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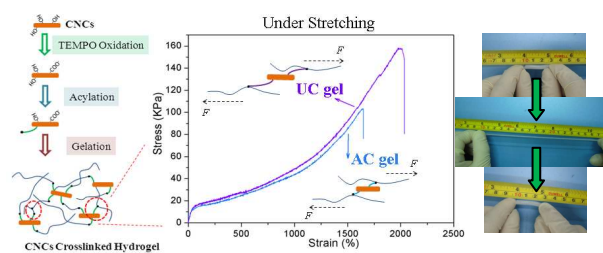


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A new and efficient strategy was first employed to fabricate highly elastic nanocomposite hydrogel by surface modification of cellulose nanocrystal.

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ARTICLE TYPE

Fabrication of highly elastic nanocomposite hydrogel by surface modification of cellulose nanocrystal

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Cellulose nanocrystals (CNCs) pre-grafted with polymerizable groups have been used as nano crosslinking joints and nano reinforcements to synthesize high-elastic hydrogels. However, the polymerizable CNCs usually have dispersion problem during hydrogel fabrication because of the hydrophobicity of the grafted polymerizable groups. In this study, TEMPO oxidation was successfully utilized to overcome this problem by introducing more hydrophilic groups on the CNCs surface, facilitating their homogeneous distribution in aqueous solution and hydrogels. Furthermore, AC and UC gels crosslinked by CNCs that were pre-grafted with acryloyl chloride (AC) and 10-undecylenoyl chloride (UC) on their surfaces were fabricated for finding out a more effective way to synthesize stronger nanocomposite hydrogel. The results showed that UC gels showed both higher tensile strength and higher elongation than the corresponding AC gels. It was shown that UC gels, which had longer grafted carbon chain length on CNC surface, possessed a better energy dissipation capacity under stretching than AC gels. The water swelling ratios of UC gels (13.0-36.7 g/g) were also much higher than those of the corresponding AC gels (11.2-21.0 g/g) as a result of larger space to hold water in hydrogel network. This work gives an insight into the influence of carbon chain length on the properties of CNCs crosslinked nanocomposite hydrogel, and provides an effective way to fabricate nanocomposite hydrogel with higher mechanical strength.

Introduction

Cellulose nanocrystals (CNCs) are attractive nano materials that can be obtained from a variety of renewable bioresources, such as cotton, wheat straw, pulp and tunicates.¹ Typically, CNCs are nanoparticles with 100-300 nm in length and 5-20 nm in width, which are prepared by removing amorphous regions of cellulose using mineral acid hydrolysis.^{2,3} Because of their excellent mechanical property, low density and high surface area, CNCs are effective nano reinforcements for novel composites in many aspects, including hydrogels.⁴⁻⁷

Hydrogels are water absorbent gels that are extensively used in cosmetics, agriculture, pharmaceuticals, etc.^{8,9} However, the synthesis of hydrogels with satisfactory mechanical properties is always one of the biggest challenges, and thus the brittle nature of hydrogels hinders their applications in many fields.¹⁰ In recent years, a variety of new methods, such as interpenetrating network, polymer blending, co-polymerization and nanoparticle reinforcement, have been discussed extensively to prepare robust hydrogels.¹¹⁻¹³ As a kind of biocompatible nanoparticles, CNCs have been confirmed to be effective nano reinforcements to synthesize hydrogels with high mechanical performances.

Abitbol et al.¹⁴ prepared CNCs loaded polyvinyl alcohol (PVA) hydrogels by repeated freeze-thaw processing. Owing to the addition of CNCs, the structural stability and compressive strength of hydrogels were improved. Later in 2012, Spagnol et al.¹⁵ synthesized nano composite hydrogels, consisting of CNCs, starch and poly(sodium acrylate) (PAA). It was demonstrated that CNCs could improve the water swelling ratio, mechanical properties and porous size of hydrogels. However, in these works or other similar works, the mechanical properties of CNC reinforced hydrogels were not satisfactory enough, as CNCs only acted as fillers to reinforce hydrogels, forming non-covalent bonds in networks.^{16,17}

Recently, Yang et al.¹⁸⁻²⁰ proposed a novel route to prepare CNCs reinforced hydrogels with excellent mechanical properties. After introducing polymerizable groups onto the surface of CNCs, robust hydrogels with could be prepared by using CNCs as crosslinking joints via free radical polymerization in the absence of crosslink agents. In this case, CNCs acted as not only fillers but also crosslinking joints. Because of their extraordinary stretching properties, CNCs crosslinked hydrogels have promising applications in biological, pharmaceutical and packaging fields. However, there are some problems yet to be settled, for example, the poor water dispersibility of the modified

CNCs, and the influence of the grafted group length on the mechanical performance of hydrogels.

