BIOCOMPOSITES REINFORCED WITH CELLULOSE NANOCRYSTALS DERIVED FROM POTATO PEEL WASTE

BIOCOMPOSITES REINFORCED WITH CELLULOSE NANOCRYSTALS DERIVED FROM POTATO PEEL WASTE

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Abstract

Cellulose is the most abundant biopolymer on earth, derived from a variety of living species. An attractive source to obtain cellulose is from agriculture wastes, for instance, potato peel. Potato is one of the most important crops for human consumption, but in recent years its consumption in raw form has decreased, especially in developed countries. Many potatoes are processed into value-added products to meet the demand of fast food industries. So far the main use of the potato peel is sold for animal feed at very low prices. In addition, there are significant quantities of rotten potatoes generated during the years of heavy rain fall, which represent a substantial financial loss to the farmers unless an alternative industrial use can be found for the biomass. Therefore, extracting cellulose from potato peel and processing them into a higher valuable product is not only an environment-friendly solution to the disposal issues but also creates a non-food based economy for potatoes.

Cellulose nanocrystals (CN) are a promising material and have been widely studied over the past two decades. This material is interesting as nanofiller due to its nanoscale dimensions, high specific area, and highly rigid crystalline structure. In comparison to mineral or metal nanofillers that are industrially available, cellulose nanocrystals are prepared from renewable feedstocks, feature low density, are relatively low cost, and remain biodegradable.

This study investigated the effectiveness of cellulose nanocrystal derived from potato peel waste to improve the mechanical and barrier properties of a polymer. The nanocrystals were chemically derived from the cellulosic material in potato peel waste by alkali treatment and subsequently acid hydrolysis with sulfuric acid. Infrared spectroscopy indicated sufficient removal of lignin and hemicellulose from the raw potato peel biomass whereas X-ray diffraction confirmed that the prepared nanocrystals maintained their original crystalline lattice structure as the extracted cellulose, with a crystallinity of 85%. TEM images showed that the average fiber length of the nanocrystals was 410 nm with a diameter of 10 nm (aspect ratio of 41). Cellulose nanocrystal-filled polyvinyl alcohol (PVA) and thermoplastic starch (TPS) were prepared by solution casting method to maintain uniform dispersion of the 1-2% (w/w) fibers. An increase of 19% and 38% (starch composite) and 32% and 54% (PVA composite) in Young’s modulus was observed for the 1% and 2% CN-reinforced composites, respectively. Water vapor transmission rate measurements showed a reduction of water permeability for the PVA nanocomposite, whereas no effect was observed for starch nanocomposite.

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Abbreviation

CN	Cellulose Nanocrystal
CCN	Cellulose Nanocrystal Derived from Cotton
PCN	Cellulose Nanocrystal Derived from Potato Peel Waste
TEM	Transmission Electron Microscopy
MFC	Microfibrillated Cellulose
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
ASTM	American Standard Test Method
TPS	Thermoplastic Starch
PVA	Polyvinyl Alcohol
POE	Poly Oxyethylene
WVT	Water Vapor Transmission
DP	Degree of Polymerization
LODP	Level-off Degree of Polymerization
AFM	Atomic Force Microscopy

CHAPTER 1 INTRODUCTION

1.1. Background

Composites are materials made from two or more physically distinct constituents. Usually one constituent is dispersed in the other and the dispersed material is called filler. Conventional fillers typically have dimensions in the micron scale. In 1990s, Toyota published that the mechanical properties of Nylon 6 were dramatically improved by reinforcement with low filler content of nano-clay (less than 5 wt %). (Okada et al., 1990) After that, nanocomposites have received significant attention and many studies on nanocomposites have been carried out. Because of their nanoscale sizes which result in very high surface area-to-volume ratios, nanofillers bring impressive properties to polymers. Cellulose nanocrystal (CN) is one of the emerging renewable nanofillers which have been widely studied over the past two decades. CNs are usually prepared by strong acid hydrolysis of cellulose. According to Ramires & Dufresne (2011), the first stable suspension of colloidal-sized cellulose crystals was produced using sulfuric acid hydrolysis by Rånby (1951) and closely followed by Battista et al. (1956). The amorphous regions of cellulose can be considered as imperfections which are more easily attacked and digested by strong acids, transforming the long cellulose fibrils into short crystalline whiskers.

Cellulose is the most abundant biopolymer on earth, existing in a variety of living species such as plants, animals, bacteria, algae and some amoebas. It is the principal structural component in plant cell walls. (Perez & Samain, 2010) The availability results in the low cost of cellulose. In addition of its low density, high stiffness and biodegradability, cellulose has been mentioned above as a promising raw material to produce nanofillers. An attractive source to obtain cellulose is from agriculture waste, such as potato peel. Potato is one of the most important crops for human consumption, with a world annual production of 325 million tons in 2007. (Food and Agriculture Organization of United State [FAO], 2008) However, in recent years, the consumption of fresh potatoes has decreased, especially in developed countries. Many potatoes are processed into value-added products to meet the demand of fast-food industries. Potatoes are usually peeled before processing, and as a result, large quantities of peels are produced as waste, which raises severe disposal issues. Generally, the potato peels contain about 18% dry matter, which consists of 3.4% pectin, 2.2% cellulose, 14.7% protein, 66.8% starch and 7.7% ash. (Mahmood, Greenman & Scragg, 1998) So far, the main use of the potato peels is for animal feed, sold at extremely low prices. In addition, there are significant sources of rotten potatoes generated during the years of heavy rain fall, which represent a substantial financial loss to farmers unless an alternative industrial use can be found for the biomass. Therefore, extracting cellulose from potato peel and processing them into a higher valuable product (i.e. cellulose nanocrystals) is not only an environment-friendly solution to the disposal issues but also creates a non-food based economy for potatoes.

1.2. Research Objectives

The main objective of the thesis was to transform the valueless agriculture waste, i.e. potato peel, into a high-value product, i.e. cellulose nanocrystals. This work subsequently demonstrated the effectiveness of cellulose nanocrystal derived from potato peel waste in improving the mechanical and barrier properties of polymers. The research included:

1) A review of the current techniques for extracting cellulose from bio-resources and subsequently processing the extracted cellulose into nanocrystals found in the literature.

2) Investigating the effects of hydrolysis conditions on CN synthesis using cotton cellulose as a model material. The work included preparation of CN at different conditions, characterization of CN dimensions and morphologies by TEM, and

comparison of the particle length distribution. The aim of the work was to optimize the hydrolysis conditions to produce high quality, well isolated CN.

3) A suitable synthesis method of CN from potato peel waste and comparison of its structure based on chemical composition, crystallinity and dimension in comparison to cotton cellulose-derived CN.
4) Dispersion of a CN suspension into a polymer solution and processing the mixture into a testable biocomposite by solution casting method. Mechanical properties and water vapour barrier properties of the composite films were ultimately tested.

1.3. Thesis Outline

This thesis is composed of four chapters. The first chapter is a general introduction about the research background and objectives. The second chapter is a literature review which provides more details on cellulose nanocrystal and cellulose-based nanocomposites. The third chapter is a submitted journal article manuscript, reporting the method of preparation of CNs from potato peel waste, properties of CNs and CN-based nanocomposite. The results are discussed in detail in this chapter. The final chapter summarize the thesis and recommend for the future work.

CHAPTER 2 LITERATURE REVIEW

2.1. Cellulose

2.1.1. Origin

Cellulose is one of the most widespread biopolymer found globally, existing in a variety of living species such as plant, animals, bacteria and some amoebas. (Perez & Samain, 2010) Natural fibers mainly consist of cellulose, lignin, and hemicellulose but also include low quantities of pectin, pigments and extracts. Cellulose chains are bio-synthesized by enzymes, deposited in a continuous fashion and aggregated to form microfibrils. The microfibrils further aggregate on the macroscale to form fibers. The natural fibers themselves act as composite materials, assembling in a mainly lignin matrix. (Rong, Zhang, Liu, Yang & Zeng, 2001; Satyanarayana, Sukumaran, Mukherjee, Pavithran & Pillai, 1990) The cellulose content differs for different plant species. Cotton has the highest content of cellulose (90~99%). Wood (40~50%), jute (60~70%) and flax fibers (~80%) are all main sources of cellulose. (Filpponen, 2009)

Because of the large availability of cellulose, it has always been an important material in the life of humans. Up to the early 1900s, cellulose as well as other renewable biomaterials was the main sources of fuel, chemicals and material production. However, with the rapid growth of petroleum and petrochemical industries, biomaterials were gradually replaced. Nowadays, people have shifted their attention back to renewable bio-resources due to the depletion of oil reserves and environmental concerns.

2.1.2. Cellulose Chemistry

Cellulose is the primary component of the cell walls of higher plants. In 1838, Anselme Payen (1838) coined the name cellulose, which means the sugar (the "ose") from cells. However, cellulose chemistry did not arise until Willstatter and Zechmeister (1913) established the basic chemical formula of cellulose. In 1926, the macromolecular nature of cellulose was finally recognized and accepted due to Staudinger's contribution (Staudinger, 1926). Following those studies, Freudenberg and Braun (1928) published that 2, 3, 6-tri-O-methyl glucose was the only product obtained from methylation and subsequent hydrolysis of cellulose. Their works proved that, C-2. C-3 and C-6 carbon atoms bore free hydroxyl groups that were available for reaction, and consequently confirmed that cellulose was a linear homopolymer of anhydro–D-glucose units linked together by beta-1-4-linkage, as shown in Figure 2.1. Each glucose unit is oriented 180 degree to its neighbours.

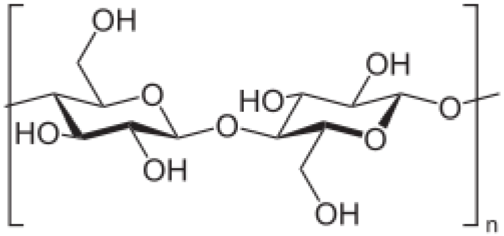

Figure 2.1: Chemical structure of cellulose. (Nishiyama, Langan & Chanzy, 2002)

2.1.3. Crystallinity and Polymorphism of Cellulose

There are three hydroxyl groups per monomer unit, so cellulose macromolecules are likely to be involved in a number of intra- and inter-molecular hydrogen bonds which play an important role in directing crystalline packing (John & Thomas, 2008). The complex hydrogen bonding network results in different ordered crystalline arrangements. The crystalline arrangements of cellulose are usually imperfect, on consideration of the crystal dimensions, chain orientation and the purity of crystalline form. The crystallinity can be determined by comparing the density of the crystalline phase and natural samples. The density of the crystalline phase is about 1.59 g/cm^3, whereas the density of the natural cellulose is about 1.55 g/cm^3, which corresponds to a crystallinity of about 70% (Hermans, 1949). Infrared spectroscopy and X-ray diffraction studies have shown that cellulose is composed of crystallites with interspersed amorphous regions, as illustrated in Figure 2.2. (Daniel, 1985) Current studies of crystallography and biosynthesis of cellulose suggest native cellulose is made up of parallel chains. (Dinand, Vignon, Chanzy & Heux, 2002; Sugiyama, Persson & Chanzy, 1991) Unlike starch, cellulose is a linear polymer, without coiling and branching. The hydroxyl groups form hydrogen bonds with oxygen atoms on the same or on a neighbour chain (Figure 2.3), holding the chains firmly together to form microfibrils with high stiffness. (Nadanathangam & Satyamurthy, 2011)

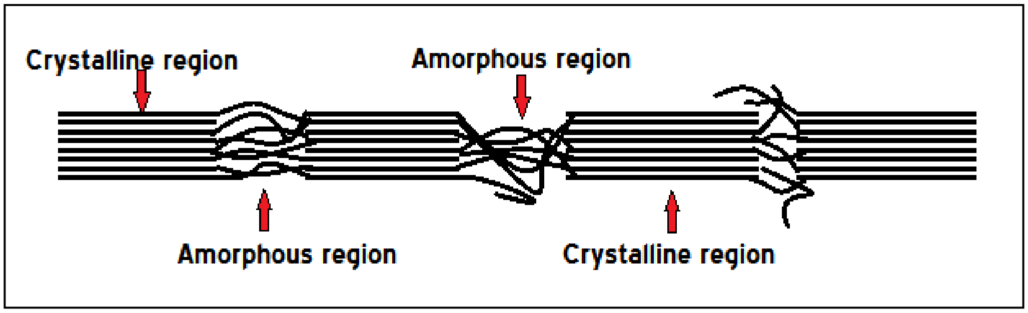

Figure 2.2: Crystalline and amorphous regions in cellulose microfibrils.

