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Novel bio-antifelting agent based on waterborne polyurethane and cellulose nanocrystals

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ABSTRACT

Novel nanocomposites made from cellulose nanocrystals and waterborne polyurethane were employed as wool antifelting agents. The cellulose nanocrystals, prepared by acid hydrolysis of cellulose microcrystalline, are in rod form with lengths of 70–150 nm and diameters of 10–20 nm in aqueous suspension, respectively. After the two aqueous suspensions were mixed homogeneously, cellulose nanocrystal reinforced polyurethane composite (nanocomposite) films were prepared and evaluated by means of transmission electron microscopy, scanning electron microscopy and dynamic mechanical analysis. Then the nanocrystal films were applied onto surfaces of wools by a pad-dry-cure process with nanocomposites containing different cellulose nanocrystal contents. The results indicated that with increasing cellulose nanocrystal content from 0 to 1.0 wt%, the area-shrinking rate of the treated wool fabrics was decreased from 5.24% to 0.70%, and the tensile strength of the fabric was increased by 14.95% and decreased about 44% use of waterborne polyurethane.

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1. Introduction

Wool is one of the most important fibers in textile industry and has been commonly used for producing high quality garments and business suits due to its properties of lightness, warmth, softness, and smoothness (Millington, 2006). However, the special scale structure in wool cuticle can cause felting shrinkage of wool fabrics under mechanical actions during laundry. Decreasing or eliminating the felting behavior is a goal of many research efforts in order to make wool fabrics machine washable (Simpson and Crawshaw, 2002; Silva, Zhang, Shen, & Cavaco-Paulo, 2006). Chlorination is a common approach that is used in the industry to reduce the shrinkage of wool fabrics; but nevertheless it produces and release harmful organohalogens into water and envrionment (Wang, Wang, & Fan, 2009). As a chlorine-free polymer and coating agent, waterborne polyurethane (WBPU) has a better anti-felting effect for wool fabrics. However, the higher concentration of WBPU was usually employed in practice (Zhang, Zhao, & Luo, 1997) in order to form a durable film and cover the scales of the surface of wool fibers. So that the WBPU concentration is high and the handle of finished fabric is hard, which limits its application. Lower concentration of WBPU could save chemical material and improve the handle if the thinner film was formed with a good mechanical performance.

Based on the idea, a nanocomposite was prepared with cellulose nanocrystals (CNCs) as a reinforcement phase in a WBPU matrix and its properties and application in anti-felting finish for wool were studied in the paper. Coating with polymer is a very important treatment in textile industry with a huge consume every year in the world. The reinforced polymer composite with nanocrystals will have a great applying foreground.

Cellulose is the most abundant biomass material in nature. More recently, cellulose nanocrystals (CNCs) have attracted interests from many researchers since CNS can serve as reinforcement fillers for many polymers due to its low cost, renewability, high availability, nanoscale dimensions, high aspect ratio, and easy of modification (Youssef, Lucian, & Orlando, 2010). Cellulose nanocrystals (CNCs), also called Cellulose Whiskers (CWs), are in rodlike shape and can be produced from various cellulose sources including wood, cotton, straw, bacteria and sea animals (Tang & Weder, 2010; Orts, Shey, Imam, Glenn, Guttman, & Revol, 2005). Depending on the source, they display high elastic modulus 100–150 GPa, aspect ratio (10–100) and wide diameters (4–20 nm) (Sturcova, Davies, & Eichhorn, 2005). Since the first report of using CNCs as a reinforcement phase in a latex matrix by Favier et al. (1995), CNCs have been widely investigated for the preparation of high performance composite materials based on a wide range of polymer matrices. Most research efforts have been focused on

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investigation of reinforcement effect and modification of CNC in nanocomposites (Samir, Alloin, & Dufresne, 2004; Pu, Zhang, Elder, Deng, Gatenholm, & Ragauskas, 2007), but no reports on applications in textile field.

