

Carboxylated Cellulose Nanocrystals Extraction from Kraft Pulp Using Ammonium Persulfate as Low Cost Source & Sustainable Method for High Quality Flexible Packaging Bio-coating

GERALD PERRY E. MARIN

MASTER'S THESIS

Packaging Logistics

Lund University



FIPDes

Food Innovation & Product Design

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Gerald Perry E. Marin



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Abstract

One of the leading challenges presented in 21st century for packaging industry is to address the growing environmental problems related to non-renewable flexible packaging. This leads to new growing interest in bio-based materials, among them cellulose nanocrystals (CNCs), which have already shown good performance in improving anti-fog and oxygen & water vapor barrier properties when applied to flexible film. A fast and low-cost CNC extraction was explored in this research by using unbleached Kraft pulp as the cellulosic source and treatment with ammonium persulfate as sustainable method for extraction. Presence of CNCs and its properties were verified and investigated using fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and x-ray diffraction (XRD). CNCs were then used to coat PET plastic film and were subjected to contact angle measurement, oxygen permeability, transparency, and haze for comparison. Tests have shown excellent barrier and optical properties, comparable to cotton linter CNC coating extracted using acid hydrolysis, even with lower amount of CNC and thinner coating used by Kraft pulp. Making CNC bio-coating more affordable can reduce the amount of plastic usage in production leading to reduction of total weight, which can provide economic benefit to producers and environmental benefit through reduced energy use during transport.

Executive Summary

Introduction

One of the leading challenges presented in 21st century for packaging industry is to address the growing environmental problems related to non-renewable flexible packaging. This leads to new growing interest in bio-based materials, particularly cellulose nanocrystals (CNCs) (see figure 1), which have already shown good performance in improving anti-fog and oxygen & water vapor barrier properties when applied to flexible film. Current existing extraction methods include use of acids, enzymes and oxidizers, by mechanical means, or combinations of these to isolate CNCs from the cellulosic material.

A fast and low-cost CNC extraction was explored in this research by using unbleached Kraft pulp as the cellulosic source and treatment with ammonium persulfate (APS) as sustainable method for extraction. APS extraction has recently been attracting attention due to its properties being ideal for CNC extraction, such as low long-term toxicity, high water solubility, and low cost compared to its sodium and potassium counterparts, as well as to other previous harsh extractive agents. Presence of CNCs and its properties were verified and investigated using fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and x-ray diffraction (XRD). CNCs were then used to coat PET plastic film and were subjected to contact angle measurement, oxygen permeability, transparence, and haze for comparison. PET film was chosen since it is one of the most common type of plastic being used in food packaging.

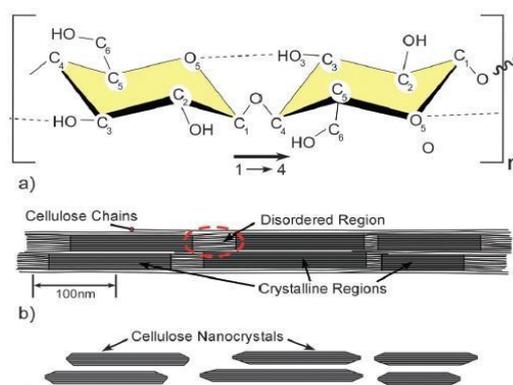


Figure 1. Simplified illustration of (a) cellulose molecule repeat unit, showing the 1-4 linkage & intramolecular hydrogen bonds (dotted line), (b) cellulose microfibril showing crystalline & disordered regions, and (c) cellulose nanocrystals after extraction, due to acid hydrolysis of the amorphous (disordered) region (Moon et al., 2011)

Materials and Methods

Characterization of kraft pulp material was performed together with InnovHub – Paper Division, who assisted in performing the experiments according to standards being used in the paper industry. For

the CNC extraction, swelling preparation was initially performed, where 10g dry weight of Kraft pulp was placed in 1000 ml beaker, diluted in 1-layer of distilled water, and stirred using magnetic stirrer. Heater temperature was increased to 70°C for 30 minutes, then cooled down in a cold water bath to reach the room temperature of 25°C. 340.5 g of ammonium persulfate (APS) was added to the cooled Kraft pulp solution to reach 1.5M APS, and was then stirred for another 30 minutes to allow the powder to dissolve completely.

APS Extraction of Kraft Pulp

This extraction method was based on patent with publication number EP 2513149 A1 filed by Leung, et al. It made use of 1.5M APS and was heated for 16 h at 70°C with high stirring speed for the cellulose nanocrystals extraction to occur completely. The sample was then removed from the heater, and was centrifuged using deionized water at 15,000 RPM for 20 minutes to concentrate the cellulose. It was centrifuged several times until it increased the pH level from around 0.2 to 3 (approximately 6 times). pH correction was then performed to the Kraft CNC solution, increasing it to pH 8 to avoid aggregation of the crystals in acidic environment. It was then subjected to ultrasonicator (UP400S 400W, hielscher Co., Germany) at 0.7 cycles of 20 minutes at 70% output to distribute CNCs evenly in the suspension. The solution was vacuum filtered using Whatman glass microfiber filter (grade GF/F, 0.7 µm) to remove fibers that did not react fully with APS treatment, and other big cellulose agglomerates and large contaminants that might have been introduced during the process. The Kraft CNC suspension was subjected to lyophilization by using a freeze drying machine (LIO-10P) for 3 days to get white Kraft CNC powder. The powder was rediluted using deionized water (18MΩ cm, Millipore Milli-Q Purification System) to reach 2.5% Kraft CNC solution, ultrasonicated for 5 minutes (0.7 cycles at 70% output), and applied to corona-treated PET film (25x20 cm²) for 20 rounds of rolling on one side of the plastic for approximately 3 minutes, improving adhesion of the nanocrystals on the surface of PET film. Automatic film applicator (ref 1137, Sheen Instruments, Kingston, UK) was used to apply the Kraft CNC solution evenly on top of the PET.

Two samples were created: sample 1 having applied only 1-layer of Kraft CNC, while sample 2 was made by directly applying another round of coating using the automatic film applicator immediately after drying the first layer. It was then dried using the blower and air-dried for 24 hours.

Results & Discussion

TEM was used to identify physical properties of Kraft CNCs extracted in nanoscale level.

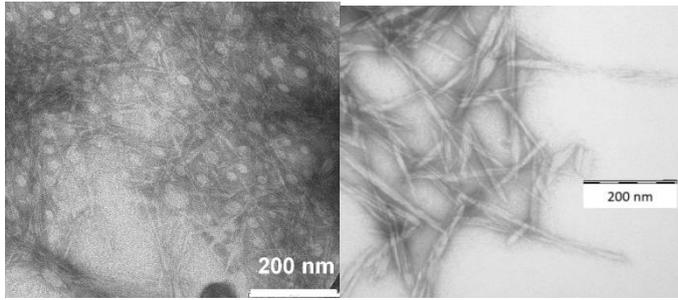


Figure 2. TEM image of Kraft CNCs (left) and cotton CNC (right) at 92,000 x magnification

Upon observing the image, it must be noted that the CNCs obtained have two distinct shapes: spherical and rod-like (see figure 2). APS concentration can influence the shape of CNC, as shown by the experiment involving different concentrations applied to a lyocell fiber matrix. It yielded a mixture of rod-like and spherical CNCs for 0.5M APS, but produced 100% spherical CNCs at 1M APS. On the other hand, acid hydrolysis extraction of Kraft pulp have yielded only rod-like crystal structure.

Table 1. Characterization of Kraft pulp raw material

Raw material	kappa number	α -cellulose %	β -cellulose %	γ -cellulose %	lignin %	Ash
Kraft pulp	35.48	86.8	0.37	13.57	7.87	0

The Kraft pulp sample obtained was carefully characterized to identify its kappa number, lignin, and α , β , γ cellulose contents (see table 1). Having a kappa number of 35.48 for the sample acquired is around the kappa number range of 30-35 for Kraft pulp that underwent conventional cooking. Having the lignin content of 7.87% shows that the Kraft pulp is subjected to an alkalinity of 20-25% in a span of 60-90 min. The high α cellulose in the resulting characterization experiment shows that previous processes have caused low degradation to the cellulose.

Table 2. Coating thickness comparison of kraft 1-layer, kraft 2-layer and cotton

Sample	Thickness (nm)
Uncoated PET	0
Kraft 1-layer coating	132.90
Kraft 2-layer coating	411.39
Cotton layer coating	660.00

The thickness values in Table 2 show that the cotton CNC coated PET film has the highest thickness, which can be explained by the total amount of CNC used in the solution.

The wettability of different samples shows that PET coated with cotton CNC has the best anti-fog property due to its very low contact angle measurement, allowing the water to spread to the solid surface. It is closely followed by Kraft 2-layers, with Kraft 1-layer exhibiting the lowest wettability. The increased amount of carboxylated CNCs in 2-layer compared to 1-layer have improved its hydrophilic interaction with polar water, thereby lowering the contact angle.

Cotton APS managed to have a high transparency, with its transparency value being close to the bare film. Kraft 1-layer and 2-layer have lower transparency values, even though both of them are thinner than cotton APS (see table 2), and lower percentage of CNCs applied in the coating (2.5% vs 7%). This can be due to the fact that in comparison to cotton linters, which has been bleached and contains >99% cellulose, the unbleached Kraft pulp as source is relatively unpure, hence ion impurities might have influenced the slight decrease in transparency.

To further verify the optical property of the samples, a sample logo with a subtitle of font 6, and website URL with font 11, were used. PET coated films still do have the same level of readability for both font sizes as compared to the bare film. This shows that in application to production, using Kraft CNC coating (both 1-layer and 2-layer at 2.5%) has almost negligible influence to transparency.

Table 3. Oxygen transmission rate values of Kraft 1-layer, Kraft 2-layer, cotton and bare PET

Oxygen Transmission Rate (O₂TR (cc m⁻² 24h⁻¹) 23°C)				
%RH	Kraft 1-layer	Kraft 2-layer	Cotton	Bare*
0				74.95
30	0.10	0.10	0.10	
40	6.72	3.94	4.2	
50	15.428	7.78	8.30	82

Given the relatively thinner size of both Kraft single and double layers as compared to cotton as seen on table 2 (132.90 nm and 411.39 nm vs 660.00 nm, respectively), and using less amount of CNC in the solution (2.5% vs 7%), the result has shown that Kraft CNC has exhibited a good potential as bio-coating source to improve oxygen barrier properties for PET film (15.43 O₂TR for Kraft 1-layer and 7.78 O₂TR for Kraft 2-layer vs 82 O₂TR for bare under measurements at 50% RH) (see table 3).

Conclusions

The experiment has exhibited that high quality CNCs can be extracted from unbleached Kraft pulp, an unpure cellulose material source, and can be utilized as a high quality bio-coating for PET to improve its packaging properties.

Ammonium persulfate has proven to be an efficient extracting agent for unbleached Kraft pulp. Kraft pulp preparation, which includes swelling using distilled water at elevated temperature (70°C) for 30 minutes, cooling down, and mixing it with APS at room temperature for 30 minutes, were shown to be important steps to execute before proceeding with APS activation via heating. Kraft CNC was successfully applied on PET, and different parameters related to packaging were performed. Oxygen permeability is an important property particularly for food packaging due to its potential effects on quality and shelf life. Kraft 2-layer showed positive results in terms of oxygen permeability rate at 30% and 40% RH. This is comparable to CNC coatings extracted using acid hydrolysis and acquired from cotton linters, which contains > 99% alpha-cellulose. Optical properties were also tested, given the transparent flexible packaging's importance to better market the products on the shelves by showing the actual product to consumers via see-through packaging, while keeping its protective barrier properties. Both Kraft 1-layer and 2-layer showed hydrophilic contact angles when in contact with water, denoting a good wettability and anti-fog property. However, more tests must be performed to verify its response when used in actual packaging. It must be highlighted that these results are based on 2.5% CNC re-dilution with distilled water after freeze drying using Kraft CNC extracted from the experiment, compared to 7% re-dilution of cotton CNC from acid hydrolysis. This re-diluted solution was used for coating application on PET film. This shows that Kraft CNC needed a lower amount of CNC concentration to achieve similar improvements observed from cotton CNC.

Utilizing unbleached and semi-processed Kraft pulp as cheaper material to extract CNC, in comparison to the heavily-processed cotton linters, was proven to be possible. Given the results, it can therefore be concluded that CNC bio-coating sourced from unbleached Kraft pulp provided a high quality bio-coating for PET, improving its optical and permeability properties. It has also provided a better alternative for a low cost extracting process at a shorter time (against acid hydrolysis, which includes dialysis step that lasts for 3-4 days). Application of this type of bio-coating can lead to reduction of total packaging weight by utilizing thinner and lighter plastics since its barrier properties were already improved. This can eventually provide economic benefit to producers and environmental benefit such as reduced energy use during transport.