Four main crystalline allomorphs of cellulose have been identified, named cellulose I, II, III and IV. Each form has its characteristic X-ray pattern. Cellulose I is referred to as native cellulose, which is obviously the most abundant form. Cellulose II is referred to as regenerated cellulose, which can be prepared from cellulose I by mercerization followed by recrystallization. (Blackwell & Kolpak, 1976; Chanzy, Nishiyama & Langan, 1999) The crystalline forms of cellulose III (III_I and III_{II}) can be prepared from either cellulose I (to obtain cellulose III_I) or cellulose II (to obtain cellulose III_{II}) by treatment with liquid ammonia or certain amines such as ethylene diamine (EDA). Cellulose IV can be prepared by heating cellulose III in glycerol for 20 minutes at high temperature. With similar notations, cellulose IV_I and IV_{II} indicate their starting cellulose form by the shown subscript. (Watanabe, Ohkita, Hayashi & Sufoka, 1975)

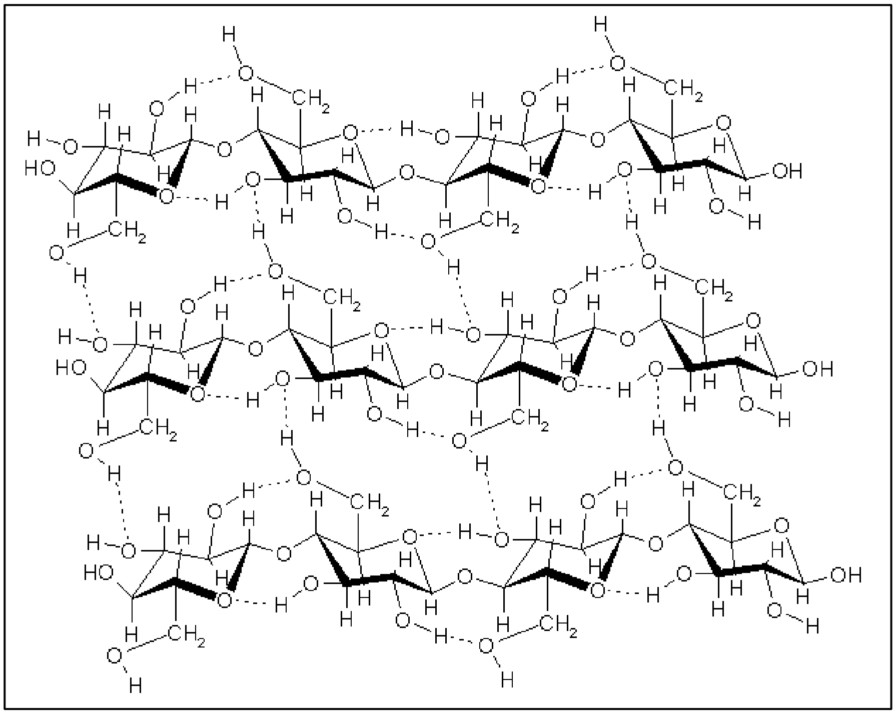

Figure 2.3: Inter- and intra-molecule hydrogen bonding of cellulose

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2.1.4. Cellulose Properties

Cellulose has no taste and it is odourless. It is insoluble in water and most of organic solvents due to its extensive hydrogen bonding and tendency to form crystalline structures. However it is soluble in more exotic solvents, such as CdO/ethylenediamine (cadoxen), aqueous N-methylmorpholine-N-oxide (NMNO), LiCl/N,N'-dimethyl acetamide, near supercritical water and in some ionic liquids. (Stenius, 2000; Turner, Spear, Holbrey & Rogers, 2004; Swatloski, Spear, Holbrey & Rogers, 2002)

Chain length or degree of polymerization (DP) is an important attribute of a polymer. Many properties of cellulose are related to its chain length. Chain lengths of cellulose are different depending on the sources. The DP of native wood is about 10,000 and it is approximately 15,000 in cotton. (Sjostrom, 1981) Chain length from the same source may also be different from different parts of the plant. Shorter chain lengths may also result from chemical and mechanical degradation during the purification and analysis processes. (Azizi Samir, Alloin & Dufresne, 2005) These smaller molecules are referred as cellodextrins, which are usually soluble in water and most organic solvents.

As mentioned earlier, high concentrations of hydroxyl groups result in strong intra- and inter-molecule forces, which have great effect on the properties of cellulose. For instance, the hydrophilic and swelling properties are strongly affected by hydrogen bonding. Cellulose is a very hydrophilic material which swells when exposed to high humidity environments. The swelling is reversible to some extent, though, it was found by Sugiyama, Vuong & Chanzy (1991), the desorption curves of cellulose have higher moisture contents than the adsorption curves. This hysteresis effect was explained as the inaccessibility of hydroxyl groups of cellulose in the dry state. In other words, hydroxyl groups are more difficult to access at dry state because hydroxyl groups satisfy each other, while at high moisture level the hydroxyl groups are easier to access as the adsorbed water breaks up the hydrogen bonding between the polymer chains.

2.2. Cellulose Nanofillers

Conventional fillers are usually in the micrometer or millimeter scale and are required at relatively high loading (10-40%) in order to significantly affect the final properties of a polymer matrix composite. In recent decades, as nanotechnology has grown enormously, nanofillers have become more and more promising. Nanofillers are defined as at least one dimension of the filler being in the nano-scale (1~100 nm). It was believed that nanofillers can greatly reinforce the properties of material due to their significantly large surface-area-to-volume ratio. The most researched example to date is nanoclay. In the early 1990s, a research team at Toyota, Japan, (Okada et al., 1990) found that a small amount (less than 5%, by weight) of an organically modified montmorillonite can enhance the stiffness, strength and increase the heat distortion temperature of Nylon 6 dramatically. After Toyota's study, more and more works on nanoclay have been reported. (Alexandre & Dubois, 2000; Okada & Usuki, 2006) Fiber-shaped fillers such as carbon nanotubes have also been studied. Due to the depletion of oil reserves as well as environmental concerns, natural fibers (i.e. cellulose) have received widespread interest. Its renewable nature, low density, abundant availability, high specific strength and low cost make cellulose a very favourable candidate for the production of nanofillers.

There are basically two classes of cellulosic nanofillers: cellulose nanocrystal (CN) and microfibrillated cellulose (MFC). Different terminologies are also used in different articles leading to confusion in the research field. For example, cellulose nanocrystals are also referred to in papers as nanocrystalline cellulose (NCC) or cellulose whiskers. The two classes of cellulosic nanofillers are distinguished by the main steps involved in their preparation, namely CNs are prepared chemically by acid hydrolysis while MFC was mainly prepared by mechanical homogenization.

2.2.1. Microfibrillated Cellulose (MFC)

MFC can be considered as cellulosic materials obtained by mechanical homogenization process. It was first extracted from wood cells by Herrick, Casebier, Hamilton & Sandberg (1983) and Tubark, Snyder & Sandberg (1983). After the mechanical treatment, the cellulose is moderately degraded, and the volume and surface area is highly expanded. (Nakagaito & Yano, 2005) MFCs are long and flexible fibrils with widths ranging from 10~100 nm and length generally in micrometer scale. As there is no chemical reaction involved in the preparation process, MFC maintains the cellulose structure, i.e. consisting of alternating crystalline and amorphous regions. Another difference from cellulose nanocrystal (CN) is that, MFC has web-like structure, while CNs are rod-like whiskers.

Two common types of equipment are used for the mechanical treatment to obtain MFC. Malainine, Mahrouz & Dufresne (2005) used a Gaulin homogenizer, at a pressure of 500 bar and at a temperature of 90~95 ^{o}C. A gel-like MFC suspension was obtained after 15 passes of homogenization. A microfluidizer is the most commonly used alternative to produce MFC. (Siqueira, Bras & Dufresne, 2009) A cellulose suspension is fed through a thin channel under high pressure. The pressure can reach as high as 30,000 psi. The high pressure pushes the suspension at an extremely high velocity, leading to high shear at the channel wall and hence, resulting in deformation of the product stream. However, high shear also causes heat generation. A heat exchanger is required to cool the product stream down to the room temperature. Both types of equipment are operated at high pressure and require repeated passes to achieve a high degree of homogenization. As a result, high power consumption is the main disadvantage of those processes.

Pre-treatments, such as mild acid hydrolysis, enzymatic hydrolysis can be combined with mechanical treatment to reduce the number of passes and hence energy consumption.

2.2.2. Cellulose Nanocrystals

Cellulose nanocrystals represent the crystalline regions extracted from cellulose, mainly by acid hydrolysis. The origin of acid hydrolysis of cellulose can be dated back to 1950s. Ranby (1951) first reported the production of stable suspensions of cellulose crystals by sulphuric acid hydrolysis of wood and cotton. The amorphous regions of cellulose are more accessible to acid attack compared to crystalline regions and therefore, under controlled conditions, the amorphous regions are assumed to be removed whereas the crystalline regions remain, as illustrated in Figure 2.4. This assumption has been proven by X-ray diffraction, which has shown that the acid treated rod-like particles have the same crystal structure as original cellulose. (Mukherjee, Sikorski & Woods, 1952; Mukherjee & Woods, 1953)

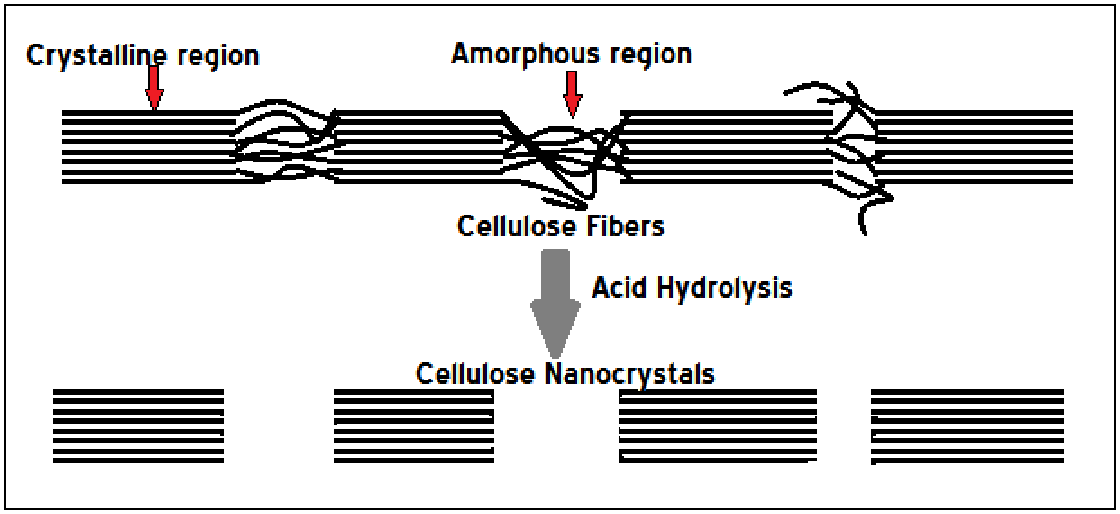


Figure 2.4: Illustration of acid hydrolysis of semicrystalline cellulose fibers.

2.2.2.1.Preparation of Cellulose Nanocrystal

Acid hydrolysis is a heterogeneous process which consists of the diffusion of acid into the amorphous regions and subsequent cleavage of glycosidic bonds. (Dong, Revol & Gray, 1998) The hydrolysis mechanism, as shown in Figure 2.5 (a), involves two paths: rapid protonation of the glucosidic oxygen (Path 1) or cyclic oxygen (path 2), followed by the addition of water to break down the glucosidic bonds. The reaction cuts the long chains into shorter fragments while the basic backbone structure remains. (Lu & Hsieh, 2010) In general, the degree of polymerization (DP) of native cellulose decreases rapidly during acid hydrolysis to a level-off DP (LODP). (Chang, 1971; Sharples, 1958) The DP reduction diminishes subsequently. The LODP is determined by the crystal size in the raw material, with a typical value of 250 being for hydrolysed cotton (Battista, 1950), 300 for ramie fibers (Nishiyama et al., 2003), and 140-200 for bleached wood pulp (Battista, Coppick, Howsmon, Morehead & Sisson, 1956). However, a wide distribution of DPs is typically observed.

The typical procedure currently applied for the production of cellulose nanocrystal is strong acid hydrolysis of pure cellulosic materials at controlled temperature and reaction duration. A resulting mixture is diluted with water, washed and separated by centrifuge to remove the acid. When the supernatant of the centrifugation product becomes turbid, dialysis against distilled water is carried out to remove acid residues, until the CN suspension reaches a relatively neutral pH. (Bondeson, Mathew & Oksman, 2006; Cao, Chen, Chang, Stumborg & Huneault, 2008) For the sulphuric acid treated CNs, the suspension is usually slightly acidic (pH~6) due to the attached sulphate groups. (Dong & Roman, 2007)

Sulphuric acid and hydrochloric acid have been commonly used for acid hydrolysis of cellulose. Phosphoric acid and hydrobromic acid have also been reported. When sulphuric acid is used as hydrolysing agent, sulphuric acid reacts with hydroxyl groups on the cellulose surface. This esterification reaction generates acid half-ester or the so-called cellulose sulphate, as shown in Figure 2.5 (b). The negatively charged surface groups aid in forming a stable CN suspensions in water due to electrostatic interactions.

The repulsive forces of the electric double layer efficiently prevent the aggregation of CNs. (Habibi, Lucia, & Rojas, 2010). However, the thermal stability of sulphuric acid treated CN is lower than that of hydrochloric acid treated CN. On the other hand, hydrochloric acid treated CNs have higher thermal stability, but there is no charged groups on the CN surface. As a result, the hydrochloric acid treated CNs are less stable in water since they tend to flocculate (Wang, Ding & Cheng, 2007). Wang, Ding & Cheng (2008) reported that a novel kind of spherical cellulose nanocrystal was prepared by hydrolysis with a mixture of sulphuric acid and hydrochloric acid under ultrasonic treatment. The hydrolysis took place with mild acid concentration so that the cellulose fibers would not be breakdown into nanosized rod-like particles. The ultrasonic treatment helped the hydrolysis to simultaneously occur at the surface and inner amorphous region, and form micrometer-sized fragments. Those fragments are further hydrolysed to form spherical particles gradually. Since the spherical cellulose nanocrystals were prepared with an acid mixture, the surface charged group were lower in concentration to those CNs prepared by sulphuric acid hydrolysis, meaning the spherical cellulose nanocrystals had better thermal stability than the sulphuric acid treated CNs.

