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Chapter

CNC Gel Rheology Meets Mechanical Characteristics

Aref Abbasi Moud

Abstract

Rheology was used to study the microstructure of cellulose nanocrystal suspensions and hydrogels before, during, and after disturbance. Rheological testing is classified into two types: linear and nonlinear tests. These tests can be carried out with either oscillatory or rotational shear deformations. This manuscript includes recent research on cellulose nanocrystals using rheology to familiarize readers with the generality of these nanoparticles and their flow behavior in aqueous media, as well as to provide a comprehensive overview of current efforts in the literature addressing these materials.

Keywords: cellulose, cellulose nano crystals, rheology, linear and non-linear viscoelastic properties

1. Introduction

Cellulose nanocrystals (CNCs) are whisker-shaped particles made of cellulose [1]. CNCs, in addition to their thin design, exhibit variable amounts of crystallinity [1]. To create a three-dimensional (3-D) structure out of CNC particles, we must gelify them. Aside from size and form, additional characteristics influencing CNC gelation include van der Waals forces, surface charges, and hydrophobic and hydrogen interactions [2].

Research revealed that changes in surface charge density, such as desulfation or high-temperature annealing, may be used to modify the electrostatic forces that keep particles apart [3]. As a result, increasing the strength of van der Waals interactions among CNCs above electrostatic repulsive forces can cause phase separation [4]. It has also been demonstrated that entering a highly concentrated regime by increasing CNC loading over 10% wt induces concentration-dependent manner aggregation [5].

Furthermore, self-similar patterns of CNC gels may be created by adding coagulants to CNC solutions, such as salts or polymers. [6] conducted research in which gel formation occurred following the addition of NaCl to the CNC solution. Chau et al. [7] showed experimentally that raising the ionic strength of suspensions weakens electrostatic repulsion among particles as compared to attractive short-range forces such as van der Waals and hydrogen bonding. It was also suggested that the stiffness of the gel is a function of the charge number of the salt as well as the radii of the injected ions. Ure a-Benavides et al. [8] hypothesized that the phase transition point for a CNC suspension coagulated with ions is roughly one order of magnitude lower

than the gelation threshold for pure CNC suspension. Regardless of recent research on the stability of various forms of nanocellulose, [6, 9–16].

As a recap, CNCs are cellulose-based whisker-shaped particles. We must gelify CNC particles to construct a three-dimensional structure. Increased van der Waals interactions between CNCs can result in phase separation. A CNC solution coagulated with ions has a phase transition point that is around one order of magnitude lower than the gelation threshold for pure CNC. It was also proposed that the stiffness of the gel is a function of the salt's charge number as well as the radii of the injected ions.

2. Methodology

Various characterization tools, including but not limited to small-angle neutron scattering [17], small-angle x-ray scattering [18], confocal laser scanning microscopy [19], rheology, and so on, have been employed to analyze CNC gels and suspensions in the literature. We concentrate on employing rheology to investigate the flow behavior and mechanical characteristics of CNC gel and suspension. The fundamentals of conducting rheological tests and their adaption to CNC may be found in Refs. [20–22] and will not be discussed further here.

3. Fundamentals of rheology and its adaptation to CNC

Rheology has been widely used to investigate the microstructural development of cellulose nanocrystals (CNC) suspensions and hydrogels before, during, and after disturbance. Because of the numerous methods of rheological tests that give important insights into the superstructures of CNC colloids at different stages. Indeed, rheological examinations may be divided into linear and nonlinear tests, each of which gives distinct information about the structural features of a system. These tests can be performed using oscillatory or rotational shear deformations. The colloidal transition, which encompasses liquid-solid and isotropic-anisotropic transitions, determines the ultimate physical characteristics and structural aspects of CNC suspensions. A lot of characteristics govern these transitions, the most important of which are CNC concentration and aqueous phase stability. In general, increasing colloidal loading or lowering CNC particle stability in water promotes the formation of colloidal glass or gel. These designs provide CNC suspensions remarkable mechanical properties, expanding their applications.

Soft solid structure formation may be easily detected using near and nonlinear rheological approaches. Qiao et al. [23] used rheological techniques to explore the colloidal behavior of CNC suspensions. The authors changed the concentration of CNC particles to alter the network structure of suspensions. They established isotropic and biphasic gel forms of CNC suspensions using rotational flow curves and oscillating frequency sweep investigations. Temperature, ionic strength, and CNC concentration can all influence the colloidal behavior of systems [24]. This section presents the rheological fingerprint of CNC suspensions as investigated by comprehensive rheological studies.

