phase separation between the soft and hard domains. The thermal stability of NCC/WPU composites decreased significantly when the content of nanoparticles was more than 1.0 wt%. With 2.0 wt% surface-modified NCC, the weight loss temperature of NCC/WPU composite was 216.2 °C.

Anti-yellowing property of NCC/WPU composites

The exposure of aromatic WPU to UV radiation leads to the photochemical degradation of the resin, which is associated with the scission of the urethane group and photooxidation of the central CH₂ group between the aromatic rings. These reactions are combined with the yellowing of WPU. The hydroxyl groups of NCC were sensitive to the UV energy and the photochemical decomposition of WPU that usually would take place due to the UV radiation was prevented by the addition of NCC. The relationship between the amount of NCC used and the UV-induced yellowing of NCC/WPU composites is shown in Fig. 6.

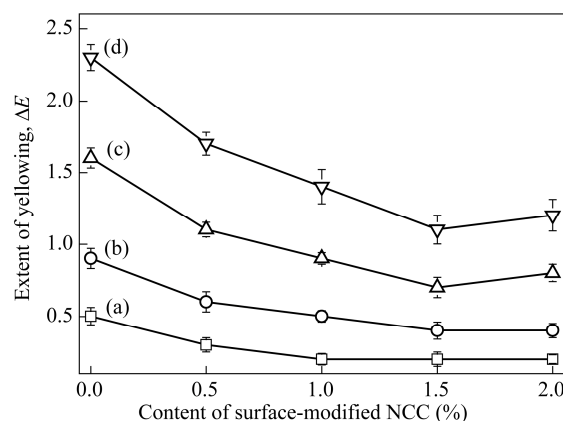


Fig. 6 Extent of yellowing of NCC/WPU composites: (a) 42 h of UV irradiation, (b) 84 h of UV irradiation, (c) 126 h of UV irradiation and (d) 168 h of UV irradiation

The anti-yellowing property of NCC/WPU composite reinforced significantly as the NCC content increased. As shown in Fig. 6(a), the ΔE of NCC/WPU composites treated with UV radiation for 42 h was decreased from 0.5 of pure WPU to 0.2 of the composite synthesized with 1.5 wt% NCC. The ΔE of samples treated with UV radiation for 84 h (curve b in Fig. 6) showed a 55.6% decrease (from 0.9 of the control group to 0.4 when the content of modified NCC was 1.5 wt%). Curves c and d in Fig. 6 presented that the yellowing values of the composites containing 1.5 wt% modified NCC were decreased by 56.3% (treated with UV radiation for 126 h) and 52.2% (treated with UV radiation for 168 h), respectively. The anti-yellowing property of the NCC/WPU composites was affected by the agglomeration of the modified nanoparticles in the matrix, and it was obvious that the contribution to the anti-yellowing property decreased when the content of modified NCC was 2.0 wt%.

Specular gloss of NCC/WPU composites

The specular gloss is an appearance characteristic of NCC/WPU composites, which is related to the structure of the composite coatings. As a kind of nanocrystals, the structure of NCC was compact and smooth. The rays irradiated on the NCC surface were able to be reflected off significantly. The well-dispersed NCC particles in the WPU matrix enhanced the reflectivity of the composite coatings and this phenomenon resulted in the improvements of the specular gloss of NCC/WPU composites.

Effects of the NCC particles on the specular gloss (60°) of NCC/WPU composites are shown in Fig. 7. The enhancements of the specular gloss were obvious when the content of surface-modified NCC was less than 1.5 wt%. Compared with the control group, the specular gloss of NCC/WPU composite was increased by 164.8% (from 12.5 of control group to 33.1 when the content of modified NCC was 1.5 wt%). When the content of modified NCC particles was 2.0 wt%, the improvement in specular gloss of the NCC/WPU composite decreased for the reunion of nanoparticles. And the specular gloss value of the composite containing 2.0 wt% modified NCC was 29.7.