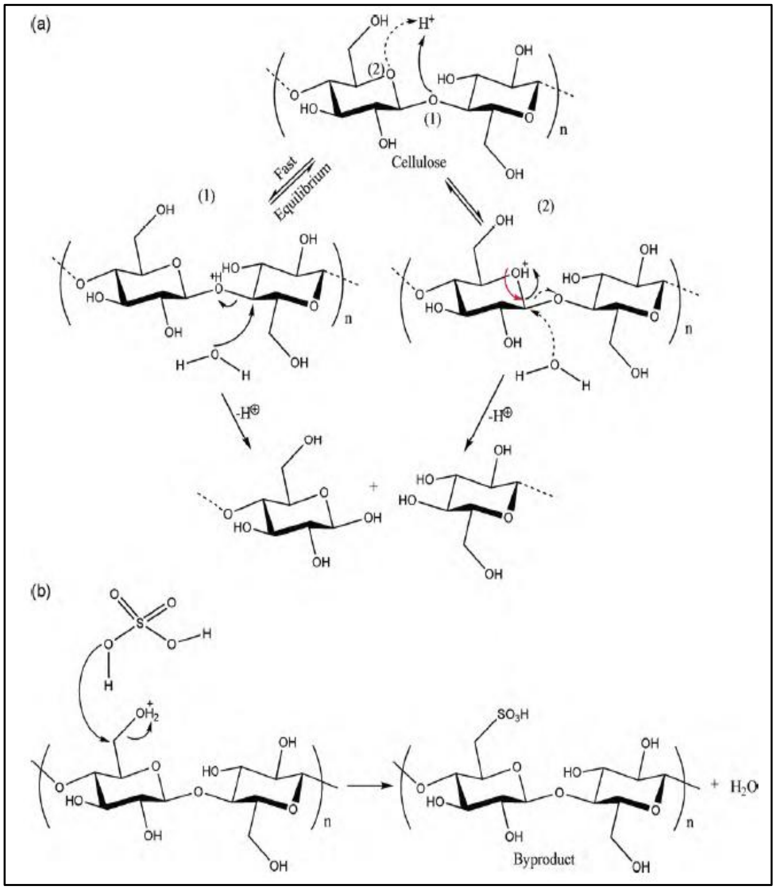


Figure 2.5: (a): Acid hydrolysis mechanism; (b): Esterification of cellulose nanocrystal surface (Lu & Hsieh, 2010)

Since a stablized CN suspension is normally preferred, hydrolysis with sulphuric acid is the most commonly used method to produce CN for the preparation of nanocomposites. Hydrolysis conditions, including acid concentration, pulp-to-acid ratio, reaction temperature and duration, can all play a significant role in the preparation of CNs. The conditions must be mild enough to avoid complete hydrolysis of the glucose. Revol et al. (1994) reported the best concentration of sulphuric acid was between 60-70 wt%. The sulfuric acid concentration used by other researchers does not vary much from 65 wt%. However, the reaction temperature varies from room temperature up to 70^{o}C and the corresponding reaction time varies from 30 minutes to overnight. Bondeson, Mathew & Oksman, (2006) performed a series of analysis and found that the optimized conditions for sulphuric hydrolysis were at temperature of 44^{o}C, an acid concentration of 63.5 wt%, a reaction time of 130.3 hours and a pulp-to-acid ratio of 1:10 g/ml with sonication time of 29.6 minutes to follow. Dong, Revol & Gray (1998) reported that at low temperature, 26^{o}C, it required 18 hours to produce ordered nanocrystals. At 65^{o}C, it was difficult to control the reaction well as side reaction, such as dehydration, which occurred producing a yellowish-coloured mixture. At 45^{o}C, the hydrolysis proceeded smoothly to produce an ivory-white suspension after a 1 hour reaction. The researchers also indicated that the particle sizes changed with the degree of hydrolysis. The longer duration the hydrolysis proceeds, the smaller the particle size will be obtained. The highest surface charge was obtained at hydrolysis time between 60-120 minutes. Beck-Candanedo, Roman & Gray (2005) reported that the effect of pulp-to-acid ratio is not large. The particle length decreases only 12.5% when doubling the pulp-to-acid ratio. However, the hydrolysis tends to be faster in a given time when larger volumes of sulphuric acid are used.

2.2.2.2.Morphology and dimensions of cellulose nanocrystal

The precise studies of morphology and dimension of cellulose nanocrystals are usually carried out using a microscopy, including TEM, AFM, E-SEM etc. or other light scattering techniques, such as small angle neutron scattering (SANS) and polarized and depolarized dynamic light scattering (DLS, DDLS). TEM is the most commonly used technique in characterization of CN dimensions. However, aggregation of particles occurs during the drying step of the preparation of test specimens. Furthermore, instrumental artifacts usually lead to an overestimation of CN dimensions. (Habibi, Lucia & Rojas, 2010) Figure 2.6 shows the TEM images of CNs from different cellulose sources: (a) tunicin, (b) ramie, (c) cotton, (d) sugar beet, (e) MCC, and (f) bacterial cellulose. (Siqueira, Bras & Dufresne, 2010)

On the other hand, AFM is another widely used technique to provide rapid indication of surface topography of CN under ambient conditions. (Miller & Donald, 2003; Hanley, Revol, Godbout & Gray, 1997) However, AFM topography may show rounded cross-section when other shapes are expected. This is probably due to substrate perturbation induced by the AFM tip and tip-broadening effect. AFM is considered as a valuable technique which can test not only the morphologies but also mechanical properties and adhesion of the cellulose nanocrystals. (Lahiji, Reifenberger, Raman, Rudie & Moon, 2010)

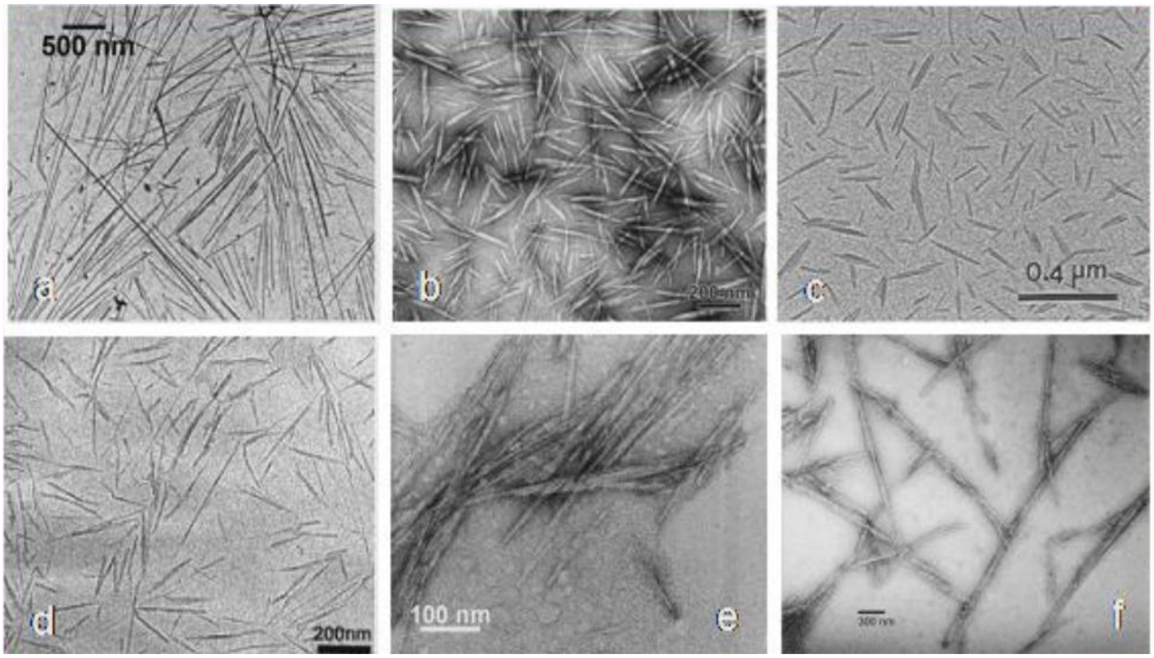
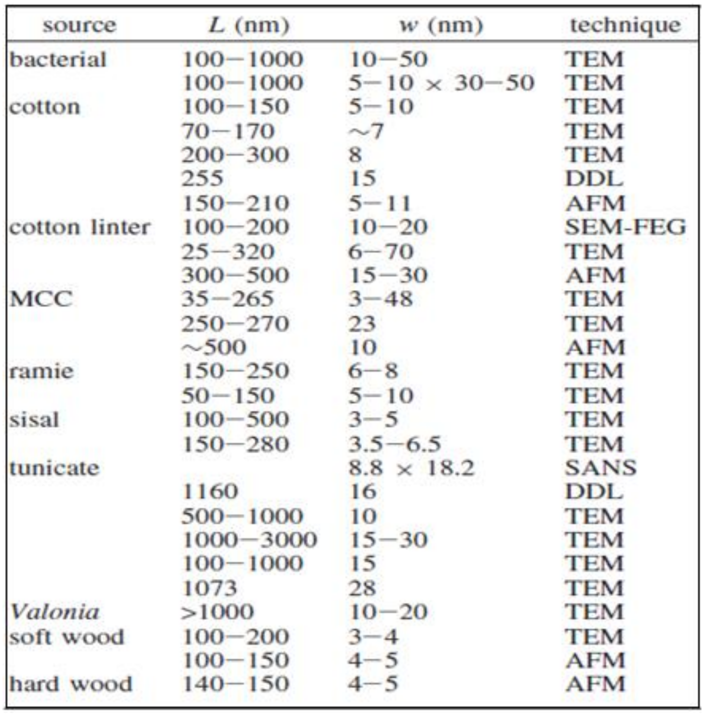


Figure 2.6: TEM images of diluted nanocrystal suspensions hydrolysed from various cellulose sources. Reprinted from (Siqueira, Bras & Dufresne, 2010)

Table 2.1 summarized the dimension of CNs found from different cellulose sources, characterized by different techniques. The dimension of CN can be seen to depend on the nature of the cellulose source as well as the analysis technique. The width is typically a few nanometers, while the length of CNs ranges from tens of nanometers to a few micrometers. For example, the CNs from wood have apparent diameters of about 3~5 nm, and length of 100~200 nm, (Bech-Candanedo, Roman & Gray, 2005) while for those from tunicate, the apparent diameter is about10~30 nm and the length ranges from 500~3000 nm. (Angles & Dufresne, 2000; Kimura et al., 2005)The aspect ratio, which is defined as length-to-diameter ratio also varies from different cellulose sources. For instance, the aspect ratio of cotton is between 10~30 and about 70 for tunicate.

Table 2.1: Examples of dimensions of CN from various cellulose sources obtained by different techniques. Reprinted from: Habibi, Lucia, Rojas, 2010



source	*L* (nm)	*w* (nm)	technique
bacterial	100−1000	10−50	TEM
	100−1000	5−10 × 30−50	TEM
cotton	100−150	5−10	TEM
	70−170	~7	TEM
	200−300	8	TEM
	255	15	DDL
	150−210	5−11	AFM
cotton linter	100−200	10−20	SEM-FEG
	25−320	6−70	TEM
	300−500	15−30	AFM
MCC	35−265	3−48	TEM
	250−270	23	TEM
	~500	10	AFM
ramie	150−250	6−8	TEM
	50−150	5−10	TEM
sisal	100−500	3−5	TEM
	150−280	3.5−6.5	TEM
tunicate		8.8 × 18.2	SANS
	1160	16	DDL
	500−1000	10	TEM
	1000−3000	15−30	TEM
	100−1000	15	TEM
	1073	28	TEM
Valonia	>1000	10−20	TEM
soft wood	100−200	3−4	TEM
	100−150	4−5	AFM
hard wood	140−150	4−5	AFM

2.3. Processing Methods of Cellulose Nanocomposites

When processing cellulose nanocomposite, properties of CNs, nature of polymer matrix, and the interfacial action between the fillers and matrix should be considered. The most challenging aspect of nanocomposite processing is dispersing CNs into a polymer matrix. Adopted processing techniques should ensure CNs to be well dispersed, to achieve good reinforcement of the materials. Casting-evaporation or solution casting is the most commonly used method in laboratory, while other processing methods including extrusion, sol-gel and electrospinning have also been studied.

2.3.1. Casting-evaporation Method

Casting-evaporation or solution casting is the most commonly used method to transfer cellulosic fillers into polymeric matrix in a laboratory due to its simplicity. (Cao, Chen, Chang, Muir & Falk, 2008; Dufresne, Dupeyre & Vignon, 1999; Lee et al., 2008; Malainine, Mahrouz & Dufresne, 2005) This method involves simply casting a mixture of CN suspension and polymer solution on Teflon or into polypropylene dishes and allowing the solvent to evaporate at an appropriate temperature. This technique can be further classified into three systems based on the types of polymer used.

