

# MICRO-HETEROGENEITY AND MICRO-RHEOLOGICAL PROPERTIES OF CELLULOSE-BASED HYDROGEL STUDIED BY DIFFUSING WAVE SPECTROSCOPY (DWS)

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Cellulose is the most plentiful biopolymer available in the world, and is a natural, biodegradable as well as inexpensive resource for biomaterials. Herein, a cellulose-based superabsorbent hydrogel (CHCCA) was prepared by crosslinking carboxymethyl cellulose (CMCNa) and hydroxyethyl cellulose (HEC) with citric acid, and its micro-heterogeneity and micro-rheological properties were explored by diffusing wave spectroscopy (DWS). The mean-square displacement (MSD) of microspheres imbedded into CHCCA hydrogels prepared at five concentrations was compared. At very low concentration, of 0.1 wt%, the CHCCA hydrogel exhibited nearly homogeneous behavior, with slight heterogeneity. The heterogeneity became larger as the CHCCA concentration increased. It was also revealed that the high-frequency viscoelastic moduli magnitude at 0.1 wt% CHCCA can be expressed by  $|G^*(\omega)| \propto \omega$ , which is characteristic of a viscoelastic fluid-like behavior. The magnitude of high-frequency viscoelastic moduli for 0.3 wt% and 0.5 wt% CHCCA can be described by  $|G^*(\omega)| \propto \omega^{3/4}$ , which is characteristic of a semi-flexible polymer. The high-frequency viscoelastic moduli magnitude for 1.0 wt% and 1.5 wt% CHCCA described by  $|G^*(\omega)| \propto \omega^{1/2}$ , was characteristic of a flexible polymer. Our results identified unique CHCCA property changes that occurred with changes in concentration, providing new insights for CHCCA derived hydrogels that will be useful in developing new CHCCA applications.

**Keywords:** cellulose, diffusing wave spectroscopy (DWS), hydrogel, micro-rheology, rheology

## INTRODUCTION

Hydrogels are unique soft materials consisting of three-dimensional polymer networks that are capable of absorbing large amounts of water.<sup>1</sup> These hydrogels can be used in a variety of applications, including drug delivery,<sup>2</sup> wound healing,<sup>2,3</sup> soil conditioners,<sup>2,4</sup> in addition to many other non-hygienic utilizations.<sup>2,5</sup> Polyacrylates or copolymers with polyacrylates are commonly used materials to prepare hydrogels.<sup>2,6</sup> However, polyacrylate and its copolymers are synthetic polymers and their resulting hydrogels can be considered harmful for the environment. At

present, scientists are seeking more environmentally friendly and low-cost materials, such as cellulose, as well as its derivatives, to develop biobased hydrogels.<sup>2,7,8</sup> Cellulose is the most plentiful biological polymer in the world, and is available from many sources, such as cotton, wood, agricultural wastes, crop residues, and some non-plant resources.<sup>2,8,9</sup> Cellulose can be a major chemical feedstock due to its low cost, large availability, and renewability.<sup>7</sup> Because cellulose is insoluble in water, cellulose hydrogels are typically developed using cellulose derivatives that

have been chemically modified through crosslinking the hydroxyl groups contained in cellulose.<sup>9</sup> However, the physical properties of these cellulose-based hydrogels are rarely reported, which are important to their understanding, and largely restricts the development of applications for these hydrogels. Currently, most studies examining the rheological properties of cellulose-based hydrogels use traditional rheological techniques, which can lead to deformation of the samples applied during rheological testing, thus limiting the understanding of the dynamic process occurring in the hydrogel.

Diffusing wave spectroscopy (DWS) is a dynamic light scattering technique that has been used to provide information concerning the micro-heterogeneity and micro-rheology of colloidal suspensions, gels, emulsions, and biopolymer samples.<sup>10</sup> An advantage of DWS is that it can be used to study a variety of materials and is non-invasive, allowing rheological properties to be measured without perturbation, making it suitable to study fragile systems. DWS tracks the thermal-driven movements of microbeads imbedded into the hydrogel, so that the mean square displacements (MSD) of the monitored microspheres over time can be tracked. From the MSD and the diffusion coefficients determined from MSD, the polymers' heterogeneity can be obtained. The viscoelastic moduli of the polymer can also be calculated from the measured MSD using the Stokes-Einstein equation.<sup>11</sup> As a result, the rheological behaviors of the hydrogel can be measured as high as  $10^6$  rad/s by DWS, which is much greater than those measured by classical rheometers. Therefore, DWS can provide more insight into the studied samples, which would be useful for us to develop and design new material applications accordingly.