Due to the fact of existence of active group –OH on the surface of CNCs, amino ($-NH_2$) and carboxylic (COOH) groups in wool, and –NCO of the WBPU, strong interactions among all three components could occur when the nanocomposite is coated on wool surfaces. Thus, WBPU/CNCs can be used as a potential “green finishing agent” in antifelting treatment of wool.

The main purpose of this study was to evaluate antifelting properties of wool fabric treated with cellulose nanocrystals composite. In this study, the WBPU/CNCs nanocomposite films were investigated by means of transmission electron microscopy, scanning electron microscopy and dynamic mechanical analysis. And then properties of wool fabric samples treated with the novel nanocomposites at different CNCs content will be discussed. The antifelting effects of the nanocomposites with different CNC contents were compared.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC, Avicel PH101) was purchased from FMC Biopolymer Corp., and the average particle size was 50 μm. Concentrated sulfuric acid (98%) was purchased from China National Medicine Corporation and used as received. All water utilized throughout the experimental procedures was deionized water.

Waterborne polyurethane (WBPU 8806) was supplied by Ruiqi Corporation, Shanghai, China. Scoured and undyed 100% wool fabric samples (204 g/m^2) were supplied by Shandong Ruyi Wool Co (Jining, Shandong Province, China).

2.2. Preparation of CNCs

A colloidal suspension of cellulose nanocrystals (CNCs) in water was prepared by acid-catalyzed hydrolysis of MCC, as described by Auad, Mosiewick, and Richardson (2009). Sulfuric acid (64%, w/w) was stirred while MCC was added in a ratio of MCC to acid of 1:8.75 g/mL. The mixture was then held at 45 °C for 2 h under strong stirring. Immediately following the acid hydrolysis, the suspension was diluted 10-folds with deionized water to quench the reaction. The suspensions were then washed with an equal volume of deionized water using repeated centrifuge cycles (15 min at 14,000 rpm). The supernatant was removed from the sediment and replaced by new deionized water, and suspension was further mixed. The centrifuge step was stopped after at least three washings, or until the supernatant became turbid. The last wash was conducted using dialysis with deionized water until a pH 5 was reached. The final suspension was freeze-dried and redispersed in water using ultrasonic treatment.

2.3. Preparation of WBPU/CNCs nanocomposite films

The compositions of dry composite films were controlled with 0–1.0 wt% of solid CNCs in the WBPU matrix by mixing various amounts of CNCs in the polymer. The mixtures were magnetically stirred for 2 h, followed by ultrasonication for 30 min in ice bath to ensure complete mixing. Then, the mixtures were cast onto a Teflon disk and dried in a vacuum oven at 25 °C for 10–20 h (depending on the water content). By changing the content of CNCs over the range of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt%, a series of nanocomposite films with a thickness of around 0.5 mm were prepared and coded as WBPU, WBPU/CNCs-2, WBPU/CNCs-4, WBPU/CNCs-6, WBPU/CNCs-8 and WBPU/CNCs-10, respectively. Before instrumental characterizations, the resulting films were conditioned at room temperature in a dessicator containing P_2O_5 with 0% relative humidity (RH).

2.4. Treatment on wool fabrics

Wool sample was treated by the mixed suspension of WBPU/CNC nanocomposites with different nanocrystals content by a pad-dry-cure process (concentration of the mixture in 50 g/L, and pick up of 70–80%). Then the samples were dried at 80 °C for 3 min and cured at 160 °C for 3 min.

2.5. Characterizations

Transmission electron microscopy (TEM). Drops of aqueous dispersions of cellulose nanocrystals (0.05%, w/w) were deposited on carbon-coated electron microscope grids (Protochips Inc.) and allowed to dry. The samples were analyzed with a JEM-2010HT transmission electron microscope (TEM) operated at an accelerating voltage of 80 kV.

Scanning electron microscopy (SEM). A scanning electron microscope TM-1000 was used to observe the WBPU/CNCs composite films and finished wool fibers. Samples were previously coated with gold.