The aim of this work was to investigate the relationships between the surface properties of CNCs and the performances of hydrogels for fabricating more robust nanocomposite hydrogel, including the surface hydrophilicity and the chain length of the grafted groups. For this purpose, TEMPO oxidation was first used to improve the dispersibility of CNCs in aqueous solution. Then two kinds of acylation agents with different lengths of carbon chain, e.g., acryloyl chloride (3 carbon numbers) and 10-undecylenoylchloride (11 carbon numbers) were grafted onto the surface of TEMPO oxidized CNCs as polymerizable groups. At last, CNCs were used as crosslinking joints to synthesize highly stretching polyacrylamide (PAM) hydrogels. It was found that, after TEMPO oxidation and then being grafted by vinylic groups with longer carbon chain length, on the surface of CNCs, a much stronger nanocomposite hydrogel could be obtained. As we known, it was for the first time to fabricate nanocomposite hydrogel by regulating the surface properties of CNCs with TEMPO oxidation and different vinylic groups. The results are encouraging and provide an effective rout to fabricate nanocomposite hydrogel with better mechanical performances.

Experimental section

Materials

Cotton linters with particle size of 200 mesh were purchased from Xuanyuan Machinery, China. The α -cellulose content was over 98 wt%. 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), NaBr and 7% NaClO solution were laboratory grade and purchased from Sigma-Aldrich Co., Ltd., China. Acrylamide (AM), potassium persulfate (KPS) and N, N-methylenebis(acrylamide) (MBA) were CP grade and provided by Aladdin Chemistry Co., Ltd., China. Acryloyl chloride (AC) and 10-undecylenoyl chloride (UC) were 98% purity and purchased from Aladdin Chemistry Co., Ltd., China. Analytical grade acetone, sulfuric acid and N, N-Dimethylformamide (DMF) were purchased from Guanghua Sci-Tech Co., Ltd., China.

CNCs Preparation

In order to prepare CNCs, cellulose was hydrolyzed by 64 wt% H_2SO_4 with a solid-to-liquid ratio of 1:10 (g/mL) at 50 °C for 90 min. After the reaction, the hydrolysis suspension was centrifuged once and dialyzed against deionized water for several days. The purified CNCs were freeze-dried, weighted and stored in a desiccators.

TEMPO Oxidation

CNCs (2.0 g) were dispersed in 150 mL water after 3-5 cycles of ultrasonic dispersion. Then 30 mg TEMPO and 0.6 g NaBr were added into the CNC suspension. After the complete dissolution of reagents, 11.6 mL 7% NaClO solution adjusted to pH = 10.0 by 0.1 M HCl was slowly dripped into the suspension. The reaction processed at 25 °C for 3 h and maintained at pH = 10.0 by adding 0.5 M NaOH. At the end of the reaction, the solution was

neutralized to pH = 3.5 by 0.1 M HCl. The suspension was centrifuged once and dialyzed against deionized water. TEMPO oxidized CNCs were freeze-dried, weighted and stored in a desiccator.

The carboxyl content of the oxidized CNCs was determined by conductometric titration according to previous literatures.^{21,22} About 20 mg oxidized CNCs were added in 20 mL NaCl aqueous solution (1 mM). Then the suspension was adjusted to pH = 2-3 by 0.01 M HCl solution. After stirring for 10 min, the suspension was titrated by 0.05 M NaOH with a speed of 0.1 mL/min. The titration curve is shown in Figure S1. The content of carboxyl groups in the oxidized CNCs was calculated to be 2.6 mmol/g.

Acylation

The reaction conditions of acylation are listed in Table S1. In the acylation reaction with AC, 100 mg oxidized CNCs were mixed into 10 mL DMF. The suspension was dispersed by ultrasonic treatment and heated to 55 °C. AC was then slowly added into the suspension and reacted at 55 °C for 3 h. After the reaction, the modified CNCs were washed with DMF once and then methanol for three times using centrifugation (10000 rpm). The UC acylation of CNCs was reacted at 30 °C for 3 h. Except for the reaction condition, the reaction process of UC acylation was similar to that of AC acylation. Solvent exchange, which was carried out by several cycles of water addition and vacuum evaporation, was applied to obtain the water suspension of modified CNCs. The CNC suspensions were stored at 4 °C.

Determination of Acylation Degree

The acylation degrees of the modified CNCs were determined according to previous method.²³ 200 mg modified CNCs were suspended in 20 mL of 95% ethanol solution with a NaOH concentration of 0.25 M. Oxidized CNCs were soaked in the same solution as blank for standardizing. The suspension was stirred for 24 h at 25 °C. Then excess standard 0.5 M HCl was added into the suspension drop-wise. After stirring for 4 h, the excess acid was titrated by 0.05 M NaOH to the phenolphthalein end point. The results are shown in Table S1.

Transmission Electron Micrograph (TEM)

The TEM observation of CNCs was performed using a JEM-2100HR (JEOL) at an acceleration voltage of 100 kV. Several drops of CNCs suspension were dripped onto a carbon-coated copper grid. Then the grid was stained with 2 wt% phosphotungstate solution for 30 s twice to enhance the microscopic resolution.

Zeta Potential Measurement

The dynamic light scattering (DLS, Zeta sizer Nano ZS, Malvern instrument) was used to evaluate the zeta potential of CNC, TEMPO oxidized CNC (CNC-T) and acylated CNC suspensions at 25 °C. All experiments were carried out in dilute CNC suspension (0.15 wt%) where CNC particles randomly oriented.

Hydrogel Preparation

As shown in Table S1, AC-T-2 (DS= 0.24) and UC-T-3 (DS= 0.25) with similar degree of substitution (DS) were selected to

synthesize hydrogels. The AC and UC gels were prepared by free radical polymerization. The preparation conditions are listed in Table S2.