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Most of all, I thank God, for His unspeakable miracles.

Introduction

One of the leading challenges presented in 21st century for the packaging industry is ensuring sustainability of the materials while maintaining high performance properties and low cost production. The majority of the world's flexible packaging materials are currently made up of petrol-based plastics, which are dependent on crude oil, a non-renewable resource. Flexible packaging can be defined as a type of packaging made of flexible or easily yielding materials that can change its shape readily once filled or closed, and its material construction can be paper, plastic film, foil or combinations of these. (Efremov, 2014) The increasing pressure to address the growing environmental problems related to oil dependency leads to new growing interest on bio-based materials for packaging, such as poly lactic acid, starch, gluten, and other bio-polymers. However, keeping a cost-effective process while improving their barrier and physical properties has been a challenge to be able to replace conventional plastics. Using bio-based coating materials, on one hand, is one step towards improving particular plastic properties, and also reducing amount of plastic usage (Li, Mascheroni, & Piergiovanni, 2015).

With cellulose as the most abundant renewable organic material produced in the biosphere (with an estimated 7.5×10^{10} tons of annual production), new researches are now geared towards utilizing its properties, particularly in the nano level, to make flexible packaging more environmentally-friendly while keeping the quality required for packaging. Recent discoveries and the advancement of nanotechnology reveal that acid hydrolysis application to cellulose fiber yields rod-like crystalline residues (see figure 1), called cellulose nanocrystals (CNCs), which are extracted crystalline regions of cellulose fibers. CNCs have been gathering attention in recent years due to its beneficial physical and chemical properties, as well as being low cost, high availability, renewability, light weight, nanoscale dimension, and unique morphology (Habibi, 2010). Given these, CNCs derived from cellulose are now being studied as potential bio-coating for flexible packaging to improve its packaging properties.

New research introduced various ways of preparing CNCs. Cellulose fibrils containing the CNs can be subjected to chemical (acidic and enzymatic hydrolysis, and TEMPO-oxidized processes) or physical treatments (refining and high-pressure homogenization, cryocrushing and grinding), to yield different CN morphological structures. TEMPO stands for 2,2,6,6-tetramethylpiperidinyloxy, and its

usage for catalytic oxidation of nanocellulose has made selective conversion chemistry of alcoholic hydroxyl groups to aldehydes, ketones and carboxyl groups possible under mild conditions (Fukuzumi, 2011). Different sources of CNCs such as cotton, bacterial cellulose, tunicate, wood pulp, and ramie also provide different dimensions, including various aspect ratio, or the ratio of length to width (Moon, Martini, Nairn, Simonsenf, & Youngblood, 2011).

CNCs proved to be a promising multi-functional coating for flexible food packaging (polyethylene terephthalate, oriented polyamide, and oriented polystyrene). It has excellent anti-fog and oxygen barrier properties, and has also led a reduction of oxygen and water vapor permeability (Li et al., 2015). When tested for overall migration level of CNCs coated on PLA, it exhibits migration limits below the requirement for food packaging materials in both non-polar and polar simulants (Fortunati, 2012). Moreover, CNCs have been tested for ecotoxicological tests on 9 aquatic species, and were found to have neither genotoxicity nor negative effects on their survival and growth (Kovacs et al., 2010). Given these, CNCs are attracting more attention as a safe nanomaterial to be used for food packaging.

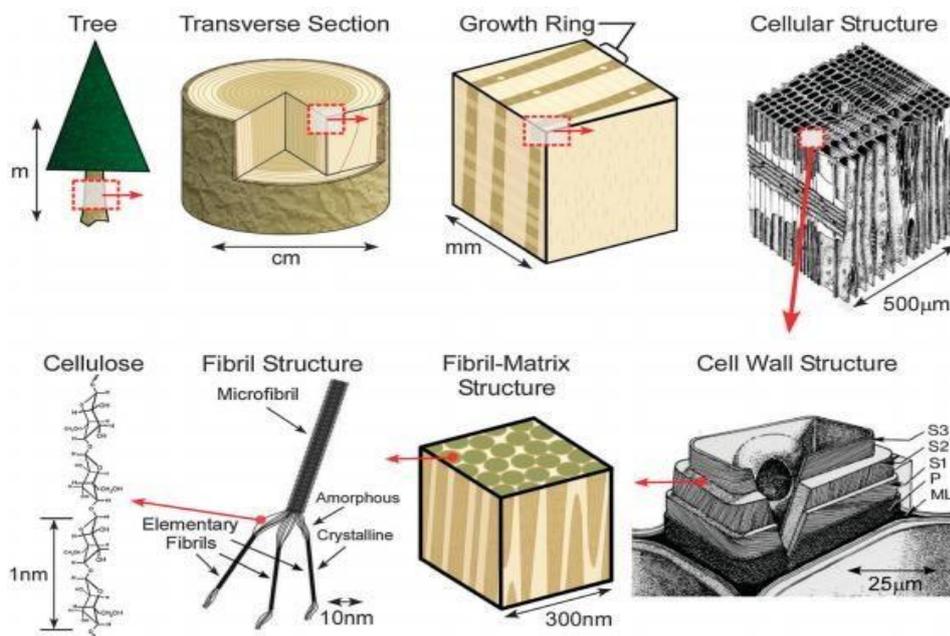


Figure 1. Schematic hierarchical structure from tree to single cellulose chain level (Postek, 2011)

High gas barrier properties is a critical component in packaging, particularly in food and drug industries. Inorganic materials such as SiO_2 (Creatore et al., 2002; Erlat et al., 1999; Haas et al., 1999)

and nanoclays (Ghasemi et al., 2012; Priolo et al., 2010; Sánchez-Valdes et al., 2006; Svagan et al., 2012) are currently being used as oxygen barriers, which can be in danger of being cracked (Priolo et al., 2010) or potential health risks (Lordan et al., 2011). Using CNCs as bio-coating is deemed to be an additional option, together with other inorganic coatings currently available, to improve gas barrier properties of flexible packaging.

Given the abundance of cellulose from paper and board, particularly in packaging, which are usually discarded as waste after usage, it is a possible CN source which can be further utilized and increase recyclability in the value chain.

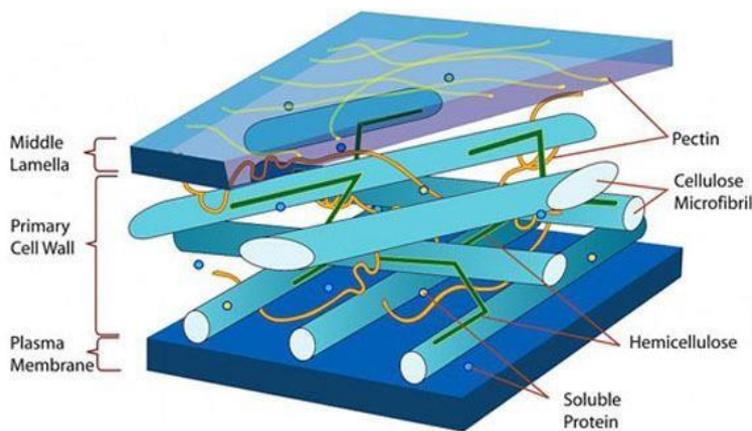


Figure 2. Superimposed layers of cellulosic microfibrils cemented together by pectins and hemicelluloses in plant cell walls. (Rampazzo, 2013)

Present procedures and challenges

Cellulose, hemi-cellulose and lignin are the main components of plant fibers (Vignon et al, 2004). Cellulose chains are connected by 1→4 linkage and intrachain hydrogen bonds (dotted line) (see figure 3a) and are arranged in the form of microfibrils enclosed by hemi-cellulose and lignin. Cellulose microfibrils range from 2-20 μm diameter and 100-40,000 nm long depending on the matrix source (Itoh, et al. 1984). These cellulose fibrils contain two regions: the highly ordered (crystalline) regions, and disordered (amorphous-like) regions (Figure 3b) (Moon et al., 2011; Nishiyama, 2009).

These crystalline regions that can be found within cellulose microfibrils are extracted, resulting in cellulose nanocrystals (CNCs) (Figure 3c).

Current existing extraction methods include use of acids, enzymes and oxidizers, by mechanical means, or combinations of these to isolate CNCs from the cellulosic material. The difficulty lies on the long process of removal of non-cellulosic contents from the source, such as lignin, hemicellulose, and wax (see figure 2), and then followed by the removal of disordered cellulose segments to break down the native semicrystalline cellulose into its elementary crystalline domains (Revol, et al., 1992; Cao, 2007; Filson, et al., 2009; Montanari, et al., 2005). What limits the CNCs for industrial commercialization and adoption by companies are the large quantities of waste chemical agents such as H_2SO_4 , as well as the huge expense related to scaling up the production (Ng, 2015).

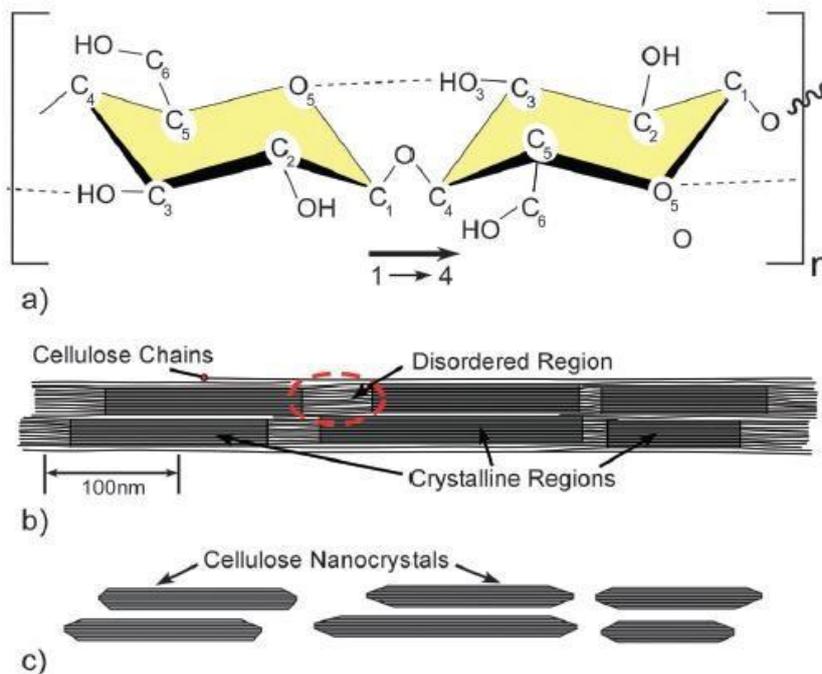


Figure 3. Simplified illustration of (a) cellulose molecule repeat unit, showing the 1-4 linkage & intramolecular hydrogen bonds (dotted line), (b) cellulose microfibril showing crystalline & disordered regions, and (c) cellulose nanocrystals after extraction, due to acid hydrolysis of the amorphous (disordered) region (Moon et al., 2011)

Extraction using Ammonium Persulfate

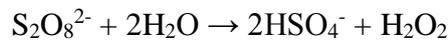
A novel procedure using ammonium persulfate (APS) as the oxidant has recently been attracting attention due to its properties being ideal for CNC extraction, such as low long-term toxicity, high

water solubility, and low cost compared to its sodium and potassium counterparts, as well as to other previous harsh extractive agents. APS has so far been used to extract CNCs from flax, flax shives, hemp, triticale, microcrystalline cellulose (MCC), Whatman CF1, wood pulp, bacterial cellulose (Leung et al., 2011), and lyocell fibers (Cheng, 2014), and the resulting mean particle length and length polydispersity were similar. As compared to acid hydrolysis, APS also cuts the production time by 3-4 days since it does not need to perform dialysis, the most time-consuming process. Yield was also improved by using APS compared to acid hydrolysis, with 28-36% for APS treatment and only 5% for acid hydrolysis from flax and hemp fibers (Leung, et al., 2011). The cross-section dimensions of CNCs prepared from APS extraction using hemp, flax, and triticale as cellulosic matrix have median around $\approx 3-6$ nm, which corresponds to elementary fibrils ($\approx 3-7$ nm in diameter) of cellulose. This is in comparison to acid hydrolysis and bleaching extraction, which yielded longer average diameters of 16-28 nm (flax) and 20-40nm (hemp). It must be noted that CNC extracted from different cellulosic matrix also showed similar mean particle length and length polydispersity with low standard deviation values. This small CNC size is desirable to serve its purpose as nanofillers and barrier properties, while its uniformity in production is important to provide consistency for mass production of CNCs.

