



# Investigation of the scaling law on gelation of oppositely charged nanocrystalline cellulose and polyelectrolyte



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## ABSTRACT

The sol–gel transition in the mixture system of oppositely charged polyelectrolyte (quaternized hydroxyethylcellulose ethoxylate, QHEC) and nanocrystalline cellulose (NCC) induced by electrostatic adsorption interaction was investigated by rheological means. Winter and Chambon theory was validated to be applicable for the critical gel point determination, and critical gel point have been successfully determined. With QHEC concentration increasing, more NCC were needed to form a critical gel, and smaller loss tangent and relaxation exponent ( $n$ ) values at the gel point were observed, indicating the elastic nature of mixture was enhanced with QHEC increase. Gel strength behaved as a function of both QHEC and NCC concentrations, suggesting the gel network at the critical point was composed of entanglements and association of QHEC macromolecular chains, as well as the electrostatic adsorption interaction between QHEC chains and NCC rods. The calculated number of NCC rods per junction decreased from 0.30 to 0.01 when the QHEC concentration increased from 1.0 wt% to 3.0 wt%, indicating the electrostatic adsorption interaction between the NCC rods and QHEC chains was less significant to gel formation at higher QHEC concentrations. Therefore, the exponents of scaling law  $\eta_0 \propto \epsilon^{-\gamma}$  and  $G_e \propto \epsilon^{-z}$  for the QHEC/NCC mixtures revealed that the scaling law  $n = z/(z + \gamma)$  between  $n$ ,  $\gamma$ , and  $z$  was only feasible at highest QHEC concentration, since the intermolecular interaction (electrostatic adsorption interaction in this article) was so weak that can be neglected and the critical gel network was dominated by QHEC chain entanglements and association.

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## 1. Introduction

Nanocrystalline cellulose (NCC) is the fundamental constitutive polymeric motif of macroscopic cellulosic-based fibers, and can be extracted by acid hydrolysis of cellulosic materials, such as bacteria cellulose, cotton, and wood pulp (Habibi, Lucia, & Rojas, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Rånby, 1949; Liu et al., 2011). This rod-shaped material has attracted a lot of attention over the past several decades because of its availability, renewability, light weight, nano-scale dimension, unique morphology and low cost (Habibi et al., 2010). Therefore, NCC has been widely employed as reinforcing agent in nanocomposites (Samir, Alloin, & Dufresne, 2005; Siro & Plackett, 2010), barrier membranes (Siqueira, Bras, & Dufresne, 2010; Paralikar, Simonsen, & Lombardi, 2008), packing materials (Yang, Tejado, Alam, Antal, & van de Ven, 2012; Azeredo, 2009; Rhim, 2007), biomedicines (Czaja, Young, Kawecki, & Brown, 2007; Liang, Hsiao, & Chu, 2007;

Woltman, Jay, & Crawford, 2007), optically and electrooptically variable materials (Beck, Bouchard, & Berry, 2011; Pan, Hamad, & Straus, 2010), bioimaging (Dong & Roman, 2007), sensors (Nielsen, Eyley, Thielemans, & Aylott, 2010), catalysts (Benaissi, Johnson, Walsh, & Thielemans, 2010; Shin, Blackwood, Bae, Arey, & Exarhos, 2007) and so forth.

Systems consisted of oppositely charged colloids and polyelectrolytes exhibited complex self-aggregation behaviors (Pickrahn, Rajaram, & Mohraz, 2010; Hoffmann et al., 2011; Kumar, Dubin, Hernon, Li, & Jaeger, 2007). The structures formed by oppositely charged macroions and polyelectrolytes vary in a large dimension range, with respect to the detailed structural organization, and such mixtures have many applications, for examples in cosmetics, paints, detergency, and drug delivery (Hoffmann et al., 2011; Wang & Roman, 2011a; Wang & Roman, 2011b; Sivakumar et al., 2009; Yap, Quinn, Ng, Cho, & Caruso, 2005; Ye, Tong, & Fetters, 1997). Therefore, they have attracted quite some interest in the past decades (Lam & Walker, 2010; Bain et al., 2010; Mezei & Meszaros, 2008). Over a finite range of polyelectrolyte and colloid concentrations, polymer-induced bridging may result in a rheological sol–gel transition (Otsubo, 1990; Larson, 1999). Colloidal

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gels formed in this way are frequently used as precursor inks for direct-write assembly of complex 3 dimensional structures with applications in advanced ceramics, sensors, and composites (Smay, Gratson, & Shepherd, 2002a; Smay, Cesarano, & Lewis, 2002b; Li & Lewis, 2003). Moreover, a remarkable attribute of the gels that make them excellent candidates for the applications is the ability to tune their rheological properties such as the zero-shear storage modulus, yield stress, and steady shear viscosity, over a relatively wide range. Therefore, a thorough understanding of the relationship between rheological transitions and microstructural changes will further advance our ability to engineer particulate materials with prescribed properties and can impact technologies ranging from food processing (Dickinson, 1992) to microfluidic separations (George et al., 2009), direct-write assembly (Smay et al., 2002a), and microextrusion (Wang, Shaw, & Cameron, 2006).

In the present paper, we investigate the gelation behavior in a mixture system composed of oppositely charged nanocrystalline cellulose (NCC) colloid suspension and polyelectrolyte (quaternized hydroxyethylcellulose ethoxylate, QHEC) aqueous solution, which was induced by the electrostatic attraction, as well as the rheological properties and scaling law application. Moreover, the microstructure and dynamics at the gel point have been as demonstrated. We hope to provide useful fundamental information on the interactions between oppositely charged colloids and polyelectrolyte, as well as the sol–gel transition behaviors, to promote the development of colloids/polymer composite materials.