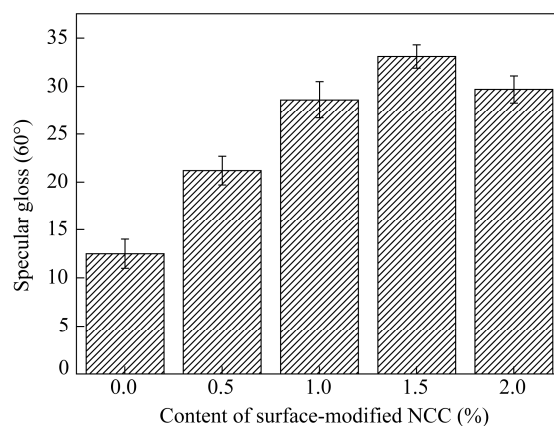


Fig. 7 The specular gloss of NCC/WPU composites with different contents of surface-modified NCC

Pencil hardness of NCC/WPU composites

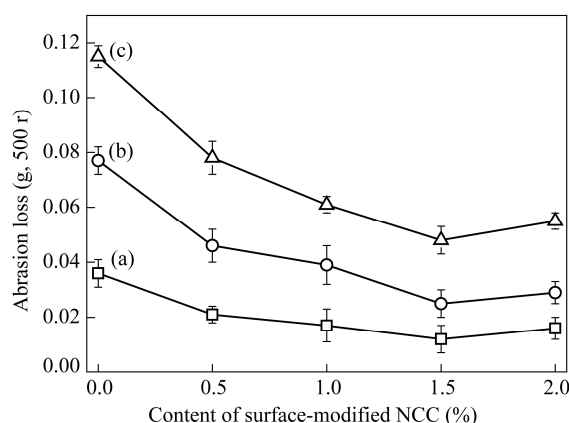
The pencil hardness of WPU coatings is influenced by the chemical structure, and the structure of the resin of linear type is unstable. The dispersion of modified NCC particles in the WPU matrix was homogenous and the chemical structure of the linear WPU coatings was supported by the well-dispersed nanoparticles effectively. The improvements in the pencil hardness of NCC/WPU composites resulting from the surface-modified NCC are indicated in Table 2. The original WPU was deformed easily and the pencil hardness of the control group was 2H. The pencil hardness of the NCC/WPU composite consisting of 0.5 wt% modified NCC was improved limitedly, while the pencil hardness was enhanced from 2H of control group to 4H when the contents of NCC were 1.0 wt% and 1.5 wt%. The agglomeration of modified NCC (when the content was 2.0 wt%) led to the decrease of the contribution to pencil hardness.

Table 2. The pencil hardness of NCC/WPU composites

NCC/WPU composites	Control group	Content of surface-modified NCC (%)			
		0.5	1.0	1.5	2.0
Pencil hardness	2H	3H	4H	4H	3H

Abrasion resistance of NCC/WPU composites

The degree of crosslinking was the main factor for the abrasion resistance of WPU. With the addition of modified NCC, the crosslinking in original linear WPU was reinforced by the cross-linked networks between WPU matrix and surface-modified NCC particles. The abrasion losses were used to indicate the abrasion resistance of the NCC/WPU composites, and the reductions of the abrasion losses resulting from the modified NCC particles are shown in Fig. 8.

**Fig. 8** The abrasion loss of NCC/WPU composites with different loads: (a) 250 g, (b) 500 g and (c) 750 g

According to the reductions of the abrasion losses presented in Fig. 8, the abrasion resistance of WPU was enhanced by the addition of surface-modified NCC. When the load was 250 g, the abrasion loss was reduced from 0.036 g of control group to 0.012 g of the composite consisting of 1.5 wt% modified NCC, and the abrasion loss of the composite (containing 1.5 wt% modified NCC) was decreased by 67.6% when the load was 500 g. Compared with the pure WPU, the abrasion resistance of the sample synthesized with 1.5 wt% surface-modified NCC was improved by 58.3% when the load was 750 g. The contribution to the abrasion resistance of WPU was influenced by the agglomeration of 2.0 wt% NCC particles.

CONCLUSIONS

NCC particles were modified by APTES and the crystallinity of surface-modified NCC was decreased with the enhancement of modifier. The grafting ratio of NCC modified by 6% APTES was 36.01% and the CA was decreased by 28.8%. From the SEM micrographs of NCC/WPU composites it can be concluded that the state of dispersion of the modified NCC particles in WPU was homogeneous. APTES-modified NCC affected the XRD diffraction peaks of the NCC/WPU composites at $2\theta = 27.3^\circ$ and 29.1° more obviously than the peak at $2\theta = 35.7^\circ$, and the thermal stability of NCC/WPU composites was enhanced by the nanoparticles visibly.

The photochemical degradation of WPU matrix was inhibited by the addition of NCC and the composites containing 1.5 wt% modified NCC showed a satisfying anti-yellowing property. The improvement in the specular gloss of NCC/WPU composites was 164.8%. The chemical structure of linear WPU was supported by the well-dispersed NCC particles and the pencil hardness of NCC/WPU composites increased from 2H to 4H. The abrasion resistance of the composites synthesized with WPU and modified NCC, influenced by the degree of crosslinking, enhanced significantly as the NCC concentration increased.

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