

Effect of Nanofillers on Carboxymethyl Cellulose/Hydroxyethyl Cellulose Hydrogels

Qizhou Dai,* John F. Kadla

Advanced Biomaterials Chemistry, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada

Received 25 September 2008; accepted 20 May 2009

DOI 10.1002/app.30789

Published online 23 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of hydrophilic nanoparticles (oxidized cellulose nanocrystals (CNC) and montmorillonite nanoclay) on the properties of a sodium carboxymethylcellulose (CMC)/hydroxyethylcellulose (HEC) hydrogel system was investigated. Visually, the CNC reinforced cellulosic hydrogel-composites were transparent over all CNC loadings, whereas those reinforced with organoclay were opaque even at low clay loadings despite the nanoparticles being well dispersed. Incorporation of CNC into the cellulosic hydrogels led to an increase in the compressive modulus of CNC-hydrogel composites, but a corresponding decrease in the swelling ratio. However, the addition of CNCs enabled a

reduction in the amount of cross-linker required to obtain a given compressive modulus and swelling behavior. It was observed that the surface charge density of the CNCs had no significant effect on the compression modulus or swelling behavior of the CMC/HEC hydrogel composites. By contrast, the organoclay reinforced CMC/HEC hydrogels did not show any trend in compression modulus or swelling ratio with organoclay content. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1664–1669, 2009

Key words: biomaterials; cellulose nanocrystals; hydrogels; nanocomposites; organoclay

INTRODUCTION

Hydrogels have received increasing attention due to their significance both in theory and application. They are currently used in a variety of applications such as matrices for controlled drug delivery; soft contact lenses and artificial tissues.^{1–3} A type of hydrogel of commercial importance are superabsorbent polymers (SAP). They are low crosslink density polymer systems that can absorb a large amount of water during a short period and keep a large amount of water even under pressure. Superabsorbents have great advantage over traditional porous water-absorbing materials such as fluff pulp and sponges due to their ability to retain large amounts of liquid, and maintain mechanical integrity when wet or under pressure.⁴ The high equilibrium swelling capacity of hydrogels is primarily attributed to polymer hydrophilicity and fixed ionic charge.⁵ Since first reported by the USDA in the 1960's, they have been used in a variety of value-added applications, including hygienic products, medical products as well as agriculture and horticulture applications.⁶

The performance of superabsorbents is determined by three features: (1) swelling capacity, (2) swelling rate, and (3) strength of the swollen gel.⁷

Natural polymers have been studied as possible materials for superabsorbent hydrogels due to their biodegradability and wide availability. One system that has shown promise is the sodium carboxymethylcellulose/hydroxyethylcellulose (CMC/HEC) divinyl sulfone (DVS) crosslinked hydrogels.^{8,9} The CMC/HEC system can absorb up to 500 g of water per gram of polymer. However, like other natural polymer based SAPs, cellulose tend to absorb relatively small amounts of fluid, lose their mechanical integrity in water and yield creamy-like gels.¹⁰

Polymer nano-composites have attracted considerable attention because of their effective reinforcement and property enhancement, higher dimensional stability, low filler loading and more uniform composites (as compared to "conventional" microfiller composites). Clay,^{11–18} mica¹⁹ and kaolin²⁰ have been used to improve the mechanical properties of synthetic hydrogels.¹⁵ The strength and the modulus increased with the addition of nano-minerals.¹⁶ However, the swellability of the hydrogel composites were limited due to the low swellability of the inorganic fillers^{4,16} and the increased crosslinking density due to the reactions between polymer and fillers during polymerization of the hydrogel networks.¹⁶

Cellulose nanocrystals (CNCs) are obtained through the acid hydrolysis of natural cellulosic

*Present address: Dentsply International, Inc., Caulk Division, 38 W Clarke Avenue, Milford, DE 19963, USA.

Correspondence to: J. F. Kadla (john.kadla@ubc.ca).

