CHEMISTRY AND APPLICATIONS OF NANOCRYSTALLINE CELLULOSE AND ITS DERIVATIVES: A NANOTECHNOLOGY PERSPECTIVE

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Nanocrystalline cellulose (NCC) is an emerging renewable nanomaterial that holds promise in many different applications, such as in personal care, chemicals, foods, pharmaceuticals, etc. By appropriate modification of NCC, various functional nanomaterials with outstanding properties, or significantly improved physical, chemical, biological, as well as electronic properties can be developed. The nanoparticles are stabilised in aqueous suspension by negative charges on the surface, which are produced during the acid hydrolysis process. NCC suspensions can form a chiral nematic ordered phase beyond a critical concentration, i.e. NCC suspensions transform from an isotropic to an anisotropic chiral nematic liquid crystalline phase. Due to its nanoscale dimension and intrinsic physicochemical properties, NCC is a promising renewable biomaterial that can be used as a reinforcing component in high performance nanocomposites. Many new nanocomposite materials with attractive properties were obtained by the physical incorporation of NCC into a natural or synthetic polymeric matrix. Simple chemical modification on NCC surface can improve its dispersability in different solvents and expand its utilisation in nano-related applications, such as drug delivery, protein immobilisation, and inorganic reaction template. This review paper provides an overview on this emerging nanomaterial, focusing on the surface modification, properties and applications of NCC.

Keywords: nanocrystalline cellulose, chemical modification, applications

INTRODUCTION

Cellulose is the most abundant natural biopolymer on earth, which is renewable, biodegradable, as well as non-toxic. It is a carbohydrate polymer made up of repeating β-D-glucopyranose units and consists of three hydroxyl groups per anhydroglucose unit (AGU) giving the cellulose molecule a high degree of functionality. The knowledge of the molecular structure of cellulose is of prime importance as it explains the characteristic properties of cellulose, such as hydrophilicity, chirality, biodegradability and high functionality. As a renewable material, cellulose and its derivatives have been widely studied, focusing on their biological, chemical, as well as mechanical properties. The materials based on cellulose and its derivatives have been used for more than 150 years in a wide variety of applications, such as food, paper production, biomaterials and pharmaceuticals (Coffey et al., 1995; de Souza Lima and Borsali, 2004).

Nanocrystalline cellulose (NCC) obtained from acid hydrolysis of cellulose fibres, has been realised as a new class of nano-materials. Compared to cellulose fibres, NCC possesses many advantages, such as nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc. These amazing physicochemical properties and wide application prospects have attracted significant interest from both research scientists and industrialists. Gray and co-workers have conducted extensive research on NCC, and they have made important contributions to the understanding of NCC. A recent review on NCC was reported by Habibi et al. (2010a), where the chemical structure, composition and their relationship to the optical and mechanical properties of NCC were discussed. At present, nanoscience and

nanotechnology are disciplines that have been highlighted for special focus by many funding agencies and government. Many novel products have been created and developed based on nanotechnology. Undoubtedly, the exploitation of NCC will become a bridge between nanoscience and natural resource products, which could play a major role in reviving the forest industry in Canada and countries with abundant forest resources.

In this review, recent developments on surface modification, physicochemical properties, and applications of NCC will be considered and discussed. Above all, the production and morphology of NCC are described, and some of their unique solution properties highlighted. A variety of surface functionalisation routes will be considered, where the focus is on improving the dispersability of NCC in different solvents, thereby expanding their applications in various market sectors. Some potential applications of NCC include nanocomposite films, drug delivery, protein immobilisation and metallic reaction template.

GENERAL ASPECT OF NANOCRYSTALLINE CELLULOSE

Nanocrystalline cellulose derived from acid hydrolysis of native cellulose possesses different morphologies depending on the origin and hydrolysis conditions. NCCs are rigid rod-like crystals with diameter in the range of 10–20 nm and lengths of a few hundred nanometers (Figure 1); e.g. crystallites from tunicates and green algae have lengths in the range of a few micrometers and crystallites from wood and cotton have lengths of the order of a few hundred nanometers, while some spherical shape NCCs were also produced during the acid treatment (Zhang et al., 2007; Wang et al., 2008). Therefore, the relative degree

of crystallinity and the geometrical aspect ratio, i.e. the length-to-diameter (L/d) are very important parameters controlling the properties of NCC-based materials. An important characteristic of NCCs, when prepared in sulphuric acid, is that they possess negative charges on their surface due to the formation of sulphate ester groups during acid treatment, which enhances their stability in aqueous solutions. In order to characterise the morphology of NCC, various types of instruments can be used. The most conventional and common one is the transmission electron microscopy (TEM) (Araki et al., 1998), which can directly provide high-resolution images. Moreover, scanning electron microscopy (SEM) (Miller and Donald, 2003), atomic force microscopy (AFM) (Pranger and Tannenbaum, 2008), small angle neutron scattering (SANS) (Terech et al., 1999) and polarised and depolarised dynamic light scattering (DLS, DDLS) (de Souza Lima and Borsali, 2002; de Souza Lima et al., 2003) were also employed to study the morphology of NCC.

PRODUCTION OF NCC

Acid treatment (acid hydrolysis) is the main process used to produce nanocrystalline cellulose, which are the smaller building blocks released from the original cellulose fibres. Native cellulose consists of amorphous and crystalline regions, and the amorphous regions have lower density compared to the crystalline regions, so when cellulose fibres were subjected to harsh acid treatment, the amorphous regions break up, releasing the individual crystallites. The properties of NCC depend on various factors, such as cellulose sources, reaction time and temperature, and types of acid used for hydrolysis. Since Rånby (1951) first reported that colloidal sulphuric acid-catalysed degradation of cellulose fibres,
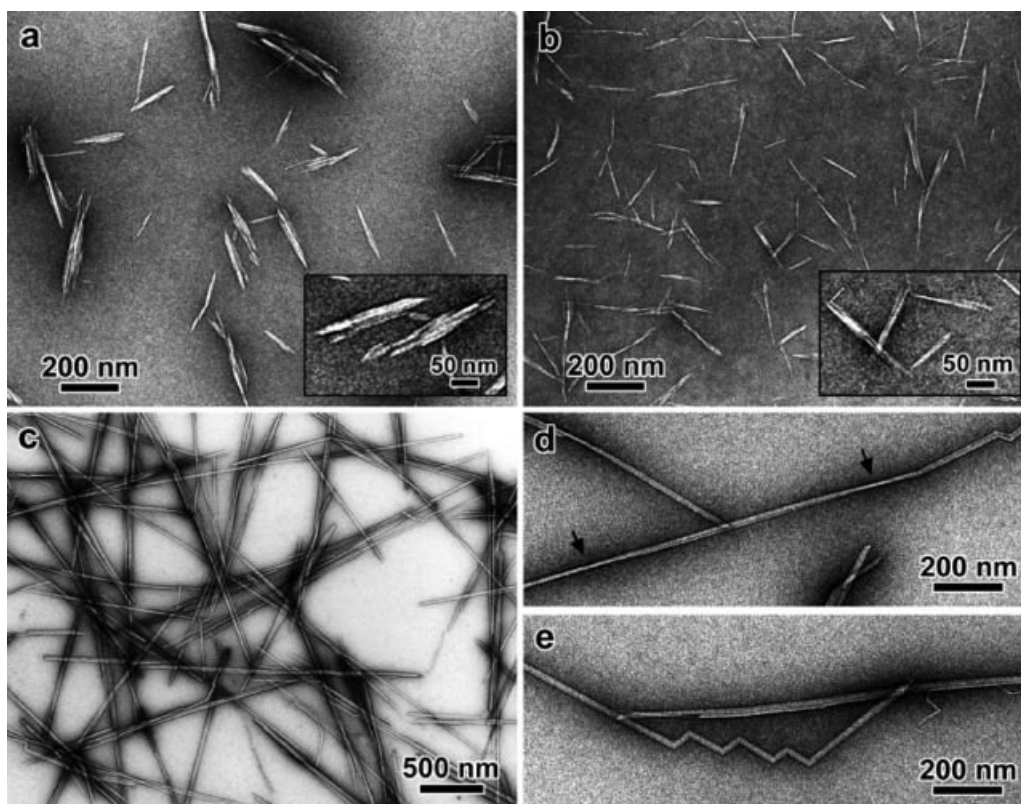
Figure 1. TEM micrographs of nanocrystals obtained by sulfuric acid hydrolysis of (a) cotton (b) avicel (c-e) tunicate cellulose. The insets of (a) and (b) provide higher resolution images of some characteristic particles (Elazzouzi-Hafraoui et al., 2008).

