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Cross-linked nanocomposite hydrogels based on cellulose nanocrystals and PVA: Mechanical properties and creep recovery

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Abstract

Cellulose nanocrystal (CNC) reinforced poly(vinyl alcohol) (PVA) hydrogels with a water content of ~92% were successfully prepared with glutaraldehyde (GA) as a cross-linker. The effects of the CNC content on the thermal stability, swelling ratio and mechanical and viscoelastic properties of the cross-linked hydrogels were investigated. The compressive strength at 60% strain for the hydrogels with 1 wt% CNCs increased by 303%, from 17.5 kPa to 53 kPa. The creep results showed that the addition of CNCs decreased the creep elasticity due to molecular chain restriction. The almost complete strain recovery (~97%) after fixed load removal for 15 min was observed from the hydrogels with CNCs, compared with 92% strain recovery of the neat cross-linked PVA hydrogels. The incorporation of CNCs did not affect the swelling ratio and thermal stability of the hydrogels. These results suggest the cross-linked CNC-PVA hydrogels have potential for use in biomedical and tissue engineering applications.

Keywords: A. Cellulose; A. Nanocomposites; B. Mechanical properties; D. Creep; E. Casting

1. Introduction

Hydrogels are three-dimensional networks that can absorb a large amount of water without dissolution [1]. Due to the high water content and elastic behavior, the hydrogels can possibly be used for biomedical and pharmaceutical applications such as contact lenses, articular cartilage, drug carriers, membranes and wound dressings [1-3].

Poly(vinyl alcohol) (PVA), a synthetic water-soluble polymer, has been widely used to prepare hydrogels by physical or chemical cross-linking mechanisms due to its advantages such as biocompatibility, non-toxicity, biodegradability and transparency [4-6]. A freeze/thaw processing has been used to prepare physically cross-linked hydrogels since the 1970s [7, 8]. When a polymer solution is quenched at low temperature, liquid phase separation occurs and ice crystals appear. Polymer segments rejected from the ice crystals are formed. With repeated freeze/thaw cycles, the number of ice crystals increases, resulting in a higher concentration of polymer segments. Subsequently, adjacent polymer chains form hydrogen bonds for physical cross-linking. The porous structure filled with water is finally obtained when the ice crystals melt [9, 10]. The mechanical properties of the hydrogels are controlled by the number of freeze/thaw cycles [11]. This method is straightforward; however, it is time- and energy-consuming. Alternatively, the use of chemical agents such as borax [4], epichlorohydrin [11] or glutaraldehyde [12] to connect the polymer chains has been found to be an efficient and feasible way to fabricate hydrogels with better properties. Due to its water solubility and high cross-linking efficiency, glutaraldehyde (GA) has been extensively applied to cross-link functional

groups of both matrix and reinforcement such as hydroxyl or amino to improve the mechanical properties of the composites [12, 13]. For examples, bacterial cellulose (BC) was cross-linked with PVA using GA [11]. The Young's modulus and tensile strength of the cross-linked BC-PVA composites were improved by 49% and 105%, respectively, compared to those of the un-crosslinked BC-PVA composites at the same cellulose content.

To date, cellulose nanocrystals (CNCs) have been used as a promising reinforcing phase in composites due to their renewability, biocompatibility, low density, high surface area and high stiffness [14-16]. CNCs can be extracted from various plants and bacterial by sulfuric or hydrochloric acid hydrolysis. The amorphous regions in the cellulose are removed, leaving rod-like particles with a high degree of crystallinity [9, 14]. It has been reported that CNCs prepared using sulfuric acid hydrolysis have sulfate ester groups on their surfaces. These generated sulfate ester groups allow CNCs to easily disperse in polar solvents such as water; conversely, more aggregations can be observed from neutrally charged CNCs produced using hydrochloric acid hydrolysis owing to the strong interaction of hydrogen bonds [17]. Rusli et al. [17] studied effect of cotton-derived CNCs prepared by sulfuric and hydrochloric acid hydrolysis on the stress transfer of nanocomposites using Raman spectroscopy. A lower stress-transfer efficiency can be observed from the nanocomposites with hydrochloric acid-hydrolyzed CNCs because of the aggregation of the CNCs caused by the strong interaction of hydrogen bonds. This resulted in a decrease in the aspect ratio and surface area contacted with the resin. This suggests that surface charges of CNCs play an important role in enhancing the mechanical properties of the nanocomposites. For these reasons, CNCs hydrolyzed by sulfuric acid were selected to reinforce the PVA hydrogels in this study.