Recently, we prepared cellulose-based hydrogels by crosslinking a mixture of sodium carboxymethyl cellulose (CMCNa) and hydroxyethyl cellulose (HEC) with citric acid, a green crosslinking agent.<sup>9</sup> The resulting cellulose-based hydrogel (CHCCA) is a superabsorbent that can absorb more than 130 times its dry weight in water and may have use in seed coating, drug delivery, wound healing and cosmetic applications.<sup>9</sup> In this work, we explored the micro-heterogeneity and micro-rheological properties of CHCCA using DWS. From this study, the micro-heterogeneity and micro-rheological properties of CHCCA were revealed. The results of this work

not only provide a deeper understanding of the physical behaviors of this hydrogel, but also are particularly important and useful for developing new usages for this cellulose-based biodegradable hydrogel.

## EXPERIMENTAL

### Raw materials

Sodium carboxymethyl cellulose (CMCNa), hydroxyethyl cellulose (HEC), and citric acid were all purchased from Sigma-Aldrich (St. Louis, MO, USA).

### Preparation of hydrogels

The CHCCA was prepared by cross-linking CMCNa and HEC with citric acid.<sup>9</sup> Concisely, CMCNa and HEC (3:1 weight ratio) were mixed to make up a 2 wt% in water solution at 23 °C. Citric acid (1.75 wt%) was added when the solution became clear, after continuously agitating (30 min). The resulting mixture was then dried at 55 °C overnight. The dried sample was then crosslinked by heating for 24 h at 90 °C. The cooled sample was ground into powder and stored. The powdered samples of CHCCA were re-dissolved in water to make five concentrations (0.1%, 0.3%, 0.5%, 1.0%, and 1.5%) (wt%) of hydrogels. The prepared hydrogels were then kept at 4 °C and used within two days.

### Measurements by attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FTIR)

The Fourier transform infrared spectroscopy (FTIR) spectra of individual samples were collected using a Thermo Fisher Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), equipped with a SensIR dATR DuraScope single-contact attenuated total reflectance (ATR) attachment (Smith's Detection; Danbury, CT, USA). The ATR attachment employed a round (2 mm diameter) diamond crystal, pressure gauge and video imaging. The FTIR spectrometer was equipped with a Globar infrared source, KBr beamsplitter, and deuterated triglycine sulfate (DTGS) detector. The powdered (freeze dried) samples were placed onto the surface of the diamond ATR crystal, pressure was applied and spectra were acquired at room temperature in the region of 4000-500  $\text{cm}^{-1}$ . A 128-scan co-added interferogram with Happ-Genzel apodization was employed for each sample at 4  $\text{cm}^{-1}$  resolution using OMNIC software (version 8.2; Thermo Fisher Scientific; Madison, WI, USA). FTIR data were collected in an enclosed room with a single operator. A background scan was performed every 5 minutes.

### Diffusing wave spectroscopy (DWS) measurements

Diffusing wave spectroscopy is an optical light scattering technique that measures Brownian movement of microspheres imbedded into the hydrogel samples.<sup>10</sup>

Briefly, a laser beam is incident on a cuvette that holds the hydrogel sample containing the optical probe microbeads, and the fluctuations in the intensity of scattered light is collected by a photon detector. The autocorrelation function ( $g_2(t)-1$ ) with the time was determined by a correlator coupled to the photon detector. The mean square displacement (MSD) of the probing beads,  $\langle \Delta r^2(t) \rangle$ , can be extracted using a root-search algorithm. The diffusion coefficient of the microbeads can be calculated as  $D(t) = \langle \Delta r^2(t) \rangle / 6t$ . The polymer sample's rheological behaviors ( $|G^*(\omega)|$ ) can be calculated from the MSD through the equation of Stokes-Einstein.<sup>10</sup> The DWS measurements for the CHCCA were carried out using a DWS RheoLab II instrument (LS Instruments AG, Switzerland). The 0.5% polystyrene microspheres (450 nm diameter) were gently mixed with the CHCCA in a cuvette. The temperature of the chamber holding the cuvette in the DWS RheoLab II was controlled at 25 °C ± 0.1 °C. Measurements were repeated at least three times using different samples to ensure relative errors were within ±3%.