Table 1. Examples of the length (*L*) and diameter (*d*) of NCCs from various sources obtained via different techniques

Source	*L* (nm)	*w* (nm)	Aspect ratio (*L/d*)	Technique	References
Bacterial	100–1000	10–50	2–100	TEM	Araki et al. (2001)
Cotton	100–150	5–10	10–30	TEM	Araki et al. (2001)
	150–210	5–11	15–42	E-SEM	Miller and Donald (2003)
MCC	~500	10	50	AFM	Pranger and Tannenbaum (2008)
Ramie	50–150	5–10	5–30	TEM	de Menezes et al. (2009)
Sisal	100–500	3–5	20–167	TEM	de Rodriguez et al. (2006)
Tunicate	1160	16	73	DDLS	de Souza Lima et al. (2003)
	100–several 1000	15–30	3–67	TEM	Kimura et al. (2005)
Valonia	>1000	10–20	50–100	TEM	Revol (1982)
Wood	100–300	3–5	20–100	AFM	Beck-Candanedo et al. (2005)

a series of NCC products were produced from a variety of sources, such as wood (Table 1) (Beck-Candanedo et al., 2005), cotton (Araki et al., 2001; Miller and Donald, 2003), sisal (de Rodriguez et al., 2006), tunicate (de Souza Lima et al., 2003; Kimura et al., 2005), bacterial (Roman and Winter, 2004), microcrystalline cellulose (Pranger and Tannenbaum, 2008), ramie (de Menezes et al., 2009) and *Valonia* cellulose (Revol, 1982).

The geometrical dimensions (length, *L* and diameter, *d*) of NCC were found to vary widely, in accordance to the examples shown in Table 1. The varieties of dimensions depend on the source of cellulosic material and conditions under which the hydrolysis is performed (Habibi et al., 2010a). It was reported that nanocrystalline cellulose derived from tunicate and bacterial cellulose is usually larger in dimension compared to those obtained from wood and cotton (Heux et al., 2000; de Souza Lima et al., 2003). This is because tunicate and bacterial cellulose are highly crystalline, hence there are lower fractions of amorphous regions that need to be cleaved resulting in the production of larger nanocrystals. Beck-Candanedo et al. (2005) compared the properties of NCC from softwood (black spruce) and hardwood (eucalyptus) produced at the same reaction time, temperature and acid-to-pulp ratios. They found that these NCC suspensions exhibited similar dimensions, surface charge, as well as critical concentrations required to form anisotropic liquid phases. It was also observed that at a higher acid-to-pulp ratio and longer reaction time, shorter nanocrystals with narrow polydispersity index (PDI) were produced and the critical concentration to form an anisotropic phase was increased. As the cleaving on cellulose chains occurred randomly during the acid hydrolysis process, the dimensions of NCC are not uniform. Bai et al. (2009) proposed a method to obtain NCC with a narrow size distribution via the differential centrifugation technique. Six different NCC fractions with narrow PDI were produced using differential angular velocities that generate relative centrifugal force (RCF) for each fraction at a constant centrifugation time.

By using response surface methodology, Bondeson et al. (2006) optimised the reaction conditions for sulphuric acid hydrolysis of MCC from Norway spruce (Picea abies). The concentration of MCC and sulphuric acid, hydrolysis time, temperature and ultrasonic treatment time were varied during the process. It was found that the reaction time, temperature and acid concentration were critical factors for the production of NCC. It was possible to produce cellulose whiskers with a yield of 30% (of initial weight) with a sulphuric acid concentration of 63.5% (w/w) in approximately 2 h to yield NCC with length of between 200 and 400 nm and diameter of less than 10 nm. Elazzouzi-Hafraoui et al. (2008) studied the effect of temperature on the size distribution of NCC produced from sulphuric acid hydrolysis of cotton, and

they demonstrated that shorter NCC was obtained by increasing the temperature. Sulphuric and hydrochloric acids are extensively used in the preparation of NCC, however, the dispersability of NCC derived from these two kinds of acids is different. Due to the abundance of charged sulphate groups on its surface, NCC obtained from sulphuric acid hydrolysis dispersed readily in water, while those produced from hydrochloric acid hydrolysis do not disperse as readily, and their aqueous suspensions tend to flocculate. In addition, differences in the thermal stability and rheological behaviour between the NCC produced from sulphuric acid and those from hydrochloric acid were observed (Araki et al., 1998). NCC has also been produced from recycled pulp using microwave assisted enzymatic hydrolysis. Filson et al. (2009) reported a method to produce NCC using endoglucanase enzyme, a constituent of cellulases. They observed that microwave heating produced NCC with greater yield compared to conventional heating since microwave heating is more selective and reduces the reaction time as well.

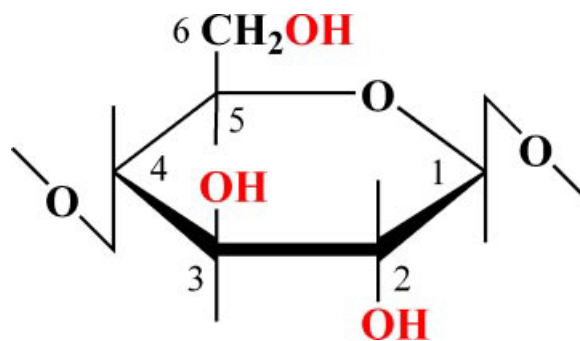## PROPERTIES OF NCC SUSPENSIONS

Nanocrystalline cellulose derived from acid hydrolysis using various forest product sources can disperse in water due to their negative charged surfaces. At low concentration, NCC particles are randomly oriented in aqueous suspension as an isotropic phase, and when the concentration reaches a critical value, they form a chiral nematic ordering, where NCC suspensions transform from an isotropic to an anisotropic chiral nematic liquid crystalline phase (Revol et al., 1992). As the concentration increased further, aqueous NCC suspensions showed a shear birefringence phenomenon. The critical concentration for sulphated NCC typically ranges between 1 and 10% (w/w), which is a function of aspect ratio of NCC, charge density and osmolarity. Theories based on different parameters have been studied to explain the phenomena (Stroobants et al., 1986).

The phase behaviour of NCC is sensitive to the presence of electrolytes and their counter ions, as well as macromolecules. The effect of added electrolyte on the phase separation of NCC was studied by Dong et al. (1996), and they found that the addition of electrolytes, e.g. HCl, NaCl and KCl significantly reduced the volume fraction of the anisotropic phase, indicating that addition of electrolytes reduces the anisotropic phase. Dong and Gray (1997) also studied the effect of counter ions on the phase separation behaviour and stability of NCC suspensions by adding inorganic counterions, weakly basic organic counterions and highly basic organic tetraalkylammonium salts. It was observed that the types of counter ions had a significant effect on phase separation behaviour of NCC suspensions. Similar to electrolytes, the phase
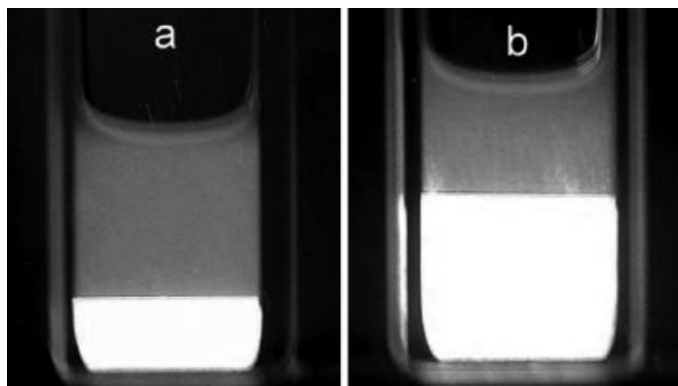
Figure 2. Phase separation observed between cross polars for different concentrations of NCC (cotton fibers) suspensions at total concentrations of (a) 19.8 wt% and (b) 25.0wt% (Elazzouzi-Hafraoui et al., 2009).

**Figure 3.** Numbering system for carbon atoms in anhydroglucose unit of cellulose.

separation of NCC suspensions is strongly affected by the addition of macromolecules. Gray and co-workers (Edgar and Gray, 2002; Beck-Candanedo et al., 2006, 2007) conducted a detailed study on the effect of dextran and ionic dyes on the phase equilibrium of NCC suspensions. Surfactant coating used to disperse NCC whiskers in non-polar solvents was first reported by Heux et al. (2000), where NCC whiskers from cotton and tunicate were mixed with Beycostat NA (BNA) surfactant. The authors demonstrated that the chiral nematic phases were formed in spite of a layer of surfactants around the NCC whiskers. Detailed exam-

ination of the chiral nematic structure (Figure 2) was recently reported (Elazzouzi-Hafraoui et al., 2009). Zhou et al. (2009) illustrated that NCC with adsorbed xyloglucan oligosaccharide-poly(ethylene glycol)-polystyrene showed excellent dispersability in non-polar solvents. In addition, the addition of surfactants enhanced the dispersion of NCC in polystyrene matrix (Kim et al., 2009).

