



## Colloidal behavior of aqueous cellulose nanocrystal suspensions



Hale Oguzlu<sup>a,b</sup>, Christophe Danumah<sup>b,1</sup>, Yaman Boluk<sup>a,b,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, T6G 2W2, Canada

<sup>b</sup> National Institute for Nanotechnology, Edmonton, Alberta T6G 2M9, Canada

### ARTICLE INFO

#### Article history:

Received 27 October 2016

Received in revised form 31 January 2017

Accepted 2 February 2017

Available online 12 February 2017

#### Keywords:

Sulfonated

Cellulose nanocrystals

Microstructure

Rheology

Gels

Electrolyte

Polymer

Depletion

### ABSTRACT

In this short review, we discuss the colloidal microstructure of sulfonated cellulose nanocrystal (CNC) suspensions and connect to their rheological behavior in the presence of electrolyte, by changing its surface chemistry and also in dilute water soluble polymer solutions. Presence of electrolyte has a significant effect depending both on the concentrations of CNC and electrolyte. The salt presence on the microstructure of CNC suspensions were successfully explained by DLVO theory. Even within the dilute concentration regime (<0.5 vol%), CNC particles can form gels either by adding high concentration of electrolyte or low concentration (around overlapping concentration) of non-adsorbing polymer. Addition of water soluble polymers may cause depletion of CNC if the polymer is not adsorbing. It is believed that the depletion flocculation is the case for the effects of carboxymethyl cellulose (CMC) polymer chains in CNC suspensions and cause significant gelling.

© 2017 Elsevier Ltd. All rights reserved.

### 1. Introduction

Cellulose is a 1,4- $\beta$ -glucan, a linear polysaccharide of D-glucose monomers which are linked by glycosidic bonds and forms crystalline microfibrils and fibers with strong intermolecular hydrogen bonds. Conventionally cellulose is used as a raw material in two forms: 1) in its native form; 2) derivatized versions. Native fibrous structure of cellulose is preferred for the production of construction, paper and board materials. Since unique structure makes cellulose infusible at high temperatures and insoluble in conventional organic solvents, cellulose can be used for the production of polymers only after conversion to cellulose derivatives such as cellulose ethers and esters or by regeneration [1]. Later advancement of synthetic polymers from petrochemicals eclipsed the utilization of cellulosic polymers and plastics. Nevertheless, cellulose becomes an attractive material recently again for several reasons. First of all, it is renewable, and also available from abundant wood and other plant fibers supplies. Secondly it is a non-toxic and biocompatible material for the human body and biodegradable. Lastly, but most importantly, cellulose can be converted to cellulose nanocrystals (sulfonated CNC) and cellulose nanofibers

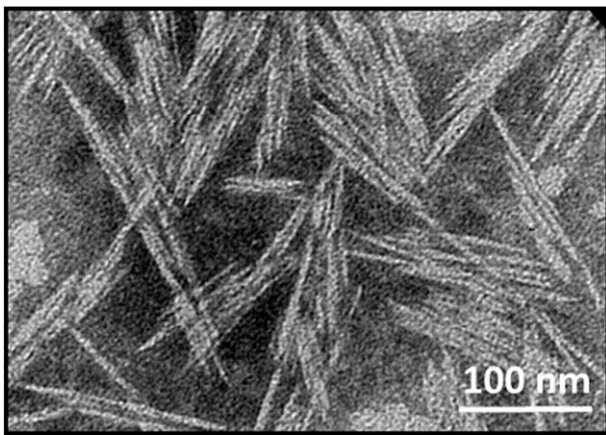
(CNF) by top down procedures very unique to its own structure [2,3,4,5]. Hence, various forms of nanocellulose such as sulfonated CNC, CNF and other versions are expected to bring new life into cellulose next to conventional utilization of cellulose in the form of macroscopic fibers and derivatized and regenerated polymers.