Contract grant sponsor: Canadian Natural Science and Engineering Research Council (NSERC).

materials to produce highly crystalline well-defined rigid rods.²¹ Also known as cellulose whiskers, CNC are about 15 nm in width and 100–500 nm in length. The crystallites form a colloidal suspension in water and are stabilized by the negative surface charges introduced during the isolation procedure. Cellulosic nanocrystals have been widely used to enhance thermoplastic polymer materials.^{22–24} By modifying the surface of CNCs by either steric grafting^{25,26} or surfactant addition,²⁷ CNCs can be readily suspended in organic solvents, and used to reinforce hydrophobic materials.²⁸

To our knowledge, the use of CNC to reinforce hydrogels has not been previously reported. In this article, we compare the effect of CNC addition on cellulosic hydrogel properties, and contrast those to results obtained using a commercial organoclay.

EXPERIMENTAL

Materials

CNCs were prepared from Whatman No. 1 filter paper (*vide infra*). Cloisite NA+ nanoclay (2–13 μm dia; 100–500 nm thick; surface charge ~ 900 meq/kg) was obtained from Southern Clay Products Inc (Austin TX) and used as received. Sodium carboxymethyl cellulose ($M_w \sim 700,000$; degree of substitution ~ 0.9) and 2-hydroxyethyl cellulose ($M_w \sim 250,000$; degree of substitution ~ 1.0 ; molecular substitution ~ 2.0) were purchased from Sigma-Aldrich (Oakville, ON). All other chemicals were chemical pure grade and obtained from Sigma-Aldrich and used without further purification.

Preparation of CNC

CNC were prepared according to Araki et al.²⁵ Specifically, Whatman No. 1 filter paper (Sigma-Aldrich) was ground to 20 mesh using a lab scale Wiley Mill. The resulting cellulose powder (10 g) was hydrolyzed with 100 mL 3 N HCl at 100–110°C for 1 h. The hydrolyzate was thoroughly washed with deionized water by centrifugation (3–5 times). The cellulose suspension (1–1.5% solid content) was then homogenized with a blender for 30 min. The cellulose suspension (500 mL) was mixed with 0.5 g TEMPO and 5 g NaBr and a desired amount of a NaClO solution ($\sim 5\%$) drop-wise in 4 equal portions at time 0, 0.5, 1, and 2 h. The degree of carboxylation was controlled by the amount of NaClO added. The mixture was stirred at room temperature and pH adjusted to 10–11 with 3 N NaOH, and left stirring overnight. The reaction was stopped by adding ~ 30 mL methanol and 30 g NaCl to the suspension. The suspension was then centrifuged, and the CNC was repeatedly washed with 1 M NaCl

solution. The suspension was dialyzed in deionized water for at least 72 h. The water was changed twice daily. After dialysis, the product was well dispersed and translucent, and the suspension was finally concentrated to 3–4% solids content.

Preparation of hydrogel nanocomposites

The nanoparticle (CNC or Nanoclay) suspension with $\sim 4\%$ solid content was sonicated with a Fisher 450 Sonifier at 75% power output. The suspension was centrifuged to remove undispersed particles. After dispersion in water, the CNC suspension was transparent, while the organoclay suspension was opaque.

In a typical experiment a desired amount of CMC and HEC (CMC/HEC = 1/1, w/w) were dissolved in a 0.1 N NaOH solution to form $\sim 4\%$ wt homogeneous solutions in a 50 mL centrifuge tube (Fisher-brand). The CMC/HEC solution was then mixed with a certain amount of nanoparticle suspension and crosslinker divinyl sulfone (DVS). The mixture was subsequently diluted with 0.1 N NaOH to a polymer concentration (CMC and HEC) of 2% and a pH of 12–13. The reaction mixture was centrifuged to remove bubbles and left for at least 20 h at room temperature to form a hydrogel. The resulting hydrogels were isolated from the centrifuge tubes (cut open) as 19 mm diameter cylinders. The CNC-reinforced hydrogels were transparent, while the organoclay-reinforced hydrogels were opaque.

General analysis

The swelling ratio of the hydrogels was determined gravimetrically from the ratio of the weight of the fully swollen gel to that of the completely dry gel. The dry gel was prepared by solvent exchange of the fully swollen gels using acetone, or if the hydrogels were swollen in NaCl solutions deionized water first, then acetone followed by air-drying overnight. All analyses are the average of a minimum of three replicates.