Tensile test. The mechanical behavior of the wool fabric was performed at 20 °C using a universal testing machine (H5KS) in accordance with a testing standard, ASTM D5035-95. The fabric was 25 mm × 75 mm and crosshead speed of 100 mm min^{-1}. An average value of at least five replicates for each sample was taken.

Dynamic mechanical analysis (DMA). The dynamic mechanical behavior of the nanocomposite films was determined using a dynamic mechanical analyzer (TA instrument DMA Q800) in tensile mode at 1 Hz and a heating rate of 5 °C/min in the temperature range of −60 to 80 °C. The samples were prepared by cutting 6 mm wide strips from the films.

Felting shrinkage was determined according to a machine-washable technical standard of Woolmark TM 31 with washing cycles of $1 \times 7A + 3 \times 5A$. The area shrinkage was measured as follows:

$$\text{Area dimensional change} \quad (\%) \approx \text{WS} + \text{LS}$$

where WS is the mean width direction size (%) and LS is the mean length direction size (%).

The fabric whiteness was measured by using a Datacolor 65 color measurement spectrophotometer. The whiteness of the treated samples were measured before washing and all samples were conditioned for 24 ± 4 h (Hu & Yan, 2008) at 65 ± 2% relative humidity and 21 ± 1 °C.

ATR-FTIR spectroscopy was performed on a Nicolet ATR-FTIR spectrometer outfitted with a Smart OMNI-Sampler at room temperature. The finished fabrics were placed flat on the crystal surface. The data were collected over 16 scans with a resolution of 4 cm^{-1}. The background spectra were recorded with Ge crystal contacting air in the absence of samples.

3. Results and discussion

3.1. Morphology of CNCs and WBPU/CNC nanocomposites

The rod-like CNCs produced from sulfuric acid hydrolysis of MCC were characterized by TEM as shown in Fig. 1. The width varied from 10 to 20 nm whereas the length varied from 70 to 150 nm. These dimensions agreed well with the literature values reported for CNCs produced from the same cellulosic

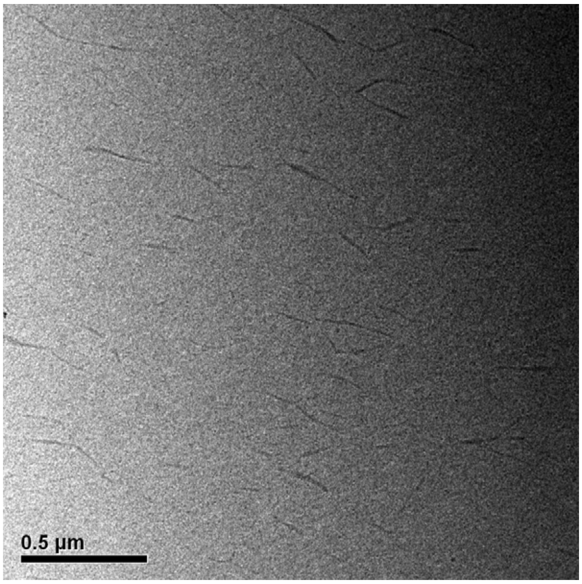

Fig. 1. TEM image of CNCs hydrolyzed from MCC.

material under similar conditions (Auad et al., 2009). However, a wide distribution of CNCs size, especially the length, is inevitable owing to the diffusion-controlled nature of the acid hydrolysis.

Fig. 2 shows the films SEM images of (a) WBPU matrix and nanocomposites filled with (b) 0.2, (c) 0.6, and (d) 1.0 wt% CNCs in WBPU matrix, respectively. As compared to the WBPU film, the morphology of the CNCs can be easily identified as white dots. As the concentration of CNCs in the composites increased, the surface appeared dots on the nanocomposites increased as well. These white dots are corresponding to the nanocrystals in the perpendicular plane of the nanocomposite films (Favier et al., 1995). No large aggregates and a homogeneous distribution of the CNCs in the WBPU matrix were observed in all nanocomposites, implying good adhesion between the nanocrystal fillers and the matrix, which should be attributed to the hydrophilicity of both WBPU and CNCs and the hydrogen-bonding interactions existing among filler/filler and filler/matrix. Such an even and uniform distribution of the fillers in the matrix could play an important role in improving the mechanical performance of the resulting nanocomposite films and their antifelting effects.

