



The role of hydrogen bonding in non-ionic polymer adsorption to cellulose nanocrystals and silica colloids



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ABSTRACT

A piqued interest in nanocellulose has recently arisen due to the growing need to use sustainable and renewable materials in place of those that are derived from petrochemical resources. Although current commercial uses of nanocellulose remain limited, research over the past two decades demonstrates numerous applications including reinforcing agents in polymer and cement composites, coatings, foams, gels, tissue scaffolds, and rheological modifiers, amongst others. Because of the hydrophilic nature of nanocellulose many of the potential uses will likely be in water-based formulations or employ water-based processing methods. Thus understanding the interactions between nanocellulose and water-soluble polymers is critical. Although polyelectrolyte adsorption to cellulose is well understood, adsorption of non-ionic polymers is less clear, with hydrogen bonding often cited as a governing factor. Recent work suggests that in fact hydrogen bonding does not play a significant role in nanocellulose systems, and that non-ionic polymer adsorption is largely entropically driven. Herein we review current literature that investigates non-ionic polymer adsorption to cellulose nanocrystals (CNCs) and draw upon previous papermaking research to better understand the mechanisms involved. Additionally we analyze recent work that compares the adsorption of polyethylene glycol (PEG) to CNCs and fumed silica that provides further insight into this phenomenon. Our findings, along with current literature, suggest that hydrogen bonding does not significantly impact polymer adsorption in aqueous media despite reports to the contrary.

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1. Introduction

The appetite for “green” materials and technologies is more apparent now than ever. Not only limited to public opinion, the push for sustainable practices is a major driving force for innovation in both academia and industry. The American Chemical Society’s 12 Principles of Green Chemistry outline areas in which scientists and engineers can make steps towards earth-friendly technologies [1]. Of these principles, the use of renewable feedstocks is perhaps the most readily achievable.

Derived from the most abundant polymer on earth, nanocelluloses, including cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs) and bacterial cellulose (BC) are renewable and sustainable materials that have received growing interest over the last decade [2]. Originally investigated for their chiral nematic liquid crystalline properties, nanocelluloses are now studied as reinforcing agents, rheological modifiers, emulsion stabilizers, biological and electrical scaffolds and structured templates amongst others leading to a rapid increase in publications over the last two decades (Fig. 1a) [3,4]. Additionally,

patents surrounding nanocelluloses have greatly increased (Fig. 1b) with many potential applications in foods, cosmetics, cements, biomedical devices, coatings and rigid polymer nanocomposites [5]. Due to the hydrophilic nature of nanocelluloses, the most readily attainable applications will be aqueous based and will likely contain a complex mixture of polymers and surfactants [3]. As a result, thorough understanding of the interactions between water-soluble polymers and nanocellulose is critical for the development of these applications.

The field of nanocellulose research has the luxury of standing on nearly a century of papermaking know-how. Many of the findings regarding lignocellulosics and cellulose fiber behavior can be paralleled to CNCs and CNFs. This is largely not the case for materials such as carbon nanotubes, graphenes and metal nanoparticles, which are relatively recent discoveries. As we traverse the literature it is important to be mindful of decades-old research while being aware of potential new mechanisms, behaviors, and sophisticated measurement techniques. Herein we focus specifically on CNCs, as they are (relatively) short rigid colloids, which unlike CNFs and BC show no evidence of entanglement and their interactions in suspension are governed by DLVO theory.

First isolated from cotton cellulose via acid hydrolysis by Nickerson and Habrle [6] and imaged by Rånby and Ribi [7] CNCs have since

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been produced from numerous cellulose sources including, woods, grasses, BC and tunicate, amongst others [8]. Typically, CNCs are extracted via strong acid hydrolysis, that selectively hydrolyzes amorphous regions of cellulose fibers yielding highly crystalline (>80% cellulose I) rod shaped particles which range from 50 to 3000 nm in length and 3–20 nm in cross section [9]. Acid hydrolysis, additionally grafts anionic half ester groups (OSO_3^- or OPO_3^- depending on the acid) to the cellulose surface, which serve to electrostatically stabilize particles in aqueous environments. Recently, there has been a growing interest in developing more environmentally conscious CNC extraction methods using organic acids and hydrothermal processes. Chen et al. demonstrated that CNCs and CNFs can be produced via hydrolysis using dicarboxylic acids which can be efficiently recovered and recycled following nanocellulose production [10]. Additionally, the nanocelluloses produced showed improved thermal properties, in comparison to sulfuric acid extracted CNCs, and were colloidally stable resulting from grafted carboxyl groups on the CNC surface. Hydrothermal processes have been investigated with [11] and without [12] the use of acids and both methods exhibit improved thermal properties in comparison to sulfuric acid-extracted CNCs; however, colloidal stability is unclear as the CNCs remained uncharged by some production methods.

Traditionally, CNCs have been produced at the bench scale in academic laboratories but recently industrially produced CNCs have become more common making CNCs more commercially relevant [13, 14]. Currently, in North America sulfuric acid extracted CNCs are produced by CelluForce, InnoTech Alberta (formerly Alberta Innovates - Technology Futures) and the US Department of Agriculture Forest Products Labs (supplied by the University of Maine). In addition to acid hydrolyzed CNCs, Bluegoose Biorefineries, American Process Inc., Renmatix and others are currently producing CNCs and other nanocelluloses via less conventional methods [13].

