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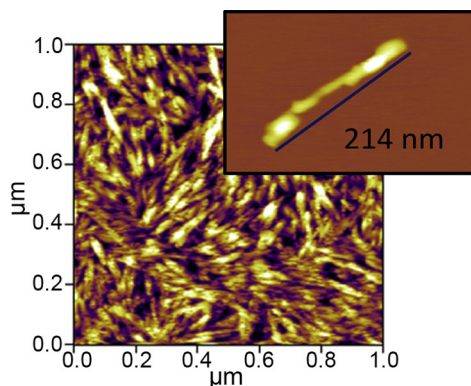
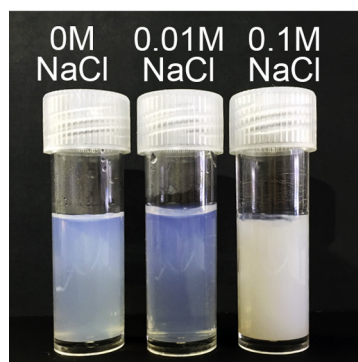
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Regular Article

Rheology and microstructure of aqueous suspensions of nanocrystalline cellulose rods

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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Nanocrystalline cellulose (NCC) is a negatively charged rod-like colloid obtained from the hydrolysis of plant material. It is thus expected that NCC suspensions display a rich set of phase behaviour with salt and pH because of its anisotropic shape and electrical double layer that gives rise to liquid crystallinity and self-assembly respectively. It should thus be possible to tune the rheological properties of NCC suspensions for a wide variety of end-use applications.

Experiments: Rheology and structural analysis techniques are used to characterise surface-sulphated NCC suspensions as a function of pH, salinity (NaCl) and NCC concentration. Structural techniques include atomic force microscopy, Zeta potential, dynamic light scattering, and scanning electron microscopy.

Findings: A phase diagram is developed based on the structure-rheology measurements showing various states of NCC that form as a function of salt and NCC concentration, which go well beyond those previously reported. This extended range of conditions reveals regions where the suspension is a viscous fluid and viscoelastic soft solid, as well as regions of instability that is suggested to arise when there is sufficient salt to reduce the electrical double layer (as explained qualitatively using DLVO theory) but insufficient NCC to form a load bearing network.

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1. Introduction

Nanocrystalline cellulose (NCC) are nano-scaled (colloidal) rod-like particles of cellulose obtained from hydrolysis of plant mass. They are attracting increasing scientific and engineering attention since the influential works of Revol et al. [1] on nematic self-ordering of NCC in aqueous suspension and Favier et al. [2] on NCC's significant reinforcement of polymer composites. The advantages of NCC as an advanced material are their high strength, abundance, biodegradability, non-toxicity, good thermal stability and relatively low cost [3,4]. Its large aspect ratio and the high density of surface hydroxyl groups enable NCC suspensions to have unique rheological properties, whereby isotropic rod-like particle suspension behaviour occurs at low concentrations, and a chiral nematic liquid crystalline structure is observed over a certain concentration range that is followed by gelation at higher concentrations. In addition, colloids rods are more efficient at building low-shear viscosity, yield stress and gel strength in suspension than spherical particles [5]. Thus NCC has potential to be used in many application fields for rheological control, including within consumer products, drilling fluids [6], drug delivery [7], and in artificial tissue formation [8]. In order to tune their ability to control the rheology in a wide variety of applications, it is necessary to understand its relationship to the underlying microstructure and how this is influenced by inter-particle forces between the colloidal rods. The specific objective of this study is to map the structure and rheology of NCC suspensions in aqueous media as a function of pH, salt, and NCC concentration.

Recent research on the rheology of NCC suspensions has focused on its liquid crystalline or self-ordering behaviour and its gelation properties [9,10]. Their large aspect ratio and the presence of surface hydroxyl groups play an important role on the interactive forces between NCC particles and thus suspension rheology [11]. Surface hydroxyl groups render NCC colloidal rods to be negatively charged, which electrostatically stabilises the suspension in aqueous media. They assemble into a gel structure provided there is a sufficient salt concentration to screen surface charges so as to promote adhesive interactions to occur [12].