3.2. Dynamical mechanical analysis (DMA)

The storage modulus (E′) of WBPU/CNCs nanocomposite films with different CNCs loading as a function of temperature is shown in Fig. 3. In contrast to the pure WBPU, the storage modulus increases largely with the addition of cellulose nanocrystals. The WBPU-CNCs-10 in Fig. 3 shows the highest storage modulus during the entire temperature range, being approximately 482% higher than the pure WBPU. This behavior can be contributed to the incorporation of hydrophilic nanofillers of high stiffness with high interfacial area into waterborne polyurethane produces considerable improvements in the modulus.

The storage modulus is representative of the elastic character of the material. As compared to the pure WBPU film, if the mechanical performance of nanocomposite films such as elastic property was greatly improved, the finishing process indubitably did not need so much concentration WBPU for a better anti-felting effect and a nature soft handle of wool could be kept after finish.

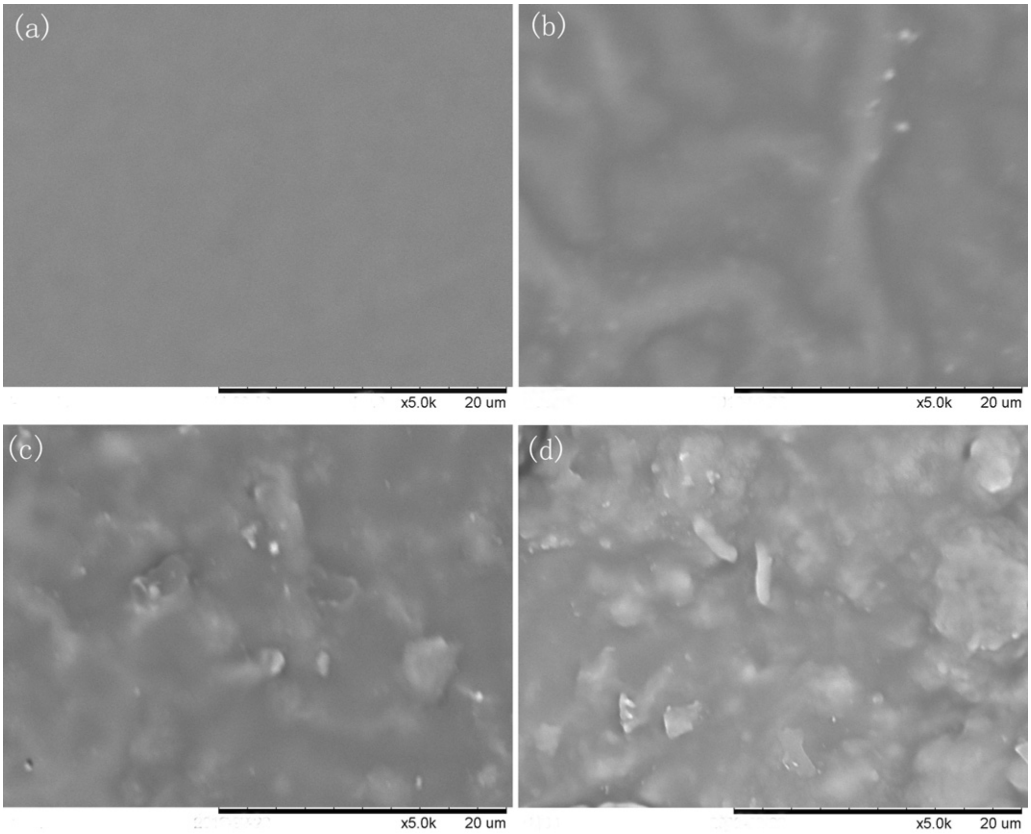

Fig. 2. SEM images of the WBPU/CNC nanocomposites with different CNCs contents: (a) 0 wt%; (b) 0.2 wt%; (c) 0.6 wt%; (d) 1.0 wt%.

