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A MINI-REVIEW ON PROPERTIES OF NANOCRYSTALLINE CELLULOSE AND ITS POTENTIAL APPLICATIONS

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Abstract: This work compiles a revision of the more relevant work done on the field of nanocrystalline cellulose (CNC). Including manufacture methods and a variety of material sources for its production, CNC properties and their effect on selected applications are presented. Several approaches on CNC surface modification are discussed, as a tool towards enhanced performance in relevant applications. Finally, self-assembly of CNC behaviour is discussed, together with its implications on rheology and stability of CNC dispersions, as well as optical properties.

Keywords: Nanocellulose, nanocrystals, whiskers, nanowhiskers

1. INTRODUCCIÓN

Further processing of lignocellulosic materials either by strong acid, mechanical or enzymatic treatments yields different degrees of nanocellulose. By controlling and choosing carefully the processing parameters and according to the properties of the resulting material, microfibrillated, nanofibrillated and nanocrystalline cellulose (CNC) can all be obtained. (see Figure 1)

This article will focus on nanocellulose obtained by chemical cleavage of the amorphous region of the cellulose structure, nanocrystalline, also known as cellulose whiskers. Among the different hydrolysis parameters that affect the size, size distribution and the degree of aggregation of the CNC suspension are: the nature of the raw material, reaction parameters (time, temperature, acid-to-pulp ratio and type of acid used. (Postek et al. 2010) Precise knowledge of the size and morphology of the CNC is needed to facilitate product development and provide quality control

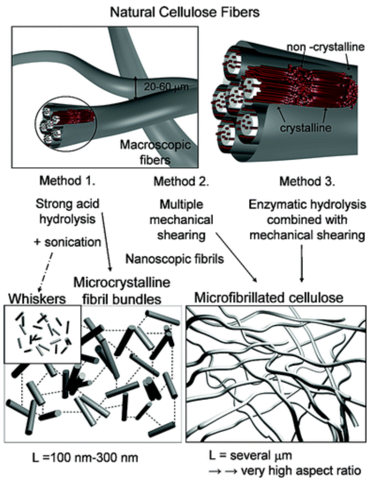

Figure 1. Methods for the disintegration of cellulose fibers. (Pääkkö et al. 2007)

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for manufacturing. Size, polydispersity, morphology of the CNC and aggregation and particle-density of suspension are key properties determining the functionality and prospective application of the material.(Postek et al. 2010)

1.1. Raw materials and production methods

Although treatment of the raw material with strong acid at controlled temperature, agitation and time is the most typical treatment for CNC production, specific protocols were developed for different starting materials.(Habibi, Lucia & Rojas 2010) Among the most common raw materials utilized are plant-based materials such as cotton,(Dong, Revol & Gray 1998) cotton linters,(Roohani et al. 2008) ramie,(Habibi et al. 2008, Peresin et al. 2010b, Zoppe et al. 2009) flax,(Cao et al. 2008b) hemp,(Cao et al. 2008a) sisal, (Siqueira, Bras & Dufresne 2008) wheat straw, (Helbert, Cavaille & Dufresne 2004) palm, (Bendahou et al. 2009) softwood and hardwood, (Beck-Candanedo, Roman & Gray 2005) sugar beet, (Samir et al. 2004) and microcrystalline cellulose. (Bondeson, Oksman 2007a) Additionally, CNC can be obtained from bacterial cellulose,(Araki, Kuga 2001, Araki, Wada & Kuga 2001, Grunert, Winter 2002, Tokoh et al. 1998) tunicates,(Angles, Dufresne 2001, Elazzouzi-Hafraoui et al. 2007) and valonia.(Hanley et al. 1992, Revol 1982)

While the properties of CNC, such as morphology and crystallinity will depend on the source of raw material utilized for its manufacture (see Table 1), remaining charge and colloidal behaviour will be primarily affected by the acid used in the production. Sulphuric and hydrochloric acids are the most widely reported but phosphoric acid (Koshizawa 1960) and hydrobromic acid (Filpponen 2009) were as well utilized.

First introduced by De Nooy et al. TEMPO-mediated surface oxidation of polysaccharides, selectively converts the primary hydroxyl group to a charged carboxyl entity, while the secondary hydroxyl moieties present in the cellulose molecule remain unmodified.(De Nooy, Besemer & van Bekkum 1995) TEMPO-mediated oxidation of native cellulose using NaBr and NaClO in water at room temperature and pH ranges between 9 and 11 were first reported by Saito et al. (Saito, Isogai 2004) TEMPO-mediated oxidation was also performed directly on nanocrystalline cellulose surfaces and the reaction conditions were optimized in order to selectively oxidize the crystal surfaces while keeping the crystal untouched while improving significantly the dispersability of crystals.(Habibi, Chanzy & Vignon 2006, Montanari et al. 2005)

Table 1. Comparison of cellulose nanocrystals properties obtained from different sources. (Moon et al. 2011)

Particle type	L (μm)	W (nm)	H (nm)	Degree of crystallinity (%)
Wood/ plants	0.05-0.5	3-5	3-5	54-88
Tunicate	0.1-4	~20	~8	85-100
Valonia	>1	~20	~20	--
Bacterial	>1	30-50	6-10	63