#### Rheology measurements by classical mechanical rheometer

Rheological properties measured by a classical mechanical rheometer were conducted by a strain-controlled Rheometric ARES rheometer (TA Instruments, New Castle, DE, USA) using a 5-cm diameter parallel-plate geometry.<sup>9</sup> A water circulation system was used to keep the sample at 25 °C ± 0.1 °C.

Mineral oil was used to seal the plates' edges to retain the moisture. The sample's viscoelasticity linear range was first determined by conducting a strain sweep test, then a linear strain was adopted for the other dynamic oscillatory experiments with new samples. The linear dynamic oscillatory experiments provided the sample's elastic/storage ( $G'$  - storage) and loss/viscous ( $G''$ -dissipative) moduli. The magnitude of complex modulus, ( $|G^*(\omega)| = (G'^2 + G''^2)^{1/2}$ ), is characterized as the total resistance to deformation of the material.<sup>10</sup> Experiments were repeated at least three times, using different samples, to ensure relative errors were all within ±7%.

#### RESULTS AND DISCUSSION

The dry powder of studied CHCCA (using 1.75% citric acid as cross-linker) can absorb 139 times its dry weight (swelling ratio = 139) after immersion in water for 24 hours at room temperature. Figure 1 shows the FTIR spectra of CMCNa, HEC, citric acid, and CHCCA. A comparison of the spectrum of CHCCA in the region of 500  $\text{cm}^{-1}$  to 1800  $\text{cm}^{-1}$ , as well as from 3200  $\text{cm}^{-1}$  to 3500  $\text{cm}^{-1}$ , with the corresponding bands of CMCNa, HEC, and citric acid, clearly reveals that CHCCA is a cross-linked material.

The micro-rheological properties of the CHCCA hydrogels were determined from time-dependent MSD of 450 nm diameter microspheres imbedded into the CHCCA hydrogels.

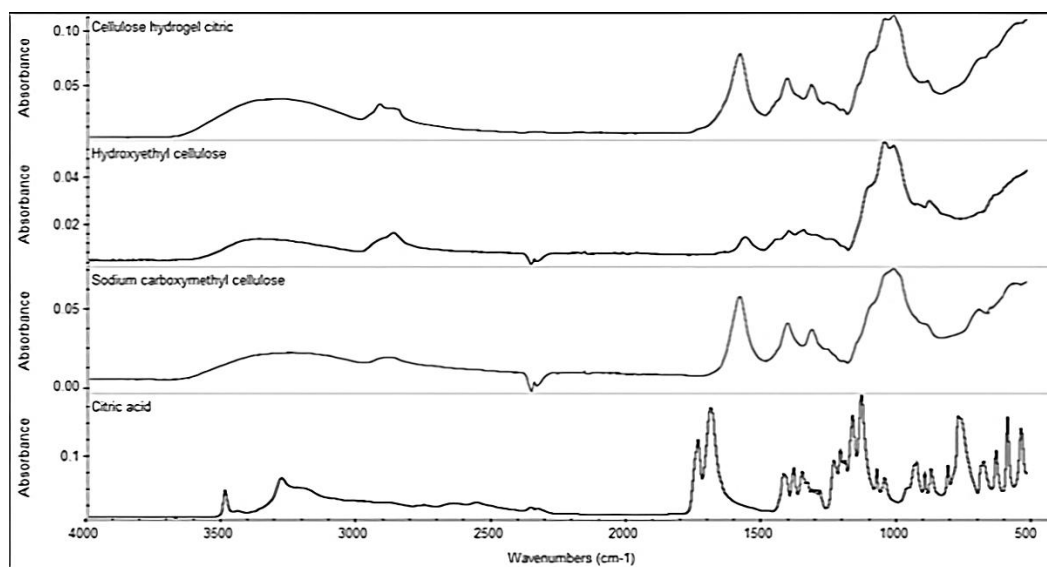


Figure 1: FTIR spectra of CHCCA (1.75 wt% citric acid cross-linked cellulose-based superabsorbent hydrogel (CMCNa/HEC = 3/1)) and its components: hydroxyethyl cellulose (HEC), sodium carboxymethyl cellulose (CMCNa) and citric acid

