Binary Mixtures of Colloidal Cellulose Nanocrystals and Laponite for Preparation of Functional Nanocomposites

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ABSTRACT

Cellulose Nanocrystals (CNCs) are attractive substances with interesting colloidal self-assembly behavior and rheological properties due to their rigid rod morphology. In this paper, the aqueous dispersion characteristics, as well as the rheological, optical, and structural properties of binary mixtures CNCs and Laponite (L) are investigated in detail. We obtain various complex structures by using the binary mixtures of CNCs and Laponite. A phase diagram consisting of sol, isotropic gel and birefringent nematic gel phases is obtained. Our findings envisage that this system will serve as a model binary system of 1D and 2D with complex interactions. To go further, we demonstrated the fabrication of nanocomposite thin films and aerogels from the binary colloidal mixtures. For the former, they can be used as

efficient absorbers of model pollutants such as Nile blue and Rhodamine B dyes in the solution while as-obtained aerogels display enhanced flame retardation behavior.

Keywords: *Cellulose nanocrystals, Laponite nanoclay, phase behavior, birefringent gels, aerogels, thin films, dye removal, flame retardants*

INTRODUCTION

Driven by concerns about the depleting resources and the environmental hazards, the researchers are now focusing on the implementation of renewable resources for the production of highly performing, sustainable materials. Recently, scientists are excited by the tremendous properties and applications of Cellulose Nanocrystals (CNCs) as it is renewable, biodegradable and non-toxic^{1,2}, which have attracted a lot of attention due to its ability in forming liquid crystals^{3,4}, its application in nanocomposites⁵⁻⁸ and photonic metamaterials^{9,10}. CNCs are crystalline nanomaterials and obtained typically from wood, bacteria, tunicate and linen by hydrolysis with sulfuric acid^{11,12}. This results in nanocrystals possessing rod shape, which bear sulfate ester groups rendering the surface of CNC negatively charged (Scheme 1).

Even though Marchessault *et al.*¹³ reported the formation of colloidal dispersions of CNCs since 1952, it took another forty years to understand the ordering in chiral nematic structure of CNC, proposed by Revol *et al.*¹⁴ in 1992. The formation of self-organized chiral nematic domains depends on several parameters such as the aspect ratio of CNCs, the surface chemistry or the ionic strength of the medium¹⁵. As the concentration is increased, aqueous suspensions of CNCs may undergo a first order transition from isotropic to pure liquid crystalline phase¹⁶, typically above 6.0 wt% for CNCs from wood pulp¹⁷⁻²⁰. At higher concentration, the liquid

crystalline sol turns into a birefringent gel above 10.0 wt% ²¹, like for clay colloids, with different crystallography ^{22–25}. The gel phase refers in the following to a state where particle motion is kinetically arrested. By definition, these colloidal gel phases display a high viscosity at rest (solid-like behavior), which decreases upon shearing after reaching a critical shear stress while fluid CNC phases present a finite viscosity at low shear stress.

Scheme 1. Crystal structures of (*left*) cellulose nanocrystals (CNCs) with sulfate ester group and (*right*) Laponite clay nanosheets. Illustration of the procedure used to prepare composite films and aerogels from binary colloidal mixtures of CNC and Laponite.

As the larger CNC particles form the liquid crystalline phase, the smaller particles remain in the isotropic phase, at critical concentration when isotropic to biphasic transition takes place ²⁶. Thus, size distribution plays an important role in the phase behavior exhibited by the CNC dispersions. From an application point of view, CNCs can be shaped in the form of fibers ²⁷ and films ^{28,29} and these regenerated cellulose materials are suitable for wrapping cardboard boxes or for packaging drugs ^{30,31} and food items ³². The high aspect ratio, high specific moduli and stiffness makes CNCs suitable as nanofillers in polymer matrices ^{33,34}, so that the mechanical, optical and rheological properties of the obtained nanocomposites can be enhanced ^{35,36,37}.

Meanwhile, inorganic nanofillers have gained prominence nowadays, especially layered aluminosilicates used extensively in polymer nanocomposites ^{38,39}. Among them, Laponite, a synthetic clay mineral having a disk shape morphology, possesses appealing properties like biocompatibility ⁴⁰, hydrophilicity ⁴¹ and biodegradability ⁴². A positive charge deficiency is created in the Laponite sheet by substituting lithium atoms in place of few magnesium atoms in the octahedral layer (Scheme 1) ⁴³⁻⁴⁵. The anisometric shape of the Laponite nanoparticle has a different charge contribution between the surface (negative) and the rims (pH dependent). Hence, the phase diagram of aqueous dispersions of Laponite is rather complex, exhibiting a variety of phase behaviors ranging from isotropic fluid to kinetically arrested phases ^{46,47}. Laponite dispersions exhibit an improvement in its physical properties like relaxation time and mechanical properties with increasing time and is an obvious consequence of physical aging in spin and molecular glasses ⁴⁶⁻⁵⁰. The colloidal and rheological behaviour of aqueous

suspensions of Laponite has been extensively addressed in the scientific literature⁵⁰. Depending on the waiting time, at concentration lower than 1 wt%, it is observed that aqueous dispersions undergo a slow phase separation process into clay-rich and clay-poor phases. Above this threshold, Laponite dispersion forms a repulsive arrested phase.