Where: L = length, W = width, and H = height

Highly dispersible in water nanocrystals suspensions were obtained by TEMPO-mediated oxidation of regenerated cellulose (4-acetamide-TEMPO/NaClO/$NaClO_2$ at 60 ^{o}C and pH = 4.8). The high degree of dispersion, as demonstrated by light transmittance measurements correlates with the higher amount of carboxyl groups present on the crystals, as well as the high shear stress and viscosity values observed on the samples.(Hirota et al. 2010)

Stable dispersions of CNC in water with high content of carboxyl groups were as well reported to be obtained by TEMPO-oxidization assisted with ultrasonic treatment.(Qin et al. 2011)

1.2. Properties of cellulose nanocrystals

Cellulose nanocrystals are low density materials that can be considered stronger than steel (elastic modulus of 145 GPa), and stiffer than aluminum (7.5 GPa).(Eichhorn et al. 2010). Properties are summarized in Table 2. Aspect ratio of nanocrystals is defined as L/d, where L = length and d = diameter), depends on the source and can vary from 1 to 100 (See Table 1).(Samir, Alloin & Dufresne 2005) Aspect ratios also influence properties of the final uses of the nanocrystals, such as percolation threshold and the corresponding reinforcing effect when utilized in nanocomposites. (Habibi, Lucia & Rojas 2010) This is attributed to the fact that a high interfacial area and a high degree of dispersion are reached when the nanocrystals physically interact with the continuous phase where they are contained.(Brechet et al. 2001)

2. USE OF CNC IN DIFFERENT TYPE OF NANOCOMPOSITES AND FUNCTIONAL MATERIALS

CNCs are strong, light and highly resistant to temperature, wear, erosion and corrosion, inexpensive, properties that positionate them as highly competitive when compared to the most popular inorganic fillers currently utilized, such as carbon nanotubes, hydroxyapatite, gold, silver, clay, or silica.(Samir, Alloin & Dufresne 2005)

Thus, CNC are a promise in the field of nanomaterials, not only for their incredibly high reinforcing effect at low dosage,(Postek et al. 2010) but also for being non-toxic, renewable and generally biocompatible and also for having established manufacturing processes.(Postek et al. 2010) Several groups had focused during the last decade, to mimic biocomposites by blending CNC of a variety of sources in different polymer matrixes.(Samir, Alloin & Dufresne 2005) A comparison between CNC properties and those of alternative reinforcing materials is provided in Table 2.

However, in order to transfer CNC properties to higher order structures, a well-controlled alignment and distribution of cellulose nanocrystals within a matrix is absolutely mandatory. This is usually a challenge since CNC tend to agglomerate in non-polar matrix materials.(Li, Yue & Liu 2012) In order to tackle these issues many strategies to selectively modify the nanocesytals surfaces had been attempted.

One of the strategies commonly used is the coating of nanocrystalline cellulose surface by using polymers or surfactant. Successful dispersions in toluene and cyclohexane were obtained after coating CNC with a sufficient amount of commercial surfactant in alkaline form, which were stable even after several weeks.(Elazzouzi-Hafraoui, Putaux & Heux 2009) An addition of anionic surfactant was also added to a CNC dispersion, prior to freeze-drying and it proved to be in the later compounding of the powder with poly-lactic acid (PLA). Although the mixture of CNC in PLA was more homogeneous, some mechanical properties of the CNC/PLA composite were adversely affected due to PLA chain scission in the presence of the anionic surfactant.(Bondeson, Oksman 2007a)

Table 2. Comparison of cellulose nanocrystals properties and alternative reinforcing materials. (Filpponen 2009, Moon et al. 2011, Mitchell 2003, Hussain et al. 2006, Lahiji et al. 2010, Rusli, Eichhorn 2008)

Material	Density (g/cm^3)	Tensile strength (GPa)	Axial Modulus (GPa)	Transv. Modulus (GPa)
Kevlar-49 fiber	1.1-1.4	3.5	124-130	2.5
Carbon fiber	~2,5	~3.5-4.5	72	--
Steel wire	7.8	4.1	207	--
Clay Nano-platelets	--	--	170	--
Carbon nano-tubes	2.1	11-73	270-970	--
Glass fiber	2.6	4.8	86	
CNC	1.6	7.5-7.7	110-220	10-50

In a similar attempt, CNCs were also modified with poly vinyl alcohol (PVA) before incorporating them in PLA. However, important phase separation was observed due to the inmiscibility between the two polymers, leading rather poor mechanical performance of the composites.(Bondeson, Oksman 2007b) Better results were obtained with polyethylene oxide (PEO) coating on CNC prior to its incorporation to low density polyethylene matrix.(Ben Azouz et al. 2011)

PEO (1%) coated CNC (up to 9% in LDPE bases) were utilized to reinforce LDPE and composites were obtained by melt extrusion by freeze-drying the composite dispersion prior to the extrusion process. Contrary to that observed in the case of PLA/CNC-PVA composites, the homogeneity of the extruded materials was excellent and materials with up to 9 % in weight of PEO-coated CNC, and the films were completely transparent, oppositely to that observed in the absence of