For AC gels, 3.0 g AM and 15 mL water were added into each tube. 1.00, 0.50, and 0.25 mmol AC modified CNCs (the mole number of modified glucose ring) were added to prepare different samples. The corresponding hydrogels were designated as A1, A2, and A3, respectively. After the addition of CNCs, the suspensions were adjusted to pH = 7 by 0.1 M NaOH. The suspensions were dispersed by ultrasonic treatment for 3-5 cycles and deoxygenated with nitrogen gas for 20 min. Then 600 μ L of 0.02 g/mL KPS was added into each suspension and continued to deoxygenate for 10 min. Thereafter, the tubes were sealed and immersed in water bath (30 $^{\circ}$ C) for 24 h. The hydrogels crosslinked by UC-T-3 were prepared by the same method. 1.00, 0.50, and 0.25 mmol UC modified CNCs (the mole number of modified glucose ring) were added into each sample. The corresponding hydrogels were designated as U1, U2, and U3, respectively. PAM hydrogel that crosslinked by MBA (0.02 g/mL, 600 μ L) instead of CNCs was also prepared by the same process for comparison and designated as B gel.

All hydrogels were soaked in distilled water for 48 h to remove the unreacted monomers. Then the swelling hydrogels were dehydrated in 95% ethanol for 24 h and oven dried at 40 $^{\circ}$ C for 48 h. The purified and dried hydrogels were stored in desiccators for further use.

FT-IR

The FT-IR spectra of modified CNCs were recorded from a KBr disc containing 1% finely grounded samples on a Nicolet 750 FT-IR spectrophotometer. Thirty-two scans were taken for each sample recorded from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode.

Mechanical Properties

Cylindrical hydrogels with diameter of 4 mm without any purification or water swelling after preparation were used for stretching test. A universal instrument of mechanical properties (Instron, 5565, USA) with a 50 N loaded cell was used to determine the elastic modulus and elongation at break in a constant stretching speed of 20 mm/min. The samples were clipped by two clamps on the instrument with the protection of cotton in order to alleviate the clipping stress on testing samples. The elastic modulus was calculated from the slope of the stress-strain curves within the range of elastic limit of stretching.

Compressing test was also operated on a universal instrument of mechanical properties (Instron, 5565, USA) in compressive mode at a constant speed of 5 mm/min. The purified and dried hydrogels were firstly soaked in water for 72 h to reach equilibrium water swelling ratio. Then the hydrogels were cut into cylindrical shape with a height of 20 mm. The diameter of the cross section of each sample was measured before testing. No water was squeezed out from hydrogels and no fracture happened to hydrogels during compressing test. Mechanical tests were carried out at 23 ± 0.5 $^{\circ}$ C and $50 \pm 5\%$ RH and were repeated for at least 5 times for each sample.

Swelling Ratios of Hydrogel

The purified and dried hydrogels were soaked in distilled water to determine their swelling ratios at room temperature. During this process, the hydrogels were taken out at certain time and weighted. Excess water on the surface of hydrogel was removed with filter paper. The swelling ratio was defined as $W_{\text{swelling}}/W_{\text{dry}}$, in which W_{dry} and W_{swelling} were the weights of hydrogels before and after swelling. The swelling process was repeated for three times. The average values are listed in Table 1.

Thermogravimetric Analysis (TG)

TG was performed in an aluminum pan by TA TG-Q200, US. Nitrogen was used as the purge gas at a flow rate of 25 mL/min. The hydrogels were finely grounded to avoid the inaccuracy that caused by hydrogel expansion. In the first period, sample was preheated to 105 $^{\circ}$ C at a rate of 20 $^{\circ}$ C/min to remove water. After cooling to 80 $^{\circ}$ C, the sample was then heated to 700 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

Results and Discussion

Dispersion of Nanoparticles

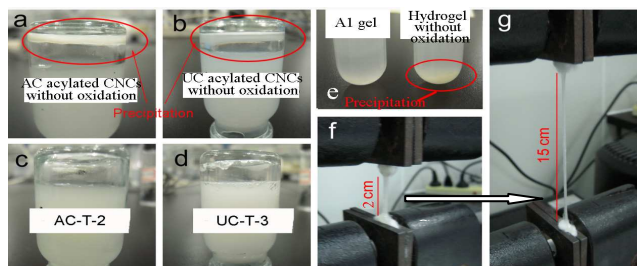


Figure 1 Pictures of CNCs suspensions and CNCs crosslinked hydrogels. (a), (b), (c), and (d) show the water suspension of acylated CNCs with or without TEMPO oxidation; (e) shows the hydrogels prepared by AC acylated CNCs with or without TEMPO oxidation; (f) and (g) show the stretching and elasticity of A1 gel.