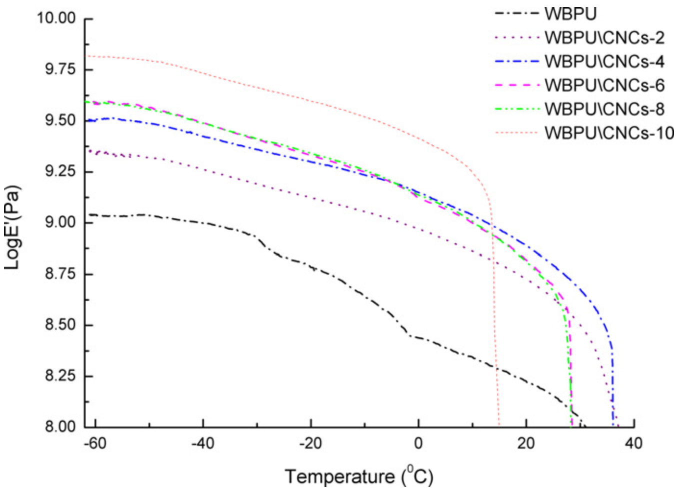

Fig. 3. Temperature dependence of E′ for WBPU/CNCs nanocomposite films.

3.3. Antifelting effect of treated wool fabrics

The antifelting effects of wool fabrics treated with different content of nanoparticles are shown in Table 1.

Table 1 shows the values of shrinkage in width, length and area of treated wool fabrics after 1 × 7A + 3 × 5A washing cycles according to Woolmark TM 31 (see also Section 2.5). When the anti-felting treatment with the concentration of pure WBPU in 50 g/L, the length-shrinking rate of the treated fabric was 3.73% and was not accord with the technical standard in less than 3.0% of machine-washable wool products. Increasing more nanoparticles in the WBPU matrix as a nanocomposite, the area-shrinking rate of the treated fabric was further decreased. When the CNCs content reached 1.0%, the length and area of shrinkage rates were separately reduced to 0.7% and 0.4%, reaching the technique standard. It can be seen in Table 1 that such a result could be obtained when 90 g/L pure WBPU were used to get the same antifelting result. Addition of 1 wt% CNCs can reduce about 40 g/L of the pure finishing agent. With the improved antifelting effect, the fabrics will exhibit improved washing durability inevitably.

Surfaces of wool fibers are covered by a layer of overlapping scales (the cuticle), with curved edges pointing to the tip of the fiber. This particular cuticle structure could result in frictional constraints on fiber movement in the direction of the fiber tip but not in the direction of the root; therefore, the effects of random forces transmitted to the fibers during washing cause the fibers to slip over each other and move preferentially in the root direction. The waterborne polyurethane (WBPU 8806) is a reactive agent due to existence of isocyanide group (–NCO) and thus is capable of crosslinking cellulose at a curing temperature. The polymer can form a uniform thin layer on the surfaces of wool fibers and cover the scales. Moreover, the –NCO group of the WBPU can simultaneously interact with active groups of the wool fibers, such as $-NH_2$, –OH, –SH, etc., to form firm covalently bonds. Thus, the coating of the polymer on the surfaces of wool fibers can cover the scales and reduce the resistance of the scales to movement of the fibers at certain directions. Additionally, the polymer coating is extremely durable due to the covalent bonding between them.