PEO. Additionally, increase in the thermal stability of the CNC was observed in the presence of PEO which is ascribed as well to the protective role of PEO on the CNC surface. It is expected that this method could help the incorporation of CNC in polymeric matrix at industrial scale, based on its simplicity and relative low cost.(Ben Azouz et al. 2011)

Another approach to improve dispersability and compatibility of CNC into more hydrophobic matrices is surface grafting. Grafting of N-octadecyl isocyanate on CNC surface was performed and the hydophobized CNC incorporated into a poly-caprolactone (PCL) matrix. However, a high degree of aggregation was observed leading to a limited reinforcing effect when compared to the same procedure but utilizing nanofibrillated cellulose instead of CNC.(Siqueira, Bras & Dufresne 2008)

CNC were reported to be used as reinforcing agent of hemicelluloses hydrogels. CNC were first coated with 2-hydroxyethylmethacrylate modified hemicelluloses and methacrylic functional groups were grafted from the surface, serving as a template for polymerization and nextwork formation. Hydrogels with excellent mechanical, recovery, water holding capacity were superior to hydrogels obtained by traditional methods and with no CNC addition. Furthermore, some of the measured properties were comparable to natural tissue with hydrogel-like properties, thus this material is envisioned as a potential replacement for articular cartilage.(Karaaslan et al. 2011)

Partially silylated CNC was reported to be dispersible in various solvent of low polarity while keeping the nanosized structure and optical properties on the dispersed state. However, long reaction times were reported to destroy both, morphology and crystalline structure of the particles, evidencing the need of controlled reaction conditions for a successful modification. An additional disadvantage of this approach is the use of toxic solvents such as toluene.(Goussé et al. 2002)

Modified CNC with sizing agents such as alkyenyl succinic anhydride (ASA) followed by drying, heating and freeze-drying were completely dispersible in dioxane with no changes on their crystalline structure. Heating time was observed to strongly influence dispersibility degrees.(Yuan et al. 2006)

It was also reported that aqueous suspensions of unmodified CNC were freezed dried and successfully re-dispersed in DMF. In this case, homogenization of the dispersion was assisted with vigorous magnetic agitation and ultrasonic treatment and the stabilization of the dispersion was explained due to the high value of the solvent dielectric constant.(Samir et al. 2004) In a similar attempt, freeze-dried CNC were directly mixed with DMSO and formamide followed by strong sonication treatment.(Viet, Beck-Candanedo & Gray 2007)

An alternative and effective approach to deal with the aggregation drawback of CNC after drying was reported using fast freezing of sulphate groups esterified CNC, thus entrapping the nanocrystals in ice cubes and then freeze-drying them. During the process, shrinkage was not observed and CNC with different shapes (rod, spheres and network) were obtained and their dispersibility was fully recovered, maintaining crystalline structure and high surface area.(Lu, Hsieh 2010)

Among the different polymeric matrices reinforced by different approaches with CNC are poly (lactic acid) (PLA) solution,(Li 2010) polyacrylamide nanocomposite in the form of a hydrogel,(Zhou, Wu & Zhang 2011) poly(3-hydroxybutyrate-co-3-hydroxyvalerate,(Ten et al. 2012) waterborne polyurethane (WPU) based on castor oil (CO)/polyethylene glycol (PEG),(Gao et al. 2011, Yu et al. 2012) epoxy resin,(Wu et al. 2011) polystyrene,(Rojas, Montero & Habibi 2009) poly(ε-caprolactone),(Zoppe et al. 2009) and even cellulose itself,(Vallejos, Peresin & Rojas 2012) among others. Due to its natural affinity through hydrogen bonding, poly(vinyl alcohol) is one of the polymeric matrices more used to be reinforced with CNC, in both cast films (Li et al. 2011, Paralikar 2006) and electrospun nonwovens.(Peresin et al. 2010b, Peresin et al. 2010a)

2.1. Hybrid materials

By mixing CNC with amorphous calcium carbonate (ACC), hard and transparent hybrids with high content of inorganic matter (up to 53%) were obtained. Such materials are of potential interest in packaging and labelling industries. (Gebauer et al. 2011)

Hybrid materials containing CNC were utilized as electrochemical sensors to selectively detect DNA hybridization. Silver nanoparticles were reported to be obtained onto TEMPO-mediated oxidized CNC by using $NaBH_4$ as a reducing agent. The presence of CNC proved to be useful in avoiding the aggregation of the nanoparticles.(Liu et al. 2011)