The surface charge of the CNC was determined conductivity titration.²⁵

Thermal mechanical properties of the hydrogels were measured with a submersible compression clamp using a TA Instruments Q800 dynamic mechanical analyzer. The fully swollen hydrogel disks, 19 mm in diameter and 13 mm in thickness were loaded onto the submersible clamp and immersed in deionized water. The compression clamp was lowered onto the sample and a compressive force was applied. The compression clamp was compressed at a speed of 5 mm per minute. The Young's Modulus before yield was recorded as the compressive modulus of the hydrogel, and calculated from the slope of the stress–strain curves (Fig. 1).

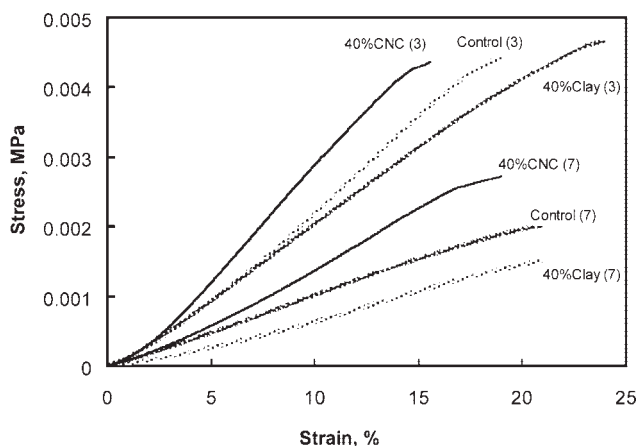


Figure 1 Effect of nanoparticle addition and crosslinker (OH/DVS) on stress vs strain of nanoparticle reinforced CMC/HEC hydrogel composites.

Thermogravimetric analysis was performed using a TA Instruments Q500 thermogravimetric analyzer (TGA). Fully swollen gels were freeze-dried prior to analysis, and measured over the temperature range of 50–800°C with a heating rate of 10°C/min under a dry nitrogen atmosphere.

Wide-angle X-ray diffraction profiles were recorded on a Bruker D8 Discover X-ray diffractometer equipped with GADDS detector. All scans were collected at 40 kV and 20 mA using CuK α radiation over the 2 θ range of 4–40°. Fully swollen gels were freeze-dried prior to analysis.

RESULTS AND DISCUSSION

CNC are generally prepared from cellulosic sources using either a one-step concentrated sulfuric acid or phosphoric acid hydrolysis,²⁹ or a two-step hydrolysis-oxidation/carboxylation process.²⁵ In both methods, stable nanocrystal suspensions are formed owing to the surface charge arising from sulfate and carboxylic acid groups, respectively. However, the surface sulfate ester groups that stabilize the acid-hydrolyzed CNCs are unstable and readily desulfonate at high temperature and/or high pH conditions. As the CMC/HEC hydrogels are formed at relatively high pH (pH > 12), desulfonation will likely occur and likely lead to destabilization and poor nanocrystals reinforcement. By contrast, the hydrolysis-oxidation method utilizes the introduction of carboxylic acid groups at the C6 position of the anhydroglucopyranose unit to introduce surface charge and stabilize the nanocrystals suspension, and consequently is very stable under alkaline conditions. For that reason, the latter was utilized in this study.

Effect of nanofiller and crosslink density on hydrogel performance

The properties of CMC/HEC/DVS hydrogels are affected by the ratio of CMC to HEC, as well as the extent of crosslinking.⁸ Generally, the higher the degree of crosslinking, the higher the rigidity of the hydrogel and the lower the water absorption capability. Theoretically, in the fully crosslinked CMC/HEC/DVS hydrogel, the OH/DVS (crosslinker) ratio is two, where OH is the total amount of hydroxyl groups in both the CMC and HEC. In this study, the OH/DVS ratio was varied from 3 to 7. Interestingly, all of the prepared gels showed similar compressive strengths, likely an artifact of the soft gels, which easily buckle under load before breaking, thereby increasing the apparent compressive strength of the soft gels. As a result, compressive modulus was used to compare the mechanical properties of the various hydrogels.