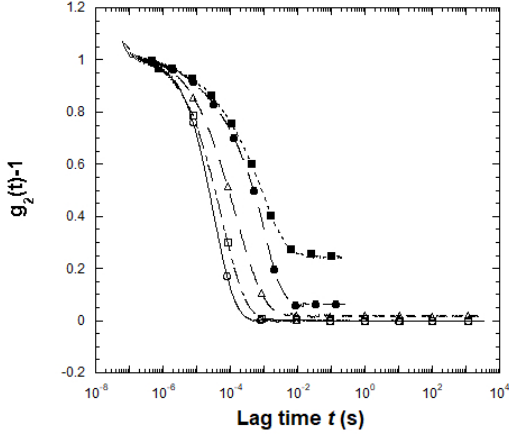


Figure 2: Autocorrelation function ( $g_2(t)-1$ ) of the light intensity scattered by 450 nm diameter microspheres in 0.1 wt% (○), 0.3 wt% (□), 0.5 wt% (Δ), 1.0 wt% (●), and 1.5 wt% (■) cellulose-based hydrogels CHCCA at 25 °C

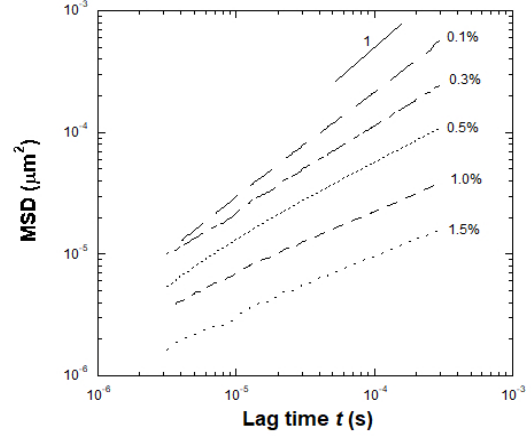


Figure 3: MSDs of 450 nm microspheres imbedded in 0.1 wt%, 0.3 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt% CHCCA at 25 °C (the straight solid line shows a slope of one)

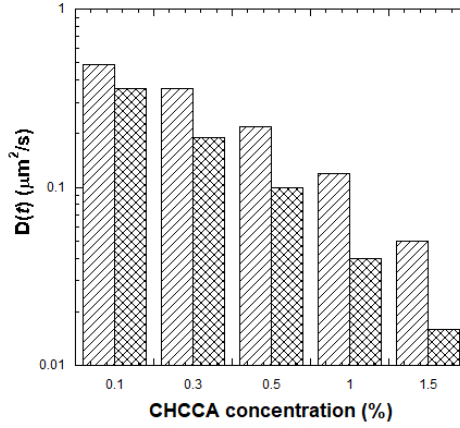


Figure 4: Diffusion coefficient  $D(t) = \langle \Delta r^2(t) \rangle / 6t$  of the microspheres imbedded in the four measured concentrations of CHCCA at time of  $10^{-5}$  and  $10^{-4}$  s at 25 °C (the first and second columns at each concentration correspond to measurements at  $10^{-5}$  s and  $10^{-4}$  s, respectively)

The MSDs,  $\langle \Delta r^2(t) \rangle$ , can be extracted from the measured autocorrelation function ( $g_2(t)-1$ ) of the multiple light scattered by the microbeads imbedded in the hydrogels. Five concentrations of CHCCA at 0.1 wt%, 0.3 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt% were evaluated by this technique.

The normalized autocorrelation functions ( $g_2(t)-1$ ) of the imbedded microbead tracer particles versus lag time are displayed in Figure 2. The autocorrelation function intensity for the 0.1 wt% CHCCA fully relaxed to zero, but as the concentration of CHCCA increased the ( $g_2(t)-1$ ) retarded. The autocorrelation function intensity for the 0.3% CHCCA slightly retarded, but still relaxed to zero. The autocorrelation function intensity for the 0.5% CHCCA delayed further and did not relax to zero. The relaxation of the autocorrelation function ( $g_2(t)-1$ ) intensity for the

highest measured concentration (1.5 wt%) CHCCA was significantly retarded and did not relax to zero. As expected, the autocorrelation functions ( $g_2(t)-1$ ) for the 1.0 wt% CHCCA sample fell between those of 0.5% and 1.5% samples (Fig. 2). More cellulose filament interactions and entanglements at the higher concentrations will account for this effect.<sup>10</sup>