Photocatalytic and photoelectronic properties of nanosized TiO_2 particles, make them very attractive in application areas such as catalysis, gas sensors, solar energy conversions. Moreover, the morphology of the TiO_2 particles has a great influence on their performance, and they are synthetized in several shapes such as spheres, rods, needles, etc. The synthesis of TiO_2 nanocubes is reported as a long, time consuming and performed in extreme reaction conditions reaction.(Chemseddine, Moritz 1999, Kuznetsova et al. 2005) CNCs were used as morphology-inducer and coordinate agent for the synthesis of TiO_2 nanocubes, in milder reaction conditions. TiO_2 nano-cubes obtained with this method were uniform in size and with a narrow particle size distribution. Crystallinity of the nano-cubes was observed to be high and no evidence of the presence of CNC was observed based on thermal analysis, implying that the CNC are embedded on the TiO_2 nano-cubes. Although the reaction mechanism of nano-cube synthesis in presence of CNC is not yet totally understood, nucleation of the CNC and stabilization of the formed nanoparticles are speculated to be the reason.(Zhou, Ding & Li 2007)

Additionally, CNC were utilized as reducing agent for synthesising Pt nanoparticles, taking advantage of both, the reducing end-group present of cellulose and the high surface area of CNC. (Johnson, Thielemans & Walsh 2011) This procedure was utilized to produce Pt-NPs supported in carbon black for electrocatlysis applications. Such material was successfully tested as catalyst for oxygen reduction reaction with specific activity similar to existing methods. It was demonstrated that naturally abundant, renewable and low cost CNC is a feasible alternative to the traditionally used reducing agents.(Johnson, Thielemans & Walsh 2011)

2.2. Stimuli-responsive materials

CNC has a great potential to be used in bottom-up engineering of nanoscale devices such as mini-sized electronics, sensors, and biomedical devices.(Dong, Roman 2007) Following, some relevant examples of such applications are included.

TEMPO-oxidized CNC were grafted with single stranded oligonucleotides with an amino modifier. After this and using the molecular recognition ability of the oligomeric base pairs, they were duplexed with complementary oligonucleotides grafted onto separate CNC batch. With this study, the concept of self-assembly of CNC with alternative bio-nanoparticles via DNA-coupling is proven. Such hybrid materials have a wide potential in the areas of tissue engineering and bio-medicine.(Mangalam 2008)

By using double-click chemistry, cellulose nanoplatelet gels were obtained through grafting amine-monomers on the surface of TEMPO-oxidized CNC. By this method, it was possible to obtain a regularly packed arrangement of crystals, demonstrating a degree of molecular control for creating these structures at the nano-level.(Filpponen, Argyropoulos 2010) Based on this approach, fluorescent coumarin and anthracene chromophores were attached to TEMPO-oxidized CNC via double-click chemistry. Posterior UV-irradiation induced the dimerization of the installed side chains of individual crystals, forming CNC nano-arrays. Potential applications of such materials include photo-recording devices, liquid crystal displays and additional photo-sensitive uses.(Filpponen, Sadeghifar & Argyropoulos 2011)

pH responsiveness of CNC with either carboxylic acid or amine moieties on their surfaces was demonstrated by modified properties displayed by CNC dispersion. While in acidic conditions amine modified-CNC inhibited aggregation of the dispersion, based on electrostatic repulsions, at neutral pH, hydrogels were formed, induced by hydrogen-bonding attractive forces. As expected, opposite behaviour was observed for carboxylic acid modified CNC. Incorporation of these pH responsive CNC into poly(vinyl acetate) matrix proved a higher value added to the already mechanically adaptive nanocomposite. (Way et al. 2012) pH sensors were also obtained by dual fluorescent labelling of CNC by labelling the CNC with analyte responsive dyes bearing a suitable functional group. Activity of the modified CNC was proven by exposure of the dispersions to different pH and measuring corresponding fluorescent emission intensities at different wavelengths.(Nielsen et al. 2010)

Stimuli-responsiveness of rubbery polymers when doped with CNC was demonstrated based on the three-dimensional network formed by the CNC and how it responds towards the effect of a chemical regulator. This study was inspired on the sea cucumber's dermis property of reversibly switching its stiffness, mechanism regulated by a switchable interaction between collagen fibrils reinforcing a low-modulus polymeric matrix. Ethylene oxide-epichorohydrin copolymer was reinforced with CNC, exhibiting a reversible decrement of tensile modulus by a factor of 40 based on interaction with water.(Capadona et al. 2008) These concept was proven in electrospun PVA nanofibers mat weinforced with CNC, which showed a fully reversible mechanical response under the effect of humidity cycles.(Peresin et al. 2010a) A step ahead, a recently published work introduces the development of a nanocomposite material with a rapidly switchable shape memory combined with specific programming, once again based on water as the chemical actuator.(Zhu et al. 2012) Shape memory of CNC-reinforced polyurethane films was also observed as a result of temperature change and water immersion. Such rapid switchable water sensitive shape-memory materials could broaden the application of CNC in smart textiles, e.g. breathable clothing, (Zhu et al. 2012) Following the same line of research, more advanced and recent studies lead to the development of microelectromechanical systems (MEMS) based on poly(vinyl acetate)-CNC reinforced materials towards the development of intracortical neural recording probes(Hess et al. 2011) demonstrating the versatility and potential of this material.

3. SELF-ASSEMBLY OF CNC SUSPENSIONS

Hierarchical bottom-up assembly of anisotropic materials are a hot-topic nowadays when it comes to the development of functional devices such as sensors, electro-optical devices, transistors and structural materials. All rod-like materials present the particularity of forming lyotropic liquid crystalline phases at a given concentration, (Davis 2011) and CNC are not an exception.