As expected, increasing the OH/DVS ratio decreased the corresponding compressive modulus of the hydrogels (Figs. 1 and 2). The compressive modulus decreased from ~ 28 kPa to ~ 10 kPa as the OH/DVS content increased from 3 to 7. At the same time, the corresponding swelling ratio increased from ~ 100 to almost 400 (Fig. 3), as the decrease in crosslinking results in a less rigid gel, more amenable to water uptake and swelling.

The addition of nanoparticles to the CMC/HEC/DVS hydrogel system dramatically affected the hydrogel properties. At low OH/DVS (OH/DVS = 3) compressive modulus of the hydrogels increased by ~ 20% with CNC addition, while decreasing ~ 20% with organoclay addition. As the ratio of OH/DVS increased the effect of CNC addition on hydrogel compressive modulus increased. At OH/

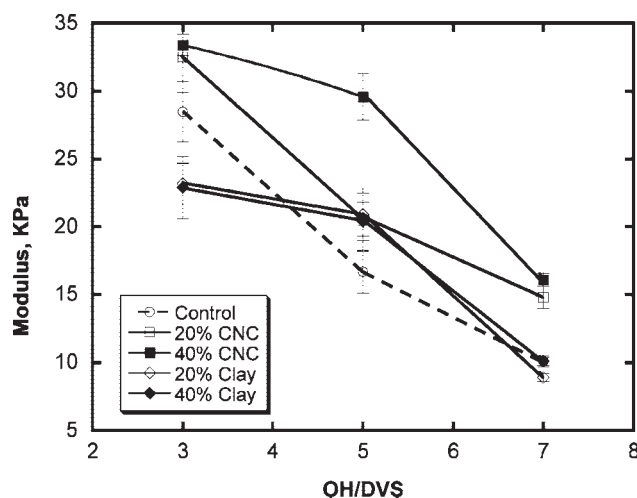


Figure 2 Effect of nanoparticle addition and crosslinker (OH/DVS) on compressive modulus of nanoparticle reinforced CMC/HEC hydrogel composites.

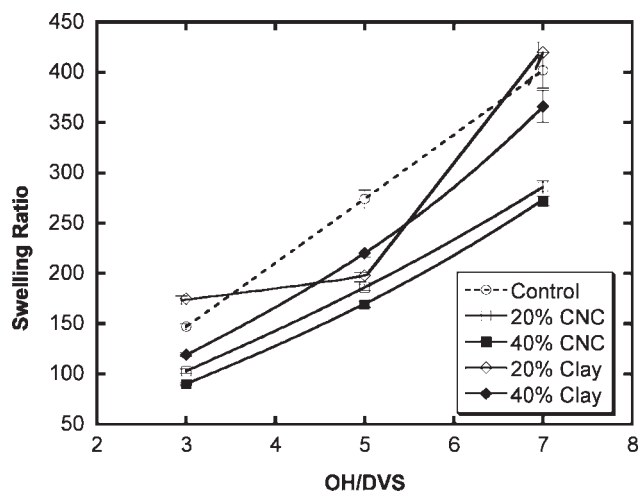


Figure 3 Effect of nanoparticles on swelling ratio for CMC/HEC hydrogels at various OH/DVS ratios.

DVS = 5, the hydrogel composites with 40% CNC have the same modulus as the reference gel with OH/DVS = 3. Similarly, with OH/DVS = 7, hydrogel composites with 40% CNC have the same modulus as the reference gel with OH/DVS = 5. By contrast, the organoclay does not appear to provide any significant reinforcement to the composite hydrogels.

With the exception of the 20% organoclay hydrogel composites, both CNC and 40% organoclay hydrogel composites have lower swelling ratios than the corresponding control hydrogel. Again, an increase in the swellability of the nanoparticle reinforced hydrogels was observed with increasing OH/DVS ratio. All of the composites had lower swelling ratios than the control, with the exception of the 20% clay. However, at the same modulus ~ 29 kPa, the 40% CNC, OH/DVS = 5 reinforced hydrogel had a slight increase in swelling ratio as compared to the control hydrogel (OH/DVS = 3). The same was observed for the higher OH/DVS = 7 CNC reinforced hydrogel, which had the same modulus as the OH/DVS = 5 control hydrogel. The organoclay hydrogel composites did not show any particular trend in relation to the reference gels. At the same crosslinker content (OH/DVS), the organoclay hydrogel composites showed higher and lower swelling ratios as compared to the reference hydrogels, even though the clay itself is an unswellable mineral.

