Designing pH-responsive and dielectric hydrogels from cellulose nanocrystals

XIAOYUAN GAO, KISHOR KUMAR SADASIVUNI, HYUN-CHAN KIM, SEUNG-KI MIN and JAEHWAN KIM*

Center for EAPap Actuator, Dept. of Mechanical Engineering, Inha University, 253 Yonghyun-Dong, Nam-Ku, Incheon 402-751, South Korea
e-mail: jaehwan@inha.ac.kr

Abstract. We report the fabrication and characterization of a pH-responsive hydrogel with improved mechanical and dielectric properties from cellulose nanocrystals. X-ray diffraction and SEM observations were used to analyze the sample morphology. The resulting pH detector exhibits a pronounced change in their swelling index in response to variation in pH. It was used singly and in combination with other nanomaterials to optimize smart material designs. The applications of the developed material are anticipated in chemical, environmental and biological systems.

Keywords. Cellulose; Cellulose Nanocrystals; Hydrogels; pH-responsive; Dielectric property

1. Introduction

Cellulose is the most abundant and low-cost natural polymer on earth. By virtue of its non-toxicity, biocompatibility and degradability cellulose has broad applications in the food, pharmaceutical and chemical industries. However, economically feasible and environmentally friendly chemical processes are required for more efficient utilization of cellulose.[1,2] These properties make cellulose a soft electroactive material. The cellulose nanocrystals (CNCs) obtained from cellulose possess low density, high mechanical strength, thermal stability, and chemical resistance.[3] CNCs can be isolated at a low cost from renewable natural sources such as cotton, wood, bananas, tunicates, and many other species.[4–7] They have a typical diameter of 5–50 nm and a length of 100–3000 nm, depending on the source and the processing conditions. The rod-like, highly crystalline CNCs are synthesized by breaking natural cellulose fibers with acid hydrolysis These CNC nanoparticles show good piezoelectric response making them applicable in sensors and actuators and biomedical fields.[8]

The interest in nanoparticle (<100 nm) filled polymer composites has emerged tremendously in recent years.[9] The CNCs that are derived from abundant and renewable sources have drawn increasing attention in this regard due to their high aspect ratio,

low density, and eco-friendliness.[10–12] Many reports have come out in which the CNCs enhance the polymer properties.[13] For instance the Young's modulus of extruded starch plastic was increased significantly when 10.3% (w/w) CNC derived from cotton was added.[14] A 5% CNC loading of the solvent casted polyurethane film increased its tensile strength and strain from 39 to 257 MPa and 157 to 237%, respectively.[15] The amphiphilic CNCs can be easily functionalized as well for achieving better compatibility with the polymer matrix. As mechanical and dielectric properties of the nanocomposite fibers are governed by the interfaces between the nanofillers and polymer matrix, stronger interactions are more beneficial.[16] By incorporating CNCs into polyacrylamide, abundant hydrogen bonding between the hydroxyl groups on the CNC surfaces and carboxylic acids along the polymer chain facilitated the dispersion of CNCs in the polymer solution.

The surface modifications of CNCs for pH-sensing have also been investigated[17] and several of these have been extensively researched in terms of miniaturized pH sensor.[18–20] The pH value is a quantity commonly used to monitor the properties of solutions, and it is one of the most critical measurable parameters in many fields such as medicine, chemistry, biology and material science.[21] A popular approach that exploits metal oxide as pH sensor is the ion sensitive field effect transistor.[22] In contrast to metal oxide and other toxic carbon materials, whose acute toxicity precludes their utilization *in vivo*, CNCs appear to be rather benign.[23–25] In

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*For correspondence

addition, strong hydrophilicity of cellulose promises reduced nonselective adsorption of biological materials that often causes degradation of transducer surfaces.[26] The advantages of biodegradable cellulose/CNC hydrogels include its applicability in controlling the size with pH variation and the electric responsive character simultaneously due to the electromechanical nature of cellulose.