Homogeneous dispersion of CNCs is always the foremost mission for CNCs reinforced hydrogels.^{24,25} Lots of factors are shown to influence the water dispersibility of CNCs, such as the surface properties, the dimension of CNC and the ionic strength of water solution.¹ CNCs that prepared from sulfuric acid hydrolysis have sulfate groups on their surfaces. The zeta potential of CNC suspension was -40.3 mV, showing negative charge surface of CNCs in water. The electrostatic repulsion of anionic sulfate groups could help CNCs homogeneously disperse in water.²⁶ However, as shown in Figures 1a and 1b, acylated CNCs without TEMPO oxidation were inclined to precipitate in water, due to the hydrophobic nature of AC and UC groups on CNC surface. In this case, the inhomogeneous hydrogels would be synthesized, as shown in Figure 1e. Therefore, the dispersion of CNCs in aqueous solution should be improved in order to synthesize nanocomposite hydrogel with high mechanical properties.

During TEMPO oxidation, the hydroxyl groups of C-6 can be partly oxidized into carboxyl groups, making the oxidized CNCs more hydrophilic.²⁷ As shown in Table S1, the zeta potential of CNC-T suspension was -59.5 mV, indicating more negative

charge surface of CNC-T in water than that of CNCs. The oxidized CNCs will have a better dispersion in water as the carboxyl groups are able to enhance the electrostatic repulsion between CNCs.^{15,28} CNCs after acylation (AC-T-2 and UC-T-3 in Table S1) in aqueous solution also showed more negative charge surface (-58.4 mV and -57.1 mV, respectively) than CNCs. Figures 1c and 1d illustrate that TEMPO oxidation greatly facilitate the dispersion of CNCs in aqueous solution, which is in sharp contrast with the suspension of CNCs with vinylic groups but without TEMPO oxidation (Figures 1a and 1b). The excellent dispersion of CNCs will undoubtedly improve the mechanical performances of nanocomposite hydrogel.

FT-IR Spectra of CNCs

The acylation condition and quantitative results of DS are listed in Table S1. Among these products, AC-T-2 and UC-T-3 had similar DS, and thus were selected as crosslink joints in order to discuss the influences of grafted groups on the properties of hydrogels. Figure 2a shows the FT-IR spectra of different CNCs. In the spectrum of pure CNCs, the absorptions at 3340, 1450, 1315, 1150, 1050, and 1020 cm^{-1} are typical bands of cellulose. The peak at 1150 cm^{-1} arises from C-O asymmetric bridge stretching vibration. The C-O-C pyranose ring skeletal vibration gives a band at 1050 cm^{-1} .²⁹ A peak at 1600 cm^{-1} could be observed, which represents the C=O stretching in carboxyl group as anion. This signal confirmed that in oxidized CNCs the hydroxyl groups in position C-6 were selectively oxidized.^{21,30} After acylation, the spectra of CNCs shows a strong peak at 1740 cm^{-1} , indicating the formation of ester bonds.³¹ The peak intensity at 1740 cm^{-1} could qualitatively indicate the successfully grafting of AC or UC. The quantitative results of DS are listed in Table S1. DS increased with more addition of AC or UC. Among these products, AC-T-2 and UC-T-3 had similar DS, and thus were selected as crosslink joints in order to discuss the influences of grafted groups on the properties of hydrogels.

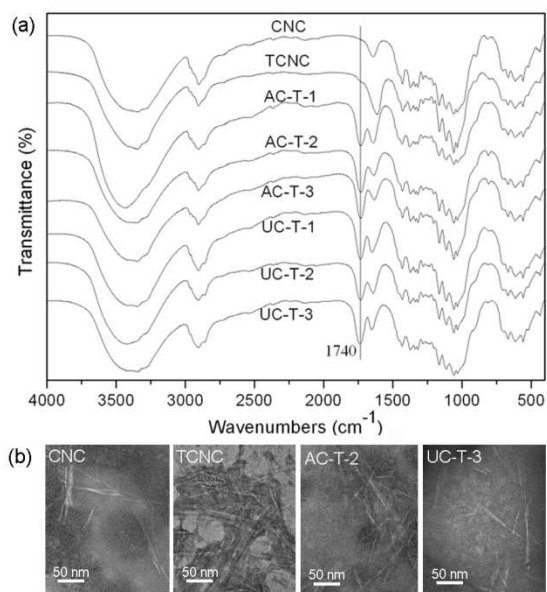


Figure 2 FT-IR spectra (a) and TEM images (b) of CNCs.

TEM Images of CNCs

Figure 2b shows the TEM images of CNCs and the modified CNCs. CNCs obtained from sulfuric acid hydrolysis had dimension of 100-200 nm in length and 5-10 nm in width. After TEMPO oxidation and mild acylation, CNCs still maintained their initial rod-like morphology when dispersed in water, indicating that TEMPO oxidation and acylation mainly occurred on the surface of CNCs.

Mechanical Properties of Hydrogels

Table S2 shows the synthesis conditions of various composite hydrogels, while Table 1 lists the mechanical testing results and Figure 3a shows the representative stress-strain curves of PAM hydrogels with or without modified CNCs. It was shown that B gel (the circled red curve), which was crosslinked by MBA rather than modified CNCs, showed a tensile stress of 20.1 KPa and an elongation at break of only about 150%, illustrating the fragility of traditional PAM hydrogels. In addition, B gel was more or less deformed before testing when clipped onto the machine due to its brittle nature. By contrast, all CNC crosslinked hydrogels exhibited very high tensile strengths (71.5-171.9 kPa) and elongations at break (1080-4540%).

Table 1 Mechanical Properties and Swelling Ratios of Hydrogels.