A lyotropic liquid crystal is by definition a dispersion of anisotropic macromolecular entities in a solvent. In such system, phase transitions are governed by changes of the anisotropic mesogen concentration (being a mesogen the fundamental unit of a liquid crystal that induces structural order in the crystals). A second category of liquid crystal is called thermotropic; it consists in small molecules with rigid cores, which phase changes respond to changes in temperature. (Davis 2011) In the case of CNC, discussion will focus on lyotropic systems.

Depending on particles properties and external conditions, the liquid crystalline ordered phase can be described as:(Donald, Windle & Hanna 2006) nematic (rod-like molecules oriented along the director with a long range orientational order but a short range positional order), chiral nematic or cholesteric (the nematic microstructure is twisted along an axis perpendicular to the director. Self-ordering of nanocrystals in these suspensions results in the formation of chiral nematic liquid crystal phases. This phenomenon has made possible new applications based on optical properties of the solidified liquid crystals.(Hasani et al. 2008)) or smectic (has both longe range orientational and positional order).(Dong et al. 1996)

Phase transitions of lyotropic suspensions are strongly influenced by aspect ratio of the nanorods, and depend on the concentration of the nanoparticles in suspension.

In dilute systems, the nanoparticles rotate freely purely by Brownian motion. However, in a semi-dilute system, the rotation of the particles start to get inhibited until the concentration reache the limit where the particles motion is confined to small volumes (known as isotropic concentration). Once a critical concentration is reached, the system is in the biphasic region, where there exists the equilibrium between some particles in an anisotropic phase with those in the isotropic phase. Once a second critical concentration is reached, the system becomes fully liquid crystalline (see Figure 2)

The tendency of CNC to self-assemble along a vector director is inherent to its rod-like rigid particles nature.(de Souza Lima, Borsali 2004)

Due to the birefringent characteristic of cellulose, the alignment of CNC create a microscopic birefringence that can be observed though cross-polarizers.(Habibi, Lucia & Rojas 2010)

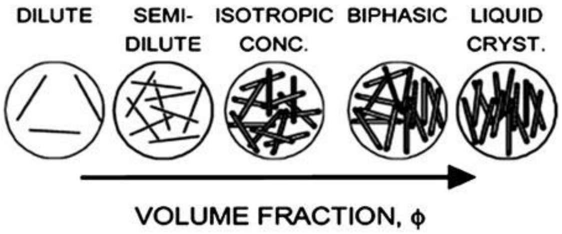

Figure 2: Phase behavior of fluid dispersed rods. (Davis et al. 2004) Reproduced with permission of American Chemical Society. Copyright © ACS 2004

Aqueous diluted supensions of CNC do not maintain an order (isotropic phase). However, at increasing concentrations, domains of CNC coalesce to form unidirectional and self-oriented phase (anisotropic). Figure 3 shows a schematic representation of isotropic and anisotropic (chiral nematic) arrangement of rod-like nanoparticles.(Habibi, Lucia & Rojas 2010, Araki et al. 2000)

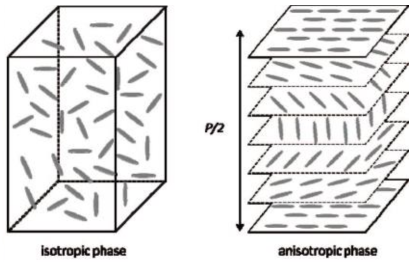

Figure 3. Schematic representation of CN orientation in both the isotropic and anisotropic (chiral nematic) phases (Habibi, Lucia & Rojas 2010) Reproduced with permission of American Chemical Society. Copyright © ACS 2010

Above certain critical concentration of chiral nematic formation, suspensions of CNC in water can form shear birefringence, while after a certain period of time at rest, the suspension can spontaneously separate into an isotropic and an anisotropic.(Habibi, Lucia & Rojas 2010, Araki et al. 2000)

Ordered nematic phases in suspensions free of electrolytes can present critical concentrations between 1 and 10% wt. depending on the charge density of the system.(Habibi, Lucia & Rojas 2010) It was demonstrated that in the case of acidic CNC suspensions, while the total concentration of nanocrystals was maintained below 4.55 % wt. the suspension was completely isotropic (monophasic). With increasing concentration, a biphasic system was formed until a critical concentration was reached (in this system, equivalent to 13.1 % wt.) where the system showed complete anisotropy. As opposite to that observed with neutral rods, the concentration in each phase of the biphasic stage, was proportional to the concentration of the total suspension.(Dong et al. 1996)

Equilibrium concentration, where isotropic and anisotropic phase coexist can be affected by several parameters such as hydrolysis conditions, mineral acid used in the hydrolysis, size of the particles, concentration, temperature, ionic strength and external forces.