Here, we introduce a pH-responsive and highly dielectric hydrogel where cellulose forms the base matrix and CNCs the filler. The morphology and structural property relationship of the cellulose/CNC hydrogels were determined with the help of X-ray diffraction (XRD) studies and scanning electron microscopy (SEM). The proposed cellulose/CNC hydrogel works as a strong transparent pH-responsive hydrogel and a good dielectric material.

2. Experimental

2.1 *Materials*

Cotton pulp (MVE, DPw-4580) was supplied by Buckeye Technologies Co. Ltd. (US). N,N-Dimethylacetamide (DMAc), sulphuric acid (H_2SO_4), and sodium hydroxide (NaOH) were procured from Sigma-Aldrich, South Korea. Lithium chloride (LiCl) and Isopropanol (IPA) were purchased from Dae Jung chemicals & metals Co. Ltd.

2.2 *Preparation of cellulose solution*

The preparation of cellulose solution using DMAc/LiCl solvent has been reported previously and this is a brief summary.[27] The cellulose (1.5%) was dissolved in the mixed solvent system of DMAc/LiCl with LiCl concentration 8.5%. Then the mixed pulp with DMAc/LiCl was heated at 80°C for 3 hours with mechanical stirring. After that, by raising the reaction temperature to 150°C and keeping the temperature for 15 min the heater was turned off and allowed slowly to reach room temperature with stirring for 24 hours. Then the reaction temperature was raised to 100°C, kept it for 6 h, then turned off the heater and let it slowly cool to room temperature. Thereafter, stirred for 12 h and kept it in a bottle leaving for at least 3 weeks for aging. Finally, the pure and transparent cellulose solution was obtained through centrifuging process.

2.3 *Synthesis of CNC*

The CNC nanoparticles used in this study were prepared by H_2SO_4 (175 mL of 30% (v/v) with water) for hydrolysis of 98% pure cotton pulp (20.0 g) under mechanical stirring (200 rpm, 6 h) at 60°C. An alkaline (1M NaOH) treatment on the cotton cellulose fiber was also carried out to remove the non-cellulosic components prior to acid hydrolysis. The hydrolysis left a suspension which was further successively centrifuged with distilled water to attain neutrality and then homogenized (10 min, 11000 rpm) and dialyzed overnight.

2.4 *Fabrication of cellulose/CNC hydrogels*

Initially, CNC in 3 and 5 wt% dispersed in DMAc by 3 hours of sonication was mixed with cellulose/DMAc solution and cast into a petri dish, followed by curing with the mixture of deionized water and IPA in a ratio of 4:6 for 3 h. This slow curing process prevents aggregation of CNCs and eliminates remnant LiCl and DMAc. Finally the cured hydrogel was rinsed in two different deionized water baths for making hydrogel of pH=7. For SEM, XRD, mechanical pull test, UV-visible and dielectric constant measurements, the solution was cast on glass using doctor blade and dried in a vacuum oven overnight at 60°C, resulting in film formation.

2.5 *Characterization*

Sample morphology was checked with the help of AFM, TEM and SEM. The FE-TEM micrographs of the CNCs were analyzed with JEOL, JEM 2100F and the FE-SEM images of the hydrogel films with a field emission scanning electron microscope (Hitachi S-4300 microscope). XRD patterns were checked with a thin film X-ray diffractometer using CuKα target radiation at 40 kV and 50 mA, at a scanning rate of 0.015°/min. The diffraction angle was varied from 5 to 40°. Optical transmittance of the samples was studied using UV-visible spectrophotometer. For this the spectra of the films in the range of 200-800 nm were recorded with a Hewlett Packard (8452A) diode array. The mechanical test was conducted according to ASTM D-882-97 using a universal testing machine. The samples were put between two plates; the upper plate would press the sample until it reached a fixed value. Test was performed under room temperature and at compressing rate of 0.005 mm/s. Dielectric constant was measured using HP 4284A LCR meter between 20 and 4000 Hz frequency with 1 V. The hydrogels were cast as films using a doctor blade and gold electrodes were coated on both sides of them.
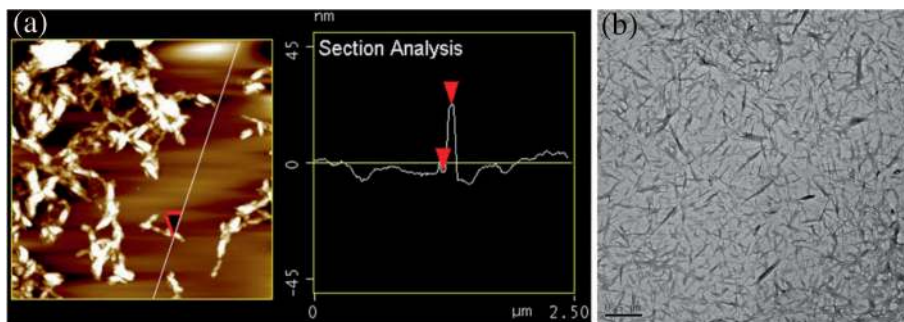
Figure 1. (a) AFM and (b) TEM images of the synthesized CNC.