2.3.1.1. Hydrosoluble or Hydrodispersible Polymer

Water is a preferred processing medium because of the good dispersion and high stability of the hydrophilic CNs in water, especially for the CNs prepared using sulphuric acid. However, this limits the choice of polymer as the matrix, i.e. only water soluble polymers can be used. Hydrodispersible polymers may also be used, as the hydrophilic polymer disperses well in water and achieve a homogenous composite with well dispersed CNs. The preparations of CN reinforced starch (Angles & Dufresne, 2000), silk fibroin (Noishiki, Nishiyama, Wada, Kuga & Magoshi, 2002), poly oxyethylene (POE) (Azizi Samir, Alloin, Paillet & Dufresne, 2004), polyvinyl alcohol (PVA) (Paralikar, Simonsen & Lombardi, 2008; Peresin, Habibi, Zope, Pawlak & Rojas, 2010), hydroxypropyl cellulose (HPC) (Zimmermann, Pohler & Geiger, 2004), carbonmethyl cellulose (CMC) (Choi & Simonsen, 2006) and soy protein isolate (SPI) (Wang, Cao & Zhang, 2006) are available in literature. The main drawback associated is that water soluble polymers are usually very sensitive to humidity. The absorbed water acts as plasticizers and strongly affects the properties of composites. Therefore, the prepared composites require to condition under specific environments.

2.3.1.2. Polymer Emulsion or Polymer Latex

Polymer emulsion or polymer latex is the stable dispersion of polymer microparticles into an aqueous medium. When polymer emulsion is mixed with CN suspension, both polymer particles and CNs stably disperse in water, as shown in Figure 2.7. The main interest of an emulsion system is to use non-polar, i.e. non-water sensitive polymers while keeping good dispersion of nanoparticles in solvent. Favier et al. (1995)

first reported the preparation of tunicin nanocrystal reinforced polymer latex, poly[S-co-BuA], a synthetic latex produced by copolymerization of styrene (35%) and butyl-acrylate (65%). Afterwards, other latexes, such as poly (β-hydroxyoctanoate) (PHO) (Dufresne, Kellerhals & Witholt, 1999), polyvinyl chloride (PVC) (Chazeau, Cacaille, Canova, Dendievel & Boutherin, 1999), polyvinyl acetate (PVAc) (De Rodriguez, Thielemans & Dufresne, 2006), natural rubber (Siqueira, Abdillahi, Bras & Dufresne, 2010), and waterborne epoxy (Ruiz, Cavaille, Dufresne, Craillat, & Gerard, 2001) have been processed into nanocomposites and showed that CNs suspensions were dispersed with the polymer emulsion in aqueous medium.

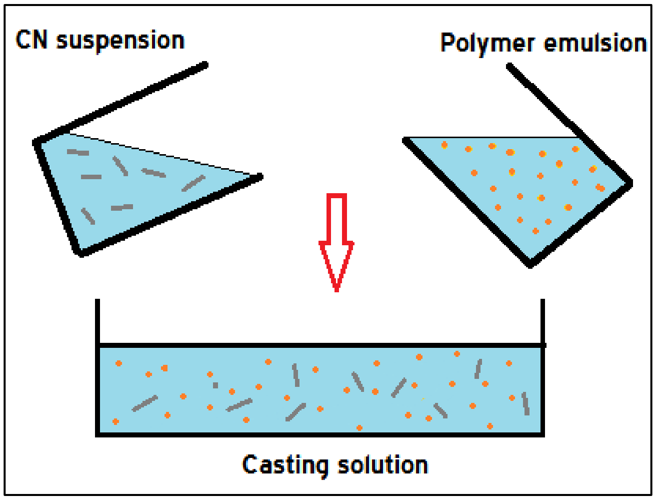


Figure 2.7: Illustration of casting-evaporation processing: emulsion system

2.3.1.3. Non-aqueous Systems

Besides hydrosoluble and dispersible polymers, a large range of polymers are soluble only in non-aqueous system. Due to the surface charge, CNs may disperse in polar solvent and dispersion is better in solvent with higher polarity. Azizi Samir, Alloin, Sanchez, EL Kissi & Dufresne (2004) dispersed freeze-dried tunicin CNs in N, N-dimethylformamide (DFM) without any coating surfactants or surface chemical modifications. The prepared suspension was sonicated to isolate nanocrystals. Viet, Beck-Candanedo & Gray (2007) obtained stable dispersion of cotton CNs in dipolar aprotic solvents (DMSO, DMF and formamide) by adding the freeze-dried CNs into the organic solvents, followed by sonication. A small amount of water was added to stabilize the CNs in solvent. In polar aprotic solvents, the negative surface charge will be the determining factor of dispersability. In protic solvents, the effect of surface charge is not obvious because the hydrogen bonds between nanocrystals are effectively disrupted, dispersing both charged or non-charged CNs. (Van den Berg, Capadona, Weder, 2007)

Coating surfactants are used in an another processing method to disperse CNs in organic solvents. For instance, Bonini et al. (2002) mixed CNs with poly(ethylene oxide)(9)nonylphenyl (PEPNP) in a ratio of 4:1 (PEPNP: CN, by weight) and freeze-dried the product. The coated CNs were then dispersed into toluene and obtained a suspension. However, due to the high specific area of nano-particles, large quantities (usually several times more than CNs) of surfactants are required. This is the main drawback of the method.

Surface chemical modification is another method to disperse nanocrystals in organic solvents. Due to the abundant availability of hydroxyl groups at the crystal's surface, different methods have been attempted, including esterification, etherification, oxidation, silylation, polymer grafting, etc. The main purpose of surface chemical modification is to enhance the dispersability of nanocrystals into organic solvents, as well as to improve the compatibility between nanocrystals and polymer matrices. (Siqueira, Bras & Dufresne, 2010)

2.3.2. Extrusion

Twin extrusion is the most commonly used process to produce composite in industrial scale, however, very few studies have been carried out concerning the extrusion process of cellulose nanocrystal reinforced composites. Due to the hydrophilic nature, CNs aggregate during drying or in non-polar matrix. Therefore, it is suggested that the CNs in aqueous suspension are first coated with a suitable surfactant and then pumped into a polymer melt. This method shows better dispersability than the freeze-drying/extrusion process but compatibility is still low. (Oskman, Mathew, Bondeson & Kvien, 2006)

2.3.3. Sol-gel Processing

A sol-gel processing approach has been recently reported by Capadona, Shanmuganathan, Tyler, Rowan & Weder (2008). This method mainly consists of forming a template of CN and filling the template into a polymeric matrix. The well individualized CNs are first formed in a three-dimensional template by self-assembly through a sol-gel method. This is basically achieved by a solvent exchange process with a water miscible solvent (e.g. acetone) in which the CN can form a well dispersed homogenous gel. The filler template is then immersed into a polymer solution, which must be miscible with the template solvent and will not re-disperse the CN.

2.3.4. Electrospinning

Electrospinning is a versatile method to prepare very fine fibers (with diameters ranging from several microns down to 100 nm) from a liquid, through the action of electrostatic forces. Electrospinning is particularly suitable to the production of fibers using large and complex molecules because the process is non-invasive and use of coagulation chemistry or high temperature is not required. (Ziabicki, 1976) Cellulose nanocrystal reinforced PVA (Medeiros et al., 2008), POE (Park, Kang, Kim & Jin, 2007), polystyrene (PS) (Rojas, Montero & Habibi, 2009) and polycaprolactone (PCL) (Zoppe, Peresin, Habibi, Venditti & Rojas, 2009) fibers were reportedly prepared by electrospinning.

2.4. Properties and Applications of Cellulose Nanocomposites

Microcrystalline cellulose has been widely used industrially while no practical application was envisaged for cellulose nanocrystals. However, several potential applications such as mechanical reinforcement, barrier materials, optical and biomedical applications may be cited.

2.4.1. Mechanical Properties of Cellulose Nanocomposites

In comparison to mineral or metal nanofillers that are industrially available, cellulose nanocrystals are prepared from abundant feedstocks, feature low density, are relatively low cost, and remain biodegradable (Azizi Samir et al., 2005; Dufresne, 2010; Podsiadlo et al., 2005). Due to these advantages, CNs are now being intensely examined as suitable fillers for mechanical reinforcement of a polymer matrix. The nanoscale dimensions along with their high inherent rigidity make them highly attractive for increasing the stiffness of polymer composites. The Young’s modulus of a CN is estimated to be 167.5 GPa which is comparable to that of Kevlar (Tashiro & Kobayashi, 1991). Favier et al. (1995) first reported the significant increase in storage modulus of a styrene/butyl arylate copolymer (poly [S-co-BuA]) matrix reinforced with low content of tunicin nanocrystals. Similarly, Cao, Dong, & Li (2007) reported a significant increase in Young's modulus and tensile strength with the incorporation of flax cellulose nanocrystals into waterborne polyurethane (WPU). An increase in Young's modulus was also observed using ramie cellulose nanocrystals to reinforce PVA composites (Peresin, Habibi, Zoppe, Pawlak & Rojas, 2010). The outstanding reinforcing effect of cellulose nanocrystal is due to a percolation phenomenon. Above a critical volume fraction, a rigid continuous percolation network can be formed by strong interaction (i.e. hydrogen bonds) between nanoparticles. The percolation was mainly determined by two factors: (1) shape and orientation of particles, and (2) interparticle interaction.

Higher aspect ratio means high surface area-to-volume ratio leading to stronger interfacial interactions, and therefore CN fillers with a high aspect ratio will be expected to provide the best reinforcing effect. The dimension of CN directly depends on the crystallinity and shape of crystal lattice in the original cellulose sources. Moreover, Eichhorn & Young (2001) reported that the Young's modulus of CN was decreased when the crystallinity of the CN decreases. Processing conditions, such as processing time and viscosity of the system, govern the possible formation of the continuous nanocrystal network and thus influence the final properties of nanocomposite materials. Hajji, Cavaille, Favier, Gauthier & Vigier (1996) found that processing conditions have a significant effect on the mechanical properties of Latex/cellulose whisker nanocomposites and classified them in ascending order of their reinforcement efficiency: extrusion < hot pressing < casting-evaporation. Generally, the slower processes such as solution casting method give better reinforcement, particularly in terms of mechanical properties. During such slow processes, CNs have more time to interconnect and form a percolation network. With the solution casting method, the viscosity of the system remains low until the end of the process. This allows the rearrangement of the CNs by Brownian motion. Conversely, in extrusion processes the high viscosity of polymer melt limits the random movement and consequently hinders the interconnection between CNs. (Ramires & Dufresne, 2011) The CN network is formed via hydrogen bonds, therefore the interfacial interactions play a significant role in mechanical properties of nanocomposites. Comparable competition between matrix/CN and CN/CN interactions is desired to achieve optimal mechanical properties.

2.4.2. Barrier Properties of Cellulose Nanocomposites

The incorporation of cellulose nanocrystal into a polymer may also improve its barrier properties because it was believed that gas molecules experience difficulty penetrating through the rigid crystalline domain of cellulose nanocrystals. A percolating CN network will force gas molecules to traverse a tortuous path to pass through the polymer film and thus act as a barrier layer. Improvement to the barrier property of a polyvinyl alcohol membrane was demonstrated by Paralikar, Simonsen & Lomdardi (2008) who experienced a reduction in water vapor and organic vapor (i.e. trichloroethylene) transmission for a 10% loading of cotton CN compared to the neat polymer. Pereda, Amica, Racz & Marcovich (2011) found that barrier properties to water vapor transmission improved up to 1% loading of CN in caseinate films but then decreased due to increased defects in the matrix.

2.4.3. Other Possible Applications

Cellulose nanocrystals have liquid crystal behaviour: they are orientated randomly in water suspension at low concentrations, while above a critical concentration a colloidal chiral-nematic phase can be observed. (Beck-Candanedo, Roman & Gray, 2005; Dong, Revol & Gray, 1998) The solidified liquid crystal can be utilized for optical application such as decorative coatings and security paper to prevent counterfeiting. (Revol, Godbout & Gray, 1997) In addition, due to the availability of hydroxyl groups, cellulose nanocrystal may also be functionalized and used in biomedical area. (Dong & Roman, 2007; Generalova et al., 2009; Noorani, Simonsen & Atre, 2009)

CHAPTER 3 RESULTS AND DISCUSSIONS: BIOCOMPOSITES REINFORCED WITH CELLULOSE NANOCRYSTALS DERIVED FROM POTATO PEEL WASTE

This chapter is a submitted journal article manuscript reporting the preparation and characterization of cellulose nanocrystal and cellulose-based nanocomposites. The results will be discussed in detail in this chapter.

Author contributions: Dan Chen performed all the lab experiments, characterizations and manuscript preparation. Dr. Michael Thompson supervised the work and participated in manuscript revision. Dr. Qiang Liu participated in some discussion of the work.

3.1. Abstract

This study investigated the effectiveness of cellulose nanocrystals derived from potato peel waste to improve the mechanical and barrier properties of a polymer. The nanocrystals were chemically derived from the cellulosic material in potato peel waste by alkali treatment and subsequently acid hydrolysis with sulfuric acid. Infrared spectroscopy indicated sufficient removal of lignin and hemicellulose from the raw potato peel biomass whereas X-ray diffraction confirmed that the prepared nanocrystals maintained their original crystalline lattice structure as the extracted cellulose, with a crystallinity of 85%. TEM images showed that the average fiber length of the nanocrystals was 410 nm with a diameter of 10 nm (aspect ratio of 41). Cellulose nanocrystals-filled polyvinyl alcohol (PVA) and thermoplastic starch (TPS) were prepared by solution casting method to maintain uniform dispersion of the 1-2% (w/w) fibers. An increase of 19% and 38% (starch composite) and 32% and 54% (PVA composite) in Young's modulus was observed for the 1% and 2% CN-reinforced composites, respectively. Water vapor transmission rate measurements showed a reduction of water permeability for the PVA nanocomposite, whereas no effect was observed for starch nanocomposite.