No.	SEM ^a (kPa)	STS ^b (kPa)	SE ^c (%)	CEM ^d (kPa)	WS R ^e
B	28.7±4.7	20.1±4.2	150±70	47.4±6.9	10.1
A1	9.6±0.4	109.1±12.1	1080±180	13.5±2.1	11.2
A2	6.3±0.9	107.3±16.8	1540±190	7.4±1.0	14.7
A3	1.8±0.3	71.5±9.4	4040±490	5.0±0.5	21.0
U1	11.1±0.4	171.9±8.7	1130±80	8.4±0.6	13.0
U2	6.0±0.4	159.3±19.5	2080±490	3.4±0.2	23.7
U3	1.9±0.1	92.1±0.2	4560±390	3.1±0.5	36.7

^a Stretching elastic modulus; ^b Stretching tensile strength; ^c Stretching elongation; ^d Compressing elastic modulus; ^e Water swelling ratio (60 h).

The high mechanical performance of CNCs crosslinked hydrogels can be explained by energy dissipation process.^{32,33} At the beginning of the stretching process when the stretching stress is low, non-covalent interactions in hydrogel network, including physical entanglement, hydrogen bond and Van der Waals force, are firstly damaged to dissipate the stress, leading to reversible deformation. When the stress becomes higher, the covalent bonds begin to dissociate to withstand the crack propagation in hydrogel network. The break of covalent bonds, mainly at crosslinking joints, can consume a great deal of energy to avoid fracture, which is irreversible and will lead to the permanent deformation of hydrogel network.³³ In CNCs crosslinked hydrogels, besides the covalent bonds between PAM chain and CNC, entanglement between PAM chain and neighboring CNC formed a large amount of non-covalent bonds. According to the energy dissipation process mentioned above, the presence of CNCs can efficiently increase the non-covalent interactions. Under stretching, non-covalent interactions would first withstand stress at low stress and then were continuously dissociated at high stress to effectively dissipate the energy, while covalent interactions withstand the stress at higher stress. Besides, CNCs give more space for the rearrangement of hydrogel network to prevent the fracture from growing. Therefore, CNCs crosslinked hydrogels showed high

elongation and elasticity, as shown in Figure 1. For B gels, however, stress was more likely to localize in certain crosslinking joints. Therefore, the fracture growth was much faster than CNCs crosslinked hydrogels.³⁴

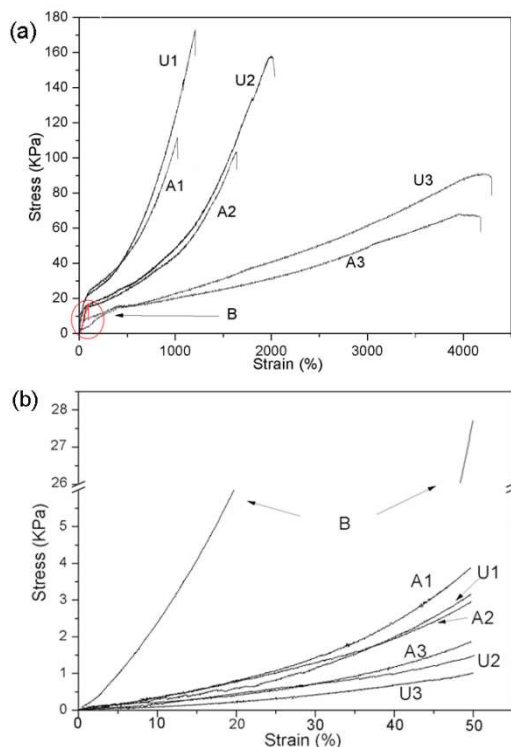


Figure 3 Stress-strain curves of stretching (a) and compressing test (b).

In stretching test, the elongation of CNCs crosslinked hydrogels increased from 1080-1130% to 4040-4460% and the tensile strength decreased from 109.1-171.9 kPa to 71.5-92.1 kPa when CNC dosage was reduced from 1.00 mmol to 0.25 mmol. The results indicated that the crosslinking network was more rigid at higher CNCs concentration. The gelation process of hydrogels crosslinked by nanoparticles had been described in previous literatures.^{34,35} Large amounts of monomers and initiators firstly gather around the surfaces of nanoparticles. Then polymer chains gradually grew from the free radical site on the surface of nanoparticles. These chains are able to interconnect with neighboring nanoparticles via covalent crosslinks or non-covalent interactions. In CNCs crosslinked hydrogels, the average distance between neighboring CNCs would become shorter (higher crosslinking density in hydrogel network) at a higher CNCs concentration. Therefore, the hydrogel had higher stress but lower strain.