CNC nanorods would easily be blended with Laponite without doing organic modification beforehand, in order to obtain favorable nanofiller-matrix compatibility and interaction. Electrostatic interactions between Laponite and CNC surfaces as well as hydrogen bonding between the hydroxyl groups present on their surfaces should promote the formation of complex self-assembled structures. CNC included composite systems are of great importance today as they enhance the rheological properties by forming complex network structures within the system. Trindade *et al.* reported that CNCs could be developed into excellent fire-retardant material by adding sodium fluorohectorite (NaFH) clays⁵¹. In that case, NaFH nanolayer provides a planar anchoring to rod shaped CNCs and the evaporation of water leads to the formation of colored films, which could exhibit the property of fire retardancy. Recently, it has been proposed that aerogels of amine-modified CNCs are excellent absorbers of CO₂⁵².

In this work, we propose a systematic analysis of the optical, structural and rheological properties of the composite gels and proposed a phase diagram. We observed a drastic change in the microscopic properties of the composite when clay nanosheets are added to CNC aqueous dispersions. To this end, we demonstrate the realization of functional thin-films and aerogels from CNC/L mixtures. We investigate the efficiency of the nanocomposite films for the removal of pollutants such as dyes (Rhodamine B and Nile blue) as well as the kinetics of dye adsorption. In parallel, we investigate the enhancement of fire-retardant property of CNC aerogels with the incorporation of clay particles. Our results should be useful for the

applications, where there requires an increase in properties like yield stress, viscosity and elastic modulus and for which the organic modification of CNC particles is not needed in preparing composites.

MATERIALS AND METHODS

Sample preparation

CNC powder was purchased from CelluForce (Canada). Laponite[®]RD was procured from BYK Additives & Instruments (Germany) and was used as received. The purity of both samples was determined by Wide Angle X-ray scattering measurements (Figure S1). Particle size and zeta potential of both samples were measured using Anton-paar Litesizer 500. The main physical properties of CNCs and Laponite are summarized in Table 1. Milli-Q purified water was used to prepare the CNC/L composite suspensions. To this end, stock solutions of Laponite (0.1-3.0 wt%) were prepared by dilution in water and appropriate amount of CNC powder (1.0-3.0 wt%) was added slowly during stirring.

Preparation of nanocomposites

Thin-films were obtained by pouring CNC and CNC/L composite samples into 6 cm diameter petridish. Solid flexible films were recovered and stored after solvent evaporation (Scheme 1). For aerogels, CNC/L composite samples and the pure CNC samples were frozen by dipping the vials containing the samples in liquid nitrogen. The caps of the vials containing samples were removed and were covered it using kim wipes. The frozen samples were kept immediately in Virtis S P Scientific (Bench top lyophilizer with a temperature of -104 °C and pressure of 23 mT) for freeze-drying overnight (Scheme 1).

Table 1. Characteristic properties of CNC and Laponite used in this work.

Materials Properties	Cellulose Nanocrystals (CNCs)	Laponite (L)
Molecular formula	$[(C_6O_5H_{10})_{22-28} SO_3 Na]_{4-6}$	$Na_{0.38} Si_8 (Mg_{5.72} Li_{0.18}) O_{20}(OH)_4$
Specific Density	1600 kg/m ³	2700 kg/m ³
Size	Length: 100-300 nm Diameter: 2-20 nm	Diameter: 25 nm Thickness: 0.92 nm
Zeta potential	-31.6 mV	-36 mV
pH (in water)	7.0 - 8.5	8.0 – 10.0

Optical observations

The composite samples of CNC/L were transferred to 10 ml glass vials and were allowed to rest for at least 2 days at room temperature. Polarized optical observations were first carried out by naked-eye inspections on vial samples placed between crossed-polarizers in a home-made setup equipped with a Panasonic DMC-FZ18 camera. Microscopic observations were performed on a polarizing microscope (BX51-P, Olympus) coupled with an Olympus XZ-1 F1.8 camera. In this

case, samples were sucked in flat capillaries (VitroCom, 0.2 x 2 mm) that were flame-sealed. The samples were observed immediately under the microscope. A retardation filter (λ -plate) was inserted at 45° with respect to the polarizers to identify preferential orientation of CNC and/or Laponite particles in the birefringent domains.

Rheological measurements

Rheological properties of CNC/L composite system were studied using AntonPaar MCR302 rheometer with cone-plate geometry having a nominal angle of 2°. All the experiments were conducted at room temperature. The composite system of CNC/L was investigated with loading and trimming the samples in the rheometer following a standardized procedure. In order to avoid the evaporation of samples, a thin layer of silicone oil was applied on the edges of the samples and an evaporation trap was used to cover the samples placed on the rheometer. Sol/gel transition and yield stress values were extracted by fitting the flow curves describing the shear viscosity versus shear stress. These experiments were completed with oscillation sweep measurements. We first performed amplitude sweep measurements at 0.1 rad/s frequency. The constant linear region observed in the variation of storage modulus (G') and loss modulus (G'') with oscillation stress allowed determining the linear viscoelastic region (LVR) of each sample. In order to evaluate the viscoelastic properties of the system, small deformation oscillatory measurements were carried out by choosing the stress value from LVR. In that case, G' and G'' moduli were recorded in an oscillatory frequency sweep using angular frequency ranging from 0.1 to 100 rad s⁻¹.