## 2. Experimental section

### 2.1. Materials

Cationic polyelectrolyte quaternized hydroxyethylcellulose ethoxylate (QHEC) was purchased from Sigma–Aldrich (St. Louis, MO, USA) (Sameer Dalvi & Rajesh Dave., 2009). Lyophilized nanocrystalline cellulose (NCC) particles were supplied by Alberta Innovates Technology Futures (Edmonton, Alberta, Canada). The fabrication procedure was as follows: NCC particle sample was prepared by acid hydrolysis of commercial dissolved softwood pulp. Pulp was hydrolyzed with 64% sulfuric acid at 50 °C for 40 min, and then diluted with de-ionized water to stop the reaction. The suspension was then centrifuged, neutralized with Na<sub>2</sub>CO<sub>3</sub> and dialyzed to remove the salts. Finally, the suspension was further dispersed in an ultrasonic bath to achieve 1–2% concentration stable colloidal suspension. NCC particles were obtained in powder form by lyophilizing the suspensions. Detailed preparation method was discussed elsewhere (Bondeson, Mathew, & Oksman, 2006; Boluk, Zhao, & Incani, 2012). NCC particles in aqueous solutions carried negative electrical charges due to the sulfate surface groups. All materials were used without further purification.

### 2.2. Samples preparation

QHEC/NCC mixture samples were prepared by mixing appropriate quantities of aqueous stock solutions of QHEC and NCC with distilled-deionized water. Water was purified by the Millipore Milli-Q system. The samples were stirred and left for equilibration at room temperature for 3 days. Four QHEC concentrations were used here: 1.0, 1.5, 2.0 and 3.0 wt%. At each QHEC concentration, NCC was added in the concentration range from 0 to 0.4 wt% to induce a sol–gel transition. And hereafter the sample composition was represented in the following way:  $c_{\text{QHEC}}/c_{\text{NCC}}$  (QHEC concentration/NCC concentration).

The phase behavior was determined by visual inspection. All the tested samples displayed one homogeneous phase.

### 2.3. Characterization

The dynamic rheological measurement of the QHEC/NCC aqueous solution was carried out on an AR-G2 rheometer (TA Instruments, USA). Cone and plate (2° nominal angle) geometry was used to measure the dynamic oscillatory parameters. The strain used for the linear viscoelastic region was determined by performing amplitude sweep experiments at a frequency of 1 rad·s<sup>-1</sup>. Temperature control was established with a ThermoCube 200/300/400 (Solid State Cooling Systems Co., USA) kept within ±0.05 °C of the desired temperature. All samples were allowed to relax for 0.5 h after the loading process, to eliminate the loading affections. In order to reduce the testing experimental error, all experiments were repeated twice.

The morphology of the NCC particles was investigated by scanning electron microscope (SEM) using a Hitachi model S-4800 apparatus (Hitachi Tokyo, Japan) equipped with a field emission source and operating at accelerating voltages of 5 kV or 30 kV (30 kV in STEM mode). For transmission electron microscope (TEM) analysis, a drop of the NCC aqueous suspension was deposited on a carbon-coated copper TEM grid for 3 min and the excess of suspension was wicked off using filter paper. The TEM grid was allowed to dry at room temperature for 3 min. The sample was then stained by depositing a drop of uranyl acetate solution (2 wt% in water) on the grid for 5 min. The excess solution was wicked off using filter paper and the grid was dried at room temperature prior to imaging.

The effective particle size of NCC particles based on translational diffusion constant was determined by dynamic light scattering (DLS). The instrument was a Zetasizer model Nano ZS from Malvern (Worcestershire, United Kingdom). The wavelength of the 4 mW He–Ne laser source was 633 nm. The particle size was measured at room temperature, and the NCC concentration was 0.1 wt%.

The zeta potential of QHEC/NCC solution was determined by Zetasizer model Nano ZS from Malvern (Worcestershire, United Kingdom). Zetasizer model Nano ZS was also a zeta potential analyzer based on electrophoretic light scattering. A 4 mW He–Ne laser source with 633 nm wavelength was used as light source. All measurements were performed at 20 °C.

## 3. Results and discussion

### 3.1. Rheological behaviors of QHEC/NCC solution

Polymeric gel is a three-dimensional network, formed from flexible chains through either chemical cross-linking or physical phase transformation. The gelation is a phenomenon in which a polymeric liquid dramatically becomes solid-like at a critical point in polymer concentration, temperature, storage time, and so forth (Lue & Zhang, 2008). Traditionally, the crossover of the storage modulus  $G'(\omega)$  and loss modulus  $G''(\omega)$  curves has been used as an indicator of the gel point (Tung & Dynes, 1982). This method is simple, however, frequency dependent. Valuable contributions to this area were made by the studies of chemical and physical gelations in Winter's laboratory (Chambon & Winter, 1985; Winter & Chambon, 1986; Chambon & Winter, 1987), and they generalized that

$$G'(\omega) = G''(\omega) \sim \omega^n \quad 0 < n < 1 \quad (1)$$

and

$$\frac{G'(\omega)}{G''(\omega)} = \tan \delta = \tan\left(\frac{n\pi}{2}\right) \quad (2)$$

for the gelling system, where  $\omega$  is the frequency,  $G'(\omega)$  is the storage modulus,  $G''(\omega)$  is the loss modulus,  $\tan \delta$  is the loss tangent, and  $n$  is the relaxation exponent at the gel point. The frequency independence of the  $\tan \delta$  in the vicinity of the gel point has been widely examined for gels and has also been employed to determine the gel

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