The stress-strain curves of compressing test are shown in Figure 3b. The elastic moduli were calculated at the range of 20-40% strain, as listed in Table 1. The curves were J-shaped, indicating that the toughness of CNCs crosslinked hydrogels increased in a higher deformation. At low compression stress, CNCs in hydrogels rotated in network. When the compression stress increased, more and more CNCs began to take up the load. CNCs, which are rigid rods with high elastic modulus, can impart significant strength to hydrogels.^{36,37} When more CNCs were

added, the elastic moduli of CNCs crosslinked hydrogels were higher in compressing test. The reason is that more CNCs could result in a higher crosslinking density of hydrogels. Besides, the high elastic modulus of CNCs is another reason. As shown in Table 1, the compressing elastic modulus of B gel (47.4 kPa) is much higher than those of CNCs crosslinked hydrogels (3.1-13.5 kPa) in compressing test, indicating a higher crosslinking density and less flexibility. Large amounts of MBA acted as crosslinking joints between PAM chains in B gel, and the distance between PAM chains were very short. Therefore the network of hydrogel was very dense as a result of low molecular weight of MBA, and the mobility of hydrogel network was very limited, leading to a hydrogel with high stiffness. However, in the case of CNCs crosslinked hydrogels, the relative large volume of CNCs contributed to the flexibility of the network, making the hydrogels softer. These results well agree with those from tensile testing.

The stretching elastic moduli of A1, A2, and A3 were 9.6, 6.3, and 1.8 kPa respectively, while the stretching elastic moduli of U1, U2, and U3 were 11.1, 6.0, and 1.9 kPa, respectively. However, UC gels showed higher tensile strength and higher elongation than the corresponding AC gels. For example, A2 had a tensile strength of 107.3 kPa and an elongation of 1540%, while U2 had a much higher tensile strength of 159.3 kPa and a higher elongation of 2080%. It is demonstrated that UC gels possessed a much more efficient energy dissipation process than AC gels, despite their similar elastic moduli. The reason should be attributed to the longer grafted carbon chain length on the surface of UC-T-3 than that on the surface of AC-T-2. CNCs with longer carbon chain length give corresponding hydrogels higher tensile strength and higher elongation. As mentioned above, most of the PAM polymer chains in hydrogels grew from the surfaces of CNCs. According to the previous theory about nanocomposite hydrogels,^{11,34} there are two kinds of PAM chains on nanoparticle surface. Some PAM chains covalently link with neighboring CNCs at their both ends, while other PAM chains only covalently link with CNCs at one end. However, this theory is hard to elucidate the differences in stretching performance between AC and UC gels. So far, no theory has been proposed to explain the relation between the grafted carbon chain length on nanoparticle surface and the mechanical performances of nanoparticle crosslinked hydrogels.

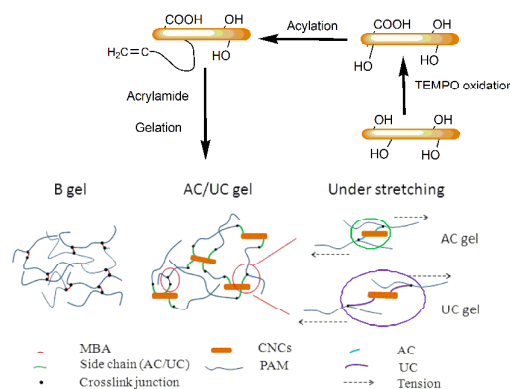


Figure 4 Network structure of B gel and CNCs crosslinked hydrogels.

As the result of this work, it is supposed that, besides two kinds of PAM chains mentioned above, some free radicals occurred along the PAM chains rather than only at the end groups. These free radicals could crosslink with polymerizable groups on CNC surface, as outlined in red in Figure 4. In this case, the importance of the grafted carbon chain length on CNC surface could be observed. As shown in Figure 4, when hydrogel is under stretching, PAM polymer chains on CNC surface would slide against each other to dissipate the energy.^{38,39} In UC gels, the longer carbon chain length on CNC surface produced larger available space to change their direction in order to reduce stress concentration and dissipate energy. From another point of view, when CNCs and surrounding PAM chains were considered as two separated parts, the carbon bridges (i.e. the grafted groups on CNC surface) between CNC and PAM could be considered as an interlayer. The interlayer would be “softer” and more “elastic” or “flexible”, if the grafted groups on CNC surface were longer, which would give more potential to dissipate the energy under stretching. In compressing test, UC gels showed lower elastic moduli than corresponding AC gels, as shown in Table 1. For example, the compressing elastic modulus of A2 gel is 7.4 kPa while that of U2 gel is 3.4 kPa. This result may also be explained by the “softer” interlayer around CNCs in UC gels, when carbon chains grafted on the surface of CNCs were longer. To sum up, in stretching test, longer carbon chain length of grafted groups on CNC surface could increase the stress and elongation of CNCs crosslinked hydrogels, while in compressing test, longer carbon chain length of grafted groups on CNC surface lead to a “softer” hydrogel.

Water Swelling Performance

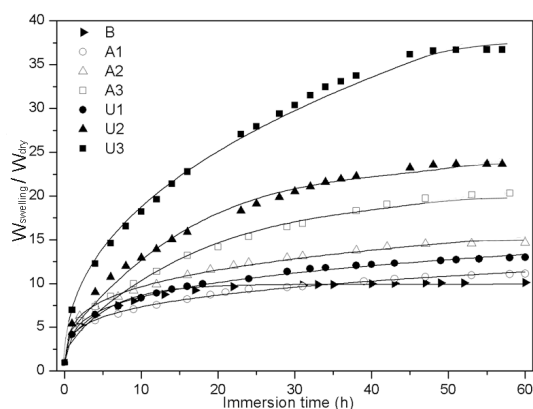


Figure 5 Water swelling ratios for different hydrogels.