During the APS treatment, the removal of lignin, hemicellulose, pectin, and other non-cellulosic contents happened thanks to the production of free radicals during heating:



And hydrogen peroxide, which happens under acidic conditions (pH 1.0):



Both SO_4^- and HSO_4^- penetrate and break down the amorphous region, isolating CNCs, as well as decolorizing the material and isolating the material by opening the aromatic rings of lignin (Leung, et al., 2011). Oxidation happened preferentially at C6 primary alcohol of crystalline cellulose. Resulting CNCs produced have carboxylic groups on the surface (see figure 4), providing active sites for surface modification, protein/enzyme immobilization, synthesis of nanoparticles, polymer nanofillers, biosensing platforms, affinity chromatography, and drug targeting / delivery (Li, 2012; Liu, 2011 and Lam, 2013).

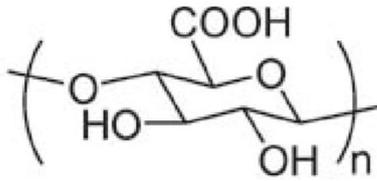


Figure 4. Cellulose with carboxyl group, adapted from a surface modification example of carboxylated CNC (Leung, 2011)

Kraft Pulp as Low Cost CNC Source

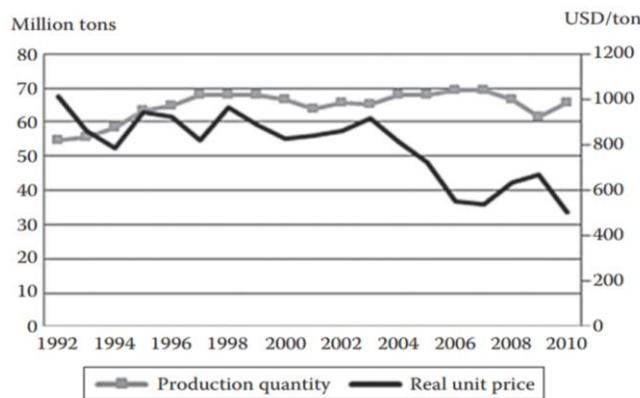


Figure 5. Production of packaging and wrapping paper in developed countries and real world price from 1992 to 2010, where real unit price went down while production quantity kept a relatively stable output (Hetemäki, Hänninen, & Moiseyev, 2014)

Pulp and paper industry is currently being challenged by the maturing stage of their products, and the decline of the graphics paper market due to increasing digital content. In this industry, the pricing differential is marginal due to low switching cost, and the negotiating power lies at the customers (see figure 5). Hence, the need for changes and innovation in the industry, such as development of new products (Hetemäki et al., 2014). The increasing concerns over sustainability has increased the usage of recovered paper in production (see figure 7). This increase in recovered paper rate lowered the demand for wood pulp from 60% in 1990 to 43% in 2010, with all grades of wood pulp showing decline in absolute volumes. On the other hand, another global trend showed that unbleached Kraft pulp price has been relatively stable in the last 20 years, and bleached wood pulp saw marginal increased demand from 14% in 1992 to 15% in 2010 (Figure 6).

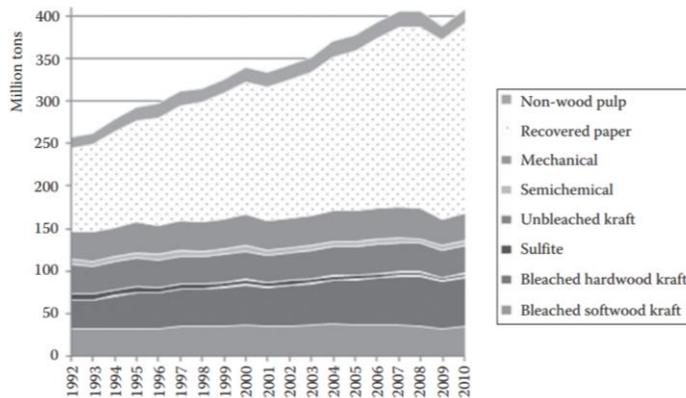


Figure 6. Global paper and paperboard input from 1992 to 2010, where the share amount of recovered paper were increasing dramatically compared to other inputs. (Hetemaki et al., 2014))

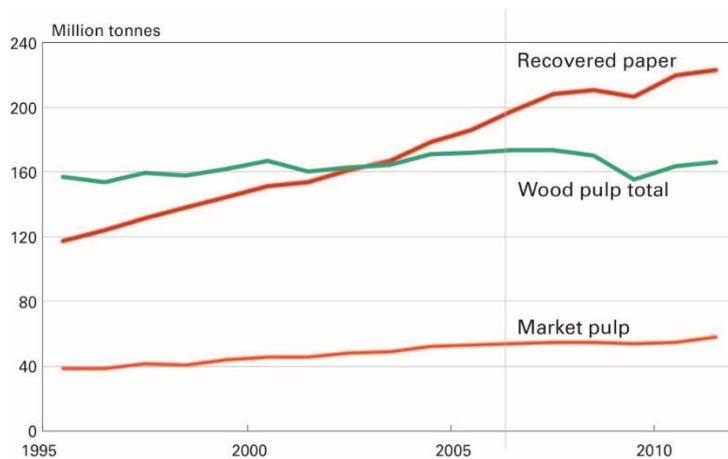


Figure 7. Global consumption of recovered pulp, wood pulp, and market pulp from 1995 to 2011, showing the recovered paper volume overtaking wood pulp within the period (Paper Industry World, 2013)

Bleached Kraft pulp was deemed to be ideal as a source of CNC given its low cellulose and lignin content (Cheng, 2014). However, given the bleaching ability of APS extraction and its ability to produce CNC even at a high 20% lignin, utilizing the unbleached Kraft pulp produced directly from paper and pulp industries is ideal to reduce cost and shorten the extraction process. To compare with acid hydrolysis, it requires pretreatment to remove the fiber contents, affecting crystallinity of the cellulose (Leung et al., 2011). So far, only acid hydrolysis have been performed using bleached Kraft pulp, and its potential applications for flexible packaging is still unexplored.

PET in Food Packaging

Polyethylene terephthalate (PET) is a type of polyester formed from the reaction between terephthalic acid and ethylene glycol. It is considered to be most commonly used polyester in food packaging, and its demand is increasing steadily. It is the most recycled type of plastic (by weight) compared to different resins according to data acquired by American Plastics Council and EPA last 2006. Its major packaging applications are containers, semirigid sheets for thermoforming (trays and blisters), and thin-oriented films (bags and snack food wrappers) (Marsh, et al. 2007). To improve PET gas barrier properties, the direct ways are to increase the wall thickness of the container, slowing down the gas transmission through the wall, and to apply barrier coating on the container itself (Bockner, 2015).

Objectives

The goals of this study are the following:

- to use ammonium persulfate as the sustainable method to make harvesting of CNCs more efficient for flexible packaging application
- to utilize Kraft pulp as an alternative cheap source for CNC production and coat it on PET film
- to perform proper characterization of Kraft pulp material (kappa number, alpha-, beta-, and gamma cellulose contents) for deeper analysis of the cellulosic material source
- to ensure high quality of harvested CNC compared against cotton CNCs from acid hydrolysis by checking its performance on different aspects: optical (transparency and haze test) and permeability (oxygen transmission rate test)

Given the 20-week duration of thesis experiment, the research was limited to investigating only Kraft pulp as the source of CNC, and was compared to past researches mainly performed in University of Milan regarding CNC application on flexible packaging, particularly on cotton linters. Cotton linters consist of > 99% alpha cellulose (Sczostak, 2009), and is heavily processed, it is being sold in the market for a high price. Only ammonium persulfate was utilized as the extraction reagent. It was only

applied to PET film due to time constraints on applying and testing its performance on other flexible packaging types. Physical properties such as retention of the CNC coating on PET film was also not studied. Due to lack of equipment, indirect thickness measurement was performed. Congestion in usage of MultiPerm permeability analyzer limited the study of barrier properties to oxygen, and water vapor barrier results are not investigated.

Materials & Methods

The unbleached softwood Kraft pulp was provided by Innovhub SSCCP (Italian Pulp and Paper Research Institute, Milan, Italy). Polyethylene terephthalate (PET) having 12.0 ± 0.5 μm thickness was sourced from Radici Film, San Giorgio di Nogaro, Italy. Reagents used for the APS extraction were purchased from Sigma-Aldrich, Italy, and were appropriate for laboratory-scale experiment, while Kraft pulp characterization was performed in the laboratory of Innovhub SSCCP.

Characterization of Kraft Pulp

The raw Kraft pulp was characterized based on its amount of alpha-, beta-, and gamma-cellulose, lignin content and its kappa number.

Delignification

Kraft pulp was initially delignified to remove the soluble lignin using the methodology being used in the pulp and paper industry (Rowell, 1997). 10 g Kraft pulp sample was diluted in 320 mL of distilled water (20° C), 2 mL acetic acid, and 4 g of sodium chlorite in a 500 mL Erlenmeyer flask. The sample was placed on a water bath, and the temperature was raised to 70°C to start the reaction. Occasional stirring was performed as the sample tend to aggregate. After 60 minutes, 0.5 mL of acetic acid and 1 g of sodium chlorite were slowly added to the solution with shaking to further continue to delignification process and degrading the polysaccharides. Careful attention must be observed and experiment must be performed under the fume hood, due to production of ClO_2 . It must be observed that the solution would turn to yellow, while the Kraft pulp would turn white during the treatment. Additional 0.5 mL of acetic acid and 1 g of sodium chlorite were added to the solution every hour until the fibers were completely separated from the lignin. The delignification process performed lasted for 4 hours with 3 additions and 1 hour without further addition, since excess chlorite can also damage the holocellulose. The samples were then cooled down to room temperature in ambient

conditions, and then vacuum filtered using Whatman glass filter paper (grade GF/F, 0.7 μm) in a Buchner funnel, cleaning the delignified Kraft pulp with distilled water until all the yellow color was removed, the holocellulose was white, and the odor of chlorine dioxide was gone. It was then washed with acetone to dry the holocellulose faster. It was air dried for 1 hour, placed in a sealed container and stored in the dessicator.

α , β , γ cellulose determination

The empirical procedure developed to perform cellulose separation of pulp into α -, β - and γ -cellulose fractions was mainly used to evaluate pulp properties such as aging characteristics and response to refining operations (Willets, 1931). α cellulose represents the undegraded, higher molecular weight cellulose content of the pulp, β cellulose as degraded cellulose, and γ cellulose as hemicellulose (Ranby, 1952 and Wilson, 1955). Alpha-cellulose is the pulp fraction resistant to 17.5% and 9.45% sodium hydroxide solution; β -cellulose is the soluble fraction identified through reprecipitation after the acidification of the solution, and γ -cellulose is that fraction of what remained in the solution.

In the beginning of the determination process, 1.5g of homocellulose obtained from delignification process was weighed and placed in a 300 mL beaker with 75.0 mL of 17.5% NaOH at 25 ± 0.2 °C. The pulp should be stirred until it is completely dispersed, then the remaining 25.0 mL of NaOH was used for cleaning the stirring rod. The suspension was placed in a water bath at 25 ± 0.2 °C. After 30 minutes, 100.0 mL distilled water was added and stirred thoroughly. The beaker was left for 30 minutes, and then transferred to a filtering funnel using Whatman paper (grade GF/F, 0.7 μm). The first 10 mL of the filtrate was discarded, and then 100 mL was collected in a filtration flask.

α cellulose determination

25.0 mL of the filtrate was pipetted, together with 0.5N potassium dichromate solution, into a 250 mL flask. 50mL of concentrated H_2SO_4 was added carefully while flask was being swirled. The solution was then cooled down for 15 minutes, then 50 mL of water was added to further bring it down to room temperature. 2-4 drops of ferroin indicator was added, and titrated using 0.1N ferrous

ammonium sulfate solution to a purple color. Blank titration was also performed, substituting the pulp filtrate with 12.5 mL of 17.5% NaOH and 12.5 mL of water.

β - γ cellulose determination

For determining the β-γ cellulose, 50.0 mL of the filtrate was collected to 100 mL graduate cylinder with glass stopper, and 50 mL of 3N H₂SO₄ were added. The solution was mixed by inverting. The cylinder was heated to around 70-90°C in a hot water bath to coagulate β -cellulose. It was then removed from water bath, and left to precipitate for several hours. Decantation was done to obtain clear solution, and 50.0 mL of the solution was pipetted to a 300 mL flask together with 10.0 mL of 0.5N K₂CR₂O₇ while carefully adding 90 mL of concentrated H₂SO₄. Solution was cooled down in 15 minutes, and then 50 mL water was added. It was then titrated with 0.1N ferrous ammonium sulfate solution while adding 2-4 drops of Ferroin indicator. Reaction would be complete once the solution turned to purple color. Blank titration was also performed, substituting the pulp filtrate with 12.5 mL of 17.5% NaOH and 12.5 mL of water.