Table 1
Influence of content of CNCs on the shrinking rate wool fabrics.[a]

Sample	CNCs content (wt%)	Shrinking rate (%)		
		Area	LS	WS
Untreated[b]	0	14.21	9.73	4.48
WBPU[c]	0	5.24	3.73	1.51
WBPU/CNCs-2	0.2	4.05	2.93	1.12
WBPU/CNCs-4	0.4	3.09	1.84	1.25
WBPU/CNCs-6	0.6	2.41	1.49	0.92
WBPU/CNCs-8	0.8	1.40	0.60	0.80
WBPU/CNCs-10	1.0	0.70	0.40	0.30
WBPU[d]	0	0.52	0.35	0.17

[a] Treating process and condition see also Section 2.4, conc. of WBPU/CNCs is 50 g/L.
[b] Raw wool fabric.
[c] Conc. of WBPU is 50 g/L.
[d] Conc. of WBPU is 90 g/L.

According to Montazer etc. (Montazer, Pakdel, & Behzadnia, 2011), there are some relation between the hydrophilicity of the treated wool and the decrease in the shrinkage. CNCs are hydrophilic and the absorbed water could play a role as a plasticizer among the surface scales of the wool, therefore, shrinkage decreased.

3.4. Whiteness and mechanical properties of treated wool

Fig. 4 shows the whiteness of wool fabrics finished by the waterborne polyurethane containing different amounts of cellulose nanocrystal. When the content of CNCs was increased to 1.0% w/w, the whiteness slightly decreased from 15.28% to 12.21%, and the whiteness of untreated wool fabric is 15.60%. The difference is too small to be identified by human eyes. Therefore, adding 1% nano fillers will not dramatically change the color of the treated wool fabrics. One report discussed potential cellulose degradation as a cause of the yellowing since cellulose nanocrystals could start to decompose around 150-200 °C (Cao, Habibi, & Lucia, 2009). When the wool fabric was cured at 160 °C, some nanocrystals will begin degradation, which could cause the slight yellowish on the treated fabrics.

Fig. 5 reveals the results of tensile strength and elongation at break of the treated fabrics. The CNCs content has a profound effect on the mechanical properties of the treated wool fabrics. Even addition of a small amount of CNCs can largely improve the tensile strength of the WBPU composite. For example, only 1 wt% of CNCs in the polymer resulted in a tensile modulus increase of about 53% based on a literature (Cao et al., 2009), which attributes to high L/D ratio of rod-like CNCs and well dispersion in WBPU show in Fig. 1. The tensile strength of the fabrics in warp direction increases with the increase of CNCs loading level in the composite coating, reaching the highest value of 2.15×10^7 N/m^2 at 1.0 wt% of CNCs, approximately 15% higher than for the fabric treated with pure

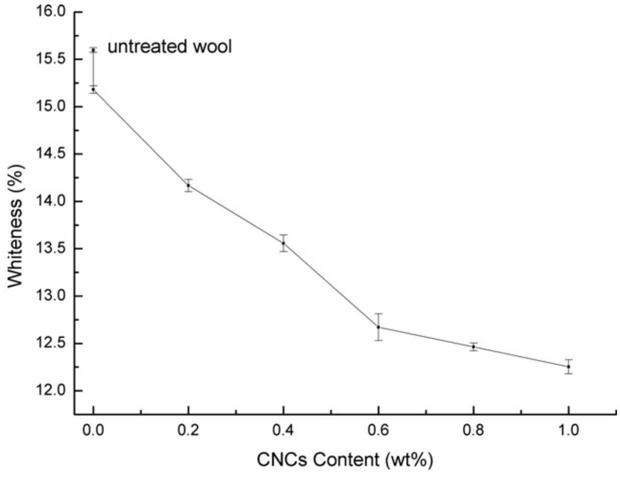

Fig. 4. The whiteness of wool fabrics finished by the waterborne polyurethane containing different amounts of cellulose nanocrystals from 0 wt% to 1.0 wt%.

