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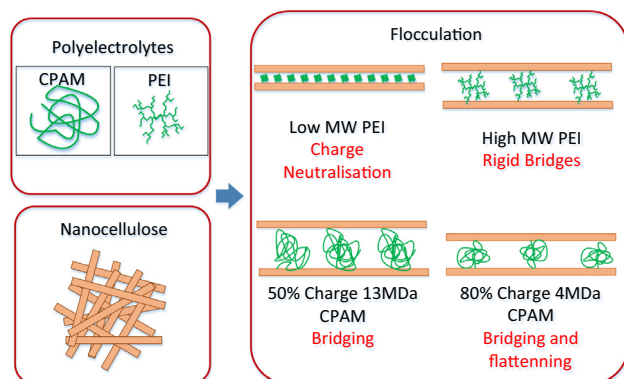
Effect of polyelectrolyte morphology and adsorption on the mechanism of nanocellulose flocculation



Praveena Raj, Warren Batchelor, Angeles Blanco, Elena de la Fuente, Carlos Negro, Gil Garnier*

BioResource Processing Research Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Clayton 3800, VIC, Australia
 Department of Chemical Engineering, Complutense University of Madrid, Madrid 28040, Spain

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of polyelectrolyte morphology, charge density, molecular weight and concentration on the adsorption and flocculation of Microfibrillated Cellulose (MFC) were investigated. Linear Cationic Polyacrylamide (CPAM) and Branched Polyethylenimine (PEI) of varying charge density and molecular weight were added at different dosages to MFC suspensions. The flocculation mechanisms were quantified by measuring gel point by sedimentation, and floc size, strength and reflocculation ability through Focussed Beam Reflectance Measurements. Polymer adsorption was quantified through zeta potential and adsorption measurements using polyelectrolyte titration. The flocculation mechanism of MFC is shown to be dependent on polyelectrolyte morphology. The high molecular weight branched polymer, HPEI formed rigid bridges between the MFC fibres. HPEI had low coverage and negative zeta potential at the optimum flocculation dosage, forming flocs of high strength. After breaking of flocs, total reflocculation was achieved because the high rigidity of polymer did not allow reformation or flattening of the polyelectrolyte adsorbed on MFC surface. The lower molecular weight branched polymer, LPEI (2 kDa) showed rapid total deflocculation, complete reflocculation and had maximum flocculation occurring at the point of zero charge. These characteristics correspond to a charge neutralisation mechanism. However, if the flocculation mechanism was purely charge neutralisation mechanism, the minimum gel point would be at the point of zero charge. Since this is not the case, this difference was attributed to the high polydispersity of the commercial LPEI used, allowing some bridges to be formed by the largest molecules, changing the minimum gel point. With the linear 80% charged 4 MDa CPAM, bridging mechanism dominates since maximum flocculation occurred at the minimum gel point, negative zeta potential and low coverage required for maximum flocculation. Reflocculation was not possible as the long linear

* Corresponding author.

E-mail addresses: ablanco@ucm.es (A. Blanco), gil.garnier@monash.edu (G. Garnier).

polymer reconformed on the MFC surface under a flat conformation. Flocculation with the linear 50% charged 13 MDa CPAM happened by bridging with the minimum gel point and maximum flocculation corresponding to roughly half polyelectrolyte surface coverage on cellulose.

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1. Introduction

Nanocellulose crystals (NCC), nanofibrillated cellulose (NFC) and microfibrillated cellulose (MFC) have emerged as a new family of high performance, renewable, biocompatible and biodegradable fibrous materials. The 3 hydroxyl groups of the anhydroglucose unit monomer enable domains of high crystallinity polymer by allowing close packing of cellulose chains [1]. This combined with their nanoscale dimensions and high aspect ratio [2], confer unique rheo-optical [3], mechanical [4], electrical and wettability properties of the materials made from them [5–9]. Nanocellulose applications are developing for biomedical devices [10,11], clear and strong films of high oxygen barrier [12–14] flexible electronics [3,15,16], intelligent packaging [1,14] and for papermaking [17–19]. Because of their high charge (–26 mV) and high surface area [20], nanocellulose suspensions form stable colloids with notoriously low drainability, and are therefore difficult to process into films or material using the efficient continuous filtration and roll-to-roll technology currently available. Polymer addition was found efficient to drastically improve drainage through controlled flocculation of the nanocellulose fibres [20,21]. Much research has targeted the optimization of nanocellulose properties with suspension drainability using a variety of polymer additives.