The following equations are used to calculate the α-cellulose content in Kraft pulp:

$$A\text{-cellulose, \%} = 100 - \frac{n6.85 (V2-V1)X n x 20}{A x W}$$

Where:

V1 = titration of the pulp filtrate, mL

V2 = blank titration, mL

n = normality of ferrous ammonium sulfate solution

A = volume of pulp filtrate used in oxidation, mL

W = oven dry weight of pulp specimen, g

$$\Gamma \text{ cellulose, \%} = [6.85 (V4-V3) \times N \times 20] / [W]$$

Where:

V3= titration of solution after precipitation of β -cellulose, mL

V4 = blank titration, mL

$$\beta \text{ -cellulose, \%} = 100 - (\alpha \text{ cellulose \%} + \gamma \text{ cellulose \%})$$

Lignin content calculation

Standard lignin content calculation procedure was performed by following the technical report NREL/TP-510-42618 from the National Renewable Energy Laboratory (Sluiter, et. al., 2008). 2 filtering crucibles were placed in the furnace at 575 ± 25 °C for 4 h minimum. Crucibles were then removed and placed to a desiccator and cool for one hour. Crucibles were weighed to the nearest 0.1 mg and weight was recorded. Crucibles were returned back into the muffle furnace at 575 ± 25 °C and ash to constant weight (less than ± 0.3 mg change)

300.0 ± 10.0 mg of Kraft pulp was then weighed into a tared pressure tube, performed in duplicates. Samples were placed in a water bath set at 30 ± 3 °C for 60 min. Samples were stirred every 5-7 minutes to ensure uniform hydrolysis. Mix 0.01 mL of 72% sulfuric acid to each pressure tube for 60 minutes, and then remove the tubes from water bath. Acid was diluted to a 4% concentration by adding 84.0 mL deionized water using burette and mixed thoroughly until phase separation between high and low concentration acid layers were removed.

Acid insoluble lignin (AIL) of the autoclaved hydrolysis solution was analyzed by vacuum filter through one of the weighed crucibles. The filtrate was collected in a filtering flask. Acid soluble lignin determination must be done within six hours of hydrolysis. Deionized water was used to quantitatively transfer all remaining solids out of the pressure tube into the filtering crucible. The solids were washed with a minimum of 50 mL fresh deionized water. The crucible and acid insoluble

residue were dried at 105 ± 3 °C until constant weight was achieved. Samples were removed from the oven and cooled in a desiccator. Weight of the crucible was recorded and dry residue to the nearest 0.1 mg. The crucibles and residue were placed in the muffle furnace at 575 ± 25 °C for 24 ± 6 hours. Samples were allowed to cool down until 105 °C, then crucibles were removed from the furnace directly into a desiccator and allowed to cool for a specific amount of time, equal to the initial cool time of the crucibles. The crucibles and ash were weighed to the nearest 0.1 mg and recorded. The crucibles were returned back in the furnace and ashing was performed until it reached a constant weight.

The following formulas were then utilized to calculate for the acid insoluble lignin content:

$$ODW = \frac{\text{Weight air dry sample} \times \% \text{ Total solids}}{100}$$

$$\% \text{ AIL} = 1 +$$

$$\frac{(\text{Weight cruc plus AIR} - \text{Weight cruc}) - (\text{Weight cruc plus ash} - \text{Weight cruc}) - \text{Weight protein}}{ODW \text{ sample}} \times 100$$

Kappa number

Kappa number is an indicative value of the lignin content in the pulp, and used in the pulp and paper industry to determine the amount of bleaching materials needed to brighten the pulp (National Council for Air and Stream Improvement, 2013). Kappa number identification was performed using T 236 om-99, which can be used for all types of chemical/ semi-chemical, and unbleached or semi-bleached pulps. Softwood Kraft pulp's kappa number is within the range of 28-34, hence the amount of sample used was 0.9 g, corresponding to the recommended amount from the standard method (Shackford, 2003). As the expected kappa number is higher, the amount of sample to be used should be lower to be able to get more accurate results during back titration in the next step.

50 ± 0.1 ml of the potassium permanganate solution (1.0N) were pipetted, and 50 ml of the sulfuric acid (4.0N) into a beaker. Temperature was set at 25 °C, quickly add the mixture to the disintegrated specimen and simultaneously start the timing device for 10 min. Beaker was rinsed with approximately 10 ml of distilled water, and the washings to the reaction mixture were added. The total volume was 500 ml. At the end of 10.0 min ± 15 s, reaction was terminated by adding 10.0 ml of the potassium iodide solution.

Free iodine was titrated to the sodium thiosulfate solution immediately after mixing. 2-3 drops of starch indicator solution (0.2%) was added when nearing the end of titration process. Volume was noted at its inflection point. Kappa number was then calculated using this formula:

$$K = \frac{pf}{w}$$

where

$$p = \frac{(b-a)N}{0.1}$$

K is the kappa number, f is the factor for correction to a 50% permanganate consumption (dependent on p value), w is the weight of moisture-free pulp in the specimen (g), p is the amount of 0.1 N permanganate consumed by test specimen (mL), b is the amount of thiosulfate consumed in blank determination (mL), a is the amount of thiosulfate consumed by test specimen (mL), and N is the normality of thiosulfate.

Table 1 provides the f value for corresponding p value calculated:

Table 1. f value determination for kappa number calculation (TAPPI, 1999)

p	+	0	1	2	3	4	5	6	7	8	9
30		0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40		0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50		1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60		1.022	1.024	1.026	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70		1.044									

Kraft Pulp Sample Preparation for APS Treatment

10g dry weight of Kraft pulp was weighed using microbalance, and then placed in 1000 ml beaker. 1-layer of distilled water was added to the sample, and magnetic stirrer was used to mix the solution. Swelling of Kraft pulp fibers was performed by increasing the temperature of the heater to 70°C for 30 minutes. After which, the solution was cooled down in a cold water bath to reach the room temperature of 25°C.

APS Extraction of Kraft Pulp

340.5 g of ammonium persulfate (APS) was added to the cooled Kraft pulp solution to reach 1.5M APS, and was then stirred for another 30 minutes to allow the powder to dissolve completely. After which, the temperature was raised to 70°C for 16 hours at high stirring speed for the cellulose nanocrystals extraction to occur completely. At the end of this stage, the brown color of Kraft pulp have changed to white by the end of the reaction. The sample was removed from the heater, and was centrifuged using deionized water at 15,000 RPM for 20 minutes to concentrate the cellulose. The supernatant was carefully decanted and the white precipitate was rediluted using distilled water, mixed, and centrifuged several times until it increased the pH level from around 0.2 to 3 (approximately 6 times). pH correction was then applied to the Kraft CNC solution, further increasing it to pH 8 to avoid aggregation of the crystals in acidic environment. It was then subjected to ultrasonicator (UP400S 400W, hielscher Co., Germany) at 0.7 cycles of 20 minutes at 70% output to distribute CNCs evenly in the suspension. The solution was vacuum filtered using Whatman glass microfiber filter (grade GF/F, 0.7 μm) to remove fibers that did not react fully with APS treatment, and other big cellulose agglomerates and large contaminants that might have been introduced during the process.

PET Bio-coating Application Using Kraft CNC

The Kraft CNC suspension was placed in an aluminum container for easier handling of the powder, frozen at -25°C overnight, and was subjected to lyophilization by utilizing the freeze drying machine (LIO-10P) for 3 days to remove water completely, leaving only white Kraft CNC powder. The powder was rediluted using deionized water (18M Ω cm, Millipore Milli-Q Purification System) to reach 2.5% Kraft CNC solution, while leftover CNC powder was stored in a tightly sealed bottle in a dessicator. It was ultrasonicated for 5 minutes (0.7 cycles at 70% output) to ensure that crystals are properly dispersed in the solution. Visual verification was also done to ensure that the solution is homogenous.

Meanwhile, PET film (25x20 cm²) was treated using the Corona treatment machine (model CG061P, ARCOTC GmbH, Germany) for 20 rounds of rolling on one side of the plastic for approximately 3 minutes, to increase the surface energy and generate a negative-charge surface, improving adhesion of the nanocrystals on the surface of PET film. Automatic film applicator (ref 1137, Sheen Instruments, Kingston, UK) was used to apply the Kraft CNC solution evenly on top of the PET.

Around 2 ml of the solution was taken and applied vertically on the beginning part of the applicator using a plastic transfer pipette. An applicator bar was used to spread out the sample evenly on the surface area of PET, with the thickness at 0.6 μm at constant speed of 2.5 mm/s. Initial drying of the Kraft CNC coated PET sample was performed using a blower (60±0.5°C) for 1 minute with a distance of 40cm perpendicular to the automatic applicator, and then air dried for 12 hours. Sample 1 was created by only applying 1-layer of Kraft CNC. The double layer of Sample 2 was achieved by directly applying another round of coating using the automatic film applicator immediately after drying the first layer, without the need for another round of corona treatment. It was then dried using the blower and air-dried for 24 hours. CNC coated film samples were properly stored at 20±2 °C temperature in a sealed anhydrous dessicator to avoid absorbance of humidity and protect from contamination from particulates in the air such as dust, before being used for analysis.

Characterization of PET Coated Films

Thickness

Thickness of the Kraft CNC coating was measured by cutting 10 x 10 cm² of the PET coated film samples, folding them twice and securing them with paper clips, and then weighing them in microbalance (m₁, g). The paper clip was used to ensure that the film would not open up and for keeping it within the weighing platform of the balance. After weighing, the samples were cleaned with soap and scrubbed using the cleaning foam to remove CNC film coating, and then dried. The bare film was then folded with paper clip and weighed (m₂, g). Using the density (ρ) of CNCs (~1.58 g cm⁻³), the thickness (L, μm) of the samples were calculated using the equation:

$$L = \frac{m_1 - m_2}{\rho} \times 100$$

Contact Angle

Surface free energy of the solid σ_s has a relationship with the contact angle θ , the surface tension of the liquid σ_l and the interfacial tension σ_{sl} between liquid and solid in Young's equation:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta$$

Identifying the surface free energy of a solid is important to understand wettability of the solid.

Wettability explains the attempt of a solid to form a common interface with a liquid which comes into contact with it (Kruss, 2015).

Characterizing the surface energy was achieved by using OCA 15 Plus angle goniometer (Data Physics Instruments GmbH, Filderstadt, Germany). The Owens-Wendt-Rabel and Kaelble (OWRK) method of calculating surface energy was used as its application is universal, such as for polymers, coating, varnishes, among others. Measurements of disperse and polar parts of surface free energy were performed at room temperature with two liquids: polar distilled water and apolar diiodomethane (DIM, 99%, Sigma Aldrich) at five different positions on each PET coated film sample. The surface energy is calculated using a linear equation, $y=mx+b$, wherein slope m and intercept b are provided by the square root of polar and dispersive components of solid surface free energy ($\sqrt{\gamma_s^D}$ and $\sqrt{\gamma_s^P}$) in this formula:

$$\frac{\gamma_l(1 + \cos\theta)}{2\sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P} \left(\frac{\sqrt{\gamma_l^P}}{\sqrt{\gamma_l^D}} \right) + \sqrt{\gamma_s^D}$$

This means that the total, dispersive and polar components of the liquid surface free energy (γ_l^D and γ_l^P) are known, and contact angle θ is measured (Nuriel, et al. 2005).

The OWRK method combined the importance of polar (containing Coulomb interactions between permanent dipoles and between permanent and induced dipoles) and disperse (interaction due to time fluctuations of charge distribution within molecules) contributions to the surface energy and surface tension by summing both parts. The softwares (SCA20 and SCA21) installed together with the instrument was then used to calculate the surface energy after using the contact angle and standard deviation of polar and apolar fluids.

Contact angle measures the angle wherein a liquid interface is in contact with a solid surface. Having a low contact angle indicates that the liquid molecule is strongly attracted to the particles in the solid surface, hence a drop of liquid will spread out on the solid surface, causing it to have a low contact angle value (see figure 8).

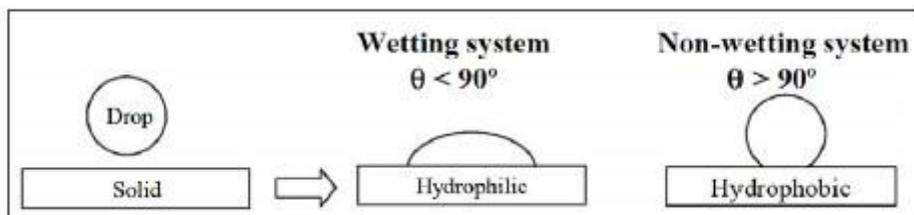


Figure 8. Wettability determination of the solid surface using contact angle measurement, showing that a wetting system can be defined when the drop formed an angle with the solid at $< 90^\circ$, and a non-wetting system if the angle formed is $> 90^\circ$ (Doriget, F. 2012)

This is related to the anti-fog property of the film, which can be important to food products with high water content. Fog formation is caused by small discontinuous water droplets that can reflect the incident light, thereby decreasing the transparency and increasing the haze (Introzzi et al., 2012; Nuraje et al., 2010).

