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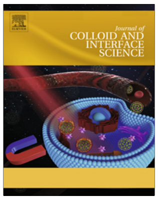

Regular Article

Gelation mechanism of cellulose nanofibre gels: A colloids and interfacial perspective

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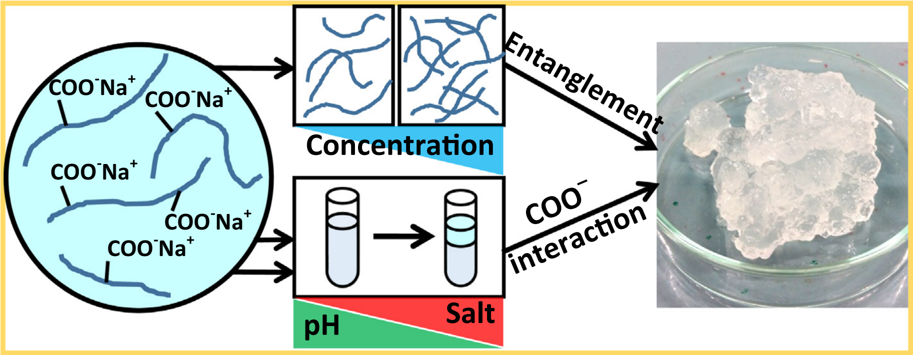
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Nanocellulose gels form a new category of sustainable soft materials of industrial interest for a wide range of applications. There is a need to map the rheological properties and understand the mechanism which provides the colloidal stability and gelation of these nanofibre suspensions.
Experiments: TEMPO (2,2,6,6,-tetramethylpiperidine-1-oxyl)-oxidised cellulose nanofibre gels were investigated at different fibre concentrations, pH and ionic strength. Dynamic and cyclic rheological studies was performed to quantify gel behaviour and properties. Gels were produced at different pH and salt contents to map and understand colloidal stability of the nanocellulose gel.
Findings: Rheology indicates gelation as a transitionary state starting at a fibre concentration of 0.1 wt.%. The colloidal stability of the nanocellulose gel network is controlled by pH and salt, whereas fibre concentration mainly dictates the dynamic rheological properties. Decreasing pH and adding salt destabilises the gel network by eluting bound water which is correlated with the decrease in electrostatic repulsion between fibres. The gelation and colloidal stability of these nanocellulose gels is driven by electrostatic forces and the entanglement ability of the fibrous system to overlap.

1. Introduction

Cellulose fibrils of nano-scale width – referred to as nanocellulose – can be extracted from plants and bacterial sources through a variety of mechanical and chemical methods [1,2]. Nanocellulose exhibits exceptional characteristics such as high tensile strength,

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ease of functionalisation, combined with its expected biological characteristics: renewability, biocompatibility, biodegradability and low toxicity [3–5]. Isogai et al. developed the TEMPO-mediated oxidation process which utilises a nitroxyl catalyst (TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl) to convert the primary alcohol groups of the cellulose D-glucose units into carboxylate groups. This provides the necessary electrostatic repulsion which allows the liberation of nanocellulose fibres [6–8]. TEMPO-oxidised cellulose nanofibres (TOCNFs) macroscopically appear as viscous and stable colloidal suspensions even at low solids content (1–2 wt.%) [9]. This surface modification produces nanofibres 3–4 nm in width and several microns in length [8,10] and is currently considered among the most effective methods for producing nanocellulose [11]. Recent TOCNF studies have focussed on biomedical applications such as drug delivery [12], wound dressing [13], tissue engineering substrate [14] and cell encapsulation [15,16], engineering reinforcement materials in plastics and paper [17–20], rheology modifier [21,22], and the development of novel materials such as aerogels [23]. Previous studies on the properties of TOCNFs investigated the structure at the individual fibril level [24], determining the fibre aspect ratio through rheological measurements [25,26] and modelling properties at the dilute and semi-dilute concentration regimes [26,27]. However, there is poor understanding on what drives the gelation and provides the colloidal stability in TOCNFs. Limited studies have analysed the properties of nanofiber cellulose gels from a colloidal and interfacial perspective.