As the mechanical properties of the hydrogels are weak, this limits the possibility of their uses. Therefore, using CNCs may be one solution to improve the mechanical properties. A few reports of the use of CNCs to improve the mechanical properties of PVA hydrogels have been investigated [18-20]. To the best of our knowledge, the preparation of GA cross-linked CNC-PVA hydrogels or how the addition of CNCs affects the creep recovery of the hydrogels has not been reported in the literature before. The main purpose of this study was to prepare PVA hydrogels with superior mechanical properties using CNCs as reinforcement and GA as a cross-linker. Physical, mechanical properties and creep recovery of the cross-linked PVA hydrogels with CNCs were investigated to understand the effect of CNCs. The high-water content CNC-PVA hydrogels with the improvement of mechanical properties, compared to neat PVA hydrogels, could broaden the use of the PVA hydrogels, and the gels prepared in this work could be easily scaled up.

2. Experimental

2.1. Materials

A commercial poly(vinyl alcohol) (PVA) resin with an average molecular weight of 89,000 - 98,000 g mol⁻¹ and a degree of hydrolysis of 99%+ for use as a matrix and glutaraldehyde (GA) (50 wt% in water) for use as a cross-linking agent for hydrogel preparation were supplied by Sigma-Aldrich. A dispersion of cellulose nanocrystals (CNCs) with a solid content of 10.3 wt% prepared by sulfuric acid hydrolysis treatment was kindly supported by Forest Products Laboratory (FPL), Madison, USA.

2.2. Preparation of cross-linked PVA hydrogels

The cross-linked PVA hydrogels reinforced with different contents of CNCs were prepared as shown in Fig. 1(a) with material combinations presented in Table 1. First,

CNCs were vigorously stirred for at least 24 h, and then sonicated using an ultrasonic device Hielscher UP200S for 10 min to fully disperse CNCs. PVA powder was gently added to the aqueous CNC suspension to prepare the suspensions of 4 wt% solid content and was continuously stirred for at least 3 h at 90 °C to obtain the transparent solution. After the suspensions were cooled to room temperature, these suspensions were placed in an ultrasonic bath for 30 min to remove all bubbles. GA (0.4 g), corresponding to 5 phr, was added drop-wise into the suspensions, and the suspensions were continuously stirred for 5 min. The pH of the suspensions was then adjusted to 1 using hydrochloric acid to initiate the cross-linking reaction. Subsequently, the suspensions were poured into molds and left for 24 h at room temperature to form hydrogels. The obtained hydrogels were then repeatedly rinsed with distilled water to remove the residual GA and acid until reaching neutral pH, and were stored at 5 °C before use (Fig. 1(c)). To prepare neat cross-linked PVA hydrogels, the same steps were followed without the addition of CNCs. The codes of cPVA0.5, cPVA1.0, cPVA1.5 and cPVA2.0 are referred to the weight fraction of CNCs up to 2 wt%, and the neat cross-linked PVA hydrogels without CNCs were coded as cPVA. The gel contents of the prepared cross-linked hydrogels with and without CNCs, determined using the following formula [21], were found to be ~ 99%.

$$\text{Gel content (\%)} = \frac{W}{W_0} \times 100 \quad (1)$$

where W is the weight of the dried gel after extraction in distilled water at 60 °C for 48 h, and W_0 refers to the initial weight of the dried cross-linked hydrogel before extraction.

To measure the diameters and lengths of the CNCs, a drop of the highly diluted CNC suspension was dried on a mica plate before the AFM measurement, and a Veeco

Multimode microscope with a Nanoscope V software in tapping mode was used. The diameters and lengths of the CNCs were found to be in the range of 5 to 13 and 185 to 568 nm, respectively. Fig. 1(b) shows the height AFM image of the CNCs.

