



Electrolyte effect on gelation behavior of oppositely charged nanocrystalline cellulose and polyelectrolyte



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ABSTRACT

The electrolyte (NaCl) influences on the sol–gel transition of the complex solution composed of oppositely charged nanocrystalline cellulose (NCC) and polyelectrolyte (quaternized hydroxyethylcellulose ethoxylate, QHEC) were investigated by the rheological means in the present paper. Winter and Chambon theory was applicable to describe the sol–gel transition, and the critical gel points have been successfully determined. When increasing the NaCl concentration, more NCC were needed to form a critical gel due to the screening of the electrostatic interaction, and the larger loss tangent and relaxation exponent (n) values at the gel point demonstrated a less elastic nature of the complex solution with more NaCl. The results indicated the gel network was composed of entanglements and association of QHEC (as polymer network), as well as the electrostatic adsorption interaction between QHEC chains and NCC rods (as cross-linking). With the addition of NaCl, the screening effect led to the enhancement of the entanglements and weakening of the electrostatic adsorption, however, the gel strength decreased with increasing the NaCl amount, suggesting the electrostatic adsorption interaction played a more dominant role than the entanglements when the gel was formed. Moreover, the exponents of the scaling law $\eta_0 \propto \varepsilon^{-\gamma}$ and $G_e \propto \varepsilon^z$ of the QHEC/NCC/NaCl solution revealed that the scaling law $n = z/(z + \gamma)$ between n , γ , and z was only feasible at the highest NaCl concentration, as a result of that the intermolecular electrostatic interaction was completely screened, indicating the scaling law was only feasible when intermolecular interaction was small enough to be neglected.

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1. Introduction

Colloidal suspensions has been extensively recruited in a wide range of applications, such as paints (Farrokhpay, 2009; McGrath, Bock, Cathcart, & Lyon, 2007), coatings (Kleinert, Kim, & Velev, 2010), pharmaceutical formulations (Qi et al., 2011; Zuzzi, Cametti, Onori, Sennato, & Tacchi, 2009), food (Canales, Hidalgo, Risso, & Alvarez, 2010) and so forth (Leunissen et al., 2005; Lee, Gradon, Janeczko, Iskandar, & Okuyama, 2010; Sabourin, Dabbs, Yetter, Dryer, & Aksay, 2009; Huang et al., 2012; Chen et al., 2011; Liu, Zhong, Chang, Li, & Wu, 2010; Liu et al., 2014). The gelation phenomenon in colloidal suspensions can be described as the aggregation of attractive particles into a network structure with mechanical stability (Whitmer & Luijten, 2011), which is relevant

in a broad range of settings, including biological systems and industrial applications (Lee, Chan, Bevan, Lewis, & Braun, 2004; Martinez et al., 2005), such as food products (Allen, Murray, & Dickinson, 2008), cosmetics (Gallegos & Franco, 1999), high-performance coatings and so forth (Larson, 1999; Russel, Saville, & Schowalter, 1989). The rheological properties of colloidal gels attribute to the micromechanical properties of the gel backbone, dominated by nano-scale particle interactions (Pantina & Furst, 2004; Liu, Chen, Yue, Chen, & Wu, 2011).

Polyelectrolyte plays an important role in diverse fields ranging from materials science and colloids to biophysics (Carrillo & Dobrynin, 2011), and complex systems composed of oppositely charged colloids and polyelectrolytes exhibit complicated self-aggregation behaviors, because of the electrostatic interactions (Pickrahn, Rajaram, & Mohraz, 2010; Hoffmann et al., 2011; Kumar, Dubin, Herson, 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 great potentials (Wang & Roman,

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2011a,b; Sivakumar et al., 2009; Yap, Quinn, Ng, Cho, & Caruso, 2005; Ye, Tong, & Fetters, 1997). Important aspects pertaining to the nature of the electrostatic interaction and its relations to phase behavior and phase structure in these systems are beginning to be understood (Hansson, 2006), and an important undertaking in this area should be to quantify the role of electrostatic interactions in complex formation between oppositely charged colloids and polyelectrolyte. More generally, the role of electrostatic interactions in the self-assembly or self-organization in charged macromolecular systems is still lacking of detailed investigation.

Addition of electrolyte to an oppositely charged colloids/polyelectrolyte complex system leads to screening of the electrostatic interactions between ionized groups, reducing the polyelectrolyte effect and affecting the conformation of polymers (Dobrynin & Rubinstein, 2005; Colby, 2010), resulting in a huge variance to the charged colloid/polyelectrolyte system and tunable rheological behavior of the complex system (Brotherson, Bottomley, Ludovice, & Deng, 2008), which is important and can be very useful in material science and technology. In the present paper, the effect of a monovalent electrolyte (NaCl) on the gelation behavior as well as the rheological properties and scaling law application of a mixture, composed of oppositely charged nanocrystalline cellulose (NCC) colloid suspension and polyelectrolyte (quaternized hydroxyethylcellulose ethoxylate, QHEC) aqueous solution, was detailed investigated. The microstructure and dynamics at the gel point have also been revealed. We hope to provide useful fundamental information about the electrolyte influences on the interactions between oppositely charged colloids and polyelectrolyte, as well as the sol–gel transition behaviors, to promote the advance and development of colloids/polymer composite materials.