Further analysis of the hydrogels swelling behavior revealed that the swelling rate of the CNC-hydrogel composite with an OH/DVS ratio of 5 and 40% CNC was approximately the same as that of the reference gel with an equivalent modulus, i.e. OH/DVS ratio of 3, despite its slightly higher swelling ratio and lower apparent crosslinking density (Fig. 4).

It is apparent that the CNC and organoclay nanoparticles show different effects on the modulus and swelling behavior of the CMC/HEC hydrogels. This

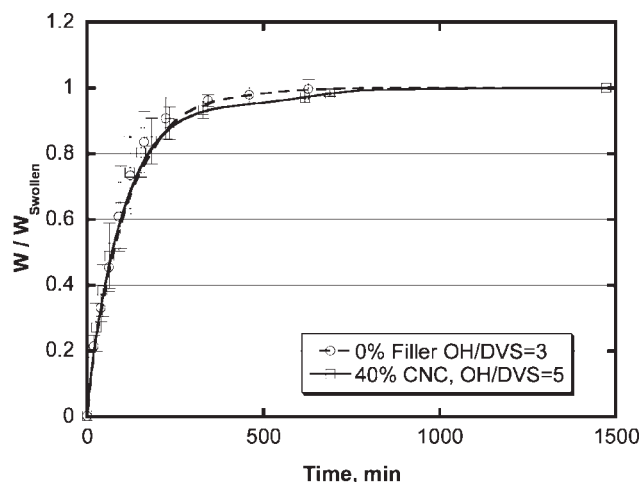


Figure 4 Comparison of swelling rate between CMC/HEC (OH/DVS = 3) and CMC/HEC + 40% CNC (OH/DVS = 5) hydrogels.

is clearly seen from Figures 5 and 6. With increased CNC content, the modulus of hydrogel nanocomposites increases and the swelling ratio decreases, which is a typical behavior of an inert filler.³⁰ By contrast, the organoclay exhibits very unusual behavior. Increasing the organoclay content results in hydrogel nanocomposites that exhibit both higher and lower modulus and swelling ratios as compared to the corresponding nonreinforced hydrogels. With the same crosslinking content (based on OH/DVS), the swelling ratio of the organoclay composites in some cases, first increases and then decreases instead of a monotonical decrease for typical inert filler.

The unique behavior of the organoclay reinforced hydrogels may be due to the reactive functional groups, e.g., OH groups, on the surface of the organoclay reacting with the DVS crosslinker. This

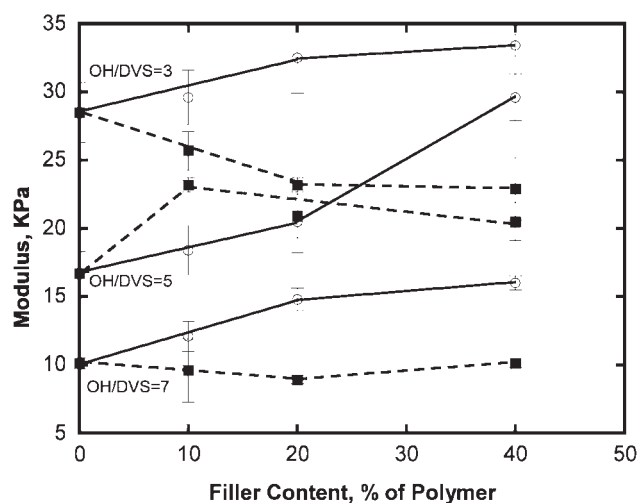


Figure 5 Effect of nanoparticle content on compressive modulus of nanoparticle reinforced CMC/HEC hydrogel composites. CNC: unfilled circle; Clay: filled square.