X-Ray Scattering experiments

All X-ray scattering experiments were performed on the MORPHEUS platform of Laboratoire de Physique des Solides. Small Angle X-ray Scattering (SAXS) measurements were carried on an in-house SAXS setup using a rotating anode generator (Rigaku Corp., Japan) at a wavelength of $\text{Cu K}\alpha = 1.542 \text{ \AA}$ delivered by a multilayer Ni/C focusing optic (Osmic)⁵³. Two-dimensional (2D) SAXS patterns were collected on a Pilatus 200K hybrid pixel array detector (Dectris) with $172 \text{ }\mu\text{m}$ pixel size, placed at a sample-to-detector distance of around 1.4 m. Wide-Angle X-ray Scattering experiments were realized on a rotating anode generator (Rigaku Corp., Japan) at a wavelength of $\text{Mo K}\alpha = 0.711 \text{ \AA}$ delivered by a multilayer W/Si focusing optic (Osmic). The 2D WAXS patterns were collected on a MAR research X-ray sensitive 345 mm plate detector with $150 \text{ }\mu\text{m}$ pixel size, placed at a sample-to-detector distance of around 250 mm. The plot of scattering intensity (I) versus scattering vector modulus ($Q = 4\pi \sin\theta/\lambda$, where λ is the wavelength and 2θ is the scattering angle), were obtained from the SAXS pattern in which azimuthal angular interaction $[0, 2\pi]$ were corrected using standard procedures implemented in Igor software.

Dye removal and kinetics

The prepared CNC/L films of different concentrations (3.0 wt% CNC with 0, 0.3, 0.7, 1.0 and 2.0 wt% Laponite) having dimensions $1.5 \text{ cm} \times 1.5 \text{ cm}$ and mass of 28 mg were dipped in 7 ml of Rhodamine B dye (S D Fine Chem Limited) and Nile Blue dye solutions of initial concentrations $0.01253 \text{ mmol L}^{-1}$ and $0.00787 \text{ mmol L}^{-1}$ respectively. Without disturbing the films, 2 ml of dye solution was taken out at different intervals over 24h. The aliquots were analyzed by UV-vis spectroscopy using a Cary 4000 UV-Vis spectrophotometer. The amount of dye adsorbed by CNC/L films at equilibrium is calculated by:

$$q = (C_0 - C)V/W \quad (1)$$

where q is the amount of dye adsorbed on the film at equilibrium (mmol g^{-1}), C_0 and C correspond respectively to the initial and equilibrium concentrations of dye solutions (mmol L^{-1}), V is the volume of solution and W the mass of the films.

Preparation of aerogel:

CNC/L composite samples and the pure CNC samples were frozen by dipping the vials containing the samples in liquid nitrogen. The caps of the vials containing samples were removed and were covered it using kim wipes. The frozen samples were kept immediately in Virtis S P Scientific (Bench top lyophilizer with a temperature of -104°C and pressure of 23 mT) and was freeze dried overnight in order to obtain CNC/L aerogels and flame test was conducted. Prepared aerogels in the nose cone shape were ignited using a torch lighter and observed the time taken for the samples to put off the flame.

RESULTS

Optical properties of gels

Having prepared CNC/L composites, we investigated the evolution of birefringence by naked-eye observations between crossed polarizers at one week, and ten months after sample preparation (Figure 1a, b and Figure S2). As mentioned before, pure CNC aqueous dispersions remain isotropic for concentration lower than 3.0 wt%, i.e., the highest concentration used in this work. Conversely, pure Laponite presents a complex phase diagram that has been largely debated^{22,46,50,54–56}. At low ionic strength ($< 10^{-3} \text{ mol. L}^{-1}$), isotropic liquid and gel phases are found at low clay concentration ($< 2.0 \text{ wt}\%$) while these dispersions form repulsive glass when the concentration of Laponite increases. For the range of concentrations, we used in this study,

the samples of pure Laponite or CNC do not exhibit any liquid crystalline behavior and hence do not show birefringence. On this basis, it is therefore not surprising to find that the CNC/L mixtures prepared with the lowest concentrations of Laponite (< 0.5 wt%) remain isotropic. However, all samples prepared above 1 wt% concentration of Laponite form arrested phases and exhibit optical birefringence with a clear evolution after ten months. This indicates the particles are locally ordered but they do not reach thermodynamic equilibrium, both rotational and translational motion of CNC and Laponite being hindered in the arrested phase.

Figure 1. Naked-eye (top) and microscopic (bottom) optical observations between crossed polarizers on binary mixtures prepared with 2.0 wt% CNC and different concentrations of Laponite. Optical textures captured after (a) one week and (b) ten months of preparation of samples. POM images (c, h) 0.7 wt%, (d, i) 1.0 wt%, (e, j) 1.5 wt%, (f, k) 2.0 wt% and (g, l) 2.5 wt%. Top panels represent images captured under cross polarizers while bottom panels

correspond to the same area with the insertion of a retardation filter (λ -plate, 530 nm) at 45° with respect to the polarizers. The orientation of both polarizer and analyzer are symbolized by white arrows with labels p and a , respectively, while the red line represents the slow axis of the retardation filter. The scale bar corresponds to 500 μm .