Transparency

Using Perkin-Elmer L650 spectro-photometer, the transmittance of PET coated samples were measured under the wavelength of 550 nm, according to ASTM D 1746-15.

Fourier transform infrared spectroscopy (FTIR)

Chemical structures of Kraft pulp raw material and Kraft CNC (in form of loose powder) were identified using Perkin Elmer Spectrum 100 FT-IR instrument. The spectral width from 650 to 4000 cm^{-1} were collected, with 4 cm^{-1} resolution and 10 scans per sample.

Haze

Haze is defined as the total transmitted light that is scattered from the incident beam by more than 2.5°, while transparence is the % of incident light that was deflected by less than 0.1° from the axis of incident light when passing through the specimen (Chevron Phillips, 2010). Perkin Elmer L650 spectrophotometer was utilized to measure the haze property of the PET coated film samples, in line with ASTM D 1003-61 (see table 2). The values yielded represent the amount of light that is scattered after passing through the film, which indicates the hazy optical effect when viewing through the plastic coated film material.

4 values of different conditions were measured per sample (single and double layer PET coated film) and 3 trials were done at room temperature (25°C).

Table 2. Haze variable conditions suggested by ASTM, D 1003-61

Variable	Sample presence	Black cover presence	White reflector presence
T1	No	No	Yes
T2	Yes	No	Yes
T3	No	Yes	No
T4	Yes	Yes	No

The following equation was used to calculate for the haze % value:

$$\text{Haze \%} = \frac{100 \times [T_4 - T_3 (T_2/T_1)]}{T_2}$$

Oxygen Permeability

Oxygen barrier property is one of the important considerations in choosing the material for packaging, particularly for food products since oxygen can change the shelf life, taste, and even the

morphological and optical properties of the product. The oxygen barrier properties of both uncoated and coated PET films were assessed on a 50 cm² surface sample using a MultiPerm permeability analyzer (ExtraSolutionR Srl, Capannori, Italy) equipped with an coulometric sensor. Measurements were performed according to the standard method of ASTM F2622-08, with a carrier flow (N₂) of 10 mL min⁻¹ at 23°C and 0% relative humidity (RH). Analyses were carried out with the coated side of each sample facing the upper semi-chamber, i.e. the chamber where the humid test gas (oxygen) was fluxed. The results were expressed as the oxygen transmission rate (OTR, milliliters per square meter per 24 h at 1 atm pressure), which has been indicated as the most suitable unit for heterogeneous materials (e.g., multilayer and coated films), that is, whenever a linear relationship between permeability and thickness is not maintained. Three conditions were set up:

- 23°C and 0% relative humidity (RH)
- 23°C and 40% relative humidity (RH)
- 35°C and 40% relative humidity (RH)

Conditioning time per sample were set at around 5-7 h depending on its stability.

Nanostructure determination using transmission electron microscope

Drops of aqueous dispersions of Kraft CNC (0.05% w/v) were placed on carbon-coated electron microscope grids that have been negatively stained using uranyl acetate. It was then dried for 10 minutes. Analysis of samples were performed using Hitachi Jeol-10084 transmission electron microscope (TEM) with 80 kV accelerating voltage.

Dynamic Light Scattering

Kraft CNC rediluted solution (prepared as mentioned in APS extraction of Kraft pulp subchapter) was transferred to a glass cuvette (1 mL), and analyzed using Malvern Zetasizer Nano ZS for Dynamic Light Scattering (DLS), and was performed in University of Milan-Bicocca Polymer Science laboratory.

Results and Discussion

Raw Material Characterization

Kraft pulp production entails using sulfite treatment and high heat to convert wood into cellulosic pulp (Sawyer, 1950). Krafting process is usually performed in an alkali solution by a combination of hot caustic soda and sodium sulfide to break down and decrease the lignin content, but still managing to preserve the cellulose content of the material.

Table 3. Characterization of Kraft pulp raw material

Raw material	kappa number	α-cellulose %	β-cellulose %	γ-cellulose %	lignin %	Ash
Kraft pulp	35.48	86.8	0.37	13.57	7.87	0

The Kraft pulp sample obtained was carefully characterized to identify its kappa number, lignin, and α , β , γ cellulose contents (see table 3). Having a kappa number of 35.48 for the sample acquired is around the kappa number range of 30-35 for Kraft pulp that underwent conventional cooking (Integrated Pollution Prevention and Control, 2001). Having the lignin content of 7.87% shows that the Kraft pulp is subjected to an alkalinity of 20-25% in a span of 60-90 min (Kiaei, Kord, & Vaysi, 2014). The high α cellulose in the resulting characterization experiment shows that previous processes have caused low degradation to the cellulose.

APS Extraction Process

CNC production using the novel Ammonium Persulfate procedure (see figure 12) was chosen given several benefits compared to acid hydrolysis and its other persulfate counterparts, which includes low long-term toxicity, high water solubility and low cost.

Reaction time, concentration of APS, and type of matrix can greatly influence the yield, dimension, and crystallinity of CNCs (Cheng, 2014). Moreover, using Kraft pulp as a source of CNCs has proven

to be challenging given the impurities of the substrate due to series of chemical and mechanical processes it was subjected to during its production. After several extraction trials in different conditions, swelling preparation of the sample by elevated temperature of 70°C for 30 minutes, as well as mixing APS in the Kraft pulp solution at room temperature for another 30 minutes has proven to be a critical factor to produce CNCs. Utilizing the method of swelling preparation from Castro-Guerrero, the extraction process yielded 21.88% of Kraft CNC (Castro-Guerrero, et al., 2014). Without swelling, CNC presence cannot be detected in FT-IR even when the concentration of solution was changed from 1 to 2M APS.

It was also possible to perform APS extraction by directly heating the beaker on top of the heater, even without using a water bath and condenser. Covering the set-up using aluminum foil was done to avoid excessive evaporation that happened in one side-experiment, wherein water was completely evaporated after 16 hours.

Once the temperature was elevated to start APS extraction, stirring the mixture at high speed was performed. It must be noted that the Kraft pulp should be visibly being stirred completely without splattering. A metal stirring rod was utilized instead of magnetic stirrer since swollen Kraft pulp has caused the stirring action to slow down and stop at various times.

After 16 hours of elevated temperature, the solution was cooled down. The solution must turn from dark brown to milky white (see figure 9). This is due to bleaching of the material due to free radicals $\text{SO}_4\cdot$ and H_2O_2 that opened the aromatic rings of lignin, decolorizing the substrate.

Performing centrifugation to isolate CNCs from the APS solution was done with utmost care, since the white precipitate is brittle and easily mixed with water even with minor shaking, and lead to loss of CNC yield. To be able to disperse the solution properly, pH correction was performed using NaOH solution, and then ultrasonication at 0.7 cycles of 20 minutes at 70% output. The samples were then viewed using optical microscope, and big fibers were still seen (see figure 10), which have not fully reacted to the APS solution to proceed to CNC extraction. Hence, filtering this dispersed solution using Whatman glass microfiber filter (grade GF/F, 0.7 μm) was performed to remove big fibers that can influence the oxygen permeability property once coated on PET film. The presence of CNC of filtrated solution was further verified using the birefringence property of cellulose nanocrystals. Light was beamed to the filtrated solution, and CNC presence was verified given the light scattering effect it caused in the solution, as compared to pure water (see figure 11).

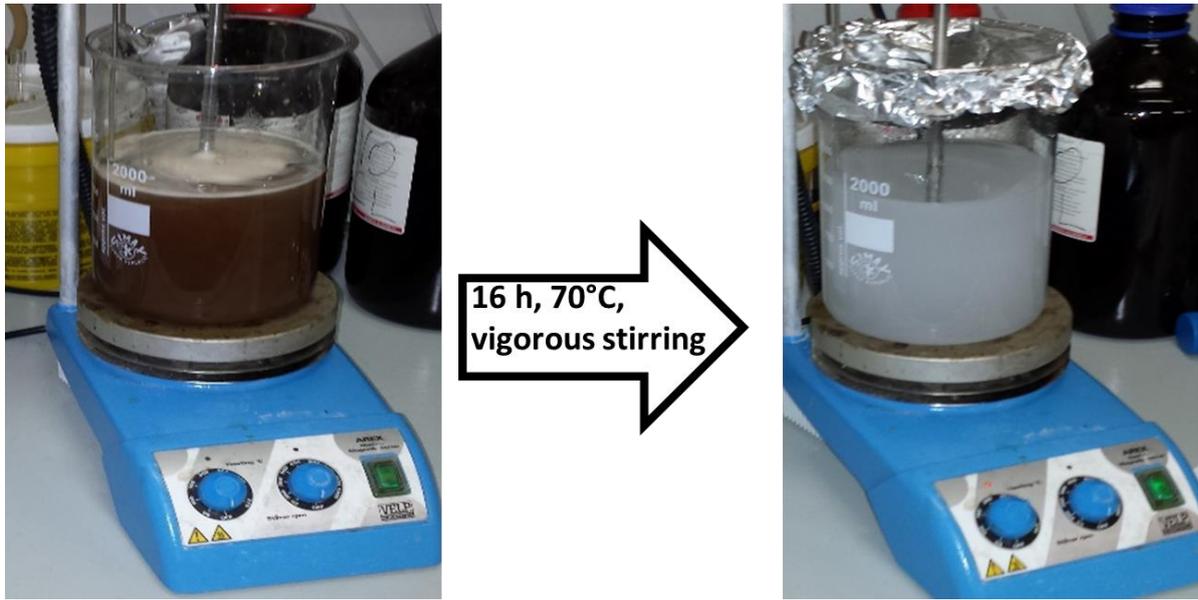


Figure 9. Color change of Kraft pulp solution after APS extraction treatment (16 h, 70°C), from dark brown to milky white

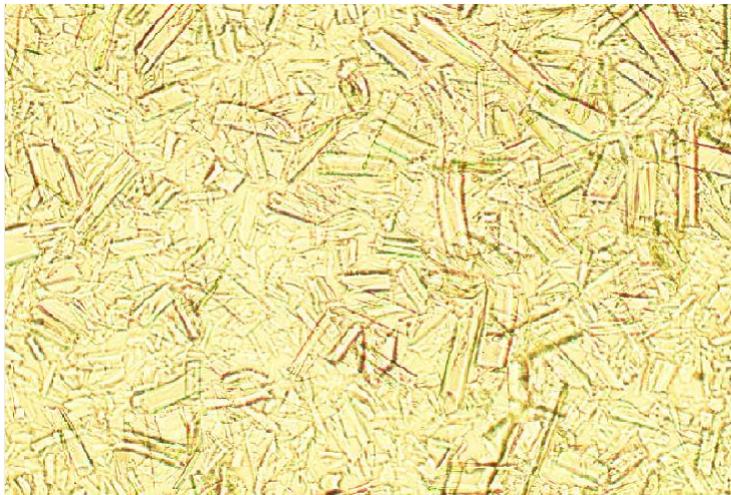


Figure 10. Large fibers visibly detected under optical microscope after APS treatment. This shows the Kraft pulp fibers that were broken down but did proceed to CNC extraction

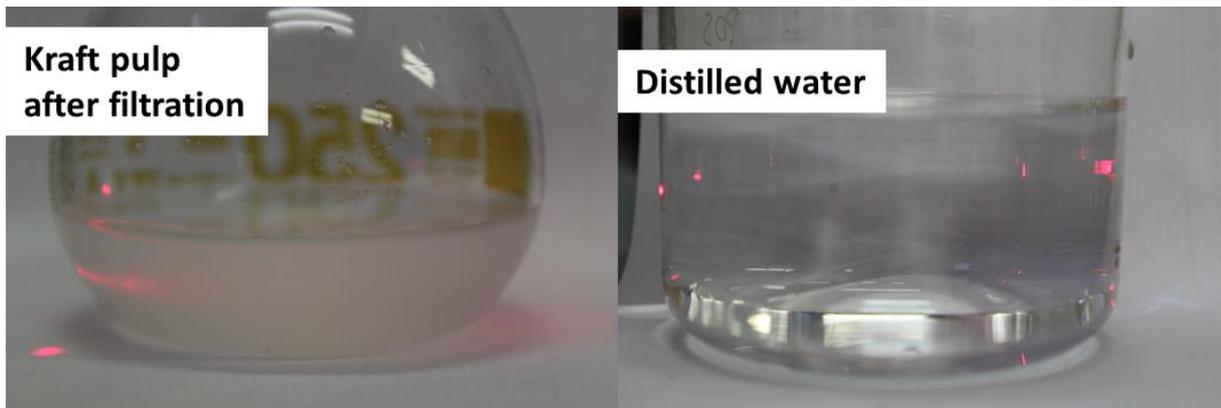


Figure 11. Light scattering effects on CNC in filtrated Kraft pulp and on distilled water, which was used to determine the presence of Kraft CNC after APS extraction

Freeze drying was then performed for 3 days to ensure that all water was removed. Coating was done by rediluting the powder to form 2.5% Kraft layer, lower than the 7% used for cotton CNC application in other literature. The % CNC used for Kraft layer was lowered down given the difficulty in the application process since it forms unequal coating visible by optical inspection. Circular blank spots were seen when 7% Kraft CNC was used, but it was resolved by dissolving the formula further down to 2.5%. Increased corona treatment from 10 to 20 times were performed to increase the polarity of the PET film surface, allowing better adhesion of Kraft CNC on the surface. This resulted to a visibly consistent CNC coating on PET film. Kraft CNC solution was observed to form a gel when at rest, but becomes a liquid once shaken or agitated by a stirring rod.