3. Results and Discussion

3.1 *Sample Morphology*

As given in the AFM of synthesized CNCs in figure 1a, they exhibit rod like nanostructures with 25–40 nm diameter. For taking AFM, CNCs were spin coated on the silicon wafer which is oxidized by piranha solution. The compact network structure of CNCs reveals the internal bondings present in it. Figure 1b illustrates the high resolution TEM (FE-TEM, JEOL, JEM 2100F) micrograph of a very dilute suspension of CNC (in Isopropanol 0.01% w/v) deposited on carbon-coated grids. The diameter of the 'rod-like' nanocrystals has wide range of distribution but the length of most of the nanocrystals lies within the range 250-380 nm.

The morphology of hydrogel was investigated by the SEM images of the pristine cellulose and its hydrogels with CNCs. Figure 2 illustrates the SEM images of the pristine cellulose and cellulose/CNC hydrogels with 3 and 5 wt % of incorporated CNCs. The hydrogels with CNC loadings (3 and 5 wt %) exhibit uniform dispersion of CNCs within the cellulose matrix, where CNCs are closely attached on the polymer matrix surface thus reinforcing the network.

One can note that the neat cellulose exhibited a relatively rough structure (figure 2a). On the other hand cellulose/CNC hydrogel surfaces are smooth, which is attributed to the attachment of CNCs on cellulose and its smoothness increased with an increase of the filler loading (figures 2b and 2c). In the cellulose/CNC hydrogel, the cellulose chains are physically linked together with strong interaction between the CNCs leading to progressively larger branches. This physical hydrogel obtained by an exceptionally simple method of mixing cellulose and CNC before network formation is schematically represented in figure 3 and the interactions between cellulose chains are effectively permanent at a given set of experimental conditions. Energetically favorable interactions existed between adjacent cellulose-CNCs, by which the interconnected network structure with a repeated distance of a few hundred nanometers was formed. Since the CNCs possess hydrophilic character they are inherently compatible with DMAc/LiCl cellulose system and this makes the homogeneous dispersal of surface charged CNCs in DMAc relatively easy. This is clear from the SEM images of figure 2 where the CNCs are uniformly dispersed within the cross-linked network under the swollen state. Formation of the cross-linked network with a small amount of CNCs indicates that the CNCs act as multifunctional cross-links with highly effective functionality.

Figure 4 shows the XRD patterns of the pristine cellulose, cellulose/CNCs with 3 and 5 wt% and pure CNCs. CNCs display four well-defined diffraction peaks at 14.7, 16.5, 22.7, and 34.5, which are typical of cellulose I.[8] Compared with those of CNCs, the mainly
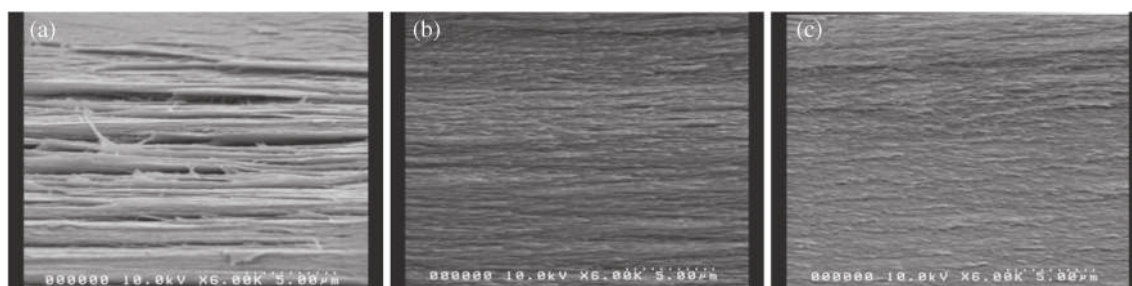