The threaded textures recognized in the observations in optical flat capillaries confirm the nematic ordering of CNC/L mixtures (Figure 1c-g and Figures S3 and S4). The position and extent of these domains, delimited by topological defects, are highlighted when a retardation filter (here a λ -plate at 530 nm) is inserted at 45° with respect to the polarizers (Figure 1h-l). If so, blue (red) colors correspond to an orientation of particles in the nematic domains with their normal parallel (perpendicular) to the slow axis of the λ -plate. These nematic domains are randomly oriented throughout the samples whatever the concentration of CNC and Laponite. Interestingly, we also evidenced the formation of small tactoids with increasing the concentration of CNC (Figure S3). These tactoids seem to be more frequent when the concentration of Laponite increases (Figure S3d) and the use of a retardation filter help us to distinguish them from the birefringent background (Figure S3h and Figure S4). Although clear tactoids were never identify in pure Laponite samples, we can assume that they are related to a nematic phase of CNC nanorods, trapped in the arrested phase of clay nanosheets. The incorporation of Laponite probably induces depletion interactions as observed in other clay-inorganic nanoparticle mixed dispersions⁵⁷⁻⁵⁹.

Small-Angle X-ray scattering experiments

We investigated the structural organization of the different binary mixtures by performing laboratory Small-Angle X-ray Scattering experiments. SAXS profiles for CNC/L binary

mixtures prepared at 2.0 wt% and 3.0 wt% of CNC are displayed in Figure 2. All curves present similar shape with a monotonous decrease of the scattered intensity I with increasing the scattering vector modulus as $I(Q) \sim Q^{-2.1}$ in the Q -range 0.02-0.12 $\text{\AA}^{-1}$. The exponent of the power law is characteristic of bidimensional objects, even if the slightly higher value of 2 seems to indicate that some more complex interplays occur between particles in these arrested phases as shown from POM observations (Figures 1 and S3). In the low Q -region, SAXS profiles are flattened due to the form factor coming from CNC nanorods. We also noticed a slight effect on the slope for CNC/L mixtures prepared at 3.0 wt% of CNC, probably due to the formation of droplets as evidenced from POM images (Figure S4). Although it is hard to extract any correlation peaks from the SAXS profiles, these results suggest that incorporation of CNCs in Laponite dispersions do not strongly modify the microstructural properties of the binary mixtures for distances between ~ 75 and 5 nm.

Figure 2. SAXS profiles for CNC/L binary mixtures prepared with *a)* 2.0 wt% and *b)* 3.0 wt% of CNC and varying concentrations of Laponite. The curves have been shifted for the sake of clarity.

Rheological study and gelation behavior

Optical observations reveal that CNC/L samples prepared with Laponite concentration higher than 0.5 wt% sustained inverted vial test, indicating gel-like formation. To characterize the gelation behavior, we performed a detailed rheological analysis of the binary mixtures. The evolution of the flow curves (viscosity η versus shear stress σ) at varying concentrations of Laponite are shown in Figure 3 and Figures S5-S6. For all mixtures, we observed a decrease in

the viscosity with increasing shear stress, indicating that the CNC/L composites exhibit a shear thinning behavior related to the alignment of the solid particles along the shear field. Whatever the CNC concentration, the flow curves still exhibit a finite viscosity at rest (η_0) when the Laponite concentration is lower than 0.5 wt% denoting the fluidity of the phase. By contrast, higher Laponite addition always led to the appearance of a yield stress (σ_y) in the flow curves with a significant shear thinning behavior. Flow curves of complex anisotropic clay dispersions can be modeled using a viscosity-shear model ^{24,58,60} inspired from the Quemada hard-sphere model ⁶¹. This model is based on the definition of an effective hydrodynamic volume fraction. It allows deriving a relevant physical interpretation of the flow curves. The viscosity is defined as:

$$\eta(\sigma) = \eta_{\infty} \left[\frac{1 + \frac{\sigma}{\sigma_c}}{\chi + \frac{\sigma}{\sigma_c}} \right]^2 \quad (2)$$

In this equation, η_{∞} corresponds to the infinite shear viscosity, σ_c represents a critical shear stress that is related to the average potential energy of the system and χ is an adimensional term whose value reflects the state of the suspension: χ is equal to 1 for Newtonian fluids. If only shear-thinning behavior occurs, χ is positive and is equal to:

$$\chi = \left(\frac{\eta_{\infty}}{\eta_0} \right)^{\frac{1}{2}} \quad (3)$$

This parameter becomes negative for solid-like dispersion and the yield stress can be determined:

$$\sigma_y = -\chi\sigma_c \quad (4)$$

Figure 3. Viscosity versus shear stress plots of a) 2.0 wt% and b) 3.0 wt% CNC at varying concentrations of Laponite. The solid lines between the data points represent the fits of the experimental flow curves to the fitting the curves to the viscosity-shear model in equation 1.

Panels c) and d) represent the variation of χ parameter and yield stress σ_y values for different concentrations of Laponite, respectively.

The flow curves were fitted with eq. 2 by adjusting the set of three parameters η_∞ , σ_c and χ using the least-squares method (Figure 3a, b and Figure S6). In most cases, good agreement is obtained between experimental and calculated flow curves, except for the highest concentration of Laponite for which the flow curves display a second inflexion close to the yield stress. This feature can be related to shear banding attributed to the breaking of large structures in the geometry gap of the rheometer^{24,62}. For this case, the flow curves were adjusted only on the high shear stress range. The evolution of the value of χ parameter is represented in Figure 3c. The sol-gel transition defined as the sign inversion of χ occurs around a Laponite concentration of ~0.4 wt%, in accordance with optical observations (Figures 1 and S3). The sol-gel transition seems however slightly shifted to lower clay concentration when the amount of CNC in the binary mixture is increased. The yield stress σ_y values obtained from the viscosity-shear model shows a linear dependence against the concentration of Laponite (Figure 3d) similar to the observations reported for pure clay dispersions^{24,63}. Remarkably, we note that the increase of CNC concentration drastically modifies the mechanical properties of the binary mixtures since the yield stress values are always higher for samples prepared with 3.0 wt% of CNC. Variation of the critical oscillation stress σ_0 with the yield stress σ_y for CNC/L aqueous suspension shows a linear behavior (Figure S7).