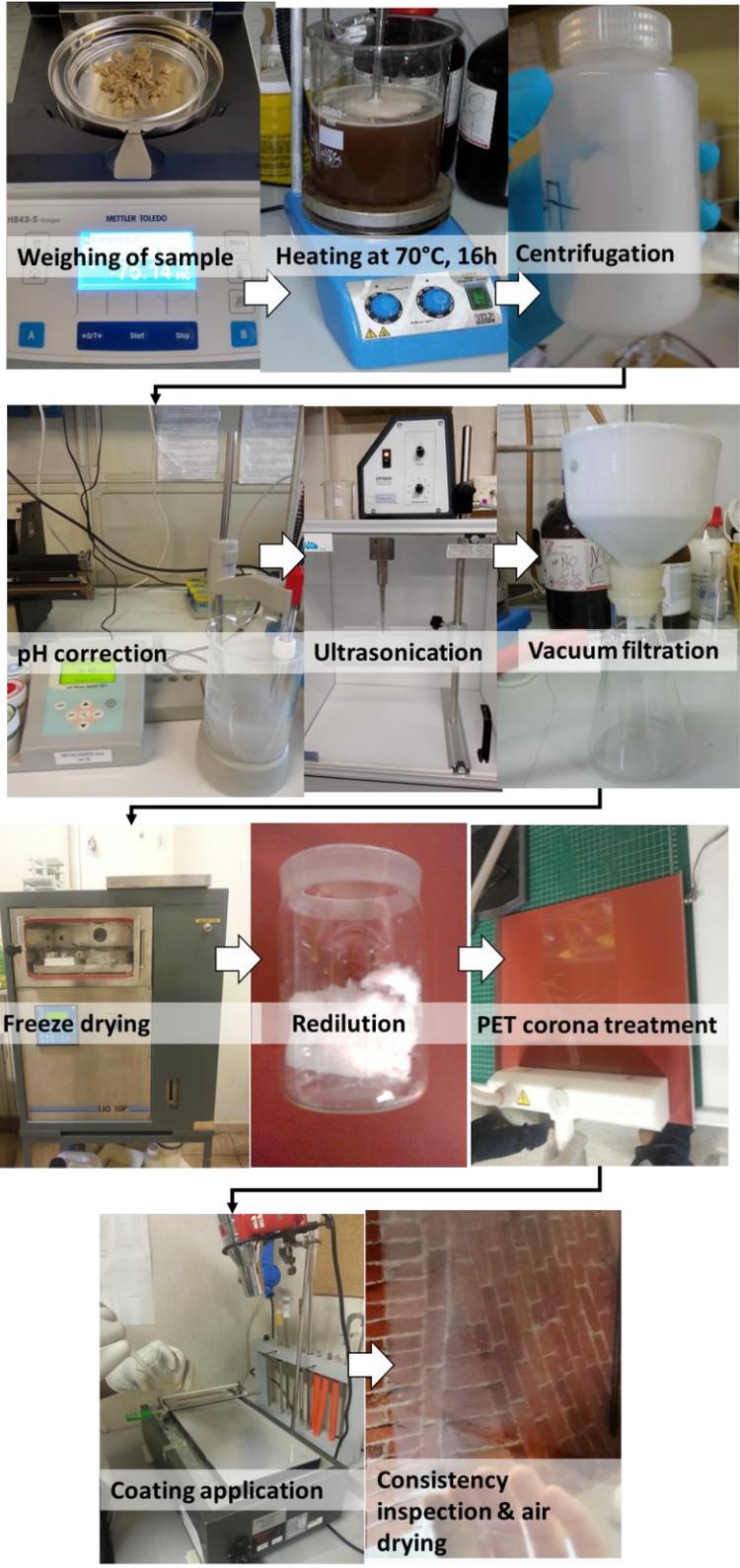


Figure 12. Step-by-step process of Kraft CNC extraction using Ammonium Persulfate

Morphology and dimension

TEM was used to identify physical properties of Kraft CNCs extracted in nanoscale level.

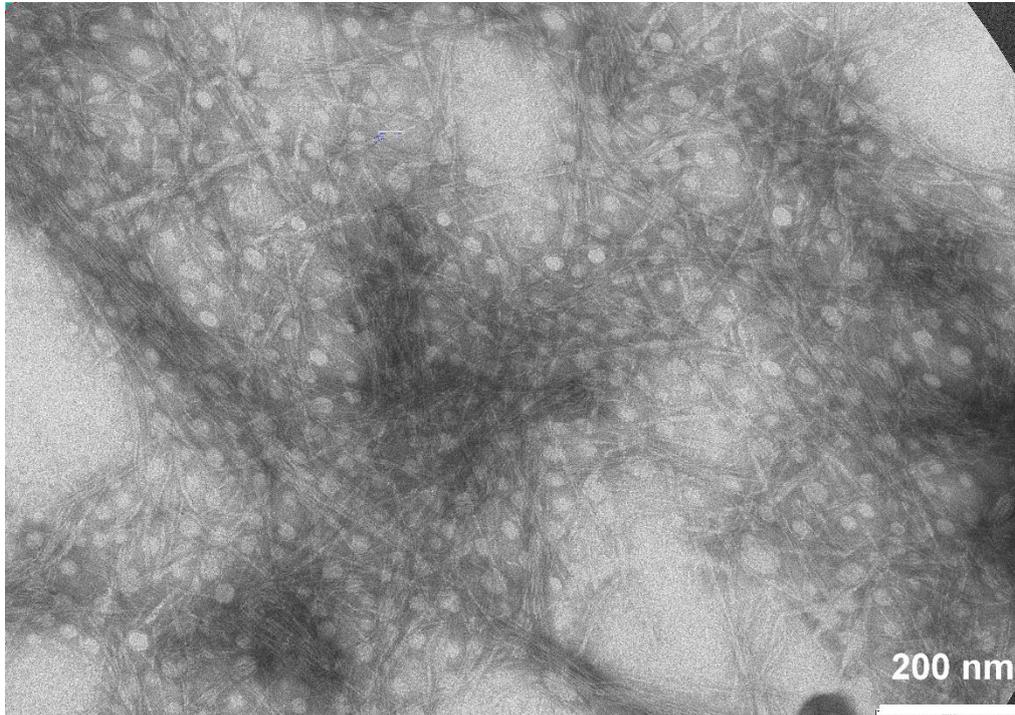


Figure 13. TEM image of Kraft CNCs at 92,000 x magnification, having a mixture of rod-like and spherical structures

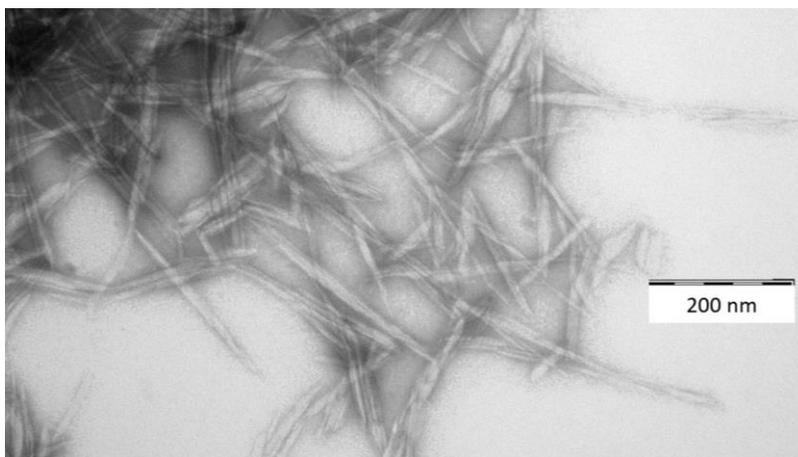


Figure 14. TEM image of rodlike cotton CNC structure

Upon observing the image, it must be noted that the CNCs obtained have two distinct shapes: spherical (Fig. 13) and rod-like (Fig. 14). APS concentration can influence the shape of CNC, as shown by the experiment involving different concentrations applied to a lyocell fiber matrix. It yielded a mixture of rod-like and spherical CNCs for 0.5M APS, but produced 100% spherical CNCs at 1M APS (Cheng, 2014). On the other hand, acid hydrolysis extraction of Kraft pulp have yielded only rod-like crystal structure (Li et al., 2015).

The presence of spherical CNCs was previously studied during MCC hydrolysis, and it was found out that spherical or rod-like CNCs could be selectively formed by changing the mixed acid concentrations of H_2SO_4 and HCl. Moreover, swelling preparation of the material in NaOH solutions or NaOH-Dimethyl sulfoxide mixtures, followed by acid hydrolysis under ultrasonic treatment various spherical CNC extraction were found out to yield spherical CNCs, as observed for microcrystalline cellulose (MCC), cotton, Avicel pulp, sesame husk, sweet potato residue, and cellulose fibers (Cheng, 2014). Kraft pulp raw material has been subjected to similar alkali conditions after its processing from wood, and then subjected to acid treatment and ultrasonication, which were similar conditions that explain the presence of spherical CNCs. No tests have been done to verify if the shapes can influence specific packaging properties when coated to a flexible film.

The FT-IR was used to further characterize the white powder extracted from the experiment, and identify the presence of cellulose by identifying key chemical compounds through its chemical bonds' absorbance of infrared radiation.

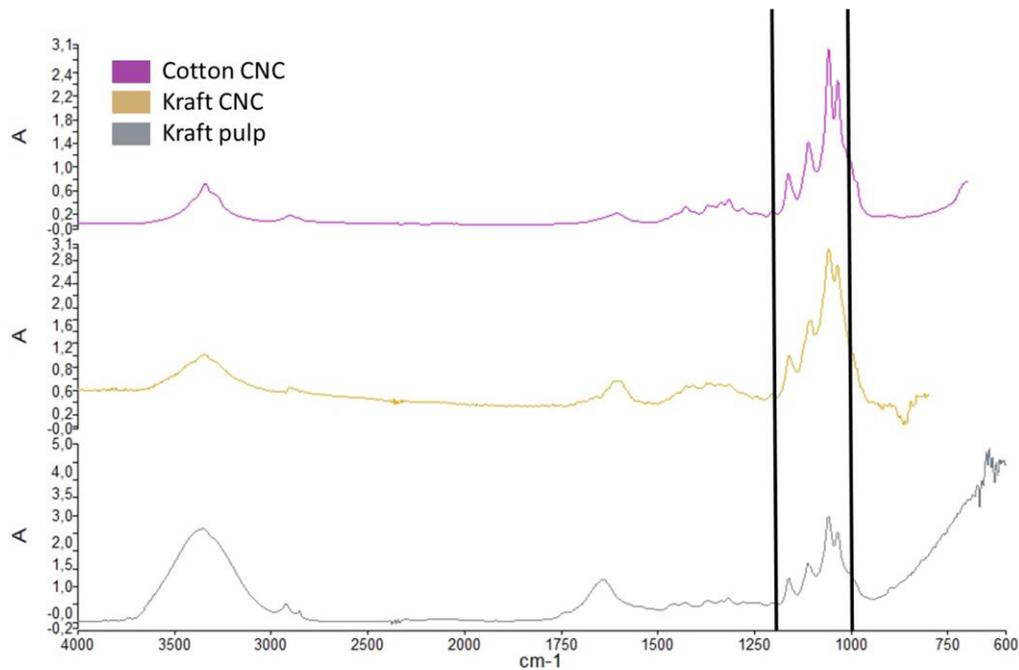


Figure 15: FTIR spectra of CNC obtained from Cotton and Kraft, and Kraft pulp raw material shows that the characteristic four peaks of cellulose between the two bars are present from the Kraft raw material until the end of the reaction, indicating APS ability to preserve cellulose during extraction process, and similar to Cotton CNC extracted using acid hydrolysis.