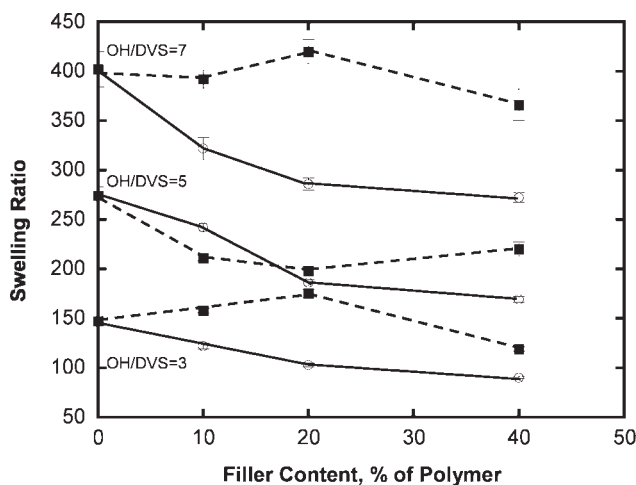


Figure 6 Effect of nanoparticle content on swelling ratio of nanoparticle reinforced CMC/HEC hydrogel composites. CNC: unfilled circle; Clay: filled square.

consumes some of the crosslinker, thereby lowering the crosslinking density, which lowers the modulus but increases the swelling ratio. Because the CNCs are highly crystalline, calculated to be above 90% from the X-ray diffraction pattern, there are not any accessible OH groups available to undergo similar reactions with the cross-linker. The result is the CNC behaving like inert fillers.

Further support of this is evident from thermogravimetric analysis of the nanocomposites, Figure 7. All of the gels show a thermal degradation around 300°C, likely degradation of the CMC/HEC network or cellulose backbone. The organoclay composite shows a second decomposition at around 500°C, which is not observed in the CNC composites. This degradation may be that of chemical bonds between the cellulosic network and organoclay.

Nanoparticle reinforced material performance is very dependent on the dispersion/exfoliation of the nanoparticles within the polymer matrix. Dispersion/exfoliation is typically determined by microscopic or diffraction analysis. Both CNC and organoclay nanoparticles exhibit characteristic X-ray

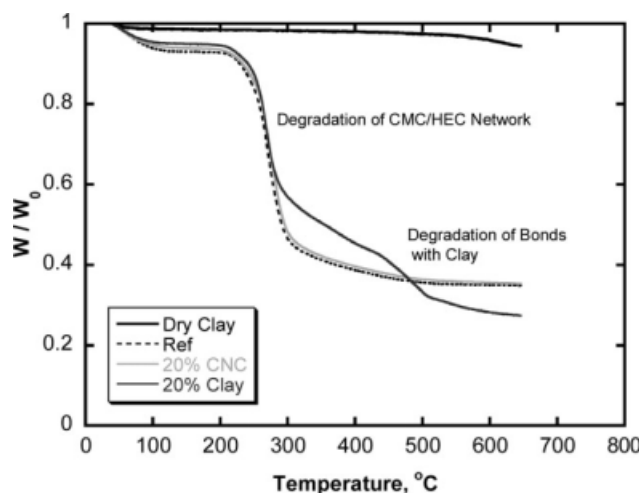


Figure 7 Thermogravimetric analysis (TGA) of nanoparticle reinforced CMC/HEC hydrogel composites.

diffraction patterns. When well dispersed/exfoliated, nanoparticles lose their characteristic X-ray diffraction patterns.^{31,32} Figure 8 shows the X-ray diffraction patterns of the CNC, CMC/HEC and CNC reinforced CMC/HEC hydrogels. The CMC/HEC network and the CNC reinforced CMC/HEC composite have the same diffraction patterns. The diffraction pattern of CNC (Cellulose I) is not visible in these composite, and indicates that the CNC particles are well dispersed in the CMC/HEC matrix. However, at high nanoparticle loadings, e.g., ~ 0.8 g CNC per gram of CMC/HEC, or under high pH conditions (pH > 13) the CNC particles tended to aggregate and the characteristic X-ray diffraction pattern of cellulose I was observed (data not shown).