Recently, the assembling behaviours of NCC under external field, such as AC electric field and magnetic field were investigated (Sugiyama et al., 1992; Fleming et al., 2000; Bordel et al., 2006). The effect of AC electric field on the alignment and orientation of NCC was investigated by Habibi et al. (2008a). They observed that the application of an AC electric field to NCC suspensions
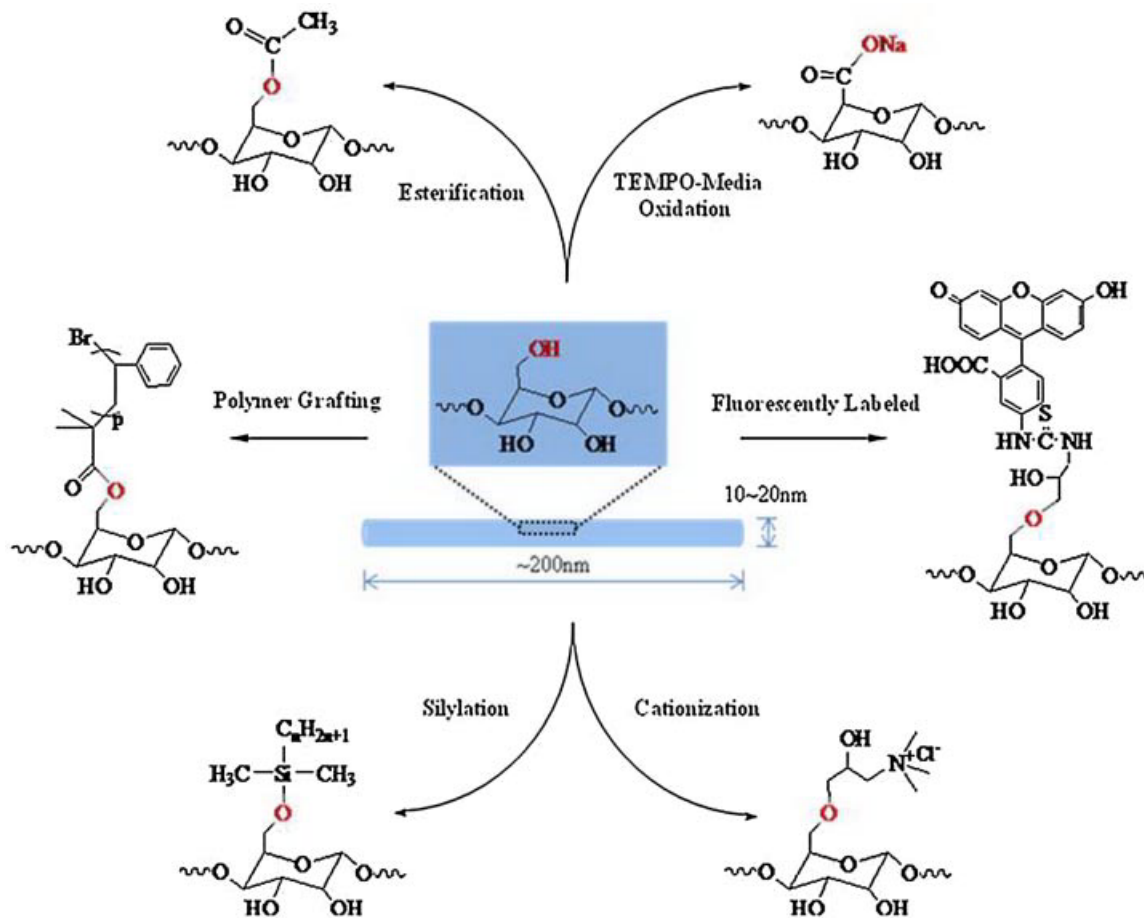
Figure 4. Schematic diagram illustrating the various types of chemical modifications on NCC surface (Braun and Dorgan, 2009; Hasani et al., 2008; Dong and Roman, 2007; Goussé et al., 2002; Habibi et al., 2006; Morandi et al., 2009).

deposited between two metallic electrodes resulted in the homogeneous alignment of NCC molecules. Moreover, the alignment of cellulose nanocrystals generated films was greatly influenced by the frequency and strength of the applied electric field, while the orientation of cellulose nanocrystals became more homogeneous with increasing electric field greater than 2000 V/cm with a frequency ranging between 10^4 and 10^6 Hz. Previous studies (Revol et al., 1994) have shown that NCC suspensions exhibited negative diamagnetic susceptibility anisotropy as they dried under the influence of a magnetic field. The authors also demonstrated that for NCC films, the presence of magnetic field did not facilitate the formation of chiral nematic phase but it only increased the chiral nematic pitch of the suspensions. Similar study was recently conducted by Pan et al. (2010), where they examined various factors affecting the chiral nematic properties of NCC films.

CHEMICAL MODIFICATION OF NANOCRYSTALLINE CELLULOSE

According to its structure, NCC possesses an abundance of hydroxyl groups on the surface, where chemical reactions can be conducted. Among the three kinds of hydroxyl groups (Figure 3), the OH group on the sixth position acts as a primary alcohol, where most of the modification predominantly occurs (Roy et al., 2009). Various chemical modifications of NCC, such as esterification, cationisation, carboxylation, silylation and polymer grafting have been reported (Figure 4) (Goussé et al., 2002; Habibi et al., 2006; Hasani et al., 2008; Braun and Dorgan, 2009; Morandi et al., 2009). Most of these focused on the improvement of its dispersability and compatibility in different solvents or matrices that are suitable in the production of nanocomposites. There is increasing research focus on modification of NCC because of the increasing potential applications of modified NCC in various industrial sectors, such as personal care, nanocomposites, biomedical, etc.

ACETYLATION AND ESTERIFICATION

Several methods had been employed to achieve acetylation and esterification of NCC. Based on a non-swelling reaction mechanism, the reaction only occurred on the cellulose chains located on NCC surface. The limitation on the extent of acetylation lies in the susceptibility and accessibility of hydrolysed NCC on the surface.

Sassi and Chanzy (1995) employed acetic anhydride and acetic acid to modify the fibrous and homogenous cellulose. They showed that acetylation commenced from the surface and proceeded through a non-swelling mechanism. Due to the low solubility, the acetylated cellulose on fibrous NCC was observed to surround the un-reacted NCC core; compared to homogenous acetylation that proceeded through dissolvation of the surface acetylated cellulose. Yuan et al. (2006) used straightforward freeze drying and heating of mixtures of alkyenyl succinic anhydride (ASA) aqueous emulsions and NCC suspensions to obtain acetylated NCC. This process imparted hydrophobicity to the NCC and rendered it soluble in a solvent with low polarity, i.e. DMSO and 1,4-dioxane. Surface acetylation of NCC whiskers (obtained from MCC) was undertaken by reacting it with vinyl acetate in the presence of potassium carbonate as catalyst (Çetin et al., 2009). By progressively increasing the reaction times, it was observed that crystalline structure of the NCC whiskers was destroyed.