2. Experimental

2.1. Materials

Lyophilized nanocrystalline cellulose (NCC) particles were supplied by Alberta Innovates Technology Futures (Edmonton, Alberta, Canada). Specifically, NCC particle sample was prepared by acid hydrolysis of commercial dissolved kraft softwood pulp. Pulp was hydrolyzed with 64% sulfuric acid using a 1:8 weight ratio at 50 °C for 40 min and then diluted with de-ionized water to quench the reaction. The suspension was then centrifuged at 6000 rpm for 10 min, neutralized with Na₂CO₃ 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), and NCC particles used in the present paper exhibited average length of 87 nm, average diameter of 16 nm, average aspect ratio of ~5.4 and ζ -potential of –58.2 mV (Lu, Hemraz, Khalili, & Boluk, 2014a). NaCl was purchased from Fisher Scientific (Fair Lawn, NJ). Cationic polyelectrolyte quaternized hydroxyethylcellulose ethoxylate (QHEC) was purchased from Sigma-Aldrich (St. Louis, MO, USA), with a molecular weight between 400,000 and 500,000, cationic substitution of about 5 wt% and charge density of 1.2 mEq g⁻¹ (Dalvi & Dave, 2009; Junka, Sundman, Salmi, Österberg, & Laine, 2014; Frenzel, Swaboda, Petzold, Emmler, & Simon, 2011; Regismund, Heng, Goddard, & Winnik, 1999). All materials were used without further purification.

2.2. Samples preparation

Water was purified by the Millipore Milli-Q system. QHEC was dissolved in NaCl aqueous solution to form QHEC/NaCl aqueous

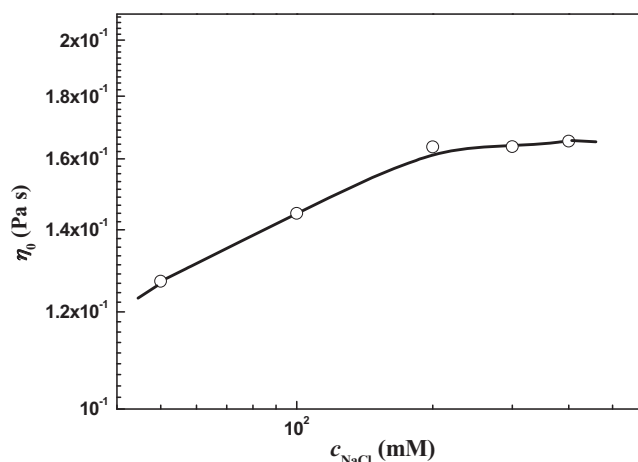


Fig. 1. Zero-shear viscosity (η_0) of 1.5 wt% QHEC in NaCl solution as a function of NaCl concentration (c_{NaCl}).

solutions, and NCC was dispersed in water to form NCC aqueous suspensions. QHEC/NCC/NaCl mixture samples were prepared by mixing appropriate quantities of aqueous stock solutions of QHEC/NaCl solutions and NCC suspensions. The samples were stirred and left for equilibration at room temperature for 3 day. In the QHEC/NCC/NaCl complex solution, QHEC concentrations (c_{QHEC}) were constant to be 1.5 wt%, due to a proper viscosity and sensitive response to the introduction of NaCl (which will be demonstrated later), while the NaCl concentration (c_{NaCl}) was various, and at each NaCl concentration, NCC concentration (c_{NCC}) was changed in the range from 0 to 0.39 wt% (during c_{NCC} range, the QHEC/NCC solution undergoes phase transition from liquid to gel, which was ready for investigation), which was influenced by the different amount of NaCl.

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/NaCl complex 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⁻¹. 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. In order to reduce the testing experimental error, all experiments were repeated twice.

3. Results and discussion

Fig. 1 shows the zero-shear viscosity (η_0) of 1.5 wt% QHEC in NaCl aqueous solution as a function of NaCl concentration (c_{NaCl}). The η_0 values increased in the beginning, followed by a plateau when c_{NaCl} was higher than 200 mM. QHEC molecular chain was electrostatically repulsed by each other in the aqueous solution as a result of the positive charge along the chains. When salt added, the electrostatic interaction between QHEC chains was partially screened, and stronger entanglement and association of the chains occurred, leading to a denser network. And the increasing viscosity was due to the denser 3-D network. When c_{NaCl} was higher than 200 mM, the electrostatic interaction was completely screened by NaCl stoichiometrically and QHEC behaved as uncharged macromolecules in the solution, therefore, further increasing c_{NaCl} made

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