Effect of CNC surface charge density on hydrogel performance

By controlling the degree of oxidation during CNC preparation, the surface charge density of the CNC can be changed. Generally, the presence of fixed charges within the hydrogel can induce an osmotic gradient and enhance the electrostatic repulsion

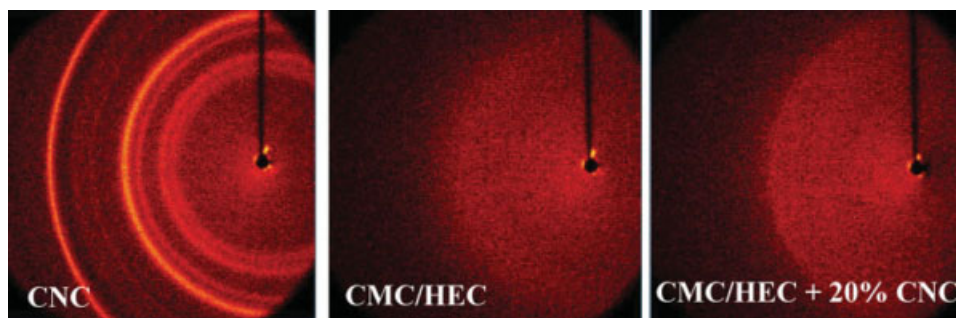


Figure 8 X-ray diffraction patterns of CNC, CMC/HEC and CMC/HEC + 20% CNC hydrogels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

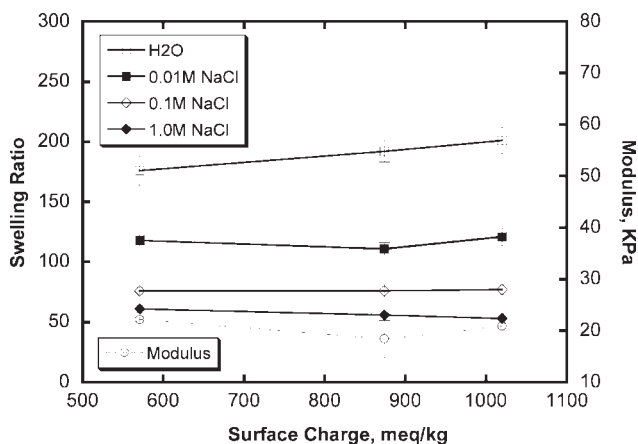


Figure 9 Effect of CNC surface charge density on CMC/HEC hydrogel swelling ratio.

within the hydrogel expanding the matrix,⁵ and thereby increasing the swelling ratio. The modulus of the CNC hydrogel composites is not significantly affected by the change in CNC surface charge (Fig. 9). In deionized water, a slight increase in swelling ratio is observed with increasing CNC surface charge. This is due to the osmotic gradient induced by the fixed ion charge on the CNC surface along with the fixed charge of CMC/HEC network. When the ionic strength of the aqueous solution is increased, the CNC composites have the same swelling ratio no matter what the surface charge density of the CNC. This is due to the screening effect of ions in water.³³ However, it was observed that the nano-reinforced hydrogels with the higher surface charge density CNC is more transparent than the others due to better dispersion of the CNC particles with the higher surface charge.

CONCLUSIONS

It is possible to reinforce CMC/HEC hydrogels using CNC nanoparticles. The hydrogel nanocomposites with CNC have similar or improved swelling properties and comparable mechanical properties to pure CMC/HEC hydrogels with higher crosslinking content, i.e. incorporating CNCs can reduce the amount of crosslinking agent used. However, the CNC loadings required for performance enhancement in this system are well beyond what is typically expected based on traditional nanofillers. As CNCs are not currently commercially produced, the cost of CNC addition relative to the savings in crosslinker cannot be determined, but will be a critical issue for the utilization of CNCs in such systems.

The surface charge density of the CNCs did not have any obvious effect on the properties of the CNC-hydrogel composites. X-ray diffraction analysis revealed the CNC particles are well dispersed

throughout the CMC/HEC matrix at lower CNC loadings, but showed clear evidence of CNC clusters and the presence of a cellulose I diffraction pattern at higher CNC loadings.

By contrast, the organoclay-reinforced hydrogels did not reveal any significant reinforcement capacity upon organoclay incorporation. This may be due to possible reaction of the reactive functional groups on the organoclay surfaces with the crosslinking agent, as evident by TGA.