2.3. Thermogravimetric analysis

The thermal stabilities of the CNCs, neat PVA powder, and cross-linked hydrogels with CNCs were investigated using a thermogravimetric analyzer TA instruments, Q-500. Approximately 7 - 10 mg of the dried samples was analyzed in the temperature range of 35 to 850 °C at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 60 mL min⁻¹.

2.4. Water content and swelling ratio

To measure the water content of the hydrogels with different contents of CNCs, the weight of the hydrogel samples was measured before (W_i) and after drying (W_d). The water content of the samples (W_c) was calculated as follows [22]:

$$W_c (\%) = \frac{(W_i - W_d)}{W_i} \times 100 \quad (2)$$

To estimate degree of swelling, the dried samples were immersed in distilled water at 25 °C for 120 h to reach swelling equilibrium. Before weighing on an analytical balance, the swollen samples were wiped with filter paper to remove excess water. The equilibrium swelling ratio (S) was calculated using the following equation [3, 5]:

$$S (\%) = \frac{(W_s - W_d)}{W_d} \times 100 \quad (3)$$

where W_s and W_d are the weights of the sample in the swollen and dry state, respectively.

2.5. Compressive testing

TA-DMA Q800 dynamic mechanical analyzer was used to investigate the effect of the CNCs on the mechanical properties of the cross-linked PVA hydrogels. Cylindrical samples with the diameter and height of ~ 11 and 4 mm were tested at 25 °C with a compressive strain rate of 10 % min⁻¹ and a preload force of 0.05 N. The compressive strength of the hydrogels was calculated at a compressive strain of 60%. At least seven specimens were tested for each material to obtain the average values of the compressive strength.

A cyclic loading-unloading experiment was also performed using a TA-DMA Q800 dynamic mechanical analyzer to study the reversible behaviors of the hydrogels. Tests were performed at a crosshead speed of 10 % min⁻¹ to 50% of the compressive strain, which was subsequently reduced to 1% of the compressive strain at the same speed. A 5-min relaxation time was applied before the beginning of the next cycle. This loading-unloading cycle was continuously repeated for five times.

2.6. Creep recovery

A dynamic mechanical analyzer TA instruments, DMA Q800, with compression mode was used to study the creep recovery of the PVA-CNC hydrogels. The fixed stress of 10 kPa was applied to the hydrogel samples for 15 min, followed by the relaxation period of 45 min. The strain was recorded with respect to time. No slippage or breakage of the hydrogels was observed during the test.

3. Results and discussion

3.1. Thermogravimetric analysis

The effect of the CNC content on the thermal properties of the cross-linked hydrogels compared to the neat PVA and CNCs was assessed. The thermogravimetric analysis (TGA)

and the derivative thermogravimetric (DTG) thermograms are shown in Fig. 2, and a summary of the onset of the thermal degradation of the materials is presented in Table 2. Generally, three main transition states can be observed from the neat PVA [23-25]. The first transition step is shown up to 100 °C due to the moisture evaporation. The second degradation transition occurs between 230 and 330 °C, corresponding to the removal of the oxygen functional groups from the PVA molecules and the formation of the polyene intermediate. The chain scission, cyclization and molecular decomposition of the PVA chains can be found when the temperature is higher than 420 °C, yielding carbon and hydrocarbon [18, 24, 25]. With the addition of the GA, the onset degradation temperature of the cross-linked PVA hydrogels was shifted to 347.4 °C from 249.5 °C of the pure PVA. This increase is an indication that the cross-linking plays an important role in improving the thermal stability of the PVA at a high temperature [18, 26]. A similar increase in the thermal stability has been observed from PVA films cross-linked with boric acid [10]. The onset degradation temperature was found to be approximately 280 °C for cross-linked PVA, compared to 230 °C for pure PVA [10]. Additionally, cross-linked PVA with glyoxal showed a higher thermal stability than neat PVA [19].