To complete this investigation, we performed dynamical rheological experiments on our different CNC/L binary mixtures (Figure 4). Oscillation amplitude sweeps were first carried out depending on the concentration of both CNC and Laponite. The evolution of elastic (G') and

viscous (G'') moduli as a function of shear strain are shown in Figure 4c and Figure S8. The G' and G'' values increase linearly with the concentration of Laponite in CNC suspension. At low shear strain, G' and G'' values are constant corresponding to the so-called linear viscoelastic region (LVR) before they cross over each other. The strain at which G' and G'' intersect is called as yielding strain. The value of shear stress at the limit of the LVR plateau is referred as the critical oscillation stress (σ_0) and is obtained using tangent analysis method. The critical oscillation stress values are plotted against the concentration of Laponite (Figure 4d). As for flow curves, σ_0 increases with Laponite concentration and can be related to the strengthening of the gel phase. Interestingly, a linear relationship is observed between yield stress values obtained from flow curves and the critical oscillation stress from dynamic rheological measurements (Figure S6). This feature confirms the consistency of the results obtained by both methods in defining the yield stress.

Storage modulus (G') and Loss modulus (G'') are plotted against angular frequency for different CNC/L mixtures (Figure 4a and S9). Based on amplitude sweep, we defined a common value of strain for frequency sweep experiments. Regardless of the concentration of Laponite and CNC, G' is always one order of magnitude higher than G'' and almost independent with frequency, for gel samples. This limited dependence of G' values indicates that the arrested phases observed from POM images display an elastic behavior. It is observed that the average values of both G' and G'' increase with the concentration of Laponite in the mixture. To illustrate this point, G' taken arbitrarily at an angular frequency (ω) of 10 rad/s, plotted as a function of the concentration of Laponite (Figure 4b). The storage modulus increases linearly with the concentration of Laponite while the effect of CNC concentration is a

slightly visible with a systematic shift of G' to higher values with increasing CNC amount in the mixtures.

Figure 4. a) Frequency sweep plots of 3.0 wt% CNC with varying concentrations of Laponite b) Elastic modulus G' versus concentration of Laponite at $\omega = 10$ rad/s c) Elastic modulus G' versus shear strain graphs of 3.0 wt% CNC with varying concentrations of Laponite and d) yield stress σ_0 versus concentration of Laponite plot with varying concentration of CNC, G' and G'' are represented by closed and open symbols respectively.

Phase diagram

The physico-chemical properties, the surface properties, dimensions of CNC particles and the ionic strength of the system has a tremendous role in the rheological properties and the phase transitions happening within the system ⁶⁴. The anisotropic shape of Laponite particles along

with its inhomogeneous charge distribution and also the large aspect ratio and easily orienting properties of CNC particles with its self-assembly behaviour makes CNC/L composite system exhibit complex interactions in aqueous systems. The relationship between structure and property as well as the processability of these composite systems can be understood by the rheological and optical studies. At lower concentrations of Laponite, we observed isotropic phases in single component system. However, when we prepared the CNC/L composite system, birefringence is observed even at low concentrations of Laponite (Figure 1). As the concentration of Laponite in CNC suspension increases, the formation of tactoids in the form of anisotropic microdroplets takes place and remain trapped in the arrested phase as evidenced from POM investigations (Figures 1 and S3). In order to form a tactoid, it needs both an attractive and a repulsive energy to gather the mesogens together in the form of a microdroplet and to arrange it in a liquid crystalline order respectively ⁶⁵. We observed that there exists a complex interplay between repulsive and attractive forces as well as the loss of rotational and translational motion in the gel phase which limit the phase separation.

The mechanical properties of CNC/L composite system have also been investigated through rheological studies. The steady state flow curves of CNC/L system shown in Figure 3 depicts the shear thinning behaviour of this system. Due to the alignment of the molecules along the shear field, the system exhibits a shear thinning behaviour as the shear rate increases. The shear thinning behaviour at low shear rates is not significant due to the weak association of the particles in the system ⁶⁶. On increasing the shear rate, there is a tremendous increase in shear thinning behaviour and can be ascribed to the restriction in the motion of particles due to the formation of network structure by CNC and Laponite particles within the system. The formation of lyotropic liquid crystalline phase due to the alignment of particles along the shear field can

also be a reason for this power-law having non-linear behaviour at high shear rates. The pristine CNC aqueous suspensions exhibit Newtonian behaviour and are isotropic till 3.0 wt% concentration ⁶⁶.