The comparative FTIR spectra of absorbance analysis from raw Kraft pulp material to Kraft CNC and Cotton CNC (see figure 15) highlights the characteristic representation of cellulose. It can be observed that the peaks have been retained, which can provide proof that the extraction process did not change the original chemical structure of cellulose moving from the native raw material to the CNC obtained after extraction. Understanding that cellulose remained intact provided an assurance that CNC can be present, which is critical before proceeding to next steps such as application to PET coating.

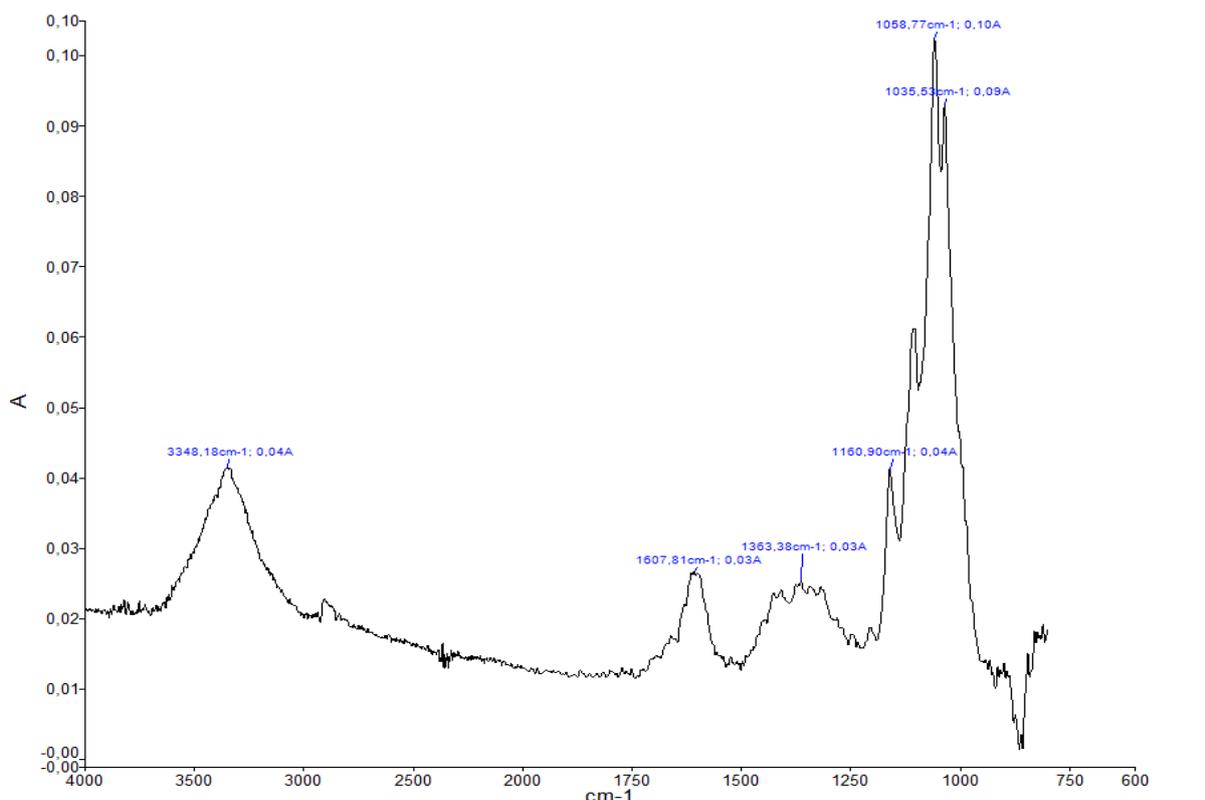


Figure 16. FT-IR absorbance spectra of freeze dried Kraft CNC, having the characteristic 4 peaks of cellulose (1000-1160 nm) and presence of C=O at 1607.8 cm-1

Inspecting closely on the absorbance of Kraft CNC (see figure 16), it was observed that it displayed characteristic peaks exhibited by cellulose nanoparticles: the four peaks 1160.9 cm⁻¹ (C-O-C ring 5), 1108 cm⁻¹ (C-O-C ring 2), 1035.53 cm⁻¹ (C-O-C bridge) and 1058.77 cm⁻¹ (C-O ring 3). Having peaks at 3,348 cm⁻¹ and at 1607.8 cm⁻¹ suggest the presence of C=O after the oxidation of Kraft pulp by APS to produce carboxylic acid reacting with C6. This carboxylation only occurs on the surface of the crystal, and the rest of C6 hydroxyl are not oxidized (Habibi, et al. 2006).

The degree of oxidation is 0.192 for the extracted Kraft CNC using the following formula (Habibi, 2006), utilizing the intensity acquired from FT-IR spectra:

$$DO = 0.01 + 0.7 (I_{1607}/I_{1058})$$

DO represents the amount of carboxyl that are produced, which is important to make nanocellulose particles become more reactive and improve its attachment to PET film during the application process. The formula using I_{1607} represents the carboxylic acid and I_{1058} as the highest absorbance peak. The cm⁻¹ of the peaks are variable depending on a variety of factors, such as the acid/base state,

temperature, and concentration (Ryu, Noda & Jung, 2015), but measurements should be performed to represent these characteristic peaks. Carbonyl groups are generated by the long interaction of cellulose and the free radicals produced by APS during hydrolysis. As can be inferred from the table 4, the reaction time, temperature and molarity can influence the degree of oxidation in APS extraction. Moon's research on table 4 showed that oxidation degradation is promoted at low temperature condition (as seen on the DO values between 70°C and 90°C, 1M at 16 h), and the increase in APS concentration has increased the DO (as seen on DO values between 0.5 M and 2.0M, 16h at 80°C).

Table 4. Different reaction conditions and its effect on extracted CNCs' crystallinity, DO, and thermal parameters (Moon et al., 2011)

Sample			DO ^b (%)
Lyocell			—
Reaction conditions			
4 h	80 °C	1.0 M	0.093
8 h			0.113
12 h			0.102
16 h			0.083
20 h			0.078
24 h			0.081
16 h	70 °C	1.0 M	0.140
	90 °C		0.058
16 h	80 °C	0.5 M	0.065
		2.0 M	0.132

In the experiment, Kraft CNC's DO of 0.192 is higher compared to that of lyocell fiber at 0.140 for 16 h reaction at 70°C and at 1M APS. It is important to note that this is the highest DO value for lyocell fiber among 10 other set-ups with varying reaction conditions. This high DO can be attributed to the fact that the experiment used more APS at 1.5M, while still maintaining 70°C, the best temperature from the conditions performed in Cheng's experiment (Cheng, 2014).

On the other hand, using 16 h was used since it provided the right compromise between the CNC diameter and % yield at 70°C. DLS particle size analyzer was utilized to verify the nanocrystal size from a properly dispersed Kraft CNC solution at 2.5%.

DLS produces sizes with respect to its intensity he values provided by DLS revealed two different CNC sizes: 53±25 and another at 215±53, which can be explained by the spherical and rod-like CNCs found using TEM. The polydispersity index (Pdl) of the result was 0.831. Pdl values closer to 1 shows a broad size distribution, and values closer to 0 means narrow size distribution (Malvern Instruments

Limited, 2015). This can be attributed to another peak being registered, which is statistically broad with a standard deviation of 263.6, hence it was considered as an outlier.

PET Coating

Table 5. Coating thickness comparison of kraft 1-layer, kraft 2-layer and cotton

Sample	Thickness (nm)
Uncoated PET	0
Kraft 1-layer coating	132.90
Kraft 2-layer coating	411.39
Cotton layer coating	660.00

The thickness values in Table 5 show that the cotton CNC coated PET film has the highest thickness, which can be explained by the total amount of CNC used in the solution. This was measured only once due to the small amount of sample available. Moreover, there is a positive correlation between the % CNC in the solution and the thickness of coating, which is can be seen in figure 17.

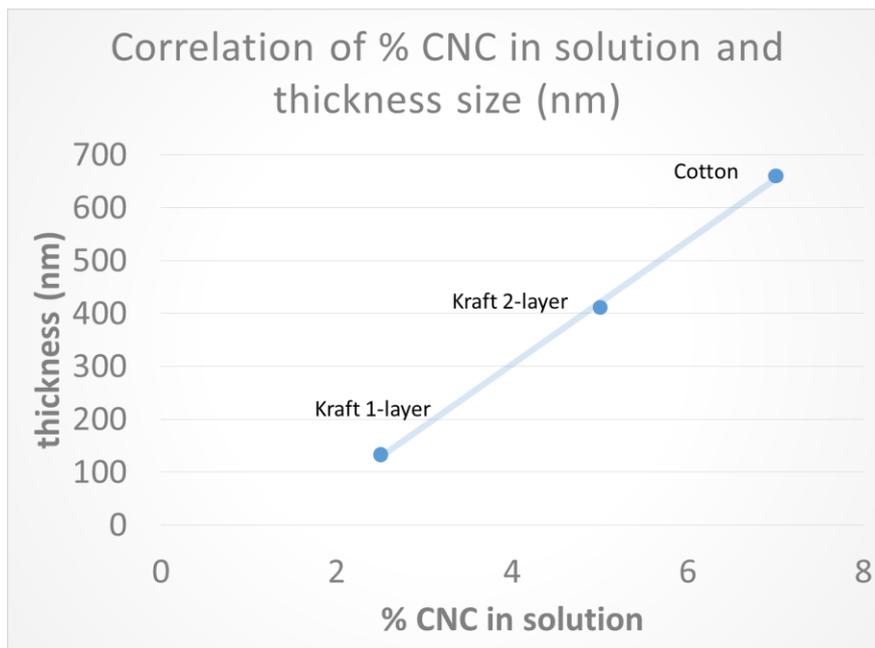


Figure 17. Positive correlation of % CNC in solution and thickness size (nm)

Table 6. Contact angle values of bare PET, Kraft 1-layer, Kraft 2-layer, Cotton CNC, and CNC free standing film.
(*Li, 2015; **Rampazzo, unpublished data)

Sample	Contact angle values				
	Water (mJ/m ²)	Diiodomethane (mJ/m ²)	Surface energy	Dispersion	Polar
	γ_1^P	γ_1^D	γ_1		
Bare PET*	57.44±5.84	22.41±2.73	50.00	47.00	3.00
Kraft 1-layer	64.07 ± 2.86	37.89 ± 2.48	50.62	40.66	9.97
Kraft 2-layer	24.8 ± 1.64	38.42 ± 2.27	71.41	40.40	31.01
Cotton CNC*	12.32±1.33	37.15±3.02	57.00	41.00	16.00
CNC free standing film**			69.50	42.00	27.50

Different literatures have shown that a cellulose nanocrystal film surface formed a contact angle between 13° and 29° when in contact with water. Kraft 2-layer is within this region, but PET with Kraft 1-layer value is higher, but still within the hydrophilic range. This may be due to the fact that the thickness of Kraft 1-layer is very low, and consequently the PET film may have also influenced the increased contact angle of Kraft 1-layer compared to 2-layer upon contact with water. Surface energies exhibited by Kraft 1-layer and cotton coated PET are similar, but Kraft 2-layer showed a higher surface energy value (see table 6), which is closer to thick self-standing CNC film generated by evaporating a 5 ml CNC suspension on a petri dish at 60°C overnight.

The wettability of different samples shows that PET coated with cotton CNC has the best anti-fog property due to its very low contact angle, allowing the water to spread to the solid surface. It is closely followed by Kraft 2-layers, with Kraft 1-layer exhibiting the lowest wettability. The increased amount of carboxylated CNCs in 2-layers compared to 1-layer have improved its hydrophilic interaction with polar water, thereby lowering the contact angle. However, further tests must be done, such as boiling water test, to verify its anti-fog property when applied in food products.

Optical Property – Transparency and Haze

Table 7. Transparency % of Bare PET, kraft 1-layer, Kraft 2-layer, and cotton APS

Transparency (%)				
	Bare	Kraft 1-layer	Kraft 2-layer	Cotton APS
AVERAGE	82.41	76.02	72.45	79.55
STD	0.47	1.00	0.80	0.01

It can be inferred in table 7 that transparency values for PET coated with Kraft CNC (both 1-layer and 2-layer) are lower than that of bare film. After running it through ANOVA in three sets (bare vs Kraft 1-layer, bare vs Kraft 2-layer, Kraft 1-layer vs Kraft 2-layer), it was verified that Kraft 1-layer and Kraft 2-layer are statistically different as compared to each other and compared to the bare values, all at 99% confidence interval.