In an attempt to avoid complex surface functionalisation routes, Braun and Dorgan (2009) recently combined the synthesis and functionalisation of NCC in a single step. By utilising a mixture of acetic acid, HCl and organic acids, NCC whiskers were synthesised and functionalised using the Fischer esterification process (Figure 5). The presence of acetate and butyrate groups affects the hydrophilicity of NCC whiskers making their aqueous solutions unstable but they possessed better dispersibaility in ethyl acetate and toluene. Apart from the solution process, Berlioz et al. (2009) demonstrated a gas phase process that makes use of evaporation of large excess of palmitoyl chloride to achieve a surface
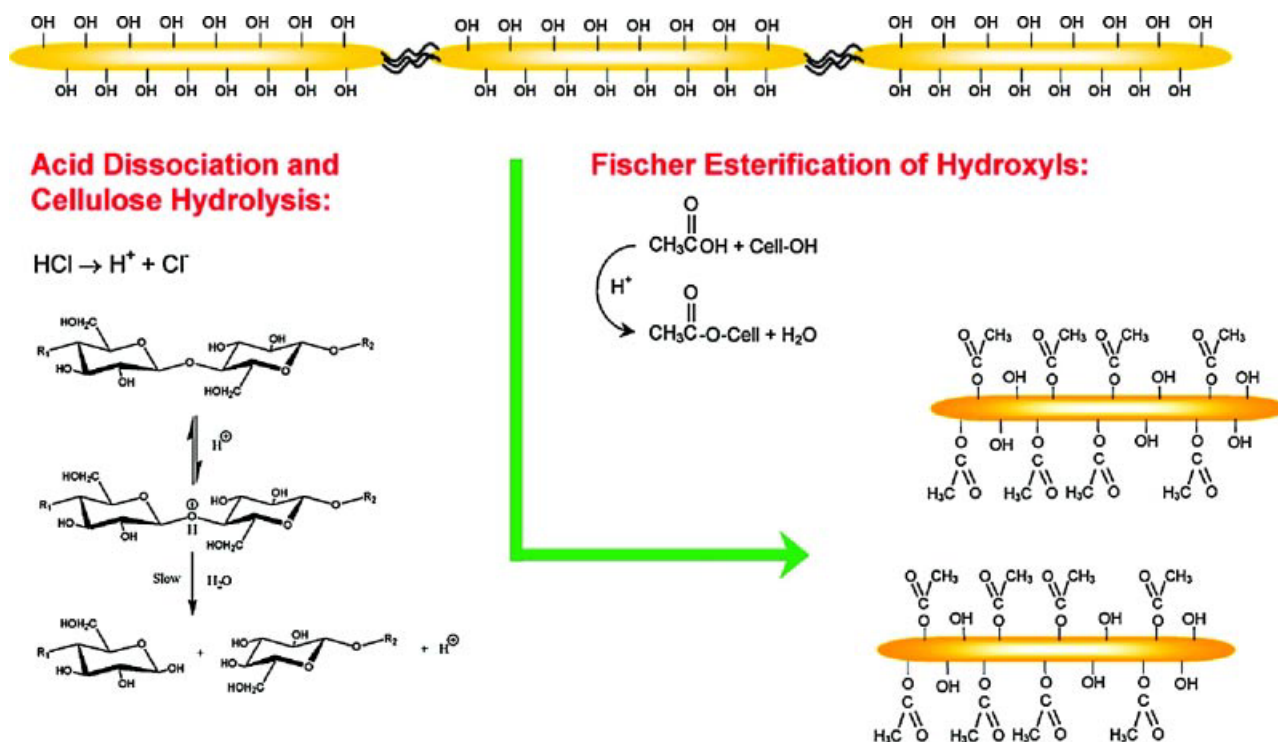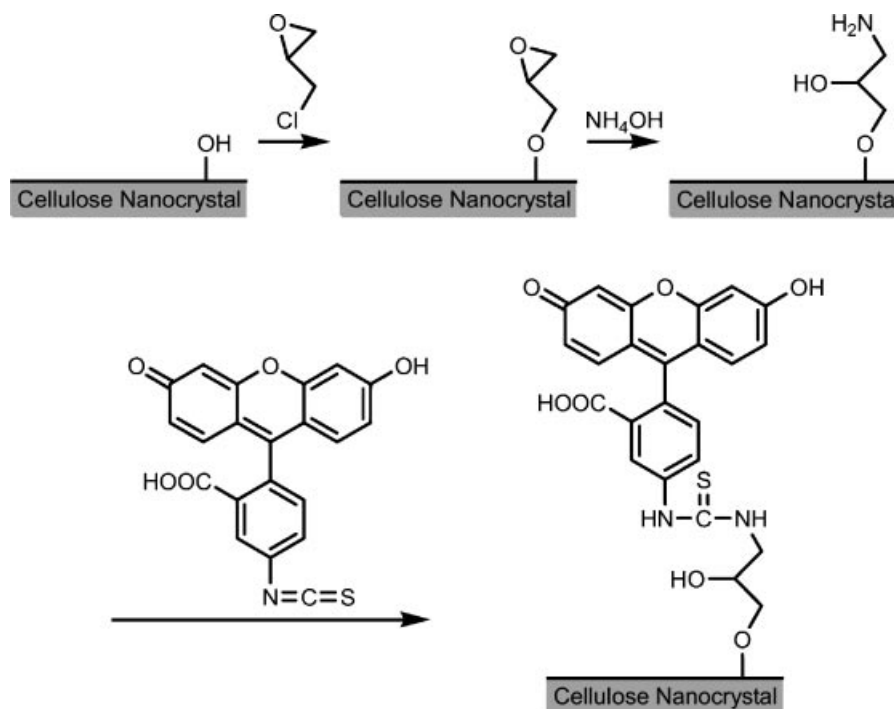

Figure 5. Single step process for cellulose hydrolysis and esterification of hydroxyl groups using a mixture of acetic and hydrochloric acid (Braun and Dorgan, 2009).

Figure 6. Reaction route for surface fluorescently labeled NCC with FITC (Dong and Roman, 2007).

to core esterification. This method can be extended to esterification of different fatty acid chlorides. The nature and treatment of the cellulose were found to be an important factor controlling the extent of esterification and the final morphology of NCC. Similar concept was applied to esterification by refluxing hydrolysed NCC in organic acid chloride (de Menezes et al., 2009). Grafting organic fatty acids of different aliphatic chain length (up to 18) was achievable; while the crystalline core was found to be un-affected. Improved homogeneity of the extruded LDPE was reported with modified NC grafted with longer aliphatic chain.

CATIONISATION

Gray and co-workers (Hasani et al., 2008) described a one step method to introduce positive charges on the surface of NCC through the grafting of epoxypropyltrimethylammonium chloride (EPTMAC) onto NCC surfaces. Such surface cationisation procedure was conducted via a nucleophilic addition of alkali-activated cellulose hydroxyl groups to the epoxy moiety of EPTMAC. This modification process reversed the surface charge and led to stable aqueous suspensions of NCC with unexpected thixotropic gelling properties. It seems that thixotropic gels inhibit the formation of chiral nematic liquid crystalline phase, because no liquid crystalline chiral nematic phase separation was detected, while shear birefringence was observed. However, mild alkaline cationisation conditions preserve the original morphology and maintain the integrity of the crystal.

FLUORESCENTLY LABELED NCC

Fluorescence techniques were extensively used to study the cellular uptake and biodistribution of nanoparticulate delivery systems, by tracking the localisation of the fluorophores. Dong and Roman (2007) described a method to label NCC with fluorescein-5′-isothiocyanate (FITC) for fluorescence bioassay and bioimaging applications. To covalently attach FITC moieties to the

surface of NCC, they developed a simple method involving a three-step reaction pathway described by the reaction route shown in Figure 6. First, the surface of NCC was decorated with epoxy functional groups via reaction with epichlorohydrin, and then the epoxy ring was opened with ammonium hydroxide to introduce primary amino groups. Finally, the primary amino group was reacted with isothiocyanate group of FITC to form a thiourea. They compared the UV/vis absorption spectrum of unlabelled and FITC-labelled NCC in their suspensions, and found the absorption peaks of FITC in the wavelength range of 450–500 nm in the spectrum of the FITC-labelled NCC.

SILYLATION

Cellulose whiskers resulting from the acid hydrolysis of tunicate were partially silylated by a series of alkyldimethylchlorosilanes, with alkyl moieties ranging from isopropyl to *n*-butyl, *n*-octyl and *n*-dodrecyl (Goussé et al., 2002). The partially silylated whiskers with degree of substitution (DS) of between 0.6 and 1 can readily redispersed in medium polarity organic solvents, such as acetone and THF. At DS of less than 0.6, the morphological integrity of the whiskers was preserved, however, it was disrupted when the DS was greater than 1. The authors developed a model with four silylating agents to describe the experimental observations at different DS. Figure 7a shows the NCC whisker at low DS that is still hydrophilic, where its structure integrity is maintained. Such NCC was found to flocculate in THF. Figure 7b shows NCC whisker with moderate DS rendering the surface hydrophobic. Some of the chains are derivatised, where the soluble chain ends stabilise the whiskers in organic solvents of low polarity. Figure 7c shows highly silylated whiskers where the surface chains are solubilised in the reaction medium and the inner core is exposed to more silylation thereby compromising its structural integrity and crystalline nature. Moreover, the partially silylated whiskers were found to be more swollen compared to the needle-like images of unmodified whiskers, indicating the occurrence of slight
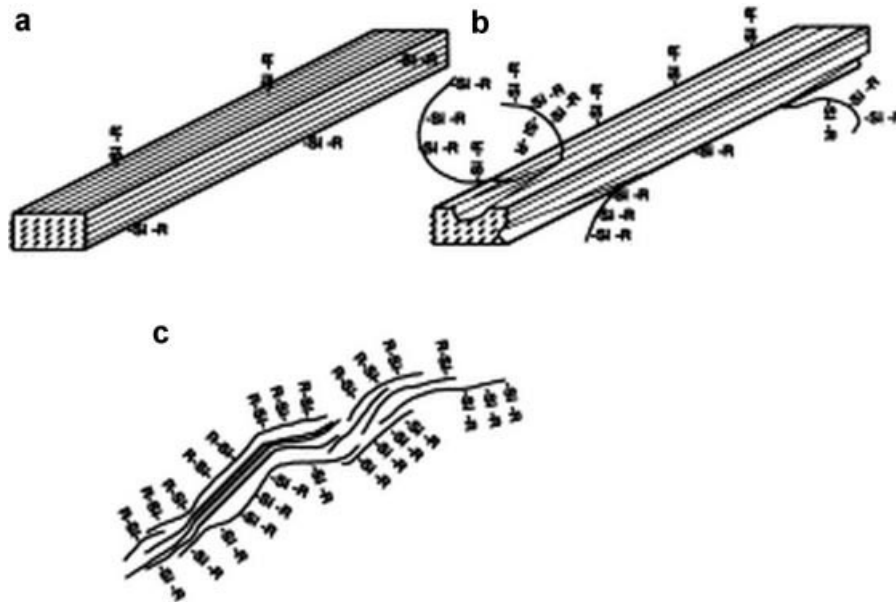
Figure 7. Model explaining the silylation of NCC whiskers (a) Onset of surface silylation. (b) Silylated with silylating agents (c) Partially silylated NCC whiskers (Goussé et al. 2002).

silylation of the NCC core. In addition, Grunert and Winter (2002) also studied the surface trimethyl silylation of NCC from bacterial cellulose, and investigated their reinforcement characteristics in nanocomposites.