Up on the addition of Laponite to CNC, this behaviour gets disturbed and at low concentrations of CNC itself, abundant variations in shear stress can be seen. This behaviour is attributed to the gelation taking place in CNC/L systems which inhibits the particle motion. This is due to the electrostatic interactions taking place between CNC surfaces and Laponite edges, which are having negative and positive charges respectively. Another reason for this is the formation of hydrogen bond between the hydroxyl groups which induces the formation of a 3D network structure. At higher concentrations of Laponite, inflection points can be seen in viscosity versus shear stress graphs (Figure 3) and is due to the process of shear banding in the system. The minimum shear stress required to disrupt the gel structure and to maintain the flow is termed to be the dynamic yield stress. Here, we determined the dynamic yield stress values of the composite system using Quemada model. They all show an increase in the yield stress values with an increase in the concentration of Laponite in CNC aqueous suspensions. This behavior was further verified by performing oscillation tests such as frequency sweep tests and amplitude sweep tests. Linear viscoelastic measurements reveal the gel nature and the complex network formation within our composite system as the G' values are higher than that of G'' and they are almost independent of the angular frequency and also the G' values increase as the concentration of CNC increases which is a clear indicative of the strengthening of the gel structure within the system.

Based on the observations, we propose a phase diagram for the binary mixture system as shown in Figure 5. Phase diagram of CNC/L system shows that it can exhibit two phases, the isotropic

suspension and the birefringent gel. At varying concentration of CNC in aqueous suspension without Laponite, behaves as an isotropic suspension. As we add Laponite to the aqueous suspension of CNC, birefringent gel formation takes place. From 0.5 wt% added Laponite onwards, the CNC suspensions even at very low concentrations exhibit birefringent gel behaviour.

Figure 5. Phase Diagram of CNC/L Composite system. It consists of colloidal fluid (★), isotropic co-gel (■) and birefringent gel states (▲). The schematics of microstructures of isotropic fluid and birefringent gels are shown.

Here, the viscoelastic nature of the system arises mainly due to the presence of CNC and Laponite particles, since water as a solvent has zero G' values at all frequency ranges, a typical property of Newtonian fluid⁴. In total, the self-assembly of CNC and Laponite particles within the CNC/L composite systems are responsible for the enhancement of optical properties as well as the rheological properties like elastic modulus, yield stress and viscosity. The hydrogen bond

which is a reversible non-covalent interaction arising between CNC and Laponite particles, and the depletion interactions between them are mainly responsible for this physical cross-linking and self-assembly of particles leading to the complex structure formation. The incorporation of Laponite probably induces depletion interactions. At low concentration of CNC and high L, it forms cooperative gels (co-gels), where we did not observe any birefringence from the gels. At high concentrations of Laponite, the gel formation is unavoidable at any pH. Hence in the birefringent gel, the structure could be that the CNC particles are trapped as tactoids in the gel formed by Laponite due to the depletion interactions (Figure 5).

The pH values of 3.0 wt% CNC with varying Laponite concentration ranges from 8.26 to 10 with their conductivity values increases in a non-linear manner from 280 $\mu\text{S}/\text{cm}$ to 640 $\mu\text{S}/\text{cm}$ (Figure S10). There is a lot of scope to go to higher concentrations and explore the phase behavior, in particular the transition from isotropic to birefringent gel. It should involve a thorough examination of the effect of aging, salt, temperature or higher concentration of the CNC/L system that will be the scope of a future study.

Elaboration of functional nanocomposites

We first investigated the fabrication of nanocomposites thin films by the solvent evaporation method. The obtained thin films made from the binary mixtures are transparent in nature. Figure 6 (a-d) displays characteristics images of transparent composite films of 3.0 wt% CNC with varying concentrations of Laponite. The transmittance curves for both 2.0 and 3.0 wt% CNC films with varying concentrations of Laponite are reported in Figure S11. The results indicate that the films are transparent over the whole range of wavelength investigated. The

corresponding POM images of the nanocomposite films are reported in Figure 6 (e-l).

Figure 6. Transparent films of 3.0 wt% CNC with a) 0 wt% b) 0.3 wt% c) 0.7 wt% and d) 1.0 wt% concentrations of Laponite. Polarized optical microscopy images of 3.0 wt% CNC with e) 0 wt% f) 0.3 wt% g) 0.7 wt% h) 1.0 wt% i) 1.5 wt% j) 2 wt% k) 2.5 wt% and l) 3.0 wt% Laponite composite films under cross polarizers and λ plate ($\lambda = 530$ nm). SEM images of (m,n) the surface morphology and (o,p) cross sections of 3.0 wt% CNC with (m,o) 0.5 wt% and (n,p) 3.0 wt% Laponite.

The colored pattern exhibited by these films indicates the presence of domains of nematic-like

structures within these films. The microstructure of CNC/L composite films are revealed by SEM images. Figure 6 (m-n) shows the surface morphology whereas figure 6 (o-p) shows the cross-sectional images of dried CNC/L composite films obtained using scanning electron microscope. As the concentration of Laponite increases in the films, the surface roughness seems to be smoother. Similar evolution was also reported for clay films made of mixture of Montmorillonite and Laponite ⁶⁷. From the cross-sectional view, the layered structures are observed in pure CNC and at low Laponite concentrations. With further increase in Laponite concentrations the films change the structure slightly where the alignment of Laponite in the films is disturbed (Figure 6p).