2. CNCs with water-soluble polymers and hydrogen bonding

Some of the most likely applications of CNCs (and generally all nanocelluloses) will involve complex mixtures of polymers, and/or surfactants in various ionic strength aqueous environments. Indeed, numerous groups have incorporated CNCs into emulsions [15–17], hydrogels [18–20], cements [21,22], and wastewater treatments [23, 24]. For hydrophobic applications, research is aimed towards covalently modifying CNC surfaces to improve compatibility with non-polar polymers [25,26]. Although significant and impressive progress has been made, surface modification of CNCs at the industrial scale has yet to be fully demonstrated suggesting that aqueous applications are closer to realization.

In aqueous environments, both polyelectrolytes and non-ionic polymers have been observed to adsorb to cellulose surfaces. Polyelectrolyte adsorption to cellulose is generally well understood with initial interaction between the oppositely charged groups of the polymer and the cellulose surface giving way to large entropic gains following the release of bound counter ions [27]. These interactions lead to strong polymer adsorption which has been used to create flocculants [28] and polyelectrolyte multilayer films [29,30] with potential optical, sensor, biomedical and coatings applications. In contrast, the adsorption of non-ionic polymers to CNCs is less clear with numerous publications questioning the role of hydrogen bonding [31,32,33–37]. The adsorption of non-ionic polymers is particularly fascinating when considering polysaccharides and the wide variety of chemical and morphological structures available. Largely, all of these polymers have the capacity to form hydrogen bonding networks with CNCs yet literature shows a diverse set of behaviors.

The first work to investigate the interactions between non-ionic polysaccharides and CNCs was conducted in Derek Gray's group at McGill University, who studied the influence of dextran on the anisotropic phase separation of CNCs [38–40]. In their work, it was observed that dextran did not adsorb to the particle surface and had limited influence on dispersion behavior. However, upon the addition of anionic blue-dextran, CNC phase separation occurred at lower concentrations resulting from increased ionic strength and depletion effects.

More recently, it has been shown that some non-ionic polysaccharides do indeed adsorb to nanocellulose surfaces agreeing with previous observations of cellulose fibers and papermaking [41]. For example Villares et al. observed xyloglucan (XG), adsorption to spin coated CNC thin films via quartz crystal microbalance with dissipation (QCM-D) (Fig. 2a) [42]. Eronen et al. reported adsorption of polysaccharides including guar gum (GG) locust bean gum (LBG) and methylcellulose (MC) to CNF thin films [36]. Hu et al. observed that non-ionic polysaccharides adsorb to CNCs in dispersion and can lower the critical concentration for anisotropic gel formation [43]. The adsorption of hydroxypropyl guar (HPG), hydroxyethyl cellulose (HEC), and LBG, measured by QCM-D (Fig. 2b), dramatically increases the effective volume fraction of CNCs in suspension, shifting the equilibrium towards anisotropic phases. No gel formation was observed for CNC/dextran dispersions indicating no polymer absorption and agreeing with previous studies [38]. The varying adsorption behaviors of chemically similar polysaccharides suggest that there are subtle differences in their interactions with the cellulose surface and that the adsorption is not driven by the common ability to hydrogen bond.

In contrast to the work by Hu et al., Boluk et al. suggest from isothermal titration calorimetry (ITC) and rheological measurements that HEC

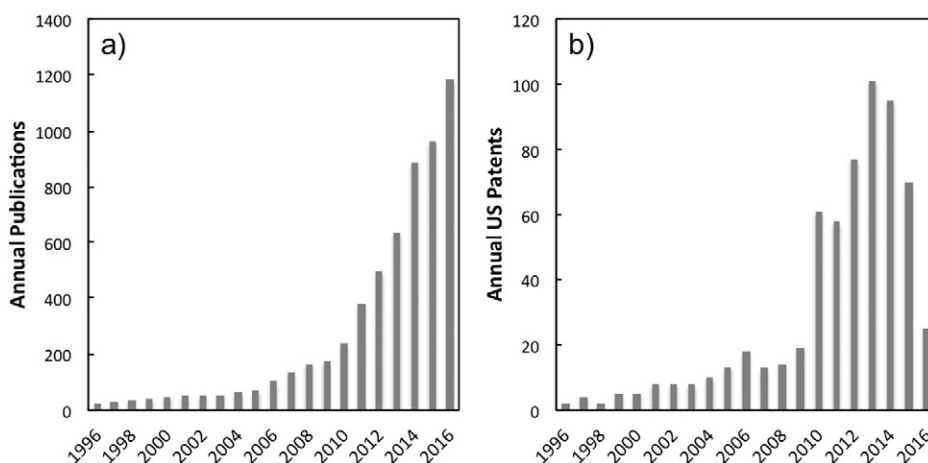


Fig. 1. Annual nanocellulose (a) publications and (b) US patent applications from 1996 to 2016. Publication and US patent claim search conducted using Web of Science and PatSnap databases, respectively, using terms: cellulose nanocrystals, cellulose whiskers, nanocrystalline cellulose, cellulose nanocrystal, nanocellulose, cellulose nanofibrils, cellulose nanofibers, nanofibrillated cellulose, cellulosic nanomaterials, cellulose nanomaterials, cellulose microfibrils, microfibrillated cellulose, nanofibrillated cellulose, bacterial nanocellulose.

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