The time-dependent MSDs calculated from the autocorrelation functions for the five CHCCA concentrations examined are shown in Figure 3. The MSDs of the microspheres imbedded in 0.1% CHCCA sample displayed a 0.87 power-law behavior that deviated slightly from a slope of one power-law behavior. The spectra for the MSDs of the microbeads imbedded in the higher concentrations of the CHCCA further deviated from the slope of unity. The MSDs of the

microspheres imbedded in 0.3% CHCCA followed a power-law behavior having a slope of 0.71. The MSDs of the imbedded microspheres at 0.5%, 1.0%, and 1.5% CHCCA further deviated from a power-law behavior of unity having slopes of 0.65, 0.51, and 0.49, respectively (Fig. 3).

The resulting diffusion coefficient ( $D(t)$ ) of the microbeads in 0.1% CHCCA was calculated to be  $0.49 \mu\text{m}^2/\text{s}$  and  $0.36 \mu\text{m}^2/\text{s}$  at  $10^{-5}$  and  $10^{-4}$  seconds, respectively, which decreased slightly with the time scale (Fig. 4). By comparison, the MSDs for the microbeads in homogeneous viscous solutions, such as water and glycerol, display a unity power-law behavior and time-independent  $D(t)$ s.

However, the MSDs for the microbeads imbedded in heterogeneous polymers would deviate from the slope of one power-law behavior, and the diffusion coefficients will be dependent on time.<sup>10,12</sup> For instance, the same beads will have the constant  $D(t)$  of  $0.97 \mu\text{m}^2/\text{s}$  in water using the  $D(t) = k_B T / 6\pi\eta a$  ( $k_B$  is the Boltzmann constant,  $T = 298$  K,  $\eta$  is the viscosity of the solvent, and  $a$  is the radius of the microspheres). Therefore, 0.1 wt% CHCCA exhibited slight heterogeneity due to the behavior of the microbeads that were imbedded in the 0.1 wt% CHCCA, with a slight deviation from those mixed in homogeneous solutions. The  $D(t)$ s of the microspheres mixed with 0.3 wt% CHCCA were  $0.36 \mu\text{m}^2/\text{s}$  and  $0.19 \mu\text{m}^2/\text{s}$ , respectively, at  $10^{-5}$  and  $10^{-4}$  seconds, showing more reduction at longer times. The  $D(t)$ s of the beads mixed with 0.5

wt% CHCCA were  $0.22 \mu\text{m}^2/\text{s}$  and  $0.10 \mu\text{m}^2/\text{s}$ , respectively, at  $10^{-5}$  and  $10^{-4}$  seconds. The diffusion coefficients of the microspheres mixed with 1.0 wt% and 1.5 wt% CHCCA were  $0.12$  and  $0.05 \mu\text{m}^2/\text{s}$ , as well as  $0.04$  and  $0.016 \mu\text{m}^2/\text{s}$ , respectively, at  $10^{-5}$  and  $10^{-4}$  seconds, showing even further dropping at longer times (Fig. 4). Thus, with the increasing concentration of CHCCA, the traces of microbeads' MSDs imbedded in CHCCA further deviated from slope of one, and  $D(t)$ s of the microspheres decreased significantly at larger time scales, showing increased micro-heterogeneous behaviors of the CHCCA at higher concentrations.

The DWS can measure high-frequency range viscoelastic behaviors of polymers that show the early dynamics of relaxation of the polymer networks. The amplitude of complex moduli ( $|G^*(\omega)| = (G'^2 + G''^2)^{1/2}$ ) represent the total resistance against deformation or external force to the material. The amplitude of the viscoelastic complex moduli ( $|G^*(\omega)|$ ) for the five concentrations of CHCCA is shown in Figures 5 and 6. The curves of  $|G^*(\omega)|$  using both classical rheometer and DWS optical measurements are shown for comparison. It can be seen that these results obtained by the classical rheometer and DWS are in good agreement, demonstrating that the DWS measurements are reasonable and accurate (Figs. 5 and 6).