TEMPO-MEDIA OXIDATION

Conversion of hydroxymethyl groups into carboxylic groups can be conducted using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) reagent (Saito and Isogai, 2004; Saito et al., 2010). This is a simple oxidative route that uses TEMPO as nitroxyl free radial to specifically oxidise primary hydroxymethyl in an environment of NaBr and NaOCl; leaving the secondary hydroxyl groups intact (Habibi et al., 2006). The morphology and crystal axis of the NCC are critical in determining the accessibility of the hydroxymethyl group. It is generally accepted that only 50% of the surface hydroxymethyl groups are accessible for the TEMPO reac-

tion. Figure 8 shows a schematic of NCC whiskers and how the surface hydroxyl groups become oxidised to carboxylic functional groups using TEMPO-mediated oxidation.

After TEMPO-mediated oxidation, NCC suspension will adopt a birefringence pattern indicating a liquid-crystal like behaviour. The NCC was found to be better dispersed in an aqueous environment; attributed to electrostatic stabilisation from negatively charged carboxylic groups. This is beneficial for further grafting of various types of functionalities. Using a carboxylation-amidation procedure, Araki et al. (2001) prepared 'brush polymer' by grafting PEG with amide linkage onto TEMPO oxidised NCC. Habibi et al. (2006) reported that by using different molar ratio of NaOCl over anydroglucose unit of hydrolysed cellulose, the degree of oxidation and solubility could be varied. Higher NaOCl resulted in an increase of carboxyl content. The degree of oxidation was determined from conductometric titration that measures the concentration of carboxylic acid. Importantly, the structural integrity
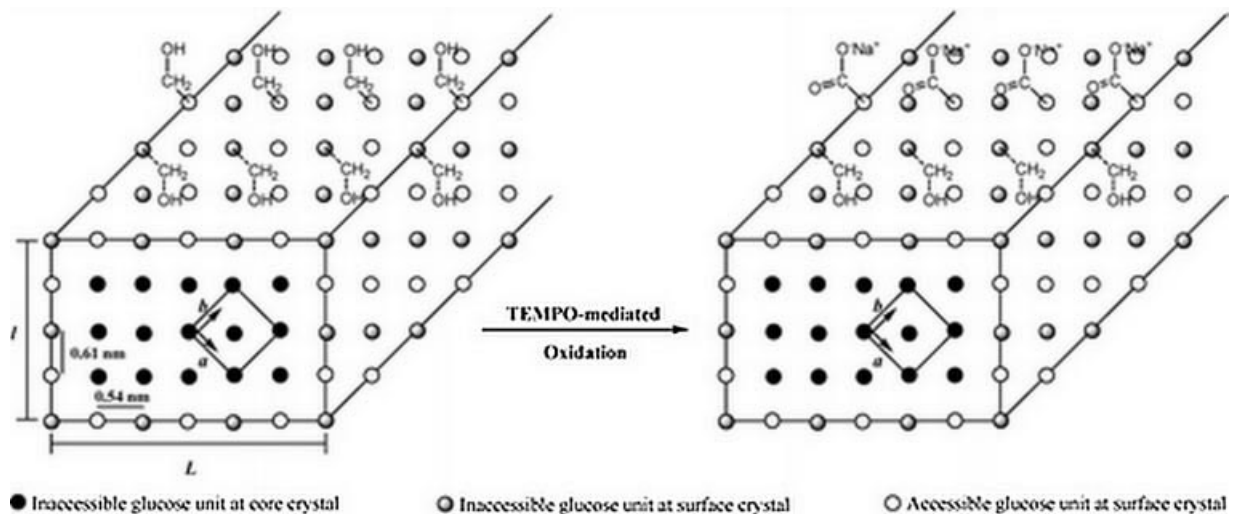
Figure 8. Schematic of the NCC whiskers before and after TEMPO-mediated oxidation (Habibi et al., 2006).
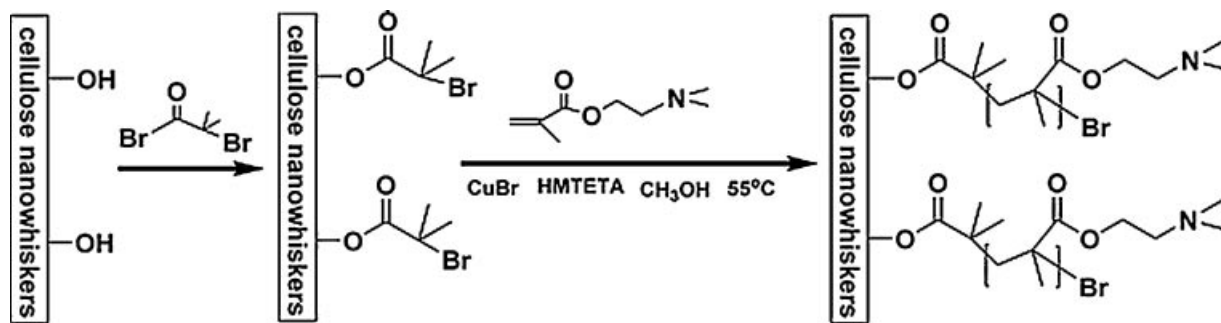
Figure 9. Formation of PDMAEMA grafted on rod-like NCC by surface initiated ATRP (Yi et al., 2009).

of NCC was retained after hydrolysis and TEMPO-mediated oxidation. However, excessive oxidation did affect the structural integrity of the original NCC; since the amorphous region of the NCC would be degraded (Montanari et al., 2005).

POLYMER GRAFTING

The methods for polymer grafting onto NCC surface are based on two approaches, i.e. 'grafting-to' and 'grafting-from'. Many techniques for surface modification of NCC whiskers involve the 'grafting-to' approach, where a polymer chain is grafted to the NCC surface. The 'grafting-to' approach was adopted by Habibi and Dufresne (2008) to graft various molecular weights polycaprolactone (PCL) to the NCC via the isocyanate-mediated coupling reaction. They found that the grafted PCL chains were able to crystallise at the NCC surface, when the grafting density was sufficiently high. Similar efforts were reported in the grafting process of presynthesised waterborne polyurethane onto the surface of NCC (Cao et al., 2009). Peptide coupling reaction was also used in the polymer grafting process of NCC. HCl-hydrolyzed NCC was carboxylated by TEMPO-mediated oxidation, and then EDC/NHS carbodiimide chemistry was used to conduct a room temperature reaction between the –COOH groups on carboxylated NCC and –NH_2 groups on PEG-NH_2 (Araki et al., 2001). The same approach was implemented by Mangalam et al. (2009), who successfully grafted DNA oligomers on the surface of TEMPO oxidised NCC. The temperature dependence and structural morphology of DNA-g-NCC composite on the nanoscale were also reported. Grafting of DNA to NCC extends the application of NCC to nucleic acid research. Ljungberg et al. (2005) investigated the process of grafting maleated polypropylene onto the surface of NCC using the 'grafting-to' approach. Recently, Azzam et al. (2010) reported the grafting of thermo-responsive polymers onto NCC via a peptidic coupling reaction. The modified NCC possesses unusual properties, such as colloidal stability at high ionic strength, surface activity and thermoreversible aggregation. They also reported a thermoreversible aggregation, which could pave the way for the design of stimuli–responsive biobased nanocomposite materials.