Figure 5 shows the water swelling ratios of hydrogels plotted according to immersion time. All hydrogels reached their equilibrium swelling ratios in 60 h without any dissolution. When 0.10 mmol AC-T-2 or UC-T-3 was added as crosslink joints (not shown in this paper), the hydrogels were partly disintegrated in water as a result of the inadequate crosslinking degree. As listed in Table 1, B gel has the lowest equilibrium swelling ratio (10.1 g/g), while CNCs crosslinked hydrogels have swelling ratio from 11.2 g/g to 36.7 g/g. As shown in Figure 4, CNCs, which have a much larger volume than MBA, could create larger space in hydrogel

network, increasing the water holding capability of hydrogels. The water swelling ability of hydrogels was higher at lower CNC concentration. The water swelling ratios were only 11.2-13.0 g/g when 1.00 mmol modified CNCs were added, and significantly increased to 21.0-36.7 g/g when the dosage of CNCs was reduced to 0.25 mmol. The reason is that the crosslinking density increases at higher CNC concentration, which limits the penetration of water into hydrogel network.⁴⁰ Table 1 also shows that UC gels have much higher water swelling ratios than the corresponding AC gels, especially at low CNCs concentration. This may be due to the longer carbon chain length of grafted groups on the surface of UC-T-3, producing more space in hydrogel network. To sum up, longer carbon chain length of grafted groups on CNC surface increased the swelling ratios of hydrogels.

Thermo-stability Study

Figure 6 shows the TGA and DTG curves of hydrogels. Both AC-T-2 and UC-T-3 showed similar thermo-stability with a significant weight loss at a wide temperature range of 200-400 °C. The weight loss of B gel can be divided into two processes at temperature ranges of 220-300 °C and 300-420 °C. According to the performances of the modified CNCs and B gels, the addition of CNCs should have lowered the decomposition temperature of hydrogels. However, as Figure 6 shown, the CNCs crosslinked hydrogels did not show any obvious difference from B gels. The reason is that the weight percentage of CNCs in hydrogels is too small to influence their thermo-stability. Thus, CNCs crosslinked hydrogels remained a relatively good thermal stability.

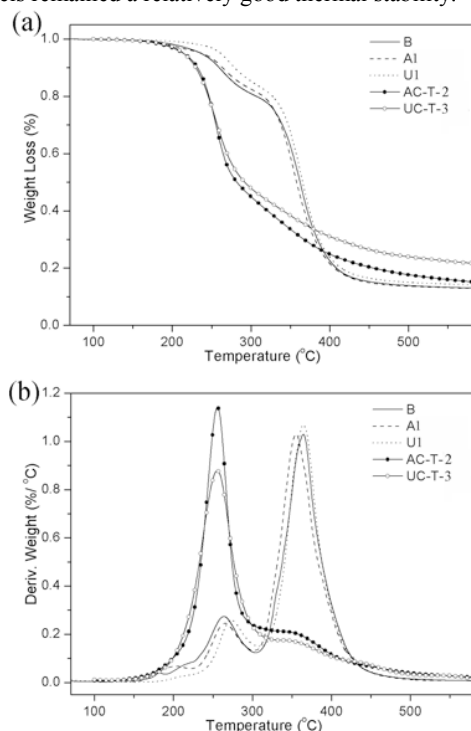


Figure 6 TG (a) and DTA (b) curves of modified CNCs and hydrogels.

Conclusions

In summary, this work shows an insight into the influence of

carbon chain length on the properties of nanocomposite hydrogel. TEMPO oxidation successfully introduced carboxyl groups on CNC surface, facilitating the homogeneous dispersion of CNCs in hydrogels. The carbon chain length of the grafted group on CNC surface significantly affected the network structure and properties of hydrogels. CNCs which had polymerizable groups with longer carbon chain length on their surfaces could significantly increase the tensile strength of PAM hydrogel. A model was proposed that longer carbon chain length on CNC surface resulted in a “softer” or more “flexible” interlayer between CNC and PAM. Therefore a better energy dissipation process could be created for CNCs crosslinked hydrogels. The water swelling ratios of hydrogels that crosslinked by CNCs with longer carbon chain length were also much higher.

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25 Notes and references

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† Electronic Supplementary Information (ESI) available: [Table S1 shows the acylation conditions of CNCs and their DS. Table S2 shows the synthesis conditions of hydrogels. Figure S1 shows the conductometric titration curve of TEMPO oxidized CNCs]. See DOI: 10.1039/b000000x/