For CNCs, there are three degradation stages, as seen in the DTG results in Fig. 2(b). The initial weight loss occurs below 100 °C due to the loss of moisture, and a sharp decrease in weight occurs at approximately 230 °C, corresponding to the cellulose degradation processes such as depolymerization, dehydration and decomposition of glycosyl units and the formation of residues. Another weight loss at approximately 360 °C is assigned to the oxidation and the breakdown of char residuals to form gaseous products with a low molecular weight [27]. At a temperature of 850 °C, approximately 20% of the

char residuals remain because the sulfate groups on the CNC surface can act as a flame retardant [27]. Compared to the nanocellulose used in other works [20, 27-29], the CNCs used in this research had significantly lower thermal stability because of the introduction of the sulfate groups on the cellulose surface during the cellulose preparation [20, 27-29]. Therefore, with the presence of the CNCs in the hydrogels, the onset degradation temperature decreased. With a higher CNC content, the onset degradation temperature of the hydrogels significantly decreased from ~ 347 °C for cPVA to ~ 320 °C for cPVA2.0. This reduction may possibly be due to the lower thermal stability of the CNCs. When the temperature increased, the CNCs initially degraded. No positive effect of the presence of the CNCs on the thermal stability of the hydrogels could be detected. However, the reduced thermal stability of the CNC-PVA hydrogels is still more than sufficient for biomaterial applications.

3.2. *Water content and swelling ratio*

The water content contained in the PVA hydrogels with respect to the CNC content is shown in Fig. 3(a). No significant difference in the water content values measured from the hydrogels with or without CNCs can be noticed. Values of $\sim 92\%$ for the water content of all of the hydrogels prepared in this work were reported. These high water contents were similar to those of the PVA hydrogels prepared using borax (Table 3). It should be noted that the water content of the hydrogel depends on the solid content in the hydrogels. With the higher solid content, the water content in the hydrogels decreases.

To study the influence of CNCs on the swelling degree of the CNC-PVA hydrogels, freeze-dried hydrogels were immersed in distilled water for 120 h to reach the equilibrium state. It should be noted that due to the sample preparation for this test, the sample structure

was changed from a 3-dimensional hydrogel to a porous material. This can explain why a value measured from swelling ratio is not similar to that of water content. Fig. 3(b) shows the swelling ratio of the CNC-PVA hydrogels. A higher swelling ratio of the PVA hydrogels cross-linked with GA could be observed, compared to hydrogels prepared by other researchers (Table 3). This is because with the lower PVA content (only 4 wt% of PVA was used in this study), the cross-linking density and entanglement of polymer chains decreases, increasing the hydrogel swelling ability [2].

The swelling ratio decreased when the weight fraction of the CNCs increased. The cPVA hydrogels showed a swelling ratio of 577%, compared to a value of 483% obtained from cPVA2.0. The swelling ratio is controlled by the hydrophilic ability of the functional groups [30]. The cross-linking between the PVA matrix and the cellulose in the hydrogels can decrease the availability of the functional groups, which interact with water, leading to the lower swelling degree of the hydrogels [30, 31]. Additionally, when the amount of CNCs in the hydrogel increases, more hydrogen bonds between cellulose and PVA are formed. This may hinder the swelling ability of the hydrogels. Similarly, the decrease in the swelling ratio of the chemically cross-linked hydrogels has been found with the presence of cellulose [30, 31]. In contrast, Abitbol et al. [32] noticed a higher amount of water absorbed by the PVA hydrogels prepared using a freezing and thawing method after CNCs were introduced. This increase in water uptake resulted from the reduction of PVA crystallinity and more pores in the structure. We conclude that the different porous structure of the hydrogels can be obtained from the physical and chemical cross-linking mechanisms. This should be further studied to understand the effect of cross-linking mechanisms on the pore structure of the hydrogels.