The 'grafting-from' approach has been used to grow polymeric chains from the NCC surface via the atom transfer radical polymerisation (ATRP). This technique allows for very precise control over the grafting process that produces well-defined monodispersed particles (Wang and Matyjaszewski, 1995). Surface initiated ATRP is a two-step process: the first step is the esterification of hydroxyl groups on NCC surface with 2-bromoisobutyryl bromide (BIBB), which is followed by the polymerisation of monomers. Styrene was used as the monomer for surface initiated ATRP by Morandi et al. (2009), and they reported a series of grafting products with different grafting effi-

ciencies and molecular weights. Yi et al. (2008) also investigated the surface grafting of NCC using styrene as a monomer, while another hydrophilic monomer, namely, N,N-dimethylaminoethyl methacrylate (DMAEMA) was also used to study the temperature-induced chiral nematic phase behaviour of suspensions of PDMAEMA-grafted NCC (Yi et al., 2009) (Figure 9). Similar to these reported studies, Xu et al. (2008) synthesised NCC whiskers grafted with azobenzene polymers to produce a novel amphotropic hairy rod-like system. This amphotropic system exhibited thermotropic and lyotropic liquid crystalline properties. Ring-opening polymerisation was also used in the 'grafting-from' approach to graft polycaprolactone (PCL) polymers onto NCC surface (Habibi et al., 2008b), where stannous octoate (Sn(Oct)$_2$) was used as a grafting and polymerising agent. To enhance the grafting efficiency, Chen et al. (2009); and Lin et al. (2009) studied similar grafting process via microwave irradiation. Recently, Siqueira et al. (2010) grafted long chain isocyanate onto NCC whiskers using two new novel methods of in situ solvent exchange in order to prevent dispersion problems in the reaction medium. A summary of various types of modifications on NCC whiskers is documented in Table 2.

APPLICATIONS OF NANOCRYSTALLINE CELLULOSE

As a result of their distinctive properties, nanocrystalline cellulose has the potential of becoming an important class of renewable nanomaterials, which could find many useful applications. The main application of NCC is for the reinforcement of polymeric matrix in nanocomposite materials. Favier et al. (1995) was the first to report the use of NCC as reinforcing fillers in poly(styrene-co-butyl acrylate) (poly(S-co-BuA))-based nanocomposites. Since then, numerous nanocomposite materials were developed by incorporating NCC into a wide range of polymeric matrices. The properties of these cellulosic nanocomposites depend on the types and characteristics of NCC and polymeric matrices (which could be both natural and synthetic polymers) (Samir et al., 2005). Chemical functionalisation of NCC improves its dispersability in organic solvents and this greatly expands its potential applications in various sectors. The following section highlights some recent studies on potential applications of NCC from a nanotechnological viewpoint.

NANOCOMPOSITE FILMS

The mechanical properties of nanocomposite films mainly depend on the morphology and dimensions of the two constituents, i.e. NCC and polymeric matrix, as well as the processing techniques. Any other factor that interferes or controls the formation of the

Table 2. Summary of various types of modifications on NCC whiskers

Type of modification	Modification agent/approach	References
Acetylation	Alkyenyl succinic anhydride (ASA)	Yuan et al. (2006)
Surface acetylation	Vinyl acetate in the presence of potassium carbonate as catalyst	Çetin et al. (2009)
Fischer esterification process	Mixture of acetic acid, HCl and organic acids	Braun and Dorgan (2009)
Surface to core esterification	Gas phase evaporation of large excess of palmitoyl chloride	Berlioz et al. (2009)
Cationisation	Grafting epoxypropyltrimethylammonium chloride (EPTMAC)	Hasani et al. (2008)
Fluorescently labelled NCC	Fluorescein-5′-isothiocyanate (FITC)	Dong and Roman (2007)
Silylation	Series of alkyldimethylchlorosilanes	Goussé et al. (2002)
TEMPO-media oxidation	Oxidation of –OH groups to –COOH using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)	Habibi et al. (2006)
Grafting of PEG-NH$_2$	Reaction of PEG-NH$_2$ and TEMPO oxidised NCC	Araki et al. (2001)
Grafting of polycaprolactone (PCL)	*Grafting-to* approach using isocyanate-mediated coupling reaction	Habibi and Dufresne (2008)
Grafting of styrene, DMAEMA or azobenzene polymers	*Grafting-from* approach using surface initiated ATRP	Yi et al. (2008); Morandi et al. (2009); Xu et al. (2008)

percolating whiskers network will also change the mechanical performance of the nanocomposite (Dufresne, 2008).

The geometrical aspect ratio, defined as the length-to-diameter (L/d), is a major factor that controls the mechanical properties of nanocompsites and determines the percolation threshold value. This factor is related to the original cellulose fibres and production conditions, which was previously discussed. Fillers with a high aspect ratio give the best reinforcing effect. It was reported that the highest modulus increase in the rubbery state of the poly(S-co-BuA) matrix and thermal stability were obtained with tunicin whiskers ($L/d \sim 67$) in comparison with bacterial ($L/d \sim 60$) or Avicel whiskers ($L/d \sim 10$) (Samir et al., 2005). de Rodriguez and co-workers (2006) studied sisal nanowhiskers with high aspect ratio as filler in the nanocomposites with polyvinyl acetate (PVAc) as the matrix. They found that the high aspect ratio could ensure percolation, resulting in mechanical improvements and thermal stability at lower fibre loadings. Dubief et al. (1999) also reported the mechanical behaviour of composites based on amorphous poly(β-hydroxyoctanoate) (PHO) when reinforced with tunicin microcrystals. They proved that tunicin whiskers with high aspect ratio led to higher mechanical properties through the formation of a rigid filler network. Similar effects on the dependence of mechanical properties of nanocomposites on aspect ratio were also reported using carbon nanotubes as fillers (Jiang et al., 2007; Wong et al., 2009).

In this section, different processing methods, such as casting evaporation, electrospinning, as well as extrusion and impregnation, were evaluated for the preparation of nanocomposite films using water and organic solvents. The resulting thermal properties, mechanical properties and applications of nanocomposite films will be discussed.

Casting Evaporation

Casting-evaporation is one of the most common techniques used to produce nanocomposite films, where the solvent is evaporated after dispersion casting. To achieve good reinforcement, the dispersability of the filler, such as NCC in both the polymeric matrix and processing solvents is critical. The water-soluble matrix is the simplest system for incorporating NCC as filler, due to the hydrophilic character of NCC. Schroers et al. (2004) studied the properties of nanocomposite films based on ethylene oxide/epichlorohydrin and NCC, which were produced by dispersion-casting of NCC fillers in THF/water mixtures. The poly-

mer grafting is beneficial for dispersing NCC and to formulate nanocomposites in non-polar solvents (Ljungberg et al., 2005). However, drying and redispersion of NCC without aggregation in casting-evaporation processing is still challenging. Habibi and Dufresne (2008) prepared nanocomposite films using unmodified and PCL-grafted NCC nanoparticles as filler and PCL as the matrix, and they that found PCL-grafted nanoparticles were easily dispersed when compared to the unmodified system. They demonstrated that the transformation of NCC nanoparticles into a cocontinuous material through long chain surface chemical modification represents a new and promising way for the processing of nanocomposite material.

Electrospinning

Electrostatic fibre spinning or 'electrospinning' is a versatile method for preparing fibres with diameters ranging from several microns down to 100 nm through the action of electrostatic forces (Dufresne, 2010). Electrospinning is a fast and simple process to produce polymeric filaments, and this approach has been widely studied. Park et al. (2007) reported on the incorporation of bacterial cellulose whiskers into polyethylene oxide (PEO) nanofibres via the electrospinning process. The authors demonstrated that electrospun PEO fibres with a diameter of less than 1 μm were successfully prepared, and the mechanical properties were enhanced by the cellulose whiskers. Nanocomposite films from polystyrene and cellulose nanowhiskers were also produced by Rojas et al. (2009) using electrospinning. They found that sorbitan monostearate, a nonionic surfactant could be used to improve the dispersion of hydrophilic reinforcing nanoparticle in hydrophobic matrix. Electrospun poly (vinyl alcohol) (PVA) (Peresin et al., 2010) and polycaprolactone (PCL) (Zoppe et al., 2009) nanofibres reinforced with NCC were also obtained by electrospinning. The new composites from PCL and NCC showed a significant increase in the storage modulus at all temperatures and possessed a nonlinear stress–strain deformation behaviour. Fibre webs from PCL reinforced with 2.5% unmodified NCC showed ca. 1.5-fold increase in Young's modulus and the ultimate strength compared to PCL webs. The reason was explained in terms of the difference in the fibre diameter, NCC loading, and crystallisation processes. A co-electrospinning technique to produce a core-in-shell nanomaterial consisting of a cellulose shell and a core containing the cellulose nanocrystals was first reported by Magalhães et al. (2009).