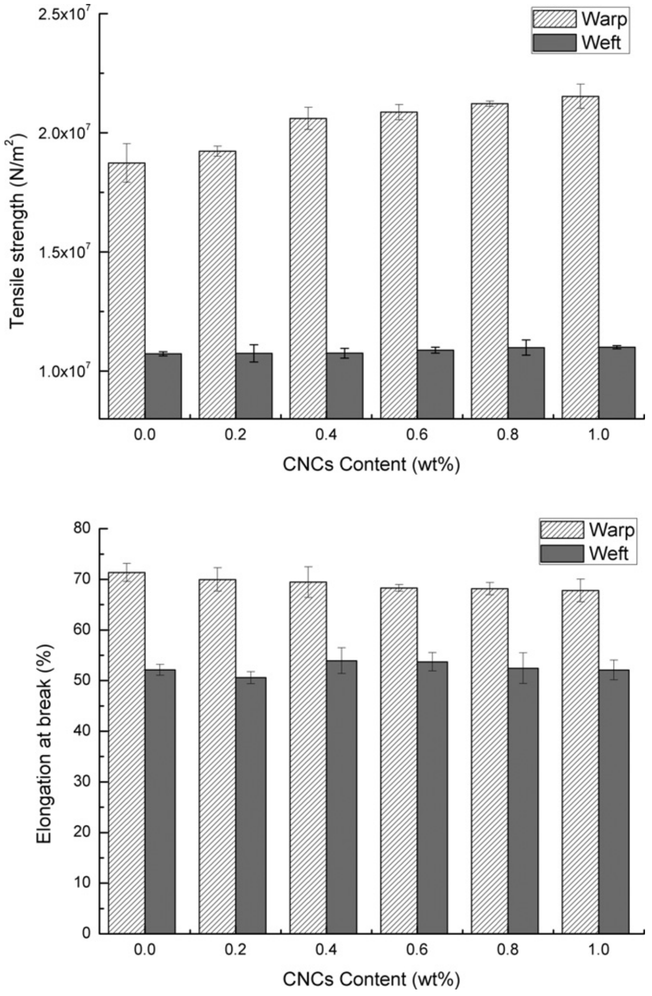

Fig. 5. The mechanical properties of wool fabrics finished by the waterborne polyurethane containing different amounts of cellulose nanocrystals from 0 wt% to 1.0 wt%.

WBPU only. The elongation at break showed an opposite result in two directions.

3.5. SEM observation

Surface morphologies of treated and untreated wool fibers are shown in Fig. 6. The pure WBPU of concentration in 50 g/L covered surfaces of the fibers reveal a thin layer covering the scales of wool fibers, which improves the smoothness of the fibers. The WBPU coating the cellulose nanocrystals provided a relatively intact layer of coating covering the surfaces of the wool fibers, higher amounts of nanoparticles absorbed on the surface of wool and, consequently, the ups and downs of the surface of wool covered completely which could further decrease Directional Frictional Effect (DEF) of wool fabrics and improve antifelting effect (Table 1).

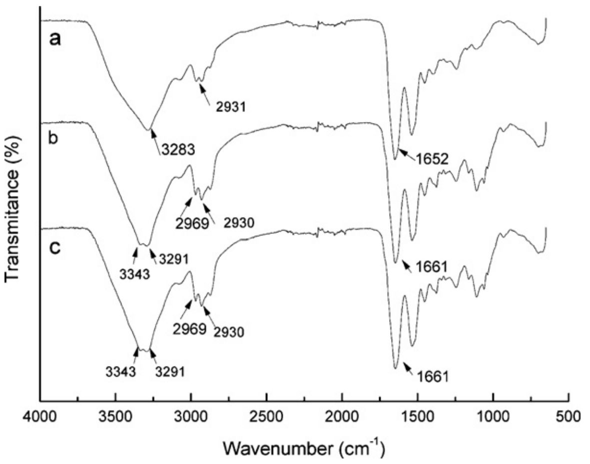

Fig. 7. ATR-FTIR spectra of treated wool fabrics (a) with 50 g/L WBPU before washed, (b) with 50 g/L WBPU/CNCs-10 before washed, (c) with 50 g/L WBPU/CNCs-10 after washed 1 × 7A + 3 × 5A.