References

- Vogelton, C. T. *Mod Drug Delivery* 2001, 4, 49.
- Fedorovich, N. E.; Alblas, J.; de Wijn, J. R.; Hennink, W. E.; Verbout, A. J.; Dhert, W. J. A. *Tissue Eng* 2007, 13, 1905.
- Grund, K. E.; Köhn, P. C.; Farin, G. U.S. Pat. 6,474,993 (2002).
- Raju, M. P.; Raju, K. M. *J Appl Polym Sci* 2001, 80, 2635.
- Sasaki, S.; Maeda, H. *J Chem Phys* 1997, 107, 1028.
- Weaver, M. O.; Bagley, E. B.; Fanta, F.; Doane, W. M. U.S. Pat. 3,981,100 (1976).
- Kabiri, K.; Zohuriaan-Mehr, M. *J Polym Adv Technol* 2003, 14, 438.
- Esposito, F.; Del Nobile, M. A.; Mensitieri, G.; Nicolais, L. *J Appl Polym Sci* 1996, 60, 2403.
- Anbergen, U.; Oppermann, M. *Polymer* 1990, 31, 1854.
- Dutkiewicz, J. K. *J Biomed Mater Res* 2002, 63, 373.
- Lee, W.-F.; Yang, L.-G. *J Appl Polym Sci* 2004, 92, 3422.
- Wu, J.; Lin, J.; Li, G.; Wei, C. *Polym Int* 2001, 50, 1050.
- Lee, W. F.; Fu, T. F. *J Appl Polym Sci* 2003, 89, 3652.
- Xia, X.; Yih, J.; D'Souza, N. A.; Hu, Z. *Polymer* 2003, 44, 3389.
- Sur, G. S.; Lyu, S.-G.; Chang, J.-H. *J Ind Eng Chem* 2003, 9, 58.
- Haraguchi, K.; Takehisa, T.; Fan, T. *Macromolecules* 2002, 35, 10162.
- Haraguchi, K.; Takehisa, T. *Adv Mater (Weinheim, Ger)* 2002, 14, 1120.
- Liang, L.; Rieke, P.C.; Liu, J.; Fryxell, G. E.; Young, J. S.; Engelhard, M. H.; Alford, K. L. *Langmuir* 2000, 16, 8016.
- Lin, J.; Wu, J.; Yang, Z.; Pu, M. *Macromol Rapid Commun* 2001, 22, 422.
- Messersmith, P. B.; Znidarsich, F. *Mater Res Soc Symp Proc* 1997, 457, 507.
- Revol, J. F.; Bradford, H.; Giasson, J.; Marchessault, R. H.; Gray, D. G. *Int J Biol Macromol* 1992, 14, 170.
- Aziz Samir, M. A. S.; Alloin, F.; Sanchez, J.-Y.; Dufresne, A. *Polymer* 2004, 45, 4149.
- Favier, V.; Chanzy, H.; Cavaille, J. Y. *Macromolecules* 1995, 28, 6365.
- Chazneau, L.; Cavaille, J. Y.; Terech, P. *Polymer* 1999, 40, 5333.
- Araki, J.; Wada, M.; Kuga, S. *Langmuir* 2001, 17, 21.
- Gousse, C.; Chanzy, H.; Excoffier, G.; Soubeyrand, L.; Fleury, E. *Polymer* 2002, 43, 2645.
- Bonini, C.; Heux, L.; Cavaille, J.-Y.; Lindner, P.; Dewhurst, C.; Terech, P. *Langmuir* 2002, 18, 3311.
- Samir, M. A. S.; Alloin, F.; Sanchez, J.-Y.; El Kissi, N.; Dufresne, A. *Macromolecules* 2004, 37, 1386.
- Dong, X. M.; Revol, J.-F.; Gray, D. G. *Cellulose* 1998, 5, 19.
- Comyn, J., Ed. *Polymer Permeability*, Chapman & Hall: London, 1994.
- Lan, T.; Wang, Z.; Shi, H.; Pinnavaia, T. *J Polym Mater Sci Eng* 1995, 73, 296.
- LeBaron, P. C.; Pinnavaia, T. *J Chem Mater* 2001, 13, 3760.
- Ken, A.; Dill, K. A.; Truskett, T. M.; Vlachy, V.; Hribar-Lee, B. *Annu Rev Biophys Biomol Struct* 2005, 34, 173.