The frequency sweep test is the most well-known small-angle oscillatory shear (SAOS) test, in which the samples' storage modulus (indicative of rigidity) and loss modulus (which quantifies how readily applied stress is relaxed or dissipated) are monitored against the frequency of deformation at a lock strain amplitude. The dynamic moduli of a liquid dominant response (e.g., at low concentrations of CNC particles) are frequency-dependent and drop as the frequency decreases, indicating

the relaxation processes in a system. Another feature of the liquid-like behavior is storage modulus < loss modulus. However, for an ideal elastic gel, the moduli are predicted to be frequency independent and storage modulus > loss modulus. As a result, the CNC particles emerge when the moduli are frequency invariant (plateau-like behavior) and conjugated with the storage modulus > loss modulus condition.

Ions, as previously indicated, can alter the structural characteristics of CNC-based suspensions and gels. Chau et al. [7] used linear rheological techniques to explore the sol/gel transitions of salt-incorporated aqueous CNC suspensions with increasing charge and cation size. In comparison to magnesium or aluminum chloride, a greater amount of sodium chloride was required to produce gelation at a constant concentration of CNCs (4 wt%) (**Figure 1a**). It is predicted that when the cation charge number grows, a stronger gel of CNC particles can develop as electrostatic repulsions between the particles decrease.

Thus, as anticipated by the DLVO theory, Van der Waals and hydrogen bonding interactions gain primacy, resulting in physical link between particles [26]. The gelation performance of different divalent positive ions differs insignificantly (**Figure 1b**). The SrSO₄ system's somewhat higher stiffness was due to its reduced solubility; that is, metal cations with bigger ionic radii and lower water solubility could bridge two nearby sulphate half ester groups of CNC particles and produce a stronger gel. Shafiei-Sabet et al. [27] looked at how the degree of sulfation affects the rheological characteristics of CNC suspension. And per the results of fast transient sweep studies at the linear viscoelastic region, the degree of sulfation has a significant influence on the critical concentrations at which the liquid-to-solid-like transition occurs. As a consequence, rheological methods were employed to show that the surface morphology of CNC particles is important in the gelation of CNC suspensions. As a consequence, rheological methods were employed to show that the surface chemistry of CNC particles is important in the gelation of CNC suspensions. To put it another way, several researchers [28–31] sought to enhance the rheological characteristics of CNC suspensions by surface modification and manipulation.

Surfactants can also be used to quickly manipulate the surface properties and hydrophilicity of CNC particles [32]. Kushan et al. [33] used cationic 1-decyl 3-methyl imidazolium chloride and 1-decyl trimethyl imidazolium ferric tetrachloride to modify the rheological properties of CNC solutions. The hydrophobic interaction of surfactant tails adsorbed on CNC particles drives the formation of network structure at low CNC ratios. Significantly, the gel network value increases in a linear proportion with the presence of positively charged micelles in the gelation.

In the case of thermal hydrogel formation (hydrothermal treatment), Lewis et al. [3] used linear rheology to investigate the hydrothermal gelation of aqueous suspensions with 4wt. percent particle loading at temperatures ranging from 60 to 90°C. They discovered liquid-like behavior in samples treated at 60°C and 70°C (frequency-dependent dynamic moduli paired with $G' > G''$ condition). The liquid-to-solid reaction happened in samples treated at 80°C, and rheological parameters increased by more than two orders of magnitude. The value of dynamic moduli was increased further by raising the treatment temperature from 80 to 90°C. The gelation of the CNC suspensions at higher treatment temperatures was explained by the surface desulfation of the particles during the hydrothermal treatment. This event, which results in the release of negatively charged sulfate groups, weakens the energy barrier between CNC particles and promotes the instability of CNC particles in suspension. The researchers also demonstrated that the rheological properties of CNC suspensions allow them to be administered through syringe injection, allowing them to be employed in biological applications such as targeted drug delivery and tissue engineering.