Polysaccharides, owing to their high degrees of polymerisation and hydrogen bonding ability, can form hydrogels through physical interactions. κ-carrageenan undergoes a coil-to-helix structural transformation as a response to temperature changes and forms gels [28]. Thermo-responsive polysaccharides, which contain methyl or other short hydrophobic groups such as methylcellulose and carboxymethylcellulose, gel through the formation of specific hydrogen bonding combined with hydrophobic associations within the cellulose backbone [29–31]. Alginates, on the other hand, require coordinating cations (i.e. Ca^{2+}) to bridge consecutive alginate polymers which induces gelation [32]. However, none of these gelation mechanisms can describe the gelation of TOCNFs. This type of nanocellulose has been known to form stable gels without the aid of temperature nor cations [27,33]. Although it is recognized that modification of its rheological properties, resulting in stiff and self-standing gels, can be achieved by manipulating pH and the addition of cations [14,34,35].

The objective of this study is to characterise the gelation mechanism of TOCNFs. These fibres, possessing nano-scale diameter and micro-scale length and strong surface charges, can be viewed as flexible colloidal particles of high aspect ratio able to interact, deform and entangle. It is desired to quantify fibre-fibre interactions and determine the factors which affect the stability of the fibres by modifying surface charge and electrical double layer thickness. This is achieved by combining rheology, atomic force microscopy (AFM) and qualitative imaging. Rheology is a well-established method to quantify the viscoelastic characteristics of complex soft materials such as gels. It provides an insight to the state of the gel network by controlled macroscopic deformation [36]. Through rheology, we can monitor the gelation state and properties of TOCNFs as a function of different variables. AFM and light scattering allows the imaging of the cellulose nanofibres enabling us to resolve the fibre dimensions. The combination of these techniques allows us to explore the source of the exceptional colloidal stability and properties of these gels.

To understand the gelation of TOCNFs, we characterised the range of viscoelastic properties in the dilute to semi-dilute range. Their rheological behaviour provides insight into how the fibres organize into a network. The effect of pH and salt on the colloidal stability of the gels was determined and analysed in terms of colloids and interfacial chemistry. We aim at relating the mechanism of cellulose nanofibre gel properties to the well-established colloid and interface science to efficiently engineer applications in food, biomedical and as rheology modifier.

2. Materials and methods

2.1. Materials

Bleached Eucalyptus Kraft (BEK) pulp of approximately 10 wt.% solids was supplied by Australian Paper, Maryvale, Australia. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and sodium bromide (NaBr) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were diluted for solutions as required and were purchased from ACL Laboratories and Merck, respectively. 12 w/v% Sodium Hypochlorite (NaClO) was purchased from Thermo Fisher Scientific and used as received.

2.2. TEMPO-mediated oxidation

The TEMPO-mediated oxidation process employed is based on the method of Saito and Isogai [6]. 100 g BEK pulp was suspended in 2500 mL water containing 0.4 g TEMPO and 2.5 g NaBr. The 12 w/v% NaClO solution was initially adjusted to pH 10 via addition of 36% HCl. To initiate the oxidation process, 75 mL NaClO was added drop-wise to the suspension whilst stirred. The pH of the reaction was maintained at 10 through the addition of 0.5 M NaOH. The oxidation process was maintained for 2 h. The oxidised fibres were recovered through filtration and stored refrigerated (4 °C).

The oxidised pulp was then dispersed in deionised water to a desired concentration. Fibrillation was accomplished through a high-pressure homogeniser (GEA Niro Soavi Homogeniser Panda) at 1000 bar. Suspensions which contain less than 1 wt.% TEMPO-oxidised pulp was homogenised for two passes. More concentrated suspensions were homogenised with only one pass. TEMPO-oxidised cellulose nanofibres (TOCNFs) possess an average length of several microns and diameter of 3–4 nm [8,10].

2.3. Determining solids concentration

The solids concentration of all samples (i.e. gel or pulp) were determined through drying. The sample was weighed before (w_i) and after (w_d) drying. Sample moisture was evaporated by drying in an oven at 105° for at least 4 h. The solids content was calculated with:

$$solids\ content(\%) = \frac{w_d}{w_i} \times 100\% \tag{1}$$

2.4. Rheology

All rheological testing of the gels were performed with an Anton Paar MCR302 rheometer. A cone (0.997°) and plate (49.975 mm) geometry were selected. Testing was done at ambient temperature (25 °C). To ensure stable temperature during the testing, a solvent trap was used.

Viscosity was measured at shear rate ranging from 0.5 to 100 s^{-1}. Oscillatory strain sweep was performed from 0.01 to 100% at a constant 1 Hz frequency. Frequency sweep was measured from 0.1 to 100 rad/s and at 0.1% strain. All measurements were in triplicates. A thixotropic loop test was performed with a 1 wt.% gel by varying the shear stress between the LVR (0.1%, 1 Hz) and the yielded region (10%, 1 Hz) for 5 cycles.