The rheology of NCC suspensions in aqueous media and their gelation behaviour is of interest in this study. NCC suspensions are considered to form liquid crystalline gels at a critical NCC concentration and a randomly entangled gel at even higher concentration [13]. The critical concentration is affected by size, aspect ratio and surface modifications of NCC as well as the ionic strength of the solution [14,15]. However, the mechanism about how, and to what extent, particle interactions affect the rheological and gelation behaviour of suspensions of NCC particles is yet to be comprehensively studied as well as the change in linear viscoelasticity of the suspension as a function of phase behaviour in terms of its colloidal stability and microstructure. In this work, we reveal structure–property relationships for NCC suspensions by investigating their rheology as a function of ionic strength, and consider the corresponding effect of NCC surface properties on the structure and morphology of NCC network via Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), scanning electron microscopy (SEM), and Zeta potential measurement. Monovalent sodium salt has been used to alter ionic strength of solution without causing ion mediated cross-links between the NCC particles.

2. Materials and methods

2.1. Materials

NCC are obtained from the primary cell wall of plants, which is made up of semicrystalline cellulose with randomly oriented

amorphous regions; these regions have a low density and are highly accessible to ionic species during acid hydrolysis [16,17]. The amorphous regions of the cellulose readily decompose under controlled temperature and concentration of inorganic acid, while the crystalline regions are left intact. The crystalline components, which are only a few nanometres in size, grow after being released from the cell wall during hydrolytic treatment. The literature NCC colloidal rods to have a diameter of 4–30 nm and length of 50–500 nm [9,18]; their size and aspect ratio are dependent on the source of primary cellulose material and the hydrolysis conditions [19,20].

The nanocrystalline cellulose used in this study was sourced from Maine University Process Development Centre (Orono, ME) as 11.9 wt% NCC aqueous suspension with 0.9 wt% sulphur on dry NCC sodium form which is equivalent to 4.62 SO₃⁻ per 100 anhydroglucose units [12]. The NCC suspension was made by re-dispersing freeze-dried powder from hydrolysis of cellulose by applying ultrasonic treatment. Sodium chloride from Merck KGaA (Darmstadt Germany) is used to investigate the effect of salt. Hydrochloric acid and sodium hydroxide (from Ajax Finechem, NSW Australia) were used to adjust pH values of suspensions. Diluted samples were produced using deionized water produced by reverse osmosis water system, which has a resistivity of 18.2 MΩ cm (Sartorius Stedim).

2.2. Preparation of NCC suspensions

The 11.9 wt% NCC suspension was diluted to 0.1, 1, 2, 3, 4, 5, 7, and 9 wt% by addition of deionized water. No ultrasonic treatment was further applied to sample i.e. particle size and aggregation pattern was unchanged during sample preparation. The resultant suspensions were at pH of 6. For studies on NCC suspension at different pH, incremental addition of 10 μL of 1 M NaOH or HCl solution were used to achieve required pH values. The volume change due to the addition of acid or base is less than 0.17 vol%, which was considered negligible. For studies on the influence of ionic strength, solid NaCl was added to NCC suspensions to levels required. For samples at very dilute NaCl (<0.01 M), salinity was adjusted by pipetting pre-prepared 0.1 M NaCl solution into corresponding NCC suspensions.

2.3. Rheological measurement

An AR1500 rheometer (TA Instrument Inc., New Castle, DE) equipped with concentric cylinder geometry was used to measure samples at room temperature. The inner and outer radii for the concentric cylinder were 14 and 15 mm respectively. For fluid-like systems in this geometry, we checked whether measurements were affected by the potential for 'slip' at smooth surfaces by comparing measurements between smooth and rough surfaces; negligible differences are observed with a result included in [Supplementary Information](#). In contrast, a vane geometry was used for thick and gel-like samples to avoid the effects of slip and structure modification during sample loading [21] in the concentric cylinder; this geometry provides an accurate means in which to determine the apparent yield stress and low-shear viscosity [21,22]. The inner (R_v) and outer R_c radii of the vane tool was 11 and 22.5 mm respectively, and height (H) is 25 mm. Since the radius-ratio between cup and vane is about 2 (R_c/R_v), the equations for Couette flow do not necessarily apply. The shear stress (σ) and apparent shear rate (γ̇) is obtained from torque (M) and vane rotation rate in s⁻¹ (Ω) using the following equations [21,22]:

$$\sigma = \frac{M}{2\pi R_v^3} \left(\frac{H}{R_v} + \frac{2}{3} \right)^{-1} \quad (1)$$

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