Size distribution plays a role on the liquid crystal phase formation;(Dong, Revol & Gray 1998, Beck-Candanedo, Roman & Gray 2005) liquid crystalline phase is first formed by larger particles while the smaller ones remain in the isotropic phase.(Dong, Revol & Gray 1998, Hirai et al. 2008) Prolonged hydrolysis times yield shorter cellulose nanocrystals with a narrower dispersity; thus in CNC suspensions with such characteristics, critical concentration was observed to be higher than in the case of suspensions with larger nanocrystals. Same tendency towards higher critical concentration was found with increasing acid-to-pulp ratio, where nanocrystals with smaller dimensions and a narrower biphasic range were obtained. Such behaviour was confirmed and comparable in the case of both softwood and hardwood as starting materials for CNC production.(Beck-Candanedo, Roman & Gray 2005) TEMPO-mediated oxidized CNC presented birefringent behaviour due to parallel alignment of individual crystals, however no chiral-nematic behaviour was observed after concentrating the suspensions. Reasons for the lack of ordering were speculated as too high polidispersity and viscosity that leads to a higher level of disorder in the suspension.(Habibi, Chanzy & Vignon 2006, Montanari et al. 2005)

Additionally to the particle size and geometry, critical concentration for phase separation was shown to be strongly influenced by the addition of electrolytes, as well as the size of the counterions, having its effect on its chiral pitch.(Dong et al. 1996) Chiral nematic pitch is directly associated to chiral twisting interactions of the system and it is one of the important properties of the chiral nematic anisotropic phase.(Dong, Gray 1997a)

An increase on the ionic strength was proved to both, decrease the cholesteric pitch of the suspensions and the fraction of particles on the anisotropic phase. This behaviour is similar to that observed in the case of polyelectric polymer dispersions.(Orts et al. 1998) Additionally, the fraction volume required for the anisotropic phase was found to increase accordingly to the counter-ion size, confirming a balance between steric repulsion and hydrophobic attractions in the case of phase equilibrium.(Dong, Gray 1997a)

A new 'birefringent glassy phase' was found when CNC suspension with reduced charge was prepared by using HCl acid instead of sulphuric acid and varying the amount of surface charge by postsulfonation treatment.(Araki et al. 2000) Neutral suspension was isotropic with shear birefringence at low solid content (ca. <1%). At slightly larger solid content (~2-3%), the suspension was still flowing but showed intricate birefringent patterns, which remained after the flow had ceased. Only at high solid content (7.1%), the suspension became too viscous to flow and showed a frozen-in birefringent crosshatched pattern. Significantly different to the behaviour of CNC obtained from sulphuric acid hydrolysis, this postsulfated suspension formed a "birefringent glassy phase" comparable to that observed for boehmite rod suspension. (Araki et al. 2000)

Shear and magnetic fields applied on CNC suspensions, were proved to alter the alignment of the CNC suspensions. Although it was demonstrated that shear applied to the suspension disrupts the cholesteric alignment,(Orts et al. 1998, Pan, Hamad & Straus 2010) it was later proved that the chiral pitch is conserved in films dried under the force of a magnetic field, however experimenting an increase.(Pan, Hamad & Straus 2010) Chiral nematic phase of an aqueous CNC dispersion can also be modified by magnetic field. The chiral nematic axis was aligned in the field direction by applying a static magnetic field, forming highly regular patterns. On the other hand, a nematic-like alignment was observed by unwinding the helixes when a rotating magnetic field was applied to the dispersion.(Kimura et al. 2005)

This discovery opens CNC applications scope towards optically active materials, for example for security papers.(Pan, Hamad & Straus 2010) Films with pitchs on the scale of light wavelength can act as interference devices that reflects circularly polarized light at a certain wavelength number,(Orts et al. 1998) therefore, the observed colour of the film will depend on the pitch and the angle of incident light.(Pan, Hamad & Straus 2010)

3.1. *Stability of CNC suspensions in different media*

Araki et al. compared CNC obtained from same raw material (bleached softwood kraft pulp) by hydrolysis with two different strong acids such as H_2SO_4 and HCl,(Araki et al. 1998) While the conductivity of HCl-treated CNC is almost undetected by conductometric titration of the suspensions, suspension of H_2SO_4 CNC has a surface charge of 84 m-equiv kg−1 dry material due to the introduction of sulfate groups. This difference in surface charge is directly responsible for the different colloidal stability of CNC dispersed in water. While both CNC suspensions form a stable colloidal suspension, HCl-hydrolyzed crystals precipitate with an addition of at about 0.4 mM electrolyte as its H_2SO_4 counterpart needs electrolyte concentrations higher than 20 mM to precipitate.(Araki et al. 1998)

Chiral-nematic structure was observed to be maintained in highly concentrated surfactant coated CNC dispersed also in non-polar solvent. Additionally, it was observed that it was possible to obtain much higher concentrations in such dispersions.(Heux, Chauve & Bonini 2000) Self-assembly and chiral nematic properties of such dispersion were studied in order to unveil the mechanism responsible for the stabilization in non-aqueous systems.(Elazzouzi-Hafraoui, Putaux & Heux 2009) Since it does not exist any electrostatic interaction between the surfactant-coated CNC, the liquid crystal phase occurrence can be explained in terms of particle-particle attractive interaction and a strong steric stabilization provided by surfactant moieties. Also, in non-polar media chiral, nematic pitches were reduced to half the values observed in the case of water, presumably due to chiral interactions in the low dielectric constant media. Same phases transitions were observed in CNC dispersed in ciclohexane than those observed in aqueous systems. Although critical concentrations for the chiral nematic phase transition were observed to be much lower than compare to aqueous dispersions.(Elazzouzi-Hafraoui, Putaux & Heux 2009)