3.6. ATR-FTIR spectra of treated wool

It is well known that the infrared spectrometer is a powerful instrument for the investigation of the surface analysis of solid. ATR-FTIR spectra of treated wool fabrics are shown in Fig. 7. For the fabric finished with 50 g/L WBPU only, the NH stretching vibration exhibits a strong absorption peak centered at around 3283 cm^{-1} arising from the hydrogen bonding between NH and carbonyl groups of the WBPU. Simultaneously, there is a prominent peak band centered at 1652 cm^{-1} assigned to the stretching vibration of both urethane and ester carbonyl was observed. After adding 1 wt% CNCs in the WBPU matrix, however, the peak of the carbonyl stretching vibration shifts to a higher wavenumber. It suggests that the incorporation of CNCs disturbs the hydrogen bonding between NH and C=O due to the strong interaction between CNCs and WBPU. The improved strength of the peak located at 2930 cm^{-1} and 2969 cm^{-1} in Fig. 7(b), which correspond to the alkane C–H asymmetric stretching vibration, indicates that there are more –CH$_2$– in the WBPU which belongs to CNCs. Fig. 7(c) is the washed fabric finished with 50 g/L WBPU/CNCs-10, the spectra is almost the same with the fabric before washed. It suggests that the wash durability is good.

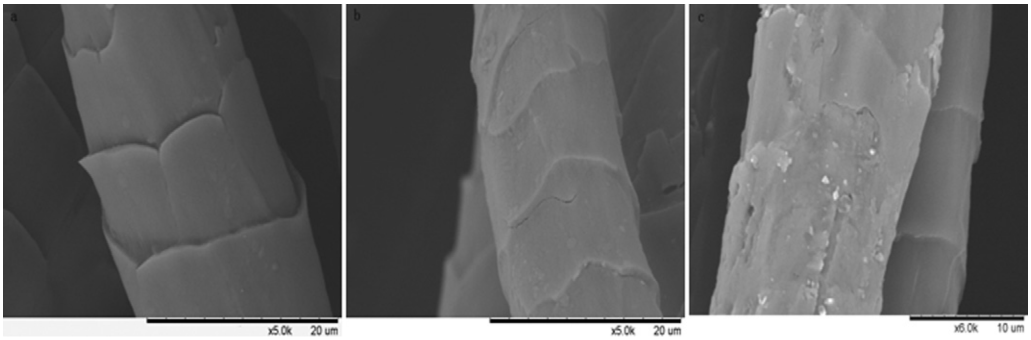

Fig. 6. SEM of surface morphologies of (a) untreated wool fabrics; (b) treated with 50 g/L WBPU only; (c) treated with 50 g/L WBPU/CNCs-10.

4. Conclusions

Nanocomposites made from cellulose nanocrystals (CNCs) and a waterborne polyurethane (WBPU) were first used as wool antifelting agents. The cellulose nanocrystals, prepared by acid hydrolysis of cellulose microcrystalline, exhibit rodlike shapes with length of 70–150 nm and diameter of 10–20 nm in TEM, respectively. SEM images showed that the CNCs were dispersed very well in the WBPU matrix. The dynamic mechanical analysis results showed that the large and strong interfacial developed between CNCs and WBPU matrix and it is one of the reasons why this nanocomposites can increase fabric's strength. The antifelting effect results indicated that with increasing cellulose nanocrystal content from 0 to 1.0 wt%, the area-shrinking rate decreased from 5.24% to 0.70%, and the tensile strength of wool fabric increased 14.95%. Addition of 1 wt% nanoparticles in the 50 g/L WBPU could achieve a result of using 90 g/L of the pure WBPU as the finishing agent. The superior properties of the new nanocomposite agent could have great potential applications in textile field.

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