Extrusion and Impregnation

Extrusion and impregnation are two methods used to prepare nano-composites comprising of a polymeric matrix and modified NCC filler. The main challenge lies in the poor dispersion and agglomeration of NCC inside the polymeric matrix, which is due to the hydrophilic nature of NCC and the formation of inter-chain H-bonding. These non-optimised conditions thus limit the mechanical properties of the prepared nano-composite. One way to address the agglomeration problem previously reported is by introducing microcrystalline cellulose at the intermediate stage during the extrusion of poly (lactic acid) (PLA), where the suspension of whiskers was pumped into the polymer melt during the extrusion process (Oksman et al., 2006). *N,N*-dimethylacetamide (DMAc) containing lithium chloride (LiCl) was used to better disperse the microcrystalline cellulose (MCC); however, it appeared to result in the degradation of the composites at high temperature. The mechanical properties did not show improvements compared to pure PLA, due to combined effect of additives and high processing temperature. Wide angle X-ray diffraction showed that the crystal integrity of the cellulose was retained after extrusion. A similar process was performed by employing poly (vinyl alcohol) (PVA) as the dispersing agent; and the MCC was distributed in the PVA phase (Bondeson and Oksman, 2007). Another method employed is the modification of surface functional groups on NCC prior to extrusion. Hydrolysis followed by grafting of organic aliphatic acid chain of different lengths was used (de Menezes et al., 2009). The mixture of modified NCC and low density polyethylene (LDPE) was extruded and improvement in the dispersion resulting in a more homogeneous mixture was observed; where better dispersion was reported in formulations with longer aliphatic chain.

Impregnation is another technique that could be used to prepare dried film or a mat comprising of NCC, before immersing the thin film in the thermosetting resin (e.g. epoxy or melamine formaldehyde). The cellulose thin film can be prepared via membrane filtration of cellulose solution or by pressing the dried cellulose. At low pressure, the resin impregnates and fills the cavities within the NCC; followed by curing to produce a composite. This technique is mostly used for sample preparation for evaluating the mechanical (Henriksson and Berglund, 2007; Iwamoto et al., 2008), thermal (Shimazaki et al., 2007), and optical (Nogi et al., 2005) properties of cellulose-filled composites. Higher degree of fibrillation of cellulose was found to be beneficial for composite strength; due to the elimination of weaker fibres acting as crack initiator. Nakagaito and Yano (2008) used NaOH treated cellulose micro-fibres impregnated with phenol–formaldehyde resin and a 20% increase in fracture strain compared to non-treated cellulose micro-fibres was observed. Composite made from the impregnation of bis-phenol A-type epoxy resin into cellulose thin film prepared from membrane filtration was found to have a high thermal conductivity and low thermal expansion (Shimazaki et al., 2007). Improvement of thermal stability was reported for composites consisting of layers of micro-size or nano-size cellulose fibres and polyurethane (Özgür Seydibeyoğlu and Oksman, 2008). The cellulose was prepared by filtering the water-cellulose slurry and the H-bonding enhanced the thin film integrity.

Monolayer Films

Interfacial behaviours of NCC were studied by Habibi et al. using the Langmuir–Blodgett (2007) and Langmuir–Schaeffer (2010) techniques. Smooth monolayer films based on NCC were prepared by Langmuir–Blodgett vertical and Langmuir–Schaeffer horizontal deposition. NCC was found to form stable layers at the air/liquid interface in the presence of dioctadecyldimethylammonium (DODA), a cationic amphiphilic molecule. Dioctadecyldimethylammonium (DODA) was used to produce NCC-DODA complexes that allowed the transfer of NCC from the air/liquid interface in an aqueous suspension to hydrophobic solid substrates. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were employed to characterise the morphology and chemical composition of NCC films. It was demonstrated that both of these two techniques could be used to prepare stable, smooth and robust monolayers of NCC. Hence, these layers offer an opportunity to investigate the interfacial properties relevant to the chemical and biological transformations of cellulose. Alternatively, these films can be used as a coating technology to modify the surface of other materials to achieve unique properties (Habibi et al., 2010b).

The self-assembly of NCC in suspension can produce iridescent chiral nematic films upon drying (Beck et al., 2011) The iridescence colour exhibited by NCC film is attributed to the ability of the NCC to reflect circularly polarised light at specific wavelengths. It was reported that ultrasound treatment increased the chiral nematic pitch in the suspension resulting in the red-shift of the reflection wavelength of NCC films as the applied energy increases.

Multilayer Films

The layer-by-layer assembly (LBL) is a unique and facile method for fabricating composite films with nanometer precision. The advantages of this approach are simplicity, universality and thickness control at the nano length scale. Two components are alternately deposited by solution-dipping or spin-coating, and usually there are strong interactions between the alternative layers. The self-assembling systems obtained from the LBL technique could be used for a wide range of applications.

LBL assembly has already been applied to prepare multilayered films based on nanocrystalline cellulose. Podsiadlo et al. (2005) first reported the preparation of NCC multilayer composites with poly (diallyldimethylammonium chloride) using LBL assembly, and they observed uniform coverage and densely packed NCC surface from AFM and SEM analyses. The feasibility of LBL assembly of NCC was demonstrated with poly-(allylamine hydrochloride) (PAH). The formation of a well-ordered alignment from anisotropic NCC suspensions and the smoothening effect of flexible PAH macromolecules was reported by Jean et al. (2008). Layer-by-layer orientated self-assembled multilayer films containing NCC and PAH were also prepared by Cranston and Gray using a strong magnetic film (Cranston and Gray, 2006a) and spin coating techniques (Cranston and Gray, 2006b, 2008). The LBL technique was also used to prepare self-organised films composed solely of anionically and cationically modified NCC (Aulin et al., 2010). The authors demonstrated that separation of surfaces covered by PEI/anionic microfibrillated cellulose (MFC) multilayers required more energy than surfaces covered by cationic/anionic MFC multilayers, because the fibrils in the PEI/anionic MFC system required more energy to be extracted from the multilayer. Biobased 'green' nanocomposite films based on alternating layers of two renewable bio-based materials (i.e. NCC and Chitosan) were prepared using the LBL technique (de Mesquita et al., 2010). The driving forces for the growth of the multilayered films are hydrogen bonds and electrostatic interactions between the two layers. In addition, LBL assembly of multilayers using two biomaterials driven by non-electrostatic interactions was recently reported by Jean et al. (2009).

DRUG DELIVERY

The materials for drug delivery seem to be one of the most interesting research fields. Abundant researches were conducted to investigate various drug delivery systems, such as liposomes, micelles, microgels (Ha and Gardella, 2005). Considering the safety and efficacy, nanocrystalline cellulose has attracted increasing attention in biomedical applications (such as a drug carrier), due to its attractive properties. The toxicity assessment of NCC in human brain microvascular endothelial cells was conducted and NCC was non-toxic to cells and could be used as carriers in the targeted delivery of therapeutics (Roman et al., 2010). Recently, a comprehensive assessment involving toxicity tests with rainbow trout hepatocytes and nine aquatic species were conducted by a team of Canadian researchers (Kovacs et al., 2010). From the initial ecotoxicological characterisation of NCC, no serious environmental concerns were observed. However, further testings will be necessary, such as the evaluation on the fate, potential NCC uptake and exposure studies, so that a detailed risk assessment of NCC can be determined.

Recently, Dong and Roman (2007) reported a method to label NCC with fluorescein-5'-isothiocyanate (FITC) for fluorescence bioassay and bioimaging applications. The interaction of labelled NCC with cells and its biodistribution in vivo by fluorescence techniques were evaluated. Shi et al. (2003) used microcrystalline cellulose as host beads, where drug nanoparticles dispersion was spray coated onto them, and they examined the morphology using scanning electron and AFM. NCC particles were incorporated into hydrogels based on cyclodextrin/polymer inclusion (Zhang et al., 2010), and they found that the new nanocomposite hydrogels can be used as a controlled delivery vehicle.

Extrusion-spheronisation is one of several methods used to produce pellets, where the excipient plays an important role as spheronisation aid. Dukic-Ott et al. (2009) discussed the properties of different materials, and they proposed alternatives for MCC, which is considered as a golden standard to produce pellets via extrusion-spheronisation. The behaviour of MCC during extrusion-spheronisation process could be explained by two proposed models: 'molecular sponge model' (Fielden et al., 1988; Ek and Newton, 1998) and 'crystallite-gel model' (Kleinebudde, 1997). In another case study with itraconazole, Van Eerdenbrugh et al. (2008) demonstrated the efficiency of MCC as a viable alternative for the preservation of the dissolution-rate of the nanoparticles upon freeze-drying.