Mechanisms of stabilization based on steric effects and enhanced electrostatic repulsion were also attempted by carboxylation or grafting on the surface of the nanocrystals.(Habibi, Chanzy & Vignon 2006, Montanari et al. 2005) Stabilization of CNC suspensions obtained by hydrolysis using sulphuric acid was reported by cationization using Epoxypropyltrimethylammonium (EPTMAC).(Hasani et al. 2008) In this case, the electrostatic stabilization is due to the trimethylammonium chloride groups present on the CNC surface, which in terms are also responsible for thixotropic gel behaviour of these suspensions. Additionally, such rheological behaviour was addressed as the reason for the particular absence in this CNC grade, of chiral nematic liquid crystalline phases at equivalent concentrations than in the case of anionic CNC.(Hasani et al. 2008)

3.2. *Rheological behavior of the CNC suspensions*

The choice of acid for the production of CNC influences the properties of the dispersion of the nanocrystals in water. This dispersability is directly related to the amount of surface charge remaining on the crystals. While CNC produced by sulphuric acid hydrolysis are esterified with sulphate groups, and this negative charge provides an inherent electrostatic stabilization when dispersed in water, CNC with reduced surface charge obtained by hydrolysis with HCl present a limited dispersability in water.(Beck-Candanedo, Roman & Gray 2005, Samir, Alloin & Dufresne 2005, de Souza Lima, Borsali 2004)

Regarding rheological behaviour, H_2SO_4-treated suspension shows no time dependence in viscosity for a wide range of concentrations (between 5 and 16 g/l), while HCl-treated suspension was thixotropic at high concentrations (> 0.5% (w/v)) and anti-thixotropic in dilute conditions (< 0.3% (w/v)) as shown by Araki et al.(Araki et al. 1998) Thyxotropy behaviour of HCl-treated CNC was ascribed to an effect of inter-particle aggregation taking place in static condition and being destroyed by shear flow. Increased distance between particles in the dilute suspension reduces the interaction between particles and it results in anti-thixotropy behaviour when the particles are aligned due to shear flow. Both CNC suspensions showed shear-thinning behaviour, however, while the shear-dependence of viscosity in the case of H_2SO_4 hydrolyzed CNC was rather weak, probably due to flow-orientation of the particles as explained by the authors, a steep decline of viscosity was observed in the case of HCl-treated CNC suspension. This behaviour is ascribed to the breakdown of flocculates that originates its thixotropic behaviour. (Araki et al. 1998)

Bercea and Navard discussed the shear rheology of CNC suspensions in terms of the orientation of the nanoparticles and concentrations. When compared to spherical particles, study of the flow of CNC particles must take into consideration the orientation vector of the particles.(Bercea, Navard 2000) At rest, the dilute case is the simplest of all since the particles are not interacting with one and other. With increasing concentration, interaction between particles has a synergetic effect on the flow behaviour, and in semi-dilute suspensions, rotational relaxation times of the rods increase with the square of the concentration of the suspension.

4. OPTICAL PROPERTIES OF CNC

Under controlled conditions, the chiral nematic order observed in CNC colloidal suspensions, can be maintained after drying. Therefore, optically active films can be prepared and its optical properties can be tuned by changing preparation conditions such as salt concentration thus, modifying the degree of order on the film.(Edgar, Gray 2001) Inherent negative magnetic susceptibility of cellulose was proved already in 1992 by Sugiyama et al.(Sugiyama, Chanzy & Maret 1992) Based on this, the chiral-nematic phase formed by colloidal CNC aqueous suspension above a critical concentration can be affected by applying a strong magnetic field.(Dong, Gray 1997b) When a magnetic field is applied during drying of the CNC suspension, it is possible to obtain films with highly ordered texture, independently of the ionic strength of the original suspension.(Edgar, Gray 2001) Aligned ultra-thin films of CNC were obtained by using a convective-shear assembly setup. By using this setup, order achieved by the CNC was similar to that obtained by high electric field. Such alignment was explained in terms of a force balance including hydrodynamic, surface tension and electrostatic interactions. Surface strength was improved as a result of the crystals alignment, which is expected to broaden application ranges of these materials.(Hoeger et al. 2011)

By increasing the ionic strength of the system, a decrease in the chiral nematic pitch of the suspension can be achieved via tightening the helix of the system.(Dong et al. 1996) In this way, it is possible to obtain films that reflect in different regions of the wavelength spectrum. While salt-free CNC suspensions reflect in the IR region, the addition of a specific amount of NaCl to the suspension yields films that reflect in the visible and ultraviolet regions of the spectra (Edgar, Gray 2001).