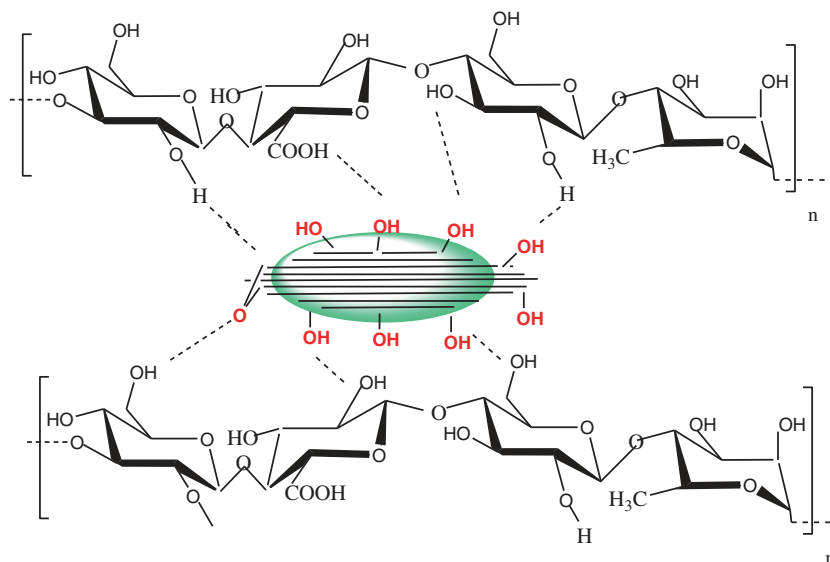**Figure 2.** SEM analysis of (a) cellulose, (b) cellulose/CNC with 3% loading and (c) 5% loading.

Figure 3. Interaction between CNC and cellulose.

strong crystalline peak appeared at around $2\theta = 21.8°$ for the pristine cellulose and cellulose/CNCs However, in the case of c cellulose/CNCs there are no characteristic peaks of CNCs. Moreover the introduction of CNCs has a negligible effect on the crystallinity of the materials based on the full width at half maxima values (FWHM).

3.2 *UV- Transmittance of the cellulose and cellulose/CNCs hydrogel films*

Figure 5 represents the UV-vis spectra and the appearance of the pristine cellulose and cellulose/CNC hydrogel films. The hydrogel film must be transparent as an optical film as they showed 88–85 % (at 550 nm) transmittance. The given transmittance versus wavelength
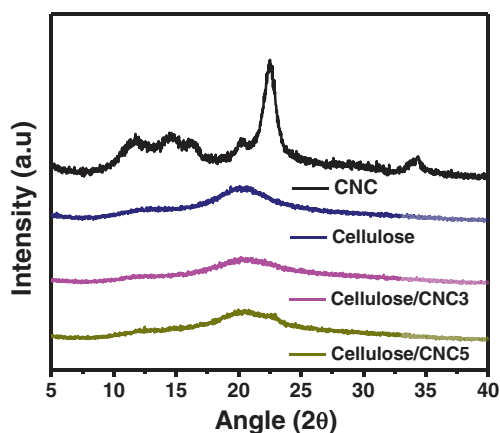
plots shows an increase in transmittance at 200–800 nm, which is approximately the lower limit of the visible region. These observations suggest an interface free structure for the materials. In other words, CNC has strong reinforcing effect and it is well dispersed in the cellulose matrix. The very small size of the nanocrystals and the low filler content (as evidenced from the AFM and TEM in figure 1) make light scattering through the film easy.