3.3. Compressive properties

The compressive strength as a function of strain was investigated to study the effect of CNCs on the mechanical properties of the cross-linked PVA hydrogels; the compressive strength is one of the most important factors for hydrogel applications. As shown in the images in Fig. 4, the cPVA1.0 sample was subjected to 60% strain without failure, and it returned to its original shape when the load was released. Fig. 5 presents the stress-strain curves of the cross-linked PVA hydrogels with different CNC contents under compression tests. The values of the compressive strength of the hydrogels were compared at 60% strain. A value of 17.5 kPa for the compressive strength of cPVA was higher than the PVA hydrogels cross-linked with borax (0.4 kPa at 70% strain) [5]. The addition of CNCs in the hydrogels had an impact on the compressive strength of the hydrogels, as shown in Fig. 6. The compressive strength of the cPVA0.5 and cPVA1.0 hydrogels was improved by 83% and 303% to 32 and 53 kPa, respectively. The improvement of the mechanical properties of the cross-linked hydrogels would result from the interactions between PVA and CNCs, which allows stress to transfer from the matrix to the reinforcement [13]. The cross-linking reactions between PVA and cellulose using GA can appear in three different types: between hydroxyl groups of PVA, between hydroxyl groups of cellulose and between hydroxyl groups of PVA and cellulose [26]. With a low content of CNCs (below 1 wt% CNCs), the covalent bonds may play a vital role for stress-transfer process in the cross-linked CNC-PVA hydrogels. However, with a higher CNC content, free hydroxyl groups of PVA and CNCs tend to link each other with hydrogen bonds. In this case, the combination of covalent and hydrogen bonds between CNCs and PVA may control the mechanical properties of the cross-linked hydrogels. Compared to other work, the strength of the

composites with 1 wt% CNCs in this study increased by around 3 times while only 33% improvement of the compressive strength was measured from the CNC-PVA foams with the same amount of CNCs [33]. This may confirm that CNCs were chemically cross-linked with PVA to provide strong interaction at the low CNC concentration.

However, when the CNC content was more than 1 wt%, the strength decreased, but it was still higher than that of the hydrogels without CNCs. Abitbol et al. [32] found a similar effect of CNCs in the hydrogels. The PVA solutions with different CNC loadings (0.75, 1.5 and 3.0 wt%) were subjected to five successive cycles of freeze-thaw. The hydrogel with 1.5 wt% CNC loading showed the optimum mechanical properties (strength and modulus). When the loading of the CNCs was greater than 1.5 wt%, the mechanical properties of the gels decreased to close to those of the gels with 0.75 wt% CNCs. This may be due to the disturbance of CNCs in the gels. Additionally, Duan et al. [31] reported that when the cellulose content in hydrogels is higher than the critical concentration, the compressive strength decreases significantly. It should be noted that the sudden decrease of the compressive strength of the hydrogels may be due to cellulose aggregates [31]. CNCs may be aggregated by hydrogen or covalent bonds. It is worth noted that no difference between strength of the cross-linked cellulose and unmodified cellulose was observed [26, 34]. Therefore, the agglomerated CNCs resulted in an inefficient reinforcement. Also, it is difficult to obtain fully dispersed CNCs when the cellulose content is high. One possibility to extend this limitation is to introduce less active functional groups on cellulose molecules. This is one of our future plans to find the most efficient way to fully disperse the CNCs in the composites.

The five compression loading-unloading cycles of the cross-linked PVA hydrogels with CNCs at a maximum strain at 50 % are presented in Fig. 7. As seen in the loading-unloading curves, the highest compressive strength was obtained from the first loading cycle. Water leached from the gel during the first loading could not re-swell the gel fast enough before the next loading began, resulting in the lower mechanical properties for the following loading cycles. Similar behavior has been reported elsewhere [35]. Notably, the trend of the five loading-unloading curves of all of the hydrogel samples were found to be identical, meaning that the hydrogels prepared in the work possess excellent elastic recovery. The collapse or the breakage of cross-linking could be predicted from a different pattern of the unloading curve, compared to the loading curve [36]. This result indicates that the structure of the hydrogels is strong enough to withstand the load and return to its original shape after the load removal.

3.4. Creep recovery

The creep behavior and strain recovery of the hydrogels with CNCs after the force removal are shown in Fig. 8. The constant force of 10 kPa was directly applied to the samples for 15 min, and the samples were further investigated for 45 min after the force was withdrawn. The CNCs were able to reduce the creep strain of the hydrogels due to their stiffness and strength and the restriction of the chain motion. Ninety-three percent of the strain recovery obtained from cPVA was reported. With the existence of CNCs in the hydrogels, values of ~97% were reported for the strain recovery. It can be said that the stiffness and load-bearing efficiency of the hydrogels can be improved by the CNCs. Also, these high values of the strain recovery behavior could be due to the high degree of cross-linking as the prepared cross-linked hydrogels had ~99% of the gel content. It has been

previously reported that the PVA hydrogels with a high degree of cross-linking showed a higher strain recovery than those with a low cross-linking degree as the decrease of the chain movement can be found in the hydrogels with a high cross-linking density [9]. The influence of the cross-linking degree on the mechanical properties of the PVA hydrogels remains a topic for future work in order to understand its relationship and fabricate hydrogels suitable for the specific purposes.