We then investigated the structure by WAXS experiments with the films placed with their normal perpendicular to the incident X-ray beam. In this case, the intensities are modulated in the reciprocal space, depending on the orientation of both CNC and Laponite. All WAXS patterns are anisotropic and display narrow arc reflections, highlighting a strong orientation of Laponite particles in the CNC matrix (Figure 7a-c). Whatever the concentration of Laponite, CNC rods are oriented with their long axis perpendicular to the 00 l axis of the clay platelets. The scattering signal $I(Q)$ was obtained by integration along two perpendicular directions of the WAXS patterns (Figure 7d,e and Figure S12). As shown previously, pure CNC films display three main peaks at 1.06, 1.16 and 1.6 Å⁻¹, which correspond to the characteristic (**1 $\bar{1}$ 0**), (**110**) and (**200**) planes of cellulose I $_{\beta}$. With increasing the concentration of Laponite, these peaks tend to decrease in line with the occurrence of the 00 l Bragg reflections of clay particles. Interestingly, the increase of Laponite concentration in the resulting films also induces a shift of the 00 l Bragg reflections to higher Q -values, suggesting a decrease of the interlamellar distance between Laponite particles. To confirm this trend, we reported in Figure 7f the evolution of basal

spacing determined from the position of the 001 reflection, such as $d = 2\pi/Q$. The d -spacing evolves from 18 to 14 Å with increasing the concentration of Laponite from 0 to 3.0 wt%, whatever the initial concentration of CNC. The lack of CNC effect indicates that this evolution is only due to the swelling behavior of Laponite. However, we obviously did not observe any effect in the other crystallographic directions.

Figure 7. 2D WAXS patterns of thin-films prepared from a 3.0 wt% CNC with a) 0 wt%; b) 0.5 wt% and c) 3.0 wt% of Laponite. Red and grey arrows indicate the hkl contributions of CNC and Laponite, respectively. Corresponding linear scans along d) a vertical line or e) a horizontal line passing through the center of the image for 3.0 wt% CNC films with different Laponite

concentrations. The dotted lines reflect the position of the ($\bar{1}10$), (110) and (200) planes of CNC. f) Evolution of the 001 Bragg reflection of Laponite with the concentration.

Applications of thin-films for the removal of cationic dyes

Rhodamine B dye removal from solution

The adsorbance capacity of CNC/L films are determined by UV-vis spectroscopic studies of films soaked in Rh B dye solution. Figure 8 (a-b, d-e) illustrates the UV-vis analysis as well as the kinetic model fittings of 3.0wt% CNC with 2.0 wt% Laponite films soaked in Rhodamine B dye solution with an absorbance peak of 554 nm. As the soaking time increases, the color of the dye solution gets faded which indicates the adsorption of dye by the films. The inset figures in the absorbance spectra illustrate the evolution of dye solution taken at different time intervals. The dye adsorption capacity of pure CNC films is very limited compared to CNC/L composite films; whose adsorption capacity increases with the concentration of Laponite. In addition, for CNC/L composite films, the adsorption capacity raises quickly within the first five hours before reaching a plateau corresponding to the maximum upload (Figure 8b). Pure Laponite films are very difficult to prepare and to handle since they start to break in the dye solution immediately after soaking.

The adsorption capacity of films is determined using two kinetic models: Pseudo first order (PFO) and Pseudo second order (PSO) kinetic models. According to PFO kinetic model,

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

where q_e and q_t represents equilibrium adsorption capacity and adsorption capacity at different

soaking times respectively (mmol g^{-1}). Here t is the time of adsorption (hours) and k_l is the rate constant (minute^{-1}) of PFO kinetics. Also, PSO kinetics is given by the equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 is the rate constant ($\text{mmol}^{-1} \text{g minute}$) of PSO kinetics^{68–70}. The rate constant and R^2 values obtained from the linear fit of the curve using PSO equation is shown in Table S1 in supporting information. As PSO kinetic model follows a better fit with the experimental data, the adsorption data can be well represented by this model suggesting the mechanism of adsorption to be chemisorption involved between adsorbate and the adsorbent.

Figure 8: a) Absorbance spectra at varying soaking times. b) C_t/C_0 vs soaking time, d) q_t versus time and e) t/q_t vs time (red line indicates the linear fit to PSO kinetics) of 3.0 wt% CNC with 2.0 wt% Laponite films soaked in Rhodamine B dye solution. c) Absorbance spectra at varying

soaking times, f) $\log (q_e - q_t)$ vs time (red line indicates the linear fit to PFO kinetics) of 3.0 wt% CNC with 2.0 wt% Laponite films soaked in Nile blue dye solution.

Nile blue dye removal studies

Figure 8 (c, f) indicates the UV-vis analysis as well as the kinetic model fittings of 3.0 wt% CNC with 2.0 wt% Laponite films soaked in Nile blue dye solution. As the soaking time increases, the color of the dye solution gets faded which indicates the adsorption of dye by the films. The inset figures in the absorbance spectra shows the pictures of films in dye solution taken at different time intervals.

Pure CNC films soaked in Nile blue dye solution started breaking from 4h onwards and there is a peak shift towards shorter wavelength region and a larger absorbance peak is observed due to the small partially dissolved pieces of pure CNC films in the dye solution. The CNC/ lower concentrations of Laponite (0.3 wt% L) composite films get swollen when soaked in Nile blue dye solution and from 3 h onwards, peak shift in the absorbance peak was observed. For CNC/higher concentrations of L (0.7, 1.0 and 2.0 wt% L) composite films, the color of the dye solution gets faded with time which indicates the adsorption of dye by the films.