3.3 *p^H response of cellulose and cellulose/CNC hydrogel*

The swelling indices of the cellulose and cellulose/CNC pH sensors calculated using Equation 1 are shown in figure 6. When CNCs were dispersed in the hydrogel,
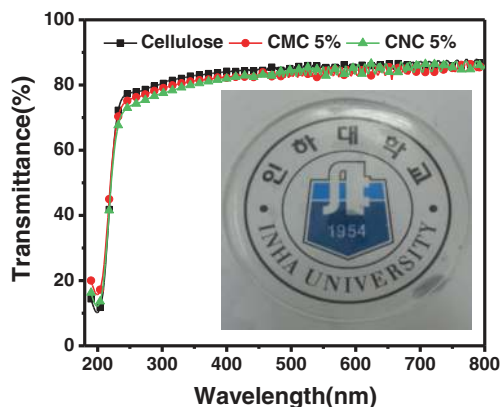

Figure 4. XRD analysis of CNC, cellulose and cellulose/CNC.

Figure 5. Optical transparency of cellulose and its cellulose/CNC hydrogels (Inset Optical image of cellulose/CNC5 hydrogel).

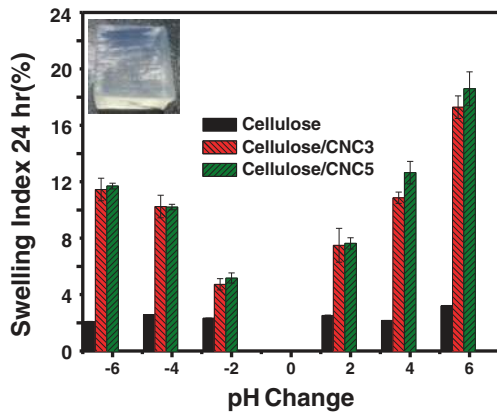**Figure 6.** P$^{\text{H}}$ sensing of cellulose and cellulose/CNC hydrogels at different pH (Initial pH of samples is 7).

Figure 7. Compressive stress-strain curves of different hydrogels.

we observed significant changes in swelling index as the pH of the solution varied:

$$Swelling Index = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_2 and W_1 are the weights of the specimen before and after swelling. W_2 is weight of the sample at pH 7 and W_1 the weight of the sample at a different pH.

Results of structural characterization indicate that the incorporated CNCs interact strongly with the cellulose matrix through hydrogen bonding. The pH sensitivity of the cellulose and cellulose/CNC can be divided into two linear regions depending on the acidic pH level. The hydrogels show a linear response with low sensitivity between pH 1 to 6. However, when the pH-responsive hydrogel senses alkaline buffer solution between pH 7 to 12, slope of the linear curve increases. Nevertheless, the hydrogel response to pH value is changed significantly compared to cellulose. For the pH sensitive hydrogels reported in this paper, functional groups are bound to the chains. Hydrogels are capable of undergoing large reversible deformations in response to changes in several environmental factors.[28] We maintained the temperature constant during measurements. Special modification of the polymer structure can also lead to gel formation that is pH sensitive to specific biological agents.[29] Swelling/deswellingphenomena occur for a hydrogel containing functional groups bound to its polymer chains when the H$^+$ or OH$^-$ comes off in basic solutions and combines with counter ion. The charge is compensated by ions that enter into the gel together with counter ions and the charge maintains neutrality. The increased ionic concentration gives rise to an osmotic pressure that causes the gel to swell/deswell. For a better understanding we considered acidic medium, in which the conjugate base of the buffer reversibly binds hydrogen ions in regions
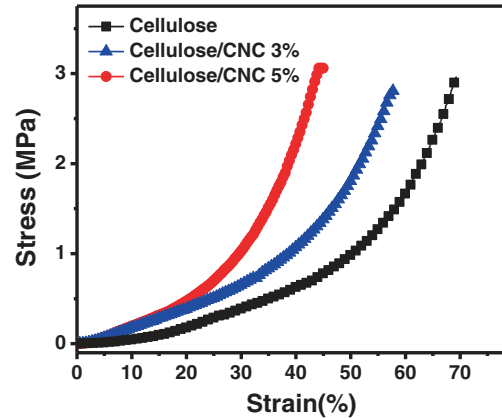
of higher concentration and releases the hydrogen ion after diffusing to a region of lower concentration.[30] Equilibrium of hydrogel occurs when the elastic restoring force of the network balances the osmotic forces and swelling index becomes constant.[30–32]