3.2. Introduction

Cellulose is the most abundant biopolymer on earth, derived from a variety of living species such as plants, animals, bacteria and some amoebas. It is the principal structural component of a plant's cell wall (Perez & Samain, 2010). An attractive source of cellulose for industrial uses is from agricultural waste, for instance, potato peel. Potato is one of the most important crops for human consumption but in recent years, its consumption in raw form has decreased, especially in developed countries. Many potatoes are processed into value-added products to meet demands of the fast food industries (Food and Agriculture Organization of United State [FAO], 2008). Potatoes are usually peeled before processing, and as a result, large quantities of peels are produced as waste. So far, the only value of potato peel waste is as animal feed which is sold at very low prices (Schieber & Saldana, 2009). In addition to food processing waste, there are significant quantities of rotten potatoes generated during years of heavy rainfall which represent a substantial financial loss to farmers unless an alternative industrial use can be found for the biomass. Therefore, extracting cellulose from the waste potato peels and processing it into a higher valuable product is not only an environment-friendly solution to disposal issues but also creates a non-food based economy for potatoes.

Cellulose microfibrils extracted from potato pulp were previously demonstrated as an effective reinforcing additive (Dufresne, Dupeyre, & Vignon, 2000). These fibers exhibited diameters in the order of 10 nm and lengths of 10-100 µm, prepared by alkaline washing, bleaching and finally mechanical attrition. However, these long fibers retain amorphous regions which weaken their strength whereas cellulose nanocrystals remove this structural defect by subsequent processing steps. This present study is the first known reference to prepare cellulose nanocrystals from potato peel waste for the purpose of being a high value-added filler in polymer matrix composite manufacturing.

Cellulose nanocrystals (CN) are a promising material and have been widely studied over the past two decades. They are commonly prepared by acid hydrolysis using strong acids (Azizi Samir, Alloin, & Dufresne, 2005). The acid digests the amorphous regions of cellulose and leaves only ordered crystalline domains as the product. This material is interesting as a nanofiller, having nanoscale dimensions, high specific area, and a highly rigid crystalline structure. In comparison to mineral or metal nanofillers that are industrially available, cellulose nanocrystals are prepared from renewable feedstocks, feature low density, are relatively low cost, and remain biodegradable (Azizi Samir et al., 2005; Dufresne, 2010; Podsiadlo et al., 2005). Due to these advantages, CNs are now being intensely examined as suitable fillers for mechanical reinforcement or to improve barrier properties of a polymer matrix. The nanoscale dimensions of CNs along with their high inherent rigidity make them highly attractive for increasing the stiffness of polymer composites; the Young's modulus of a CN is estimated to be 167.5 GPa which is comparable to that of Kevlar (Tashiro & Kobayashi, 1991). Cao, Dong, & Li (2007) reported a significant increase in Young's modulus and tensile strength with the incorporation of flax cellulose nanocrystals into waterborne polyurethane (WPU). Similarly, an increase in Young's modulus was observed in a recent study using ramie cellulose nanocrystals to reinforce PVA composites (Peresin, Habibi, Zoppe, Pawlak & Rojas, 2010). Nanofiller incorporation into a polymer may also improve its barrier properties by reducing gas transmission through increased tortuosity. Improvement to the barrier property of a polyvinyl alcohol membrane was demonstrated by Paralikar, Simonsen & Lomdardi (2008) who experienced a reduction in water vapor and organic vapor (i.e. trichloroethylene) transmission for a 10% loading of cotton CN compared to the neat polymer. Pereda, Amica, Racz & Marcovich (2011) found that barrier properties to water vapor transmission improved when using up to 1% loading of CN in caseinate films but then subsequently decreased with higher loadings due to increased defects in the matrix.

This paper establishes suitable synthesis conditions for CN derived from potato peel based on a preliminary study using cotton cellulose which has received considerable attention as a source of CN in the literature (Dong, Revol & Gray, 1998; Filpponen & Argyropoulos, 2010; Lu & Hsieh, 2010; Paralikar, Simonsen & Lombardi, 2008). Subsequently, the beneficial properties obtained by incorporating these nanoscale fibers into different polymeric materials were investigated. Purified yields of potato and cotton-derived CNs were incorporated into polymer films at concentrations from 0-2% (w/w) by the solution casting method and then tested for mechanical and water absorption/ transmission properties of the prepared nanocomposite films.

3.3. Experimental

3.3.1. Materials

Russet Burbank potatoes from Prince Edward Island, Canada were purchased from a local supermarket. A food-grade unmodified potato starch was provided by Manitoba Starch Products (Carberry, Manitoba, Canada). Polyvinyl alcohol (PVA, 87-89% partially hydrolyzed) was purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ, USA). Sulfuric acid (95-98%), sodium chlorite (>80%) and sodium sulfate (Na_2SO_4, > 99.0% purity) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), sodium hydroxide (pellet) was purchased from EMD (San Diego, CA, USA), and glycerol (99.7%) was purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada)

3.3.2. Extraction of Cellulose from Potato Peel Waste

The potatoes were hand-peeled and the removed mass was washed with water to rinse away soil and other bulk contaminants attached on the skins. The cleaned peels were added into water at a water-to-pulp ratio of 20:1 and agitated as a slurry using a blender for 10 minutes to remove the majority of potato flesh. The resulting slurry was filtered using a 250 µm sieve and repeated washed with distilled water. Potato peel waste is comprised of starch, cellulose, hemicellulose, lignin and other impurities (Arapoglou, Varzakas, Vlyssides, & Israilides, 2010), and therefore required several pretreatment steps including alkali treatments and chlorite bleaching (Dinand, Chanzy & Vignon, 1996) to isolate its cellulosic component prior to acid hydrolysis. Initially, the peel waste was treated with a 0.5 N aqueous sodium hydroxide solution at 80^{o}C for 2.5 hours under mechanical agitation. The treatment was done three times in order to completely eliminate the lignin, hemicellulose, and other impurities. After each treatment, the pulp was filtered and washed with distilled water using a 75 micron sieve to remove the alkali solution and dissolved impurities. The alkali washing was followed by bleaching with 2.3 wt% sodium chlorite solution in an acetate buffer (pH=4.9). The purpose of the bleaching was to remove any organic residues. The bleaching treatment was carried out twice at 70 ^{o}C for 2 hours each time. The extracted fibers were washed and freeze-dried.

3.3.3. Preparation of Cellulose Nanocrystals

Cotton cellulose nanocrystals were derived from bleached cellulose fibers using Whatman No.1 filter paper (Whatman Inc.; Piscataway, NJ, USA) as the source. The readily available quantities of cellulose from this source made it ideal for investigating the influence of acid hydrolysis conditions on the reaction yield in comparison to using the limited supply from our hand-peeled potatoes. Filter paper was cut into 10 mm×10 mm pieces and ground into dry pulp using a blender. The paper pulp was added into deionized water which made a dilute suspension for reaction with differing concentrations of sulfuric acid. The acid hydrolysis of cotton cellulose was carried out under mechanical agitation at different temperatures and for differing reaction times, as listed in Table 3.1. To terminate the hydrolysis reaction, an equivalent volume of distilled water was first added to the acidic solution. The cellulosic matter was separated from the mother liquor containing sulfuric acid by centrifuge, which was repeated until a turbid supernatant was obtained. The nanocrystal suspension was then dialyzed using Spectra/Por® membrane tubing rated for MWCO=12-14,000 daltons (Spectrum Laboratories Inc; Rancho Dominguez, CA, USA) immersed in distilled water for about 10 days with the water being changed frequently. Neutralization of the suspension was confirmed by measuring the pH of the dialysis water until it stopped changing (pH ~6.5), before the sample was collected. The collected aqueous suspension of cellulose nanocrystals was stored in plastic tubes at 4^{o}C till ready for use. If the fibers fell out of solution during storage, the sample was discarded. Preparation of CNs using the extracted cellulose from the potato followed the same experimental procedure, but at only one predetermined condition, namely with a 64 wt% sulfuric acid solution and using a pulp-to-acid ratio of 1:17.5 (g/ml) under conditions of 45^{o}C for 90 minutes.

3.3.4. Preparation of Thermoplastic Starch Nanocomposite Films

Thermoplastic starch being a sustainable bioplastic with increasing industrial attention due to its ready biodegradability, made it an interesting material to test as to whether CN can improve its mechanical and water absorption/transmission barrier properties. Potato starch was gelatinized at 80°C in a 4 wt% aqueous solution made from fresh deionized water and the CN/water suspension. To the solution, 30% (w/w, db=dry basis relative to the polymer matrix) of glycerol was added as a plasticizer. The gelatinized mixture was degassed by sonication for 15 minutes then by vacuum for 1 hour. Three different starch-based films were prepared with neat (0%), 1% and 2% (w/w, db) CN using a solution casting method. The water was allowed to evaporate under laminar air flow at room temperature for 3 days before the film was removed from its petri dish and then stored in an environmentally controlled room at 50% RH and 23°C for at least two days before testing.

3.3.5. Preparation of Polyvinyl Alcohol Nanocomposite Films

A 10 wt% PVA solution was made up by mixing the polymer granules with distilled water and the CN suspension. To the solution, 30% (w/w, db) glycerol was added as a plasticizer. The PVA granule was first left in distilled water at room temperature while being mechanical stirred overnight. Subsequently, the mixture was transferred to a water bath heated to 70^{o}C and mixed by mechanical agitation for 2 hours till the polymer had completely dissolved. The CN suspension (0, 1, 2% w/w, db) was slowly added into the stirred PVA solution in a dropwise manner once the polymer fully dissolved. The mixing continued for another hour, followed by 15-minute sonication. The cooled mixture was poured into petri dishes and the water was allowed to evaporate under laminar air flow at room temperature for 2 days. The films were demolded and stored in an environmentally controlled room at 50% RH and 23^{o}C for at least two days before testing.

3.3.6. Characterization

Surface morphology of the extracted cellulose was characterized with an optical microscope (VWR VistaVision) using samples which were dried on glass slides. Dimensions and the state of aggregation for the synthesized CNs were observed using a JOEL TEMScan transmission electron microscopy (JOEL Inc; Toyko, Japan) at an acceleration voltage of 80 kV. A drop of highly diluted (0.0001% w/v) CN suspension was deposited on a 100 mesh copper grid and allowed to dry. To improve the phase contrast of the fibers in the image, a drop of 2 wt% uranyl acetate was placed onto the grid and allowed to stand for one minute before the excess liquid was wicked off with filter paper. Particle lengths and diameters were directly measured from the micrographs and the length distribution was obtained by counting over 200 CNs for each sample using Image J 1.44 visualization software (National Institute of Health, US).

Fourier transform infrared (FTIR) spectra were measured from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, USA). The samples were ground into powder, mixed with KBr and pressed into thin pellets. The crystalline structures of CN were characterized by X-ray diffraction (XRD) collected on a Bruker D8 Advance Power diffractometer with Cu Kα radiation (λ=1.54Å) for a 2θ range from 5^{o} to 40^{o} at a scanning rate of 5^{o}/min. The crystallinity index was calculated using the equation by Buschle-Diller & Zeronian (1992),

$$I_c = \frac{I_{002} - I_{am}}{I_{002}} \qquad (1)$$

where I_{am} is the intensity of diffraction pattern at 2θ = 18^{o} corresponding to the baseline as characteristic of the amorphous regions in the cellulose and I_{002} is the intensity the diffraction peak at 2θ = 22.6^{o} which is associated with the crystalline region of cellulose (Ostenson, Jarund, Toriz & Gatenholm, 2006; Ramos, Frollini & Heinze, 2005).

Tensile testing was carried out with a Model 4411 universal mechanical testing system (UMTS) (Instron Corporation; Norwood, MA, USA) located in an environmentally controlled room (50% RH and 23^{o}C) according to ASTM D882. The films were cut into 5mm×80mm rectangular strips. The thickness of each specimen was measured before testing. Measurements were performed with a 30 mm grip separation, 500 N load cell and a crosshead speed of 500 mm/min for PVA films and 10 mm/min for starch films. Five specimens were tested for each sample.

The diffusion rate of water vapor through the films was determined based on a modified water method stated by ASTM E96. The exposed film area used for the tests was smaller than the stated ASTM value due to the limited space in controlled environment, but this change did not affect the analysis since the tests were done on a comparative basis. Each cylindrical glass jar was 8 mm tall and had a 3 cm diameter mouth opening, which was filled with distilled water to a level of 19 ± 6 mm. Each film sample (thickness of ~150 μm) was placed over the mouth opening of a jar and sealed with a flanged clamp. The test assemblies were weighed and placed on a horizontal surface in a controlled environment at 50% RH and 23^{o}C. The test assemblies were weighed frequently, recording the weight change. The rate of water vapor transmission (WVT) can be calculated as:

$$WVT = \left(G/t\right)A \qquad [\mathrm{g\ m^{2}\ h^{-1}}] \qquad (2)$$

where, G/t is the linear slope for the change in weight of a jar (G, in grams) relative to the time period that this change occurred (t, in hours), and A is the exposed area to atmosphere (in units of m^2).