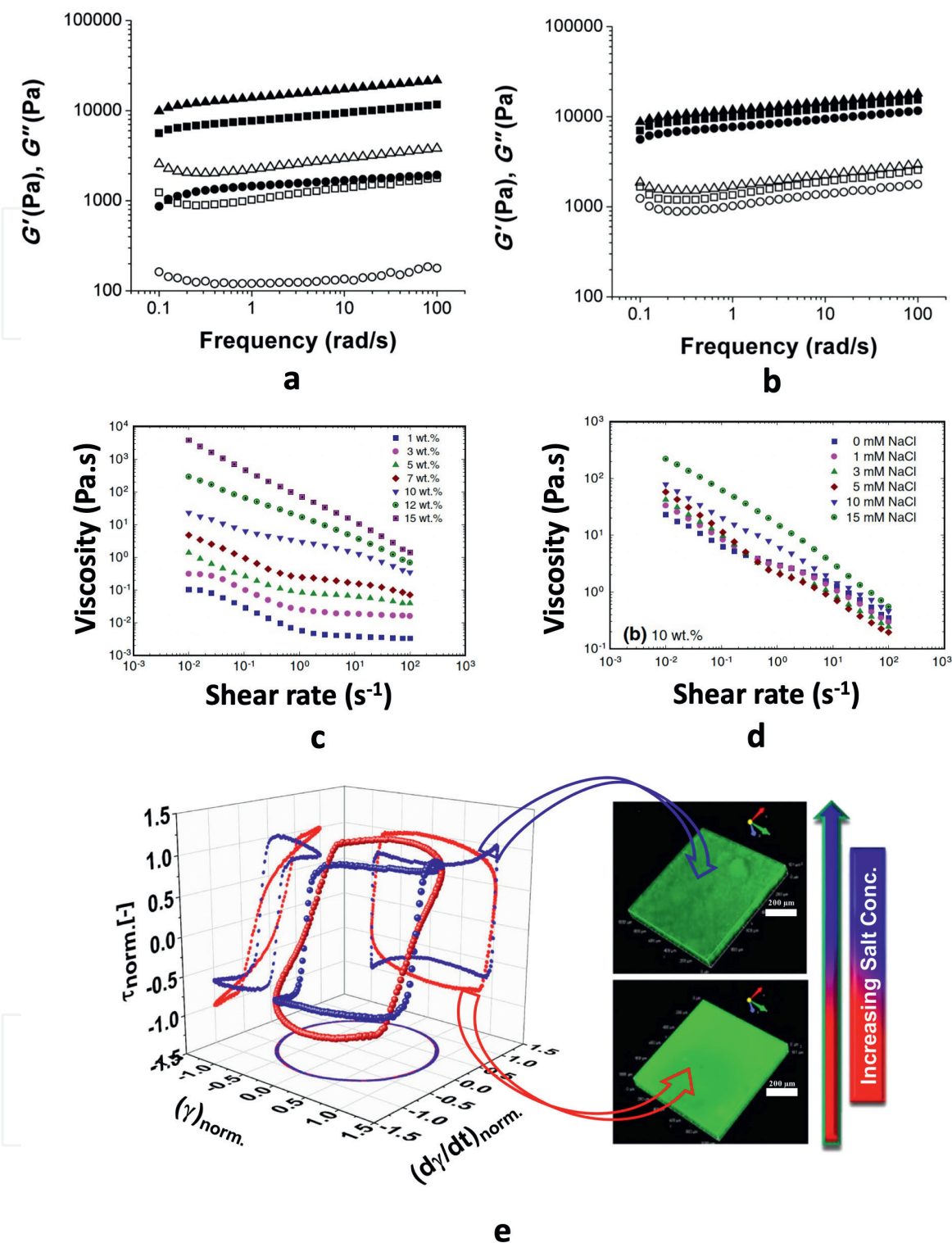


Figure 1. Dynamic frequency sweeps of 4% CNC suspensions in the presence of (a) Na⁺ (circles), Mg²⁺ (squares), Al³⁺ (triangles), (b) Mg²⁺ (circles), Ca²⁺ (squares), and Sr²⁺ (triangles). Differences in storage moduli, G', and loss moduli, G'', are represented by closed and open symbols. The dynamic frequency sweeps were carried out at a strain of 0.5 percent. (c) The material function of viscosity of CNC suspension in Deionized water at various CNC concentrations. (d) Viscosity against shear rate dependency in 10% CNC suspensions at various electrolyte concentrations. (e) Intra-cycle Lissajous-Bowditch plots of CNC suspensions at various salt concentrations, paired with confocal pictures. (a) And (b) Reprinted with permission from [7]. Copyright (2015) American Chemical Society. (c) and (d) Reprinted by permission from [Springer]: Springer Nature [Cellulose] [25], Copyright (2014). (e) Reprinted by permission from [Springer]: Springer Nature [Cellulose] [21], Copyright (2020).