3.4 *Mechanical Properties*

The mechanical properties of cellulose hydrogels with two different concentrations (CNC 3% and 5%) were investigated. Figure 7 illustrates the stress-strain curves. It is found that the addition of CNC in the cellulose hydrogel improves the mechanical property of the pristine cellulose hydrogel. Compared with the pristine cellulose hydrogel, the cellulose/CNC5 hydrogel exhibited significant improvement in Young's modulus: the Young's modulus increased from 0.40, 0.48 to 0.55 GPa for cellulose, cellulose/CNC3 and cellulose/CNC5. The high modulus is related to the high cross-linking density, where the multifunctional physical cross-links of CNCs form at the interface with cellulose matrix as per the schematic representation in figure 3. Owing to the strong interaction of CNCs through surface hydroxyl groups, they have pronounced tendency for self-association, which is advantageous for the formation of load-bearing percolating networks within the host polymer matrix.[8] It is considered that the interactions between polymer−polymer, polymer−filler, and filler−filler contribute to the mechanical properties of the hydrogels.

3.5 *Dielectric properties*

In order to check the dielectric response of the samples, dielectric constant, ε' of the cellulose hydrogels along with the CNC inclusion was measured at 25°C
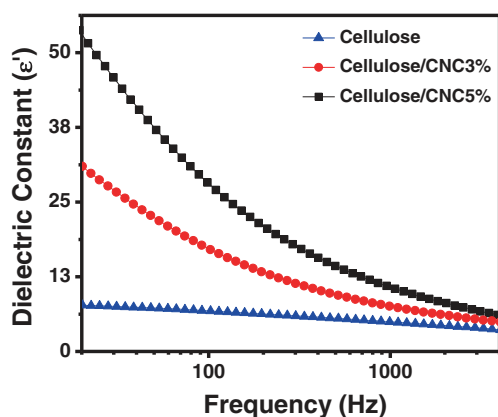
Figure 8. Dielectric property of cellulose and cellulose/CNC hydrogels.

temperature, 25% relative humidity. Figure 8 shows the measurement results The dielectric measurements show that the incorporation of the CNCs in the cellulose matrix increases ε'. When the values are compared, CNC possesses enhanced dielectric constant which is attributed to the motion of free charge carriers due to interfacial polarization effects and charges present around the CNC surface. This is possible due to the presence of moderate number of oxide functionalities (charge centers) and conjugation (carrier centers) on the CNC surface. The ε' of a microelectronic dielectric polymer depends on the amount of mobile (polarizable) electrical charges in it and the degree of mobility of these charges.[33–36] According to Maxwell-Wagner-Sillars (MWS) process polymer-filler interfacial interaction, like donor-acceptor complexes is necessary to get changes in the composite dielectric properties. The huge interfacial area of CNCs in the cellulose matrix provides numerous sites for the reinforced MWS effect.[37–39]

4. Conclusions

In summary, the cellulose/CNC hydrogels were prepared by solvent blending method and a strong and transparent pH-responsive hydrogel with good dielectric behavior has come out from this study. The results of SEM and WAXD techniques indicate homogeneous nanostructures for the obtained hydrogels and a strong hydrogen bonding interaction between CNCs and the cellulose matrix. Though long term stability in harsh environment and industrial detection protocols to provide complementary sensing information are the issues in sensor technology, the cellulose based devices have great potential for cheap, disposable and biocompatible sensors. The maximum transmittance reaches 88.7% at 800 nm for the CNC/cellulose hydrogels similar to the

pristine cellulose hydrogel. CNC/cellulose hydrogels also illustrate significant improvement in the dielectric constant and the reported pH responsive hydrogels are thus useful in energy storage applications as well.

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