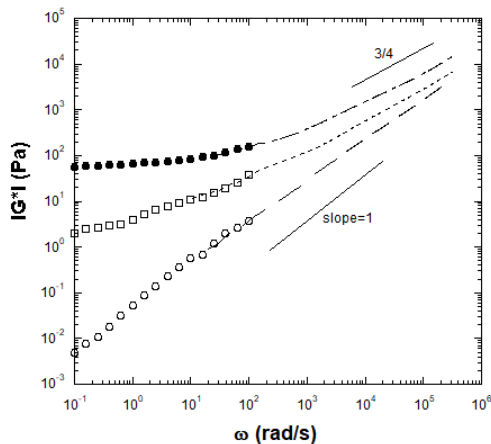


Figure 5:  $|G^*| = (G'^2 + G''^2)^{1/2}$  of 0.1 wt% (○), 0.3 wt% (□), and 0.5 wt% (●) CHCCA measured by a classical rheometer (symbols) and DWS (dashed lines) at 25 °C (two straight solid lines are showing slopes of 1 and  $3/4$ , respectively)

The magnitudes of complex moduli ( $|G^*(\omega)|$ ) at high frequencies for all measured five CHCCA

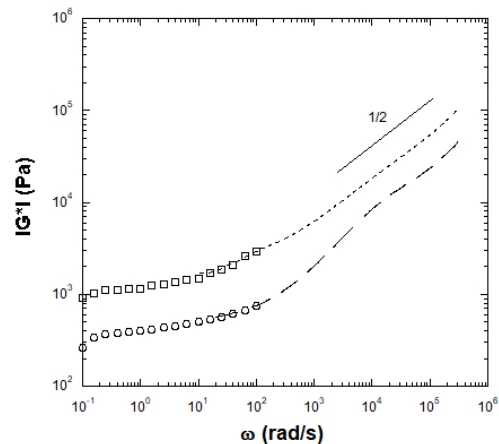


Figure 6:  $|G^*| = (G'^2 + G''^2)^{1/2}$  of 1.0 wt% (○), and 1.5 wt% (□) CHCCA measured by a classical rheometer (symbols) and DWS (dashed lines) at 25 °C (the straight line is showing a slope of 1/2)

hydrogel concentrations were large, suggesting the CHCCA total resistance to the external force was

very strong within the extremely short time. Additionally,  $|G^*(\omega)|$  was shown to increase as CHCCA concentration increased. However, as can be seen, the shape of the  $|G^*(\omega)|$  curves for different concentrations of CHCCA were totally different (Figs. 5 and 6). The  $|G^*(\omega)|$  for 0.1 wt% CHCCA measured by both classical rheometer and DWS exhibited a nearly straight line, following a power law with a slope close to unity, that is  $|G^*(\omega)| \propto \omega$  (Fig. 5). In addition,  $G''$  values were greater than those of  $G'$  over the whole frequency range measured by both rheometer and DWS (data not shown). These results indicated that the 0.1 wt% CHCCA should be a viscoelastic fluid or liquid.<sup>10,13</sup> These results suggested that at low concentration, of 0.1 wt%, the polymeric network of the CHCCA was very loose and the solution did not show strong viscoelasticity. These results also implied that CHCCA should form a gel above 0.1 wt%, which is important for designing a CHCCA hydrogel.

The  $|G^*(\omega)|$  of the CHCCA increased with the CHCCA concentration, demonstrating stronger viscoelasticity for CHCCA concentration  $\geq 0.3$  wt% (Figs. 5 and 6). Additionally, all measured  $G'$  values were higher than  $G''$  for all measured CHCCA concentrations  $\geq 0.3$  wt% (data not shown), which indicated that  $\geq 0.3$  wt% CHCCA should exhibit viscoelastic solid or gel properties. This is consistent with the increased heterogeneity observed for CHCCA concentrations  $\geq 0.3$  wt%. The high-frequency  $|G^*(\omega)|$  for 0.3 wt% and 0.5 wt% CHCCA samples displayed a behavior of  $|G^*(\omega)| \propto \omega^{3/4}$  (Fig. 5). However, the high-frequency behavior of the  $|G^*(\omega)|$  for 1.0 wt% and 1.5 wt% CHCCA had a behavior of  $|G^*(\omega)| \propto \omega^{1/2}$  (Fig. 6).