3.4. Results and Discussion

3.4.1. Effect of Hydrolysis Conditions on Cotton Cellulose

Hydrolysis conditions including acid species, acid concentration, reaction time, pulp-to-acid ratio and possibly other factors are all important to the performance of the reaction in preparing CN. Acid hydrolysis of cellulose is a heterogeneous process which involves the diffusion of acid into the amorphous regions of the fibrous material and subsequent cleavage of glycosidic bonds, both steps being dependent on the stated factors above (Dong et al., 1998). Sulfuric acid is the most commonly used acid to synthesize CNs by hydrolysis. Although hydrochloric acid and phosphoric acid have also been reported, only sulfuric acid has been found to produce negatively charged surface groups which stabilize CNs in water (Habibi, Lucia, & Rojas, 2010). Therefore, in this work only sulfuric acid was used for all reactions while other reaction conditions were varied to investigate their effects on hydrolysis performance.

The objective of these preliminary trials looking at different hydrolysis conditions with cotton cellulose were to produce high quality, long, well isolated CN, with no consideration given for optimizing the reaction yield. A robust reaction system was sought to ensure that the limited amount of cellulose extracted from potato peel would yield suitable fibers for testing. The TEM micrographs in Figure 3.1 corresponded to different hydrolysis conditions outlined in Table 3.1 with cotton cellulose. Table 3.2

gives the average fiber length of CN prepared by these different tests. The test run, Exp1 (i.e. acid concentration of 64 wt%, reaction time of 60 minutes, hydrolysis temperature of 45^{o}C and pulp-to-acid ratio of 1:17.5) was deemed to represent the baseline standard by which the other hydrolysis conditions were compared. The CNs prepared by the conditions stated for Exp1, which are shown in Figure 3.1(A), appeared as well isolated, rod-like particles with nanoscale dimensions. These nanoscale fibers were 226 ± 65 nm in length (stated uncertainty was the standard deviation of the population) and had a nominal aspect ratio of 22.6. The CN product for this condition was similar to reported dimensions in the literature (Beck-Candanedo, Roman & Gray, 2005; Dong et al., 1998; Miller & Donald, 2003). Comparatively, undesirable product was demonstrated corresponding to the hydrolysis conditions for Exp5 where the acid concentration was lowered to 50 wt% with all other conditions remained the same as Exp1. At this lower concentration of sulfuric acid, the CN morphology shown in Figure 3.1(E) revealed fibers that could not be fully isolated, showing connections to a cellulose fibril trunk. Increasing reaction temperature to 60^{o}C and extending the reaction time to 90 minutes (Exp6) could not compensate for the use of a lower acid concentration in the reaction. As shown in Figure 3.1(F), the CN produced from Exp6 still showed only partially isolated fibrils in the TEM micrograph. The reason for these results may be ascribed to the fact that lowering the acid concentration decreased the diffusion of acid into amorphous regions of the cellulose.

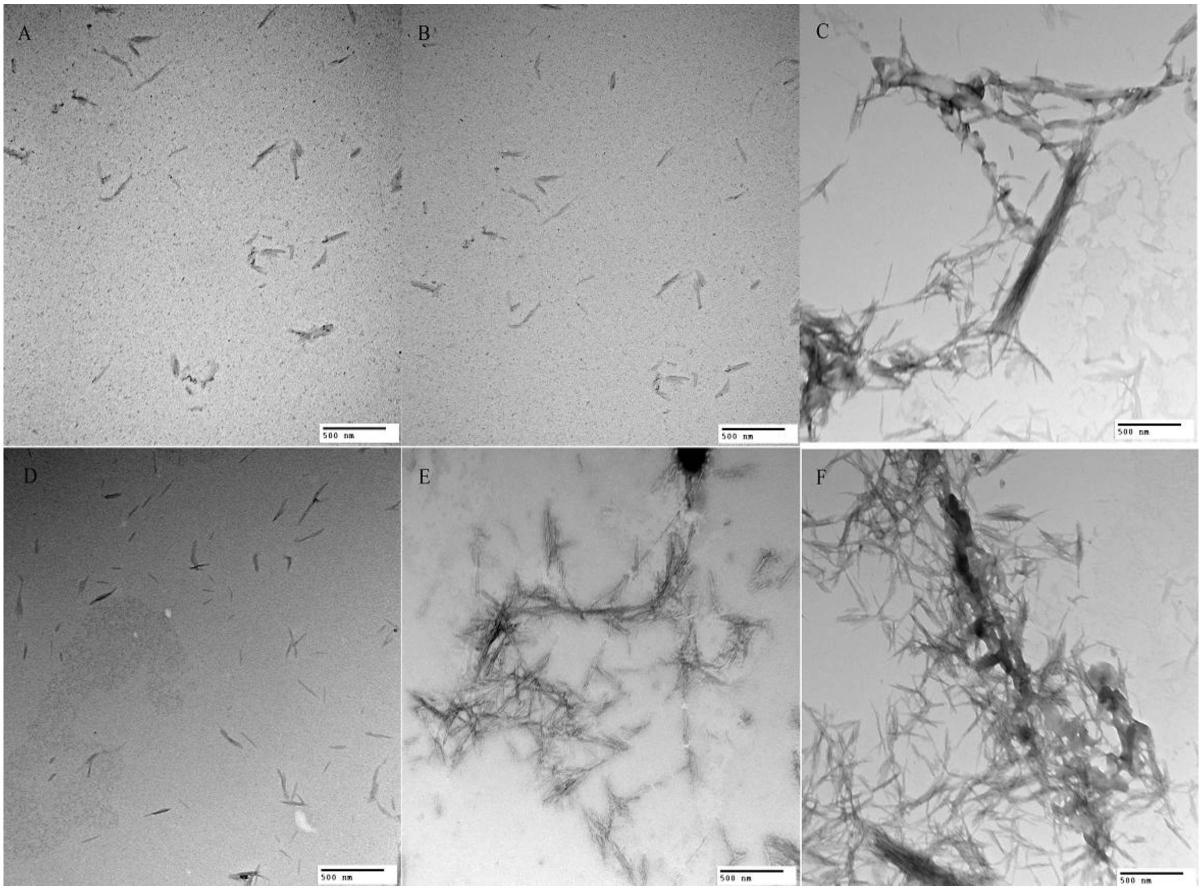


Figure 3.1: TEM images of cellulose nanocrystals prepared under different hydrolysis conditions: (A) Exp1; (B) Exp2; (C) Exp3; (D) Exp4; (E) Exp5; (F) Exp6. Scale bar=500 nm.

Table 3.1: Reaction conditions used for hydrolysing cotton cellulose

	Exp. 1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
Acid Concentration [wt%]	64	64	64	64	50	50
Reaction Time [min]	60	90	60	60	60	60~90
Hydrolysis Temperature [C]	45	45	45	60	45	60
Pulp-to-acid Ratio [g/ml]	1:17.5	1:17.5	1:8.75	1:17.5	1:17.5	1:17.5

Table 3.2: Average length of CNs prepared at different reaction time and temperature.

Exp.	Hydrolysis time (min)	Hydrolysis temperature (^{o}C)	Length of CN (nm)
1	60	45	226±65
2	90	45	183±66
4	60	60	215±71

(acid concentration: 64 wt%; pulp-to-acid ratio: 1:17.5 g/ml)

Reducing the pulp-to-acid ratio had an equally undesirable effect on CN synthesis as previously noted by lowering the acid concentration. When the pulp-to-acid ratio was decreased to 1: 8.75 in Exp3, it was directly observed during the experiment that the cellulose pulp was not thoroughly wetted by the solution initially. As the hydrolysis reaction proceeded the generated water wetted more and more of the pulp. It was apparent from these observations that the extent of reaction would likely vary throughout the product mass. Much of the cellulose fibers experienced little or no reaction time with the acid. A TEM image of CNs prepared in Exp3 is shown in Figure 3.1(C) which reciprocated this hypothesis. Whole bundles of fibrils were observed in the image, which appeared similar to the original look of the extracted cellulose microfibers.

The other two reactions which produced well isolated, rod-like CN corresponded to runs Exp2 and Exp4. The hydrolysis time was extended to 90 minutes in Exp2 from the 60 minutes used in Exp1 and reaction temperature was raised to 60^{o}C from 45^{o}C in Exp4 from Exp1. Micrographs corresponding to CN samples from Exp2 and Exp4 are shown in Figure 3.1(B) and 3.1(D), respectively. As the diameter of the cotton nanofibers did not vary among these runs, having an average value of 10 nm for Exp1, Exp2 and Exp4, only nominal length and the profile of the length distribution were useful for comparison of CN. When the reaction time was extended to 90 minutes, the particle length decreased by 19% to 183±66 nm (i.e. a fiber aspect ratio of 18.3). Conversely, with the reaction temperature raised to 60^{o}C, the particle length showed little difference from Exp1 with a length of 215±71 nm (i.e. aspect ratio of 21.5). To properly compare the nanofibers in each product, the fiber length distributions for the three samples are shown in Figure 3.2. The CN for Exp1 and Exp4 did indeed appear comparable with broad variance of fiber lengths. The CN for Exp2 gave a distinctly different distribution with a higher fraction of fiber lengths below 150 nm compared to Exp1 or Exp4.

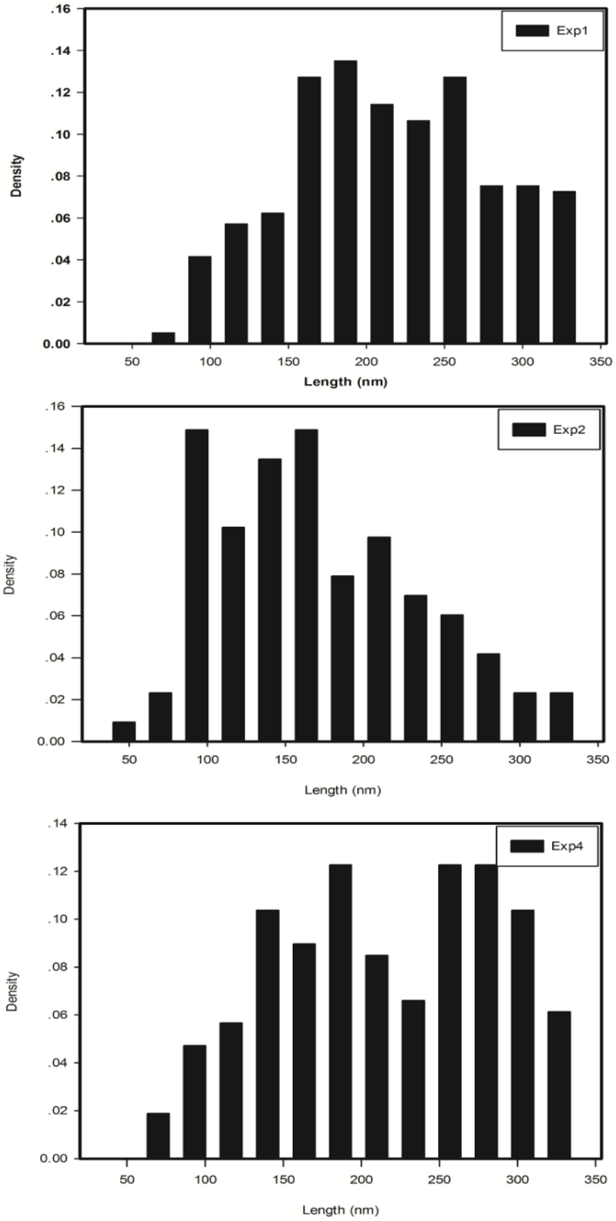


Figure 3.2: Length distribution of cellulose nanocrystals prepared at different hydrolysis conditions: Exp1, Exp2 and Exp4.

3.4.2. Morphology of CNs derived from Potato Peel

Freeze-dried and milled potato cellulose was hydrolyzed with 64 wt% sulfuric acid at a pulp-to-acid ratio of 1:17.5 for 45^{o}C; these conditions produced the longest nanoscale fibers for cotton which will be important for maximizing stress transfer as a reinforcing additive and the fibers were well isolated, improving the likelihood of a uniform dispersion when prepared in polymer films using the solution casting method. Based on the previous trials with cotton, the hydrolysis of potato cellulose was initially limited to 60 minutes (same as Exp1). However, large segments of the original microfibers were still observed in the reacting mixture after that period. The difference in performance on the same reaction condition may be ascribed to variant microstructures between the different species of cellulose. As a result, the hydrolysis was left to further proceed to 90 minutes (same condition of Exp2), with a yield of 42% (dry cellulose basis) which is comparable to that of cotton CN (43.5%). (Dong, Revol & Gray, 1998) Figure 3.3 shows a TEM micrograph of the nanoparticles prepared from potato peel which arose from the extended reaction time. The final CNs produced appeared well isolated from the cellulose microfibrils. The length distribution for CN fibers from potato peels is shown in Figure 3.4. The fibers were longer for potato CN compared to cotton CN, with a length of 410 ± 181 nm. The average diameter of the potato peel-derived CN was 10 nm giving an aspect ratio of approximately 41. This value indicates a larger surface area than that of

CNs prepared from cotton with the same hydrolysis condition (i.e. aspect ratio of 18.3), while it is similar to that of other plant-prepared CNs, such as sisal CNs (aspect ratio of 43; Siqueira, Bras, & Dufresne, 2009), wheat straw CNs (aspect ratio of 45; Helbert, Cavasille, & Dufresne, 1996) and luffa cylindrical CNs (aspect ratio of 47; Siqueira, Bras, & Dufresne, 2010).