Rod-like sulfonated CNC particles are typically prepared by employing concentrated (~64%) sulfuric acid [6,7]. The hydrolysis process removes the amorphous segments of cellulose fibrils and releases homogenous and defect free crystallites. In addition, sulfuric acid also creates negatively charged sulfate ester groups on crystallite surfaces. Sulfonated CNCs are typically 6–10 nm in width and 100–200 nm in length (Fig. 1). Although, there are many excellent studies on sulfonated CNC, which were reviewed by Habibi et al., the most of the studies on high volume applications are on organic polymer based nanocomposites, films and coatings with desired mechanical, optical and barrier properties [3]. Yet, the aggregate free dispersion of hydrophilic sulfonated CNCs in hydrophobic organic materials is the problem for those sulfonated CNCs applications hence requires additional surface modification and grafting. However, sulfonated CNC and highly negatively charged spindle shaped sulfonated CNC particles in aqueous solutions reveal unique colloidal properties [8–12]. Development of novel water based paints, coatings, pharmaceutical and personal care products, foodstuffs, drilling and fracturing fluids, concrete admixtures are new frontiers for the application of sulfonated CNC in aqueous systems. Hence, colloidal interactions of sulfonated CNC in the presence of electrolytes, polymers, surfactants, emulsions and other colloidal particles are subject to the research.

\* Corresponding author at: Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 2W2, Canada.

E-mail address: [yaman.boluk@ualberta.ca](mailto:yaman.boluk@ualberta.ca) (Y. Boluk).

<sup>1</sup> Current address: Alberta Innovates – Technology Futures, Edmonton, Alberta T6N 1E4, Canada.



**Fig. 1.** Transmission electron micrograph of sulfonated CNC produced from softwood kraft pulp.

Sulfonated rod-like sulfonated CNCs with negative surface charges result in stable suspensions in water at low ionic strengths. Sulfonated CNC suspensions generate birefringent and ordered liquid phase and separation at sufficiently high concentrations. In general, classical DLVO theory explains the stability of the dispersion of charged colloidal particles as the summation of repulsive interparticle forces, determined by the double layer interactions and attractive dispersion van der Waals forces. Colloidal stability of sulfonated CNC rods, like other rod-like colloidal particles such as tobacco mosaic virus and boehmite depends on the orientation of particles [13\*,14\*]. Thus, stability can be analyzed in low ionic strength regime, where repulsion dominates and high ionic strength regime where attraction dominates. At low ionic strength regime, rod like sulfonated CNC particles are expected to form stable dispersions within isotropic concentration, but they show phase separation into birefringent and anisotropic lower phase and isotropic upper phase at higher concentrations. In the case of high ionic strength, the double layer around particles is compressed leading to effective attractive van der Waals forces. Therefore, the rod-like colloidal particles have the affinity to form space filling isotropic gels. In addition to electrolytes, nonadsorbing macromolecules and polyelectrolytes also control attractive interactions among particles.

Rheological properties of aqueous suspensions of cellulose nanocrystals are investigated in the literature along with structural changes and phase transitions as a function of sulfonated CNC concentration under different conditions [12\*,15\*,16\*,17\*,18]. Biphasic concentrations showed three viscosity vs. shear rate regions, which are typical behavior of liquid crystals. Nevertheless, according to those studies, typical cellulose nanocrystals do not show any meaningful non-Newtonian thickening behavior, which cannot be used for practical applications in aqueous solutions below approximately 7 vol% (depending on aspect ratio) concentration. Besides, thickening behavior at high concentrations is not sufficiently shear thinning (pseudoplastic), which is always a desired to be controlled rheological property in paints, coatings, drilling fluids and other functional fluid formulations. Therefore, cellulose nanocrystals as opposed to cellulose nanofibrils have never been considered as thickeners. In our laboratories, the synergistic thickening of cellulose nanocrystals in certain water soluble polymers were discovered [19\*,20]. In our latest publications, the thickening mechanism of cellulose nanocrystals in certain cellulose ethers have been discussed [21,22\*]. Other published work focused on the thickening behavior of cationically surface functionalized sulfonated CNC, polymer grafted sulfonated CNC [23].