Besides the chemical composition of CNC particles, the rheological properties of these systems may be altered by changing their physical features, such as crystallinity and length [34, 35]. Recently, researchers [35] have shown that the aspect ratio of CNC particles has a considerable impact on their rheological reactivity. Gel-like rheological behavior, for instance, has been shown at higher concentrations with shorter CNC particles [34].

The addition of a secondary component, such as a polymer, can also cause CNC suspensions to change from liquid to solid-like [22, 36]. Much study has shown that when water-soluble polymers such as poly (vinyl alcohol) are present, the gel formation forms at lower CNC concentrations with a stronger network (PVA). Meree et al. [37] and Moud et al. [22] identified two types of networks in PVA/CNC suspensions. Their rheological findings show that polymers mediate CNC networks at lower CNC loadings, but CNC-CNC interactions are the primary source of the elastic component of networks at higher CNC loadings.

The shift between any of these networks is governed by the percolation threshold. At constant concentration, we showed that the addition of PVA enhances the storage modulus more than tenfold [21, 22]. The addition of 5% PVA, for example, increased the storage modulus of CNCs in water from 25 to 344 Pa for 30 g/L. This was attributed to CNC particles bridging with direct, primary, and secondary polymer chains. According to Zhou et al. [36], the gel-like behavior of CNC suspensions in the presence of PVA is induced by physical entanglement and hydrogen bonding between CNC particles and the PVA chain.

In linear rheological frequency sweep tests, the amount of displacement is so small that now the material is not pulled out of dynamic equilibrium. When rotating nonlinear testing, nevertheless, the entire network of the specimens is broken (e.g., steady-state shear viscosity also known as flow curve test). Flow curve tests examine viscosity at various shear rates, which is influenced by sample internal structure. The behavior of a Newtonian fluid, like very low concentration CNC suspension, is plateau-like (i.e., viscosity is independent of shear rate). The rheological response of non-Newtonian fluids, on the other hand, deviates from plateau-like behavior, following shear-thinning or shear-thickening tendencies. The nonlinear rheological response of CNC colloidal gels under rotational shearing flow, at high particle concentrations or in the presence of a polymer, was found to be shear-thinning behavior [5, 22, 23, 38]. Furthermore, as the network structure is strengthened, the degree of thinning behavior increases [25], which is advantageous to post processing techniques such as 3D printing.

Figure 1c and **d** depict the flow curves of CNC suspensions at varied salt and CNC contents. The suspensions are categorized as isotropic or anisotropic for small concentrations of CNC particles, such as 1wt. percent and 3wt. percent. Isotropic samples display (1) Newtonian plateau behavior at low shear rates, (2) shear-thinning activity at medium shear rates due to nanocrystal alignment parallel to the flow direction, and (3) a second plateau at higher shear rates due to CNC particle alignment parallel to the flow direction. A change from isotropic to anisotropic chiral nematic liquid crystal occurs between 3 and 5 wt. percent CNC levels and the viscosity profile comprises three separate zones, namely: At lower flow rates, the shear-thinning territory is caused by the conformance of chiral nematic liquid crystal domains; at intermediate shear rates, the regions are all directed along the shear direction; and at high shear rates, the shear stress is strong enough to disturb the liquid crystal domains, causing

independent nanocrystals to try to position themselves along the shear direction. Sample viscosity over 10% wt. only displays shear thinning behavior across the full shear rate window tested, indicating gel formation. See ref. for further details on the influence of salinity on the curves of CNC suspensions [25].

Scholars have been interested in nonlinear viscoelastic characterizations under large amplitude oscillatory shear (LAOS) flow since the development of better rheometers with superior torque precision and significant computing capability. In opposed to SAOS experiments, which are confined to a certain strain and/or time period, the development of LAOS flow is not constrained as long as shear flow inhomogeneities do not modify the flow dynamics and viscoelastic response. Furthermore, rotational shearing tests (e.g., flow curve) do not offer information on viscoelasticity, but LAOS may characterize nonlinear viscoelasticity in samples. Additionally, LAOS experiments are relevant to actual flow fields because most processing operations include enormous and fast deformations of materials.

The nonlinear viscoelasticity of CNC suspensions/gels under LAOS deformation in the presence of salt and PVA was recently investigated [21, 22]. Viscoelasticity tests, as demonstrated by Abbasi Moud et al. [21, 22], are very sensitive to minor changes in the interior microstructures and provide pertinent data about the filler particles network architecture.