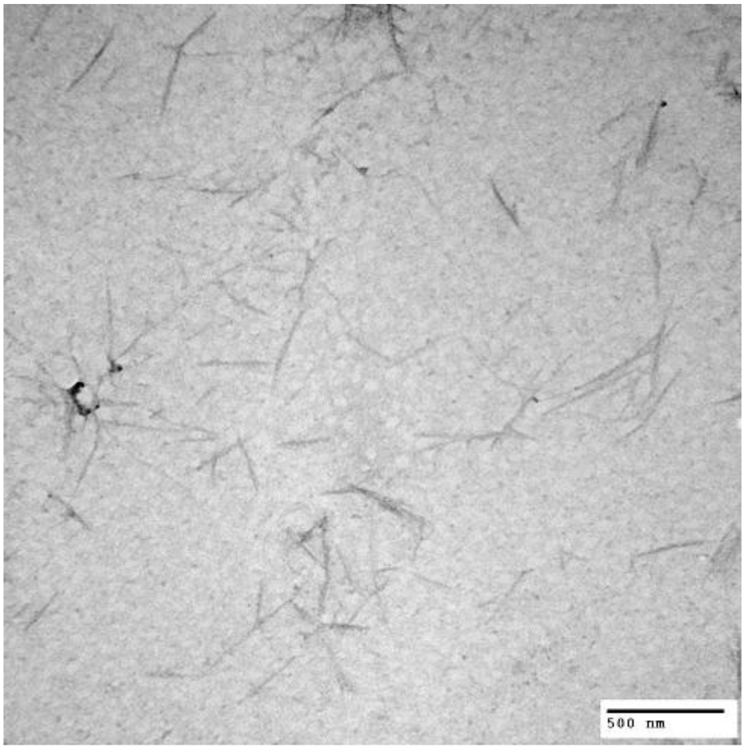


Figure 3.3: TEM image of cellulose nanocrystals prepared from potato peel, scale bar=500 nm.

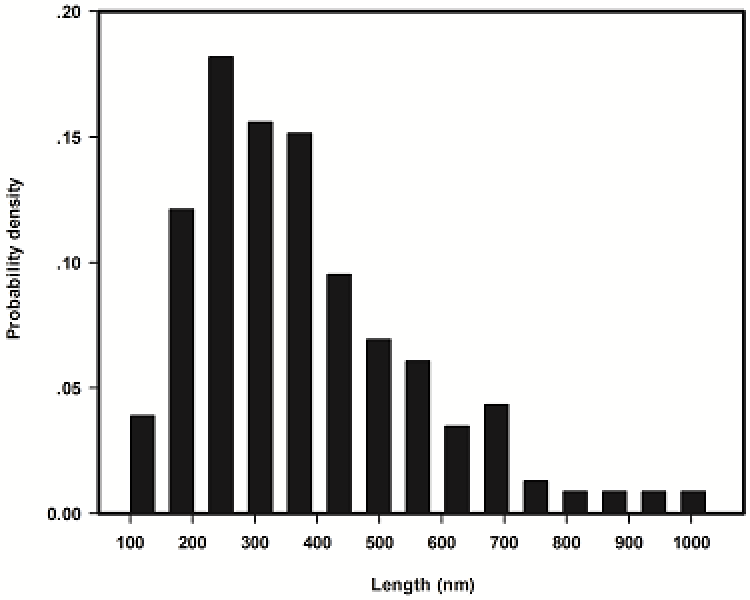


Figure 3.4: Length distribution of cellulose nanocrystals prepared from potato peel.

3.4.3. FTIR Characterization

Figure 3.5 shows the mid-range infrared spectra of potato and cotton cellulose at different stages in the synthesis procedure, namely untreated potato peel, cotton cellulose and alkali treated potato peel microfibers, as well as both CNs prepared by sulfuric acid hydrolysis followed by dialysis. The large bands at 3300-3500 cm^{-1} (assigned to O-H stretching) and near 2900 cm^{-1} (assigned to C-H stretching) were found for all characterized materials. Three vibrational bands were unique to only the untreated potato peel at 1739 cm^{-1}, 1514 cm^{-1} and 1456 cm^{-1}, with the former band attributed to the C=O stretching vibration of acetyl and uronic ester groups of hemicellulose as well as the ester linkage of the carboxyl group in lignin (Li et al., 2009; Sain & Panthapulakkal, 2006; Sun, Xu, Sun, Fowler, & Baird, 2005) and the latter two bands were assigned to the C=C vibration in lignin (Rosa et al., 2010). The region of 800-1500 cm^{-1} is a unique fingerprint region for cellulose where the majority of peaks in that range were found for all samples, indicating that regardless of alkali or acid treatment the cellulose maintained a similar chemical structure to the original untreated species. The only differences seen in the fingerprint region were for the two peaks at 1200 cm^{-1} and 810 cm^{-1} found only in the acid hydrolyzed cellulose, i.e. cotton CNs and potato peel CNs, which may be assigned to the half-ester sulfate groups produced by sulfuric acid hydrolysis (Heinze, Vieria & Heinze, 2000; Lu & Hsieh, 2010).

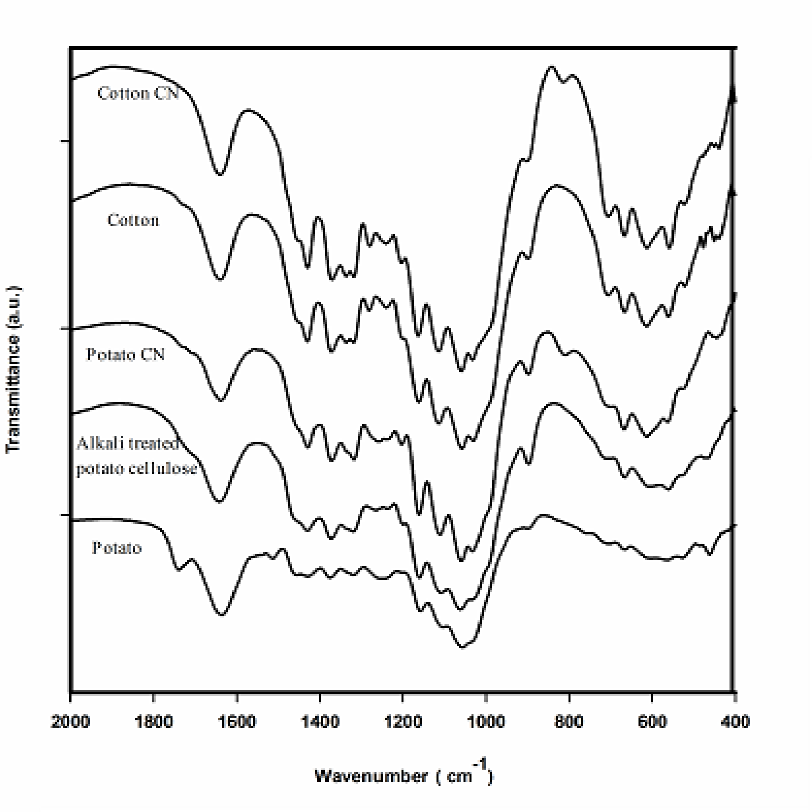


Figure 3.5: FTIR spectra of (a) untreated potato peel, (b) alkali treated potato fibers, untreated (c) cotton fibers, and CNs prepared by sulfuric acid hydrolysis from (d) potato fibers and (e) cotton fibers

3.4.4. X-ray Diffraction

Figure 3.6 shows the X-ray diffraction patterns of CNs derived from cotton (a) and potato peel (b). Both samples showed three diffraction peaks at $2\theta=14.7^{o}$, 16.4^{o}, and 22.6^{o}, which were assigned to the cellulose I crystalline structure (Wada, Heux, & Sugiyama, 2004). The result corroborated the infrared analysis in confirming the crystalline structure of both CN species were identical to their neat, untreated cellulose sources, i.e. the crystalline structure of cellulose was unaltered by acid hydrolysis in this work. The sharp diffraction peak for the (200) plane at 2θ=22.6^o indicated high perfection of the crystal lattice. The crystallinity of cotton CNs and potato peel CNs were comparable, calculated as 91% and 85%, respectively according to the Buschle-Diller and Zeronian equation.

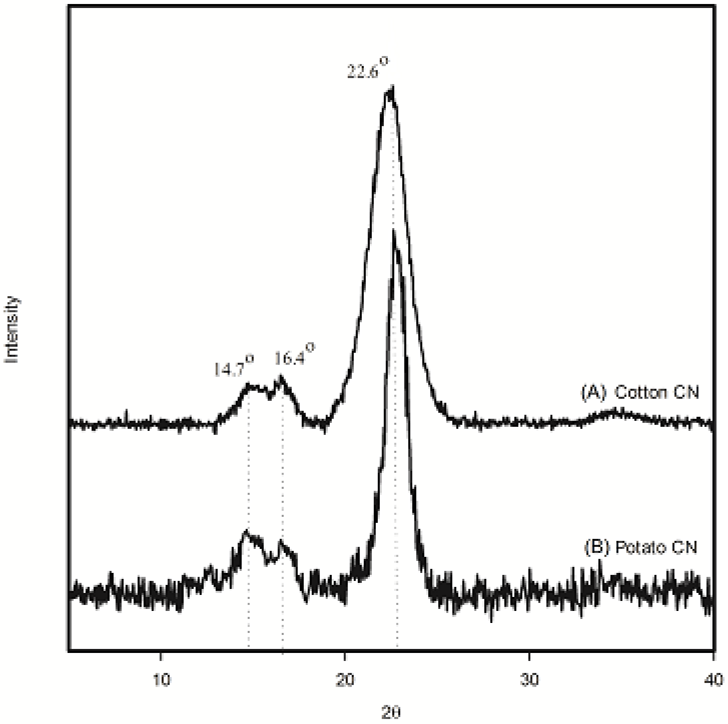


Figure 3.6: X-ray diffraction patterns of CNs derived from (A) cotton and (B) potato peel.

3.4.5. Tensile Test of Cellulose Based Nanocomposite

Four types of CN-based nanocomposites (TPS/PCN, TPS/CCN, PVA/PCN and PVA/CCN) were prepared to study the effects of CN fiber attributes and matrix compatibility on several end-use properties, where PCN refers to potato peel-derived CN and CCN to cotton-derived CN. Figures 3.7(A) and (B) show that the Young's modulus of both starch and PVA films increased with increasing PCN content. With the same plasticizer content (30 % w/w glycerol) in both materials, the matrix of gelatinized potato starch showed a higher modulus than the PVA. At 1% PCN, the modulus increased by 19% and 32% for the starch and PVA matrices, respectively. By 2% PCN, the modulus had increased by 38% and 54% for the starch and PVA matrices, respectively. The increase in tensile stiffness was significant but was small. Comparatively, the addition of CCN produced much smaller changes in the modulus of PVA (-7% and 10% for 1% and 2% CN respectively) or starch films (5% and 16% for 1% and 2% CN respectively); tensile stresses were not being as effectively transmitted across the particle-polymer interface for the CCN particles as found with PCN. This outcome could be related to differences in fiber geometry, aspect ratio, and chemistry between the CCN and PCN previously discussed in Section 3.2.

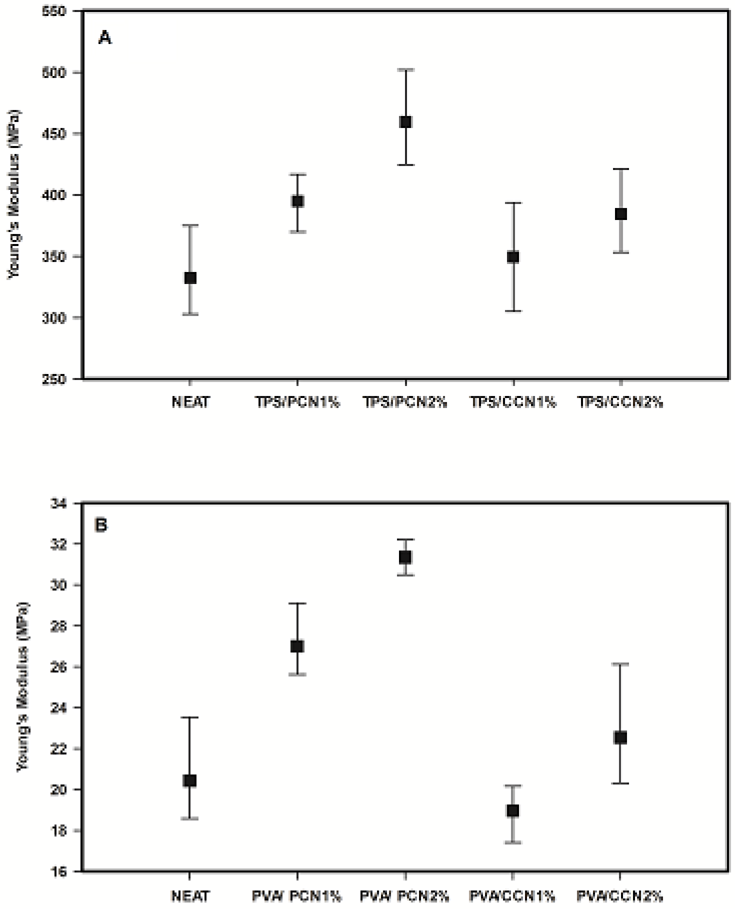


Figure 3.7: Young's modulus of (A) CN filled starch film and (B) CN filled PVA film