Conventional classical rheology measurements of the frequency dependence of the moduli for  $\omega > 200$  rad/s are nearly impossible. Thus, it is difficult to directly compare published data at high frequencies. However, the high-frequency behaviors of  $|G^*(\omega)|$  were predicted by some theoretical models. Morse<sup>14-16</sup> has constructed a model that specifically describes the rheological behavior and dynamics of semiflexible polymers in solution. This model predicts that at large frequencies,  $|G^*(\omega)| \propto \omega^\alpha$ , with  $\alpha = 3/4$ , are in excellent agreement with our DWS results for the 0.3 wt% and 0.5 wt% CHCCA (Fig. 5). Another model predicts the  $|G^*(\omega)|$  high-frequency behavior of flexible polymers as  $|G^*(\omega)| \propto \omega^{1/2}$ ,<sup>10,17</sup> which is consistent with our results for 1.0 wt%

and 1.5 wt% CHCCA (Fig. 6). These models are based on polymer physics theories, which may or may not directly apply to the CHCCA. However, the information of high-frequency moduli behavior differences for different concentrations of CHCCA does imply structural differences. The above results indicated that the CHCCA exhibited viscoelastic fluid behavior at lower concentration ( $\leq 0.1$  wt%) changing into semi-flexible polymer nature around 0.3-0.5 wt%, and then shifting into flexible polymer behavior around 1.0-1.5 wt%. At very low concentrations, intermolecular cross-linking, and cellulose fiber interactions and entanglements the CHCCA were weak, without strong network formation. Therefore, CHCCA only showed more fluid-like behavior at concentrations  $\leq 0.1$  wt%. This result was also in agreement with the result conclusion that the  $\leq 0.1\%$  CHCCA showed nearly homogenous behavior, with slight heterogeneity. When CHCCA concentrations were  $\geq 0.3$  wt%, but  $< 1.0$  wt%, the polymer chain interactions revealed semi-flexible polymer property. While at CHCCA concentrations  $\geq 1.0$  wt%, the polymer chains showed flexible behavior. When the concentration of CHCCA increased from 0.5 wt% to 1.0 wt%, the polymer chains of CHCCA behavior altered from being semi-flexible to flexible, suggesting that CHCCA should experience a structural shift within this small concentration range.

The above CHCCA property/structure information would be extremely helpful for us to design and develop different CHCCA hydrogels accordingly. Directly observing these structural differences is difficult. The possible occurrence of structure changes may be due to much stronger chain interactions that take place in the  $\geq 1.0$  wt% CHCCA. At 0.3-0.5 wt% CHCCA, the networks are relatively uniform, showing semi-flexible behavior. However, the  $\geq 1.0$  wt% CHCCA likely has more parallel chain and small bundle type interactions at greater concentrations. These parallel chains can easily pass through each other, so that the networks were relatively non-uniform, leading to a flexible polymer behavior. The technique of DWS allows the measurement of viscoelastic moduli of CHCCA at very high frequencies at certain temperature, without disturbing the CHCCA. This cannot be carried out by traditional classical rheometers. The understanding of these physical properties of CHCCA will be useful to develop new applications for such hydrogels.

## CONCLUSION

In this study, we investigated the micro-heterogeneity and micro-rheological properties of CHCCA hydrogels by diffusing wave spectroscopy (DWS) at five CHCCA concentrations – of 0.1 wt%, 0.3 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt%. The autocorrelation function ( $g_2(t)-1$ ) detected by DWS suggested the interactions and entanglements between the CHCCA cellulose filaments became stronger as the CHCCA concentration increased. The MSD behavior of the microbeads imbedded in 0.1 wt% CHCCA suggested that the nature of the 0.1 wt% CHCCA was close to homogeneous, with slight heterogeneity. However, the MSD behaviors of the microspheres imbedded in  $\geq 0.3$  wt% CHCCA implied that CHCCA exhibited larger heterogeneities, with increased CHCCA concentrations. Both low-frequency and high-frequency magnitude of viscoelastic moduli for the 0.1 wt% CHCCA can be described as  $|G^*(\omega)| \propto \omega$ , indicating that 0.1 wt% CHCCA should display more fluid-like property. The high-frequency magnitude of viscoelastic moduli for the 0.3 wt% and 0.5 wt% CHCCA can be characterized as  $|G^*(\omega)| \propto \omega^{3/4}$ , which is a semi-flexible polymer behavior. However, the high-frequency magnitude of viscoelastic moduli for the 1.0 wt% and 1.5 wt% CHCCA can be characterized as  $|G^*(\omega)| \propto \omega^{1/2}$ , which is a flexible polymer behavior. The insight gained from this study will help develop new commercial applications for CHCCA.

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