PROTEIN IMMOBILISATION

Marchessault et al. (2006) provided a description of a 'proteins fishing' phenomenon for magnetic MCC. The first step is the ferrite synthesis that yields predominantly magnetite. Two different approaches have been envisaged for preparing magnetic MCC, where the order of magnetisation and oxidation of MCC was altered, producing Mag-Oxy-MCC (oxidation first) and Oxy-Mag-MCC (magnetisation first). The results of protein binding capacities of magnetic MCC are summarised in Table 3, which were determined using bovine serum albumin (BSA) as a model protein ligand.

A novel nanocomposite consisting of NCC and gold nanoparticle was recently investigated as a matrix for enzyme/protein immobilisation (Mahmoud et al., 2009). Cyclodextrin glycosyl transferase (CGTase) and alcohol oxidase were used as test models, and they showed a phenomenally high loading rate in the matrix. The novel matrix also exhibits significant biocatalytic

Table 3. Protein binding capacities of magnetised Avicel samples (Marchessault et al., 2006)

Sample	% Bound proteins (w/w)
Mag-MCC	8.02
Mag-Oxy-MCC	21.53
Oxy-Mag-MCC	17.41

activity, and it is anticipated that the approach can be extended to other enzymes.

NANOSTRUCTURES VIA TEMPLATING WITH NCC

Since Mobil researchers reported the first synthesis of mesoporous material in 1992 (Kresge et al., 1992), this approach has attracted significant attention in fundamental and applied fields. Due to its attractive properties, NCC has already been used as a template in the synthesis of mesoporous materials. Porous titania with anatase structure was prepared using NCC as a template and aqueous Tyzor-LA solution as a cheap and stable titania precursor (Shin and Exarhos, 2007). The titania material possesses high specific surface area, and may be applied to many fields, such as catalysis, catalyst support and photovoltaics.

A new NCC-inducing route was proposed for the synthesis of shape-controlled nanoparticles (Zhou et al., 2007). The novel cubic-shaped TiO_2 nanoparticles (Figure 10) with high crystallinity and uniform size were prepared using NCC as morphology-inducing and coordinate agent at low temperature. Thermal gravimetric analysis (TGA) suggests that NCC is probably embedded in the TiO_2 nanoparticles to promote the development of regular anatase nanocubes.

Some metal nanoparticles have been synthesised on NCC surface via a reduction method, such as Ni nanoparticles (Shin et al., 2007) and Au–Ag alloy nanoparticles (Shin et al., 2008). In these processes, NCC serves as a dual role, as a matrix and a stabilising template, to produce stable dispersions of nanoparticles on NCC surface, and the crystallinity of NCC was maintained during the alloy formation (Shin et al., 2008). These reducing processes could be recognised as 'green' processes ascribed to the use of NCC and applied to the preparation of transition metal nanoparticles, which have high oxidising property without additional reducing agents.

A recent discovery of free-standing mesoporous silica films with tunable chiral nematic structures was made by the research group of MacLachlan at the University of British Columbia (Shopsowitz et al., 2010). Various types of mesoporous silica films were produced by calcinating the NCC/silica composite systems, and the transmission spectra of the mesoporous silica films are shown in Figure 11 (left panel). Photograph of the different colours of mesoporous silica films S1–S4 are shown in Figure 11 (right panel). The colours in these silica films arise only from the chiral nematic pore structure present in the materials. This discovery could lead to the development of novel materials for applications, such as tuneable reflective filters and sensors. In addition, NCC could be used as a hard template to produce other new materials with chiral nematic structures.

OTHER POSSIBLE APPLICATIONS

As more researchers become interested in NCC, many applications in diverse fields have been proposed and explored, ranging from iridescent pigments to biomolecular NMR contrast agents
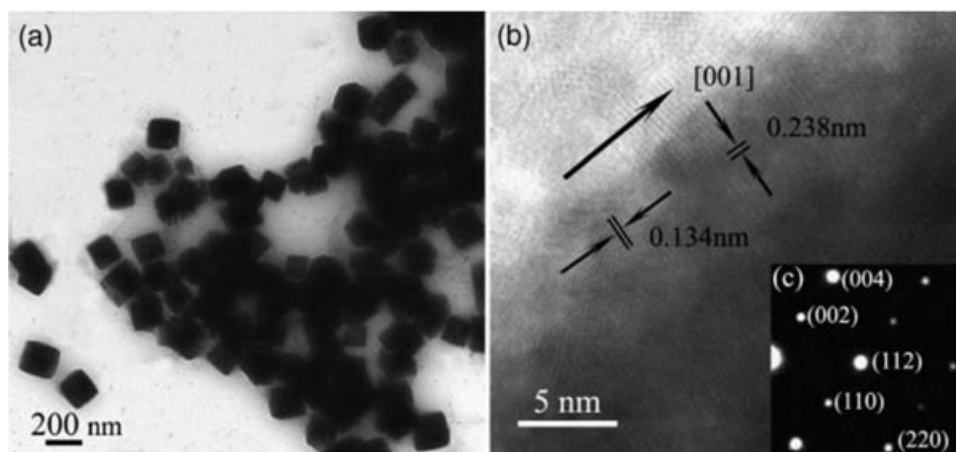
Figure 10. (a) Transmission electron microscopy (TEM) image, (b) High-resolution transmission electron microscopy (HRTEM) image, (c) selected area electron diffraction (SAED) pattern of TiO_2 nanocubes (Zhou et al., 2007).
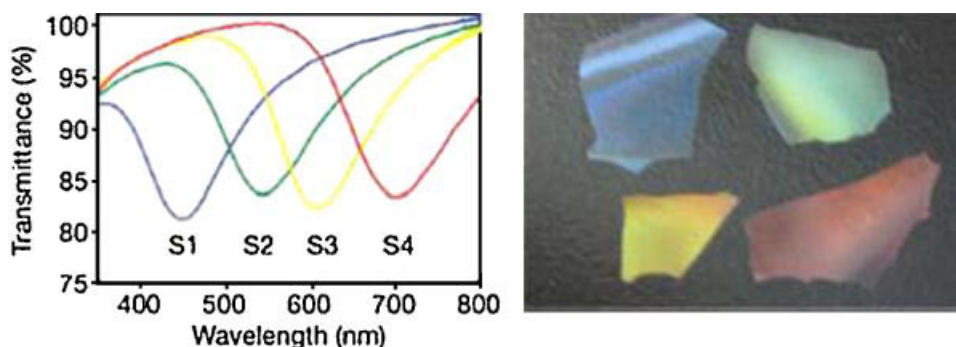
Figure 11. Optical characterization and properties of NCC/silica mesoporous films (a) Transmission spectra; (b) Photograph showing different colours of mesoporous silica films S1 to S4 (Shopsowitz et al., 2010).

(Fleming et al., 2001). In addition, NCC may be used in security paper (Revol et al., 1997, 1998), based on the solidified liquid crystals property. It is believed that NCC may be used in lithium battery products as a mechanical reinforcing agent for low-thickness polymer electrolytes (Samir et al., 2004a, b, c; Schroers et al., 2004). However, due to the duration of the preparation technique, many industrial applications of NCC have focused on nanocomposites (Samir et al., 2005).

CONCLUSIONS AND OUTLOOK

The paper reviews the recent development on the modification and applications of nanocrystalline cellulose from a nanotechnology perspective. It is shown that NCC has a distinct advantage for preparing nanocomposites with outstanding thermal and mechanical properties. Moreover, NCC may be used in drug delivery, protein immobilisation and metallic reaction template due to its attractive properties. The feasibility of its potential applications is also discussed.

Nanocrystalline cellulose is an environmentally-friendly forest-based material that could serve as a valuable renewable resource for rejuvenating the beleaguered forest industry. New and emerging industrial extraction processes need to be optimised to achieve more efficient operations and this will require active research participations from the academic and industrial sectors. The application of nanotechnology in developing NCC from the forest industry to more valuable products is required, because the availability of materials based on NCC is still limited. Increasing attention is devoted to produce NCC in larger quantities, and

to explore various modification processes that enhance the properties of NCC, making it attractive for use in a wide range of industrial sectors. Thus, the recent decision by Domtar and FP Innovations to build a demonstration pilot plant to produce larger amounts NCC will accelerate the adoption of this new renewable nanomaterial.

Thus far, most of the studies focus on the mechanical and chiral nematic liquid properties of NCC nanocomposites, however, other research directions are also being explored. In nanocomposite systems, the homogeneous dispersion of NCC in a polymer matrix is still a challenging issue, as aggregation or agglomeration of NCC is commonly encountered. We believe that appropriate modification of NCC to impart functional characteristics to this nanomaterials will be necessary if NCC is to be successfully incorporated into a specific product system. It is anticipated that nanotechnology innovations in renewable resources, such as NCC will not only improve the future viability of the forest industry in Canada, but it will also create a larger market for future products based on NCC.

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