The rate constant and R^2 values obtained from the linear fit of the curve using PFO equation is shown in Table S2 (Supporting information). As PFO kinetic model follows a better fit with the experimental data, the adsorption data can be well represented by this model. Tables S1 and S2 in Supporting information give the rate constant and R^2 values of PSO and PFO of 3.0 wt% CNC with varying concentrations of Laponite soaked in Rhodamine B and Nile blue dye respectively. Figures S12, S13, S14 and S15 in Supporting information shows respectively the UV-Vis absorbance spectra as well as the PFO and PSO kinetics of 3.0 wt% CNC with varying

concentrations of Laponite films soaked in Rhodamine B and Nile blue dye respectively. Next, we focused our studies on the composite aerogels to study their structure and flame-retardant behavior.

Flame test on aerogels

The CNC/L aerogel samples were prepared via freeze drying method, which has been found to be of light weight possessing a lot of small pores. The method of freeze drying has been used to preserve the gel structure from collapsing due to the effects of drying forces. As shown in figure 9c, the petals of a flower can hold the as prepared aerogel sample indicating that they are too light in weight. The porosity of pure CNC aerogel samples was calculated using the equation, $\text{porosity} = (1 - \frac{\rho_{gel}}{\rho_{CNC}}) \times 100\%$, where ρ_{CNC} is 1.6 g/cm³ and ρ_{gel} is the density of the prepared aerogel. Density of the prepared aerogel was measured by cutting the aerogel sample into cylindrical pieces having height and diameter 0.7 and 1 cm, respectively, and thereby calculating its volume, and the mass of the aerogel in grams is determined by Mettler Toledo weighing balance. The calculated porosity of pure CNC aerogel samples is found to be 96.4%. Similarly, porosity of CNC/L composite aerogel samples are determined using cylindrical shaped aerogel sample of 3.0 wt% CNC and 2.0 wt% Laponite. The height and diameter of the aerogel sample are measured to be 0.7 and 1 cm and the porosity was found to be 98.5 %. CNC/L composite aerogel samples exhibited an enhancement in the porosity as compared to pure CNC aerogels. We performed flame retardant tests on the as prepared aerogels. Pure CNC samples and the CNC/L composite samples were undergone flame tests and the CNC/L composite samples were found to be flame retardant whereas the pure CNC aerogel does not sustain flame test as shown in Figure 9 (d-f). Aerogels made of pure 3.0 wt% CNC, with the given size, got burnt completely

in 18 s, whereas 3.0 wt% CNC with 0.5, 1.0 and 2.0 wt% Laponite, aerogel samples became fire retardant and the images of burnt aerogels at 100s are as shown in figure 9 (g-i). With increase in the concentration of Laponite in the aerogels, they became more and more flame retardant, which is apparent from figure 9 (g-i). An in-depth analysis is needed to understand the internal structure of the aerogels. Thus, the composite aerogels can act as efficient flame-retardant materials, though more thorough tests such varying oxygen, horizontal and vertical flame tests, which may find some new applications as heat insulators in domestic and industrial appliances.

Figure 9: Flame test on pure CNC and CNC/L composite aerogels. Freeze drying process in which a) gel sample turns into b) aerogel by freeze drying method. c) Aerogel on the surface of a flower indicated the light weight of the aerogel. Flame test on 3.0 wt% CNC with d-f) 0 wt % g)

0.5 wt% h) 1.0 wt% and i) 2.0 wt% Laponite aerogel samples.

CONCLUSION

The rheological, optical and structural properties of CNC/L composite system have been carefully investigated here in this paper. We expect that as the concentration of CNC increased, the interparticle distance decreased exhibiting excellent birefringent properties which were confirmed by imaging the samples placed between cross polarizers. Most of the investigated concentrations of CNC/L, the suspensions exhibited elastic behavior since, $G' > G''$ in all the frequency sweep graphs and the viscosity profile confirmed the shear thinning behavior exhibited by the CNC/L composite systems. SAXS experiments reveal limited modifications of the microstructural properties of both Laponite and CNC. It appears that the arrested phase is mainly governed by the Laponite concentration, although the presence of CNC shifts the sol/gel transition to lower Laponite concentration. We proposed a phase diagram for the CNC/L binary system which consists of isotropic fluid, co-gels and birefringent gels. We have shown that the films made of the binary mixtures act as efficient dye removal agents. The films are able to remove cationic dyes such as Rhodamine B and Nile blue. Aerogels made of binary mixtures act as efficient flame blockers. From a fundamental point of view, in the field of colloidal binary mixtures, our system serves as a model binary system with complex interactions, and from an applied point of view, we demonstrated that the transparent composite films act as efficient dye removal agents from the solution. They may be further used in photonic applications and thin films for food packaging applications.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Wide-Angle X-Ray scattering (WAXS) experiments on the powder samples of CNC and Laponite (Figure S1), additional optical textures (Figure S2) and additional POM images of the birefringent gel samples (Figures S3, S4), additional rheological experiments of steady state flow curves (Figures S5, S6, S7), amplitude sweep (Figure S8), frequency sweep (Figure S9), electrical conductivity of the binary mixtures of CNC/L (Figure S10), transmittance of thin films (Figure S11), additional WAXS diagrams of thin-films prepared from a 2.0 wt% CNC with different Laponite concentrations (Figure S12), adsorption kinetics of composite films in Rhodamine B dye (Figures S13, S14) and Nile blue (Figures S15, S16), and R^2 and rate constant values of composite films in Rhodamine B dye (Table S1) and Nile blue (Table S1)

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