4. Conclusions

Hydrogels based on CNC-reinforced PVA with a high water-holding capability were successfully prepared with GA as a cross-linker. The compressive stress of the prepared hydrogels improved with an increasing CNC content. The maximum compressive strength at 60% strain of 53 kPa was obtained from the hydrogels with 1 wt% CNCs, which was 303% higher than that of the neat PVA hydrogel (17.5 kPa). The viscoelastic response and relaxation behavior of the PVA hydrogels were found to be enhanced by the CNCs. Approximately 97% of strain recovery after the removal of the load was measured for the PVA hydrogels with the presence of the CNCs. Although with the introduction of CNC, the thermal stability of the cross-linked CNC-PVA nanocomposite hydrogels decreased slightly, the thermal stability of the cross-linked nanocomposite hydrogels was still significantly higher than pure PVA. The nanocomposite hydrogels with CNCs prepared in this work showed high strength, elasticity and water-holding capability, which should be suitable for biomedical applications.

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Figure captions

Fig. 1. Schematic illustration of (a) the preparation of the cross-linked CNC-PVA hydrogels, (b) the height AFM image of CNCs and (c) the photograph of the prepared transparent hydrogels.

Fig. 2. (a) Thermogravimetric analysis and (b) derivative thermogravimetric curves of the cross-linked PVA hydrogels with CNCs.

Fig. 3. (a) The water content of the cross-linked PVA hydrogels with different contents of CNCs, and (b) the equilibrium swelling ratio of the hydrogels with CNCs after immersion in distilled water for 120 h. The solid line is illustrative only.

Fig. 4. Snapshots of the cross-linked PVA hydrogels with 1 wt% CNCs during the compression test: (a) before compression, (b) at 0% compression strain, (c) at 60% compression strain and (d) after load removal.

Fig. 5. Stress-strain curves of the cross-linked PVA hydrogels with varied CNC contents.

Fig. 6. Compressive strength of the cross-linked PVA hydrogels with varied CNC contents.

Fig. 7. Cyclic deformation of cross-linked CNC-PVA hydrogels between 0 and 50 % strain. The 5 min relaxation time was provided between each cycle.

Fig. 8. (a) Creep behavior of the hydrogels with different contents of CNCs and (b) recovery behavior of the cross-linked PVA hydrogels with CNCs after the hydrogels were compressed at 10 kPa for 15 min.

Table captions

Table 1 PVA and CNCs contents in the crosslinked hydrogels.

Table 2 Thermal degradation temperature of the cross-linked PVA hydrogels with CNCs, compared to pure CNCs and PVA.

Table 3 Comparison in water content and swelling ratio of the PVA hydrogels.

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(a)

(b)

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Table 1 PVA and CNCs contents in the crosslinked hydrogels.

CODE	PVA (wt%)	CNCs (wt%)
cPVA	100	0
cPVA0.5	99.5	0.5
cPVA1.0	99.0	1.0
cPVA1.5	98.5	1.5
cPVA2.0	98.0	2.0

Table 2 Thermal degradation temperature of the cross-linked PVA hydrogels with CNCs, compared to pure CNCs and PVA.

Materials	The onset thermal degradation temperature (°C)
CNCs	229.5
PVA	249.6
cPVA	347.4
cPVA0.5	328.0
cPVA1.0	323.2
cPVA1.5	320.5
cPVA2.0	320.8

Table 3 Comparison in water content and swelling ratio of the PVA hydrogels.

PVA content (wt%)	Cross-linking	Water content (%)	Swelling degree (%)	Source
2	Borax	97.1	-	[4]
4	GA	92	577	This work
10	FT 3 cycles	80	510	[2]
12	FT 3 cycles	81	165	[22]

NB: FT is the freeze-thaw method.