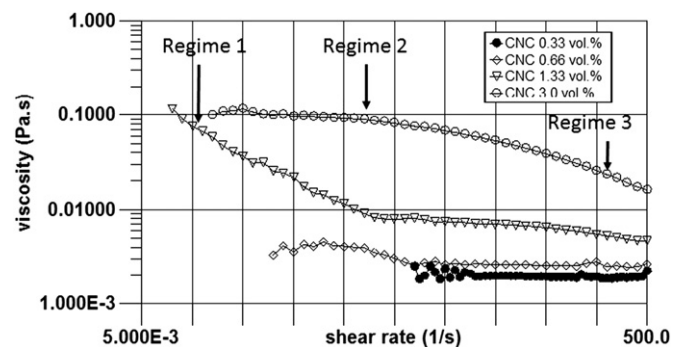
In this short review, we discuss colloidal microstructure of sulfonated CNC suspensions and connect to their rheological behavior in the presence of salt, water soluble polymers, and by changing its surface chemistry. Furthermore, we identify the possibilities for further product applications with sulfonated CNC in aqueous suspensions.

## 2. Particle concentration

The average length of sulfonated CNC particles ( $L$ ) was reported between 90 and 200 nm, which depends on the source of cellulose, acid hydrolysis conditions and measurement methods [6\*]. The transitions from dilute to semi dilute and from semi dilute to concentrated regimes occur at volume fractions of  $\phi^* \approx (d/L)^2$  and  $\phi^{**} \approx d/L$  based on rigid rod approximation, respectively [24]. Those equations suggest that the transitions from dilute to semi-dilute and from semi-dilute to concentrated regions occur at 0.44 vol% (0.66 wt%) and 6.66 vol% (10 wt%) respectively. Hence, rheological properties of aqueous sulfonated CNC suspensions reported in the literature can be summarized in dilute, semi-dilute and concentrated forms.

Boluk et al. reported Newtonian viscosities of isotropic kraft softwood sulfonated CNC suspensions ( $L/d \sim 12$ ) below 0.4 vol% concentration. Orts et al. [25\*], by using SANS experiments and Lima and Borsali [26\*], by studying steady state viscosities, show that viscosity vs. shear rate data exhibits three regimes above the semi-dilute concentration. According to their observations, at very low shear rates, the steady state flow is highly shear thinning and non-isotropic domains start to flow (Regime 1). As a further increase of shear rate, liquid crystal domains are broken up and results in a Newtonian plateau (Regime 2). At higher shear rates, the alignment of sulfonated CNC rods results in a second shear thinning region (Regime 3). According to SANS data, the most rapid ordering behavior of the sulfonated CNC whiskers occurred during the Regime 2, which suggests that the order reaches a plateau in the shear-thinning regime [25\*]. In our laboratories, we have obtained similar results which are summarized in Fig. 2. While 0.33 vol% suspension is isotropic and Newtonian, suspensions at 0.66, 1.33, and 2.0 vol% contained liquid crystals and three shear rate regimes are observable.

Urena-Benavides et al. investigated microstructure and rheological behavior of sulfonated CNC between 3.07 and 12.1 vol% concentrations [27\*]. CNCs are reported as rectangular prisms and dimensions were measured as: length =  $107 \pm 55$  nm; width =  $20 \pm 6$  nm; and height =  $8.0 \pm 2.8$  nm. As expected from the dimensional analysis of particles, suspensions between 3.07 and 10.7 vol% are above the semi-dilute transition point and phase separated into anisotropic and isotropic phases (Fig. 3). In the same study, the isotropic to biphasic region is measured by extrapolation of anisotropic volume fractions vs. CNC concentration. The transition concentration is 2.7 vol% at 20 °C and it is in good agreement with Dong and Gray's measurement of  $5.14 \times 10^{-6} \text{ nm}^{-3}$  (corresponds to 2.9 vol% for the CNC dimensions carried out) [28]. Shafie-Sabet et al. reported the limit of isotropic phase stability as 3 wt% (2 vol%) for sulfonated CNCs with dimensions of 100 nm in length and 7 nm in width [12\*]. Hard-core interactions alone are sufficient to induce an entropy-driven phase transition for rigid rod suspensions, from an isotropic phase to a liquid crystalline phase, where particles are oriented [29\*\*]. Hence, for rigid rods, the onset of liquid crystals formation concentration is predicted to be  $c_i = 4d/L$ . Bare rod diameter



**Fig. 2.** Steady state shear viscosities of softwood kraft sulfonated CNC with  $L/D = 12$  at 0.33, 0.66, 1.33 and 2.0 vol% concentrations.

Download English Version:

<https://daneshyari.com/en/article/4983611>

Download Persian Version:

<https://daneshyari.com/article/4983611>

[Daneshyari.com](https://daneshyari.com)