When both dimension and material chemistry change simultaneous, as seen in this work, it is difficult to interpret the differences seen between the two classes of CN and make statements regarding their reinforcement efficiency. In such a case, a semi-empirical micromechanics model, such as the modified Halpin-Tsai equation (Nielsen, 1974; Tjong & Jiang, 1999) can be useful in distinguishing whether the differences in mechanical properties between PCN and CCN lie in their differences in fiber geometry and aspect ratio, or their different interfacial chemistry with the polymer matrix. The model assumes a perfectly bonded interface between the matrix and reinforcing filler. It further assumes that the particles, if demonstrating an aspect ratio larger than unity, align themselves in the direction of load. The equations for the modified Halpin-Tsai model are given as:

$$\frac{E_c}{E_m} = \frac{1+\xi\eta V_f}{1-\phi\eta V_f} \tag{3}$$

in which,

$$\eta = \frac{E_f / E_m - 1}{E_f / E_m + \xi} \tag{4}$$

$$\phi = 1 + \left(1 + V_{f,\max}\right)\frac{V_f}{\left(V_{f,\max}\right)^2} \tag{5}$$

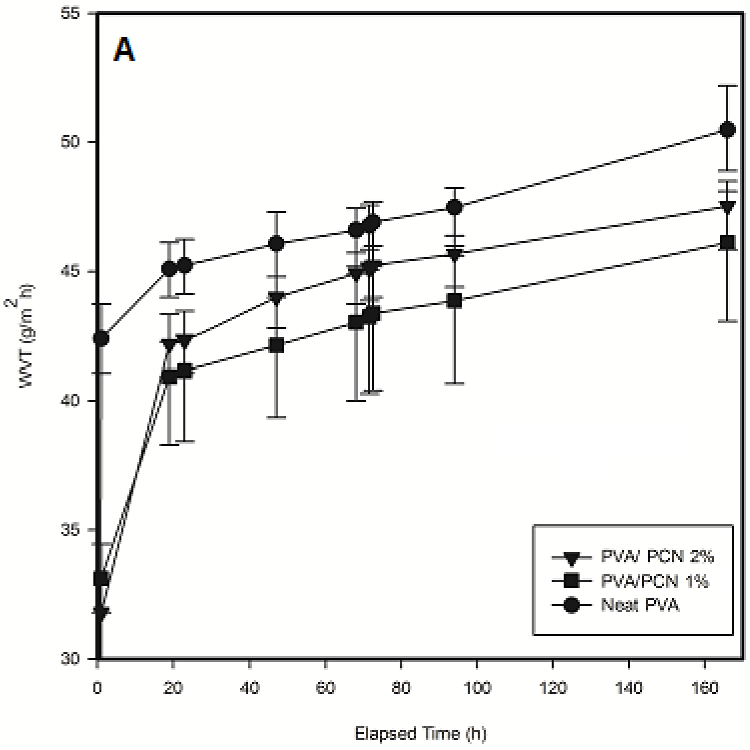
where E_c, E_m, and E_f are the moduli of the composites, matrix, and fiber respectively, V_f is the volume fraction of fibers, $V_{f,max}$ is the maximum packing volume of fibers (0.82 for random packing) and ξ is a constant related to the aspect ratio and orientation of the fiber (= 2L/D for discontinuous fibers). For the calculations, the density of both PCN and CCN were assumed as 1.59 kg/m^3 (Hermans, 1949) and a Young's modulus of 105 GPa for native cellulose crystal from cotton (Rusli & Eichhorn, 2008) was taken for both fillers; due to the slightly higher crystallinity of CCN noted by XRD compared to PCN this assumption may be overestimating the theoretical modulus for composites using the potato-derived material to a small degree. However, we are more interested in trends related to the variables of matrix polymer, CN type and CN concentration rather than absolute magnitudes in predicted modulus. The calculated and measured E_c/E_m values (ratio of Young's modulus of composite relative to the neat polymer matrix) are listed in Table 3.3. It was found that the measured values were smaller than the calculated ones in all cases, which may in part be due to the plasticizers (water and glycerol) disrupting hydrogen bonding at the interface between the matrix and CN. The difference between the measured and calculated ratio grew larger as the concentration of CN increased which suggested aggregation of the filler within the matrix. Optical microscopy indicated the absence of macro-scale agglomerates being formed as these composites were prepared, which would be most damaging to the reinforcing efficiency of fillers in a polymer matrix but sub-micron details were not be revealed visually by this technique; mechanical or rheological analysis tends to be more sensitive to microscale variations in filler dispersion in comparison to visual techniques like microscopy. Despite the higher crystallinity and seemingly more accurate value of a modulus value for CCN, the model consistently over-predicted modulus values for the composite from the experimental data, generally worse than found with the PCN composite predictions. With fiber geometry differences accounted for by the model, this poorer correspondence to predict the mechanical stiffness with CCN suggested that the lower mechanical reinforcement efficiency noted with CCN in Figure 3.7 compared to PCN should include the consideration of weaker interfacial interactions. We argue that these results point to potato peel derived CN being more effective as a reinforcing additive compared to cotton CN.

Table 3.3: Calculated and measured E_c/E_m values (ratio of Young's modulus of composite to neat matrix)

	Calculated	Measured	Percent Difference (%)
Starch/PCN 1%	1.452	1.188	26.4
Starch/PCN 2%	1.903	1.382	52.1
Starch/CCN 1%	1.232	1.051	18.1
Starch/CCN 2%	1.465	1.156	30.9
PVA/PCN 1%	1.479	1.322	15.7
PVA/PCN 2%	1.959	1.535	42.4
PVA/CCN 1%	1.219	0.928	29.1
PVA/CCN 2%	1.439	1.103	33.6

3.4.6. Water Vapor Transmission

The rate of water vapor transmission (WVT) was determined for both starch and PVA films. An improved barrier to water vapor was anticipated for these composite materials because it was believed that gas molecules experience difficulty penetrating the crystalline region of the cellulose crystals. A uniform dispersion of CN should force gas molecules to traverse a tortuous path to pass through the polymer film and thus act to retard gas transmission (Ramires & Dufresne, 2011). However, avoiding aggregate formation, which can actually improve vapor transmission, is not easy to achieve in practice. In our study, the starch films reinforced with 1 wt% and 2 wt% CN (either potato or cotton) did not show a reduced WVT compared to the unfilled plasticized starch films, which may be due to the similarity in chemical structure of the starch versus cellulose. A likely contributing issue was related to the fact that starch makes a porous matrix material when prepared from heat gelatinization due to incomplete disruption of the granular structure. This was certainly suggested by the uneven surface morphology seen by optical microscopy for the starch composites where granule boundaries were exposed. On the other hand, PCN-filled PVA films showed a decrease in WVT by 9.5% for 1% CN loading but only 6.2% for 2% CN loading after 166 h of testing. The CCN-filled PVA films showed no reduction in WVT for 1% CN loading but showed a decrease by 8.0% for 2% CN loading relative to the neat PVA film for the same testing duration of 166 h. It can be seen from Figure 3.8 which presents the WVT data with respect to time that WVT of the CN-filled PVA films (either cellulose species) were much lower than those of the unfilled PVA films, but increased rapidly within the first 20 hours. As more water was absorbed, the hydrogen bonds between PVA/PVA and PVA/CN species were disrupted and water could access further regions of the film more easily. This plasticization was evident by the center of the films which drawn downwards into the test assembly as time progressed. The rapid change in WVT that was only observed over the first 20 h was related to this saturation of the films.



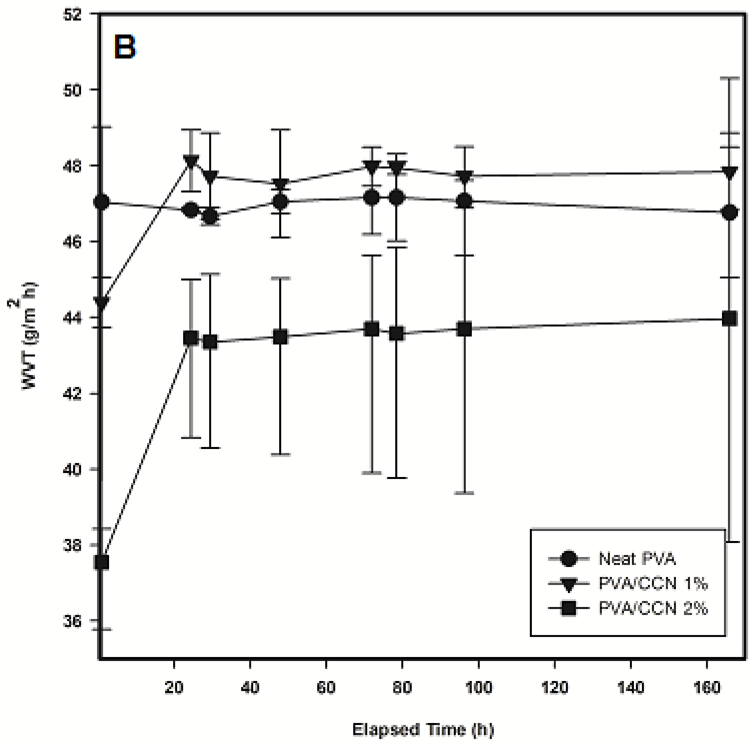


Figure 3.8: Water vapor transmission of neat, 1% and 2% (A) PCN-filled and (B) CCN-filled PVA films with respect to time.

3.5.Conclusions

In this work, cellulose nanocrystals were successfully prepared by acid hydrolysis from potato peel waste. FTIR spectroscopy indicated a sufficient removal of lignin and hemicellulose from raw potato peel by alkali treatment. X-ray diffraction confirmed that the prepared CNs remain the same crystalline lattice as cellulose. The particles have an average length of 410 nm and diameter of 10 nm (aspect ratio of 41). The crystallinity of the potato-derived nanocrystals was calculated as 85% from the peak intensities of X-ray diffraction patterns. An increase in Young’s modulus was observed for both CN reinforced starch and PVA composites. Water vapor transmission measurement showed reduced water permeability for CN-filled PVA composite, whereas no effect was observed for CN-filled starch composite.

CHAPTER 4 CONCLUSION

4.1 Conclusions

This thesis demonstrated the transformation of valueless potato peel waste into a high value cellulose nanocrystal (CN) and subsequently studied these nanoscale fibers in polymer composites. The research included preparation of cellulose nanocrystal from potato peel waste, characterization of the morphology, chemical composition and crystal structure of the CN and examined the mechanical and barrier properties of prepared CN-reinforced nanocomposites.

To produce high quality, well isolated CN, cotton cellulose was initially used to investigate hydrolysis conditions due to its availability as a source of cellulose compared to our hand-peeled potato peel. By a series of optimization trials and TEM characterizations, the hydrolysis conditions: acid concentration of 64 wt%, reaction time of 90 minutes, hydrolysis temperature of 45^{o}C and pulp-to-acid ratio (g/ml) of 1:17.5 were selected to hydrolyze cellulose derived from potato peel. TEM images showed that the average length of the CNs was 410 nm with a diameter of 10 nm (aspect ratio of 41).

Infrared spectroscopy was carried out to compare the chemical composition of untreated potato peel, alkali treated potato peel, potato CN, cotton cellulose and cotton CN. The results indicated sufficient removal of lignin and hemicellulose from the raw potato peel biomass. X-ray diffraction showed three peaks at $2\theta=14.7^o$, 16.4^o, and 22.6^o, which are assigned to the cellulose I crystalline structure. This result assisted the infrared characterization in supporting the crystalline structure of CN was identical to the untreated cellulose. The crystallinity of CN derived from potato peel and cotton were comparable, calculated as 85% and 91%, respectively from the peak intensities of X-ray diffraction patterns.

Cellulose nanocrystal-filled PVA and thermoplastic starch composites were prepared by the solution casting method to maintain uniform dispersion of 1-2% (w/w) CNs. An increase of 19% and 38% (starch composite) and 32% and 54% (PVA composite) in Young’s modulus was observed for 1% and 2% potato CN-reinforced composites, respectively. The reinforcing effect was significant but small, which could be related to the microscale aggregation of fillers. On the other hand, the addition of cotton CN did not increase the Young’s modulus significantly, for both PVA and starch composites. This may be attributed to differences in fiber geometry, aspect ratio or material chemistry but was determined through micromechanical modeling to be largely a result of weaker interfacial interactions than found with the potato-derived CN product.

Potato CN-filled PVA films showed a reduction in the water vapor transmission (WVT) by 9.5% for 1% loading and 6.2% for 2% loading; cotton CN-filled PVA films did not reduce the WVT for 1% loading but reduced the WVT by 8.0% for 2% loading, compared to the neat PVA films after 166 hours of testing. However, no significant effect was observed with the CN-filled (for either cotton or potato) starch composite, which may be caused by uneven surface morphology of starch films or similarity in chemical structures between the starch and cellulose.

4.2 Recommendations

The effectiveness of cellulose nanocrystals derived from potato peel waste to improve the mechanical and barrier properties of a polymer was relatively small. This could be related to the microscale aggregation of fillers. Improvement of filler dispersion, such as CN surface modifications could be considered for the next stage of the project. Furthermore, extrusion method is essential for scaling up the production of CN-based nanocomposite to an industrial scale in the future, but not many studies have been carried out in this field. The future work could also be focused on dispersing CN into a polymer melt and preparing CN-reinforced composites by extrusion techniques, although dispersing CN in dry state would be very challenging.

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