Additionally, improved optical activity on CNC iridescent films for covert encryption (based on the fact that the films reflect left-circularly polarized light) was obtained by addition of TINOPAl, an optical brightening agent that exhibits strong fluorescence when excited at UV wavelengths. TINOPAL doped CNC films possess a higher chiral nematic pitch, altering the domain structure of the solid film. This sort of material offers an additional feature for the development of security papers since such features cannot be photocopied.(Zhang et al. 2012)

5. USE OF CNC IN EMULSIONS STABILIZATION

Colloidal particles with the particularity of getting partially wetted by both aqueous and oil phase have the ability to stabilize emulsions, so-called Pickering emulsions.(Pickering 1907) Microcrystalline cellulose had been utilized for many years as stabilizer of oil in water (o/w) emulsions for the food industry and also as foam stabilizer.(Thomas 1982) Such stabilizing effect of MCC was shown to be based on both, the active role of the interface, together with a 3-D network formed in the continuous phase, thus retarding the coalescence of the droplets. Stabilization of emulsions was also reported in the presence of unmodified bacterial cellulose,(Ougiya et al. 1997) and hydrophobized (by silylation) degrees of microfibrillated cellulose.(Andresen, Stenius 2007, Andresen et al. 2006) Due to their smaller size, and inherent higher specific area, CNC is expected to respond superiorly in such application.

Hexane/water interface was succesfully stabilized by using unmodified nanocrystalline cellulose. The emulsions were reported stable for several months, in the form of a monodispersed emulsion with defined (4 μm in diameter) oil in water (o/w) droplets providing a promising, healthier and environmentally friendlier alternative to synthetic surfactants.(Kalashnikova et al. 2011)

Stability of pickering emulsion (30/70 ratio (o/w), with a 5 g/L suspension of CNC in the water phase) was proved at different temperatures and even after various mechanical treatments where no drop size or coalescence were observed, evidencing an irreversible adsorption of the CNC to the interface over a sensible period of time.(Kalashnikova et al. 2011)

A more accurate control of the stability of such emulsions can be attained by modifying the colloidal cellulosic particles by surface grafting of responsive polymers. Temperature-responsive Poly(N-isopropylacrylamide) (poly(NIPAM)) grafted CNC were proven as very effective on the stabilization of Pickering emulsions.(Zoppe, Venditti & Rojas 2011) Figure 4 shows optical images of emulsions prepared with two different concentrations of poly(NIPAM) grafted CNC.

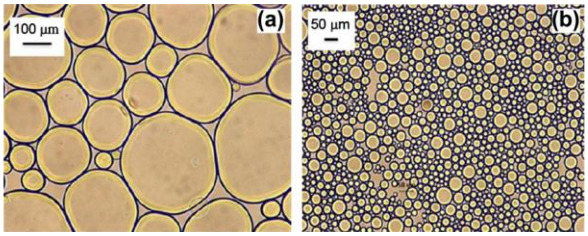

Figure 4. Optical microscopy images of emulsions prepared with 0.05% (a) and 0.5% (b) poly(NIPAM)-g-CNCs prepared with water-to-oil ratio = 1 (Zoppe, Venditti & Rojas 2011) Reproduced with permission of Elsevier. Copyright © Elsevier 2012

While the droplet size and the stability of the droplets to coalesce in the emulsion are ruled by the concentration of nanoparticles present on it, ionic strength contributes to regulate electrostatic interactions between neighbouring nanoparticles at the interface oil-water.

Independently of the poly-NIPAM-g-CNC concentration, heptane-in-water emulsions were stable up to 4 months. As expected, after heating treatment of the emulsion above the lower critical solution temperature (LCST) for only one minute, the emulsions were broken. As elucidated on rheological basis, increasing viscosity of the emulsions were observed while approaching the LCST, indicating coalescence of the oil droplets at the time of the collapse of the poly(NIPAM) brushes grafted on the CNC surface. Also, the smaller the droplet size in the emulsion, the higher the detected viscosity. The addition of salt to the system, proved to improve the stability of the emulsion, based on a reduction on steric and electrostatic repulsion between adjacent poly(NIPAM)-g-CNC particles at the interface. Such controlled stability of the Pickering emulsions could eventually improve advances in areas such as cosmetics, food industry and even bio-medicine.

6. CONCLUSIONS

Obtained by mild acid hydrolysis of cellulosic materials, nanocrystalline cellulose is an outstanding material that holds superior properties with potential application in limitless areas. With remarkable mechanical properties, CNC provides a great opportunity for incorporation as reinforcing material in many different polymers. Economic feasibility of composite materials incorporating CNC relies on enhanced properties of polymeric materials even at low dosages of CNC.

Among additional applications of CNC, their polyol nature provides a template for chemical functionalization towards more sophisticated entities with scopes of utilization in stimuli-responsive materials. Furthermore, it is possible to obtain added-value materials with optical, electrical and magnetic response due to the natural self-assembly tendency of CNC.

Based on the simplicity of their production methods of CNC and the discussed properties, there exists a great commercialization potential on CNC production with a wide scope of potential applications.

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