We have recently reported the gel point as a convenient and reliable method to measure the sedimentation of nanocellulose, with [20,22] or without polyelectrolyte addition [21,23]. The gel point, measured by sedimentation experiments, corresponds to the solids concentration at which the primary flocs are interconnected and form a self-supporting network [20,23]. Direct relationships between suspension gel point and drainage were reported using polyelectrolytes [20,24]. However, there is a poor understanding of the mechanism by which these polymers improve nanocellulose suspension drainage in terms of colloids and surface phenomena. This issue is also of fundamental interest as polyelectrolyte coagulation of flexible and long aspect ratio fibroid nanocolloids studies are also limited.

Here, we quantify the mechanisms by which two cationic polyelectrolytes families of different morphology can increase nanocellulose drainage by analysing the phenomena at two length scales. The first study, at the nanoscale, quantifies the cellulose - polymer interface in terms of polymer coverage and surface charge; the second study, at the microscale, characterizes nanocellulose flocculation in terms of floc size and flocculation/deflocculation dynamics as a function of polymer coverage and shear. The two families of polyelectrolytes investigated are high molecular weight linear polymers as cationic polyacrylamide (CPAM) and branched polyethylenimine (PEI).

In this study, we first quantify the effect of the polyelectrolyte structure, charge and concentration on the gel point of a nanofiber suspension. Second, we measure polyelectrolyte adsorption onto the nanocellulose in terms of affinity, surface coverage and zeta potential. Lastly, we assess the effect polymer type and surface coverage has on nanocellulose flocculation as a function of shear and polymer/floc reformation. It is our objective to identify the mechanisms by which polyelectrolytes adsorb onto and flocculate nanocellulose fibres to facilitate their drainage into continuous films and foster novel composite applications.

2. Experimental

2.1. Materials

Microfibrillated cellulose (MFC) purchased from DAICEL Chemical Industries Limited, Japan, (grade Celish KY-100S) with 25% solids content was used as received. MFC has an average aspect ratio of 142 ± 28 with mean fibre diameter of 73 nm as reported in Varanasi et al. [23]. Polyethylenimine (PEI) of molecular weight of 750 kDa and 2.0 kDa were purchased from Sigma Aldrich as 50 wt% solutions in H₂O and denoted as HPEI and LPEI, respectively. Cationic polyacrylamide of 50% charge, 13 MDa and 80% charge, 4 MDa (as reported by the manufacturer) were kindly supplied by AQUA+TECH Switzerland from their Snowflake product range and used as received.

2.2. Methods

2.2.1. Gel point determination

When particles are dispersed in liquid, three distinct regions can be defined based on their concentration: dilute, semi-dilute and concentrated suspensions. The boundary between the dilute and the semi-dilute regions, known as the connectivity threshold, ϕ_c , is also referred to as the gel point. Traditionally, Gel points have been obtained through a sedimentation method which was first introduced by Martinez [25]. This methodology was adopted for nanofibre suspensions by Zhang which is represented by the following equation [26]:

$$\phi_c = \phi(h_s) = \frac{d(\phi_0 h_0)}{dh_s} \quad (1)$$

where ϕ_c is the gel point, h_s is the final sediment height of the sediment bed, ϕ_0 is the initial volume fraction of solids in the original dilute suspension and h_0 is the height of the dilute suspension. The gel point is the minimum solids concentration at which the flocs are interconnected and form a network [20].

Following this method, 250 mL of MFC suspensions ranging from 0.05 wt% to 0.025 wt% were prepared. Polymer solutions of 0.5 mg/mL were added to the MFC suspension at the required dosage. Using a hand stirrer, the MFC-polymer suspensions were agitated for 2 min and then allowed to settle. After 48 h, the final sediment height was measured. Plotting a graph of the concentration of MFC versus the ratio of final sediment height to initial height of suspension, the first derivative of the curve is the gel point. This first derivative was obtained using the Matlab software as described by Raj [20].

2.2.2. Zeta potential

Zeta potential measurements were performed with a Nanobrook Omni from Brookhaven Instruments. The supplied software calculated the zeta potential based on the electrophoretic mobility using laser Doppler velocimetry and applying the Smoluchowski equation. MFC-polymer suspensions were prepared according to the method described for gel point determination. MFC-polymer suspension was then centrifuged at 4400 rpm for 20 min to remove the big aggregates and retain colloids. Zeta potential was measured in the supernatant. This methodology is further described by Raj [20].

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