40 References

- D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray and A. Dorris, *Angew. Chem. Int. Edit.*, 2011, **50**, 5438–5466.
- M. M. de Souza Lima and R. Borsali, *Macromol. Rapid Comm.*, 2004, **25**, 771–787.
- B. L. Holt, S. D. Stoyanov, E. Pelan and V. N. Paunov, *J. Mater. Chem.*, 2010, **20**, 10058–10070.
- M. A. S. Azizi Samir, F. Alloin, J. Y. Sanchez and A. Dufresne, *Polymer*, 2004, **45**, 4149–4157.
- H. Liu, D. Liu, F. Yao and Q. Wu, *Bioresource Technol.*, 2010, **101**, 5685–5692.
- M. A. Hubbe, O. J. Rojas, L. A. Lucia and M. Sain, *BioResources*, 2008, **3**, 929–980.
- B. L. Peng, N. Dhar, H. L. Liu and K. C. Tam, *Can. J. Chem. Eng.*, 2011, **89**, 1191–1206.
- G. Peng, S. Xu, Y. Peng, J. Wang and L. Zheng, *Bioresource Technol.*, 2008, **99**, 444–447.
- V. Gribova, T. Crouzier and C. Picart, *J. Mater. Chem.*, 2011, **21**, 14354–14366.
- P. Banet, P. Griesmar, S. Serfaty, F. Vidal, V. Jaouen and J. Y. Le Huerou, *J. Phys. Chem. B*, 2009, **113**, 14914–14919.
- Q. Wang, R. Hou, Y. Cheng and J. Fu, *Soft Matter*, 2012, **8**, 6048–6056.
- B. B. Mandal, S. Kapoor and S. C. Kundu, *Biomaterials*, 2009, **30**, 2826–2836.
- F. Aouada, M. Moura, W. Orts and L. C. Mattoso, *J. Mater. Sci.*, 2010, **45**, 4977–4985.
- T. Abitbol, T. Johnstone, T. M. Quinn and D. G. Gray, *Soft Matter*, 2011, **7**, 2373–2379.
- C. Spagnol, F. H. A. Rodrigues, A. G. B. Pereira, A. R. Fajardo, A. F. Rubira and E. C. Muniz, *Carbohydr. Polym.*, 2012, **87**, 2038–2045.
- R. Sanna, E. Fortunati, V. Alzari, D. Nuvoli, A. Terenzi, M. Casula, J. Kenny and A. Mariani, *Cellulose*, 2013, **20**, 2393–2402.
- M. A. Karaaslan, M. A. Tshabalala, D. J. Yelle and G. Buschle-Diller, *Carbohydr. Polym.*, 2011, **86**, 192–201.
- J. Yang, C. R. Han, J. F. Duan, M. G. Ma, X. M. Zhang, F. Xu and R. C. Sun, X. M. Xie, *J. Mater. Chem.*, 2012, **22**, 22467–22480.
- J. Yang, C. R. Han, J. F. Duan, F. Xu and R. C. Sun, *ACS Appl. Mater. Inter.*, 2013, **5**, 3199–3207.
- J. Yang, J. J. Zhao, F. Xu and R. C. Sun, *ACS Appl. Mater. Inter.*, 2013, **5**, 12960–12967.
- D. da Silva Perez, S. Montanari and M. R. Vignon, *Biomacromolecules*, 2003, **4**, 1417–1425.
- T. Saito and A. Isogai, *Biomacromolecules* 2004, **5** (5), 1983–1989.
- L. Genung and R. Mallatt, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 369–374.
- N. Ljungberg, C. Bonini, F. Bortolussi, C. Boisson, L. Heux and J. Y. Cavaillé, *Biomacromolecules*, 2005, **6**, 2732–2739.
- F. A. Aouada, M. R. de Moura, W. J. Orts and L. H. C. Mattoso, *J. Agr. Food Chem.*, 2011, **59**, 9433–9442.
- J. F. Revol, L. Godbout, X. M. Dong, D. G. Gray, H. Chanzy and G. Maret, *Liq. Cryst.*, 1994, **16**, 127–134.
- M. Hirota, N. Tamura, T. Saito and A. Isogai, *Cellulose*, 2010, **17**, 279–288.
- W. Wang and A. Wang, *Carbohydr. Polym.*, 2010, **82**, 83–91.
- N. Labbé, T. G. Rials, S. S. Kelley, Z. M. Cheng, J. Y. Kim and Y. Li, *Wood Sci. Technol.*, 2005, **39**, 61–76.
- P. Kunal, A. K. Banthia and D. K. Majumdar, *Biomed. Mater.*, 2006, **1**, 85–91.
- S. N. Bhadani and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, 1984, **102**, 255–260.
- R. E. Webber, C. Creton, H. R. Brown and J. P. Gong, *Macromolecules*, 2007, **40**, 2919–2927.
- D. Gersappe, *Phys. Rev. Lett.*, 2002, **89**, 058301.
- J. Yang, C. R. Han, J. F. Duan, F. Xu and R. C. Sun, *J. Phys. Chem. C*, 2013, **117**, 8223–8230.
- X. L. Hu, G. M. Hou, M. Q. Zhang, M. Z. Rong, W. H. Ruan and E. P. Giannelis, *J. Mater. Chem.*, 2012, **22**, 18961–18967.
- B. Chen and J. R. G. Evans, *Soft Matter*, 2009, **5**, 3572–3584.
- P. Calvert, *Adv. Mater.*, 2009, **21**, 743–756.
- J. Yang, C. R. Han, J. F. Duan, M. G. Ma, X. M. Zhang, F. Xu and R. C. Sun, *Cellulose*, 2013, **20**, 227–237.
- S. Rose, A. Dizeux, T. Narita, D. Hourdet and A. Marcellan, *Macromolecules*, 2013, **46**, 4095–4104.
- Y. H. Wu, H. B. Park, T. Kai, B. D. Freeman and D. S. Kalika, *J. Membrane Sci.*, 2010, **347**, 197–208.