This knowledge is often not obtainable via the rheological features of the linear framework. **Figure 1e**, for example, shows Lissajous-Bowditch plots and confocal images of CNC suspension with fixed particle concentrations but variable salt loadings. Confocal microscopy indicated that as the solution gelled by raising the salt content, the Lissajous-Bowditch plots took on significantly different geometries.

Other techniques, such as stress decomposition and sequence of physical processes, were used by the authors to give quantitative (e.g., inter- and intra-cycle parameters) and qualitative nonlinear analysis. All CNC/salt and CNC/salt/PVA suspensions/gels were shown to display Type III inter-cycle nonlinear behavior (weak overshoot where G' decreases while G'' first increases and then decreases). CNC-based systems' viscous and elastic intra-cycle nonlinearity was discovered to be shear-thinning and strain stiffening, respectively. Furthermore, suspensions/gels' inter-cycle nonlinearity was frequency invariant, whereas their intra-cycle response was substantially frequency dependent.

Even though nonlinear rheological procedures offer us with unique data on the inner core and processability of materials, these constructive experiments should be performed with utmost caution. Flow inhomogeneities, as previously indicated, should be avoided to acquire reliable nonlinear data. Wall depletion, shear banding, and wall sliding are examples of flow inhomogeneities discovered. Hubbe et al. expand on the influence of flow inhomogeneities on the characterization of CNC suspensions/gels [39].

Recent papers on the rheological properties of CNC suspensions/gels pave the path for sophisticated technologies of these materials. Several factors, including CNC concentration, temperature, and the inclusion of salt, polymers, or surfactants, have been shown to readily modify the viscoelasticity of CNC suspensions. The storage modulus of CNC suspensions varies from $\sim 10^{-3}$ to $\sim 10^3$ Pa by adjusting the aforementioned factors [3, 7, 40–53], As an outcome, these systems are adaptable to a variety of processing methodologies. In order to make 3D printed structures, printable inks, for example, must have precise rheological properties.

Extremely high yield stress τ_y (usually measured by a stress sweep test or by fitting rheological models, such as Herschel Bulkley, to flow curve data) confirms the strong gel-like structure, making the ink difficult to flow and thus unsuitable for 3D

printing processing techniques, despite the fact that it can cause serious problems, such as clogging the printing nozzle. Low τ_y , on the other hand, causes lateral spreading of 3D-printed inks following deposition on a substrate. It was discovered that the ideal τ_y for ink printing is around 100 Pa [54].

As a result, the controllable rheological properties of CNC suspensions (i.e., from liquid to solid dominant behavior) combined with high shear thinning and proper maximum stress allow them to flow easily during 3D printing processes, while their viscoelasticity and yield stress keep the structure of the formed filament coherent and uniform. Ma et al. [55] for example, studied the printability of CNC suspensions by improving the rheological characteristics by altering the concentration of CNC particles (0.5–25 wt percent). The greatest print quality and fidelity were determined to be 20 percent wt CNC hydrogels. The scientists also looked at the printing qualities of CNC hydrogels with high and low methoxy pectin levels. Wang et al. [56] reported another innovative rheology-related application of CNC suspensions, demonstrating the ability of CNC particles in the stabilization of magneto-rheological fluids.

4. Conclusion and future works

Rheology has been widely used to investigate the microstructural development of cellulose nanocrystals (CNC) suspensions and hydrogels. The colloidal transition determines the ultimate physical characteristics and structural aspects of CNC suspensions. Temperature, ionic strength, and CNC concentration can all influence the behavior of these systems. Ions can alter the structural characteristics of CNC-based suspensions and gels. A greater amount of NaCl was required to produce gelation at a certain particle concentration (4w. percent).

LAOS can determine the nonlinear viscoelasticity of samples. LAOS tests are relevant to real-world flow fields because materials undergo enormous and fast deformations. The viscous and elastic intra-cycle nonlinearity of CNC-based systems was revealed to be shear-thinning and strain stiffening. Several factors, including CNC concentration, temperature, and the addition of salt, polymers, or surfactants, have been shown to readily modify the viscoelasticity of CNC suspensions. As a result, these systems are adaptable to a variety of processing methodologies.

Through recap, we offered detailed instructions that walk readers through the brief steps of CNC-based system creation, from cellulosic supplies to suspension and gel forms. We presented characterization methods that provide information about the CNC's condition in either a glassy or a gel state. This review article's information appears to be well aligned with new processing techniques and applications (e.g., 3-D printing) of CNC gel inks, inspiring the interpretation of microstructural features of these complex systems to assist the community and newcomers, as well as contributing to current and future developments in the field.

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