Cotton APS managed to have a high transparency, with its transparency value being close to the bare film. Kraft 1-layer and 2-layer have lower transparency (see table 7) and higher haze values (see table 8), even though both of them are thinner than cotton APS (see table 5), and lower percentage of CNCs applied in the coating (2.5% vs 7%). This can be due to the fact that in comparison to cotton linters, which has been bleached and contains >99% cellulose, the unbleached Kraft pulp as source is relatively unpure, hence ion impurities might have influenced the slight decrease in transparency.

Table 8. Haze % of bare, Kraft 1-layer, Kraft 2-layer, and cotton APS

Haze %				
	Bare	Kraft 1-layer	Kraft 2-layer	Cotton APS
Average	2.43	11.61	14.49	6.19
STD	0.01	0.28	0.48	0.01

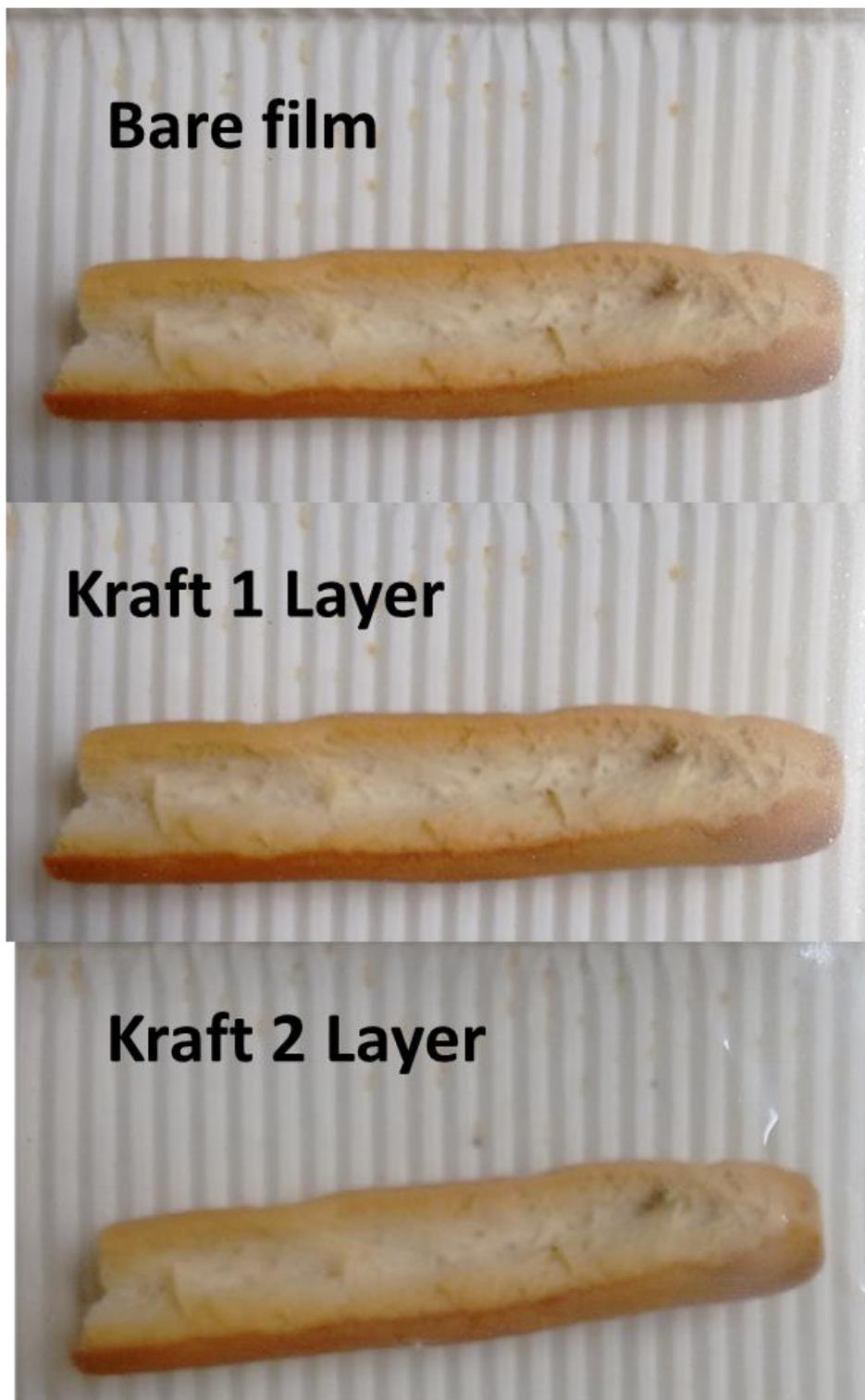


Figure 18. Application of bare film, Kraft 1-layer, and Kraft 2-layer on breadstick packaging, where the breadstick is still visible to all the samples, but with a slightly distinguishable decrease in transparency for Kraft 2-layer.



Figure 19. Text readability test (font 11 and font 6) on bare film, Kraft 1-layer, and Kraft 2-layer, showing that Kraft CNC coating (both 1-layer and 2-layer at 2.5%) has almost negligible influence to transparency.

The PET coated samples were then used to cover breadstick, which are usually packed using PET film and a white cardboard to support the product. As shown in Figure 18, the breadstick is still visible to all the samples, but with a slightly distinguishable decrease in transparency for Kraft 2-layer.

To further verify the optical property of the samples, a sample logo with a subtitle of font 6, and website URL with font 11, were used (see figure 19). PET coated films still do have the same level of readability for both font size as compared to the bare film. This shows that in application to production, using Kraft CNC coating (both 1-layer and 2-layer at 2.5%) has almost negligible influence to transparency.

Oxygen Permeability

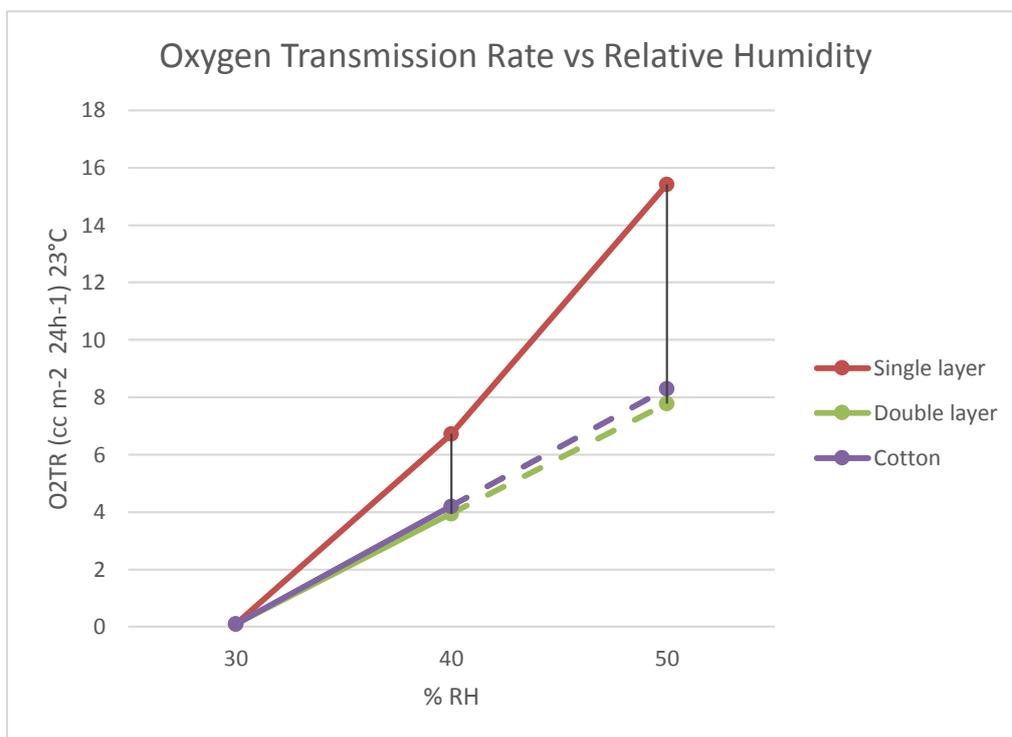


Figure 20. Oxygen transmission rate of Kraft 1-layer, Kraft 2-layer and cotton for different % relative humidity (dotted lines signify projected trend)

Table 9. Oxygen transmission rate values of Kraft 1-layer, Kraft 2-layer, cotton and bare (*) PET(Li, 2015)

Oxygen Transmission Rate (O2TR (cc m-2 24h-1) 23°C)

%RH	Kraft 1-layer	Kraft 2-layer	Cotton	Bare*
0				74.95
30	0.10	0.10	0.10	
40	6.72	3.94	4.2	
50	15.428	7.78	8.30	82

Based on table 9, Kraft 2-layer is found to have almost the same O₂TR value as cotton-coated APS. This 3.92 O₂TR can indicate a good barrier property at 40% RH, as compared to bare film at a high 84 O₂TR. Relative humidity is shown to have influenced the oxygen permeability of the values, as expressed by Kraft 1-layer. Cellulose nanocrystals are hydrophilic biopolymers, hence the reduced oxygen barrier as also shown by other literatures using CNCs as coating or filler for other polymers (Fukuzumi et al., 2011; Kato et al., 2005). Projected increase in RH was also shown by the dotted line for Kraft 2-layer and Cotton (see figure 20). However, the values are still way lower than bare PET film at 74.95 O₂TR.

Given the relatively thinner size of both Kraft single and double layers as compared to cotton as seen on table 5 (132.90 nm and 411.39 nm vs 660.00 nm, respectively), and using less amount of CNC in the solution (2.5% vs 7%), the result has shown that Kraft CNC has exhibited a good potential as bio-coating source to improve oxygen barrier properties for PET film (15.43 O₂TR for Kraft 1-layer and 7.78 O₂TR for Kraft 2-layer vs 82 O₂TR for bare under measurements at 50% RH, seen on table 9). However, further trials are suggested to verify the statistical significance of the values.

Conclusions and recommendations for further studies

The experiment has exhibited that high quality CNCs can be extracted from unbleached Kraft pulp, an impure cellulose material source, and can be utilized as a high quality bio-coating for PET to improve its packaging properties.

Ammonium persulfate has proven to be an efficient extracting agent for unbleached Kraft pulp. Kraft pulp preparation, which includes swelling using distilled water at elevated temperature (70°C) for 30 minutes, cooling down, and mixing it with APS at room temperature for 30 minutes, were shown to be important steps to execute before proceeding with APS activation via heating. Previous tests without this material preparation step have proven to be ineffective. Swelling and mixing of APS in the Kraft pulp solution allowed APS to penetrate the fibers, which allows for rapid carboxylation of Kraft pulp once the temperature was increased. However, more tests should be performed to identify the right combination of reaction time, APS concentration, and temperature to improve its current yield of 22%.

Kraft CNC was successfully applied on PET, and different parameters related to packaging was performed to ensure its quality as a coating. Oxygen permeability is an important property particularly for food packaging due to its potential effects on quality and shelf life. Kraft 2-layer showed positive results in terms of oxygen permeability rate at 30% and 40% RH. This is comparable to CNC coatings extracted using acid hydrolysis and acquired from cotton linters, which contains > 99% alpha-cellulose (Sczostak, 2009). Kraft 1-layer also displayed good barrier properties for 30% RH, but its oxygen permeability more than doubled when the relative humidity changed from 40% and 50% (6.72 to 15.43 O₂TR). However, it is still a good result, given that bare film is at a high 82 O₂TR, signifying a significant reduction in oxygen transmission rate, thanks to the coating applied.

Optical properties were also tested, given the transparent flexible packaging's importance to better market the products on the shelves by showing the actual product to consumers via see-through packaging, while keeping its protective barrier properties. Both Kraft 1-layer and 2-layer showed hydrophilic contact angles when in contact with water, denoting a good wettability and anti-fog property. However, more tests must be performed, such as boiling test, to verify its response when

used in actual packaging. Transparency and haze tests performed on Kraft 1-layer and Kraft 2-layer, and its responses to these optical tests were interpreted as slightly lower compared to cotton CNCs. Nevertheless, it was observed to have almost negligible effect on transparency compared to cotton CNC and bare film when it was applied in a breadstick food packaging and readability of text even at a minimum of font 6.

It must be highlighted that these results are based on 2.5% CNC re-dilution with distilled water after freeze drying using Kraft CNC extracted from the experiment, compared to 7% re-dilution of cotton CNC from acid hydrolysis. This re-diluted solution was used for coating application on PET film. This shows that Kraft CNC needed a lower amount of CNC concentration during the re-dilution step to achieve similar improvements observed from cotton CNC. For industrial applications, this finding can have huge economic savings when choosing the right bio-coating to achieve the same packaging requirement.

Utilizing unbleached and semi-processed Kraft pulp as cheaper material to extract CNC, in comparison to the heavily-processed cotton linters, was proven to be possible. Given the results, it can therefore be concluded that CNC bio-coating sourced from unbleached Kraft pulp provided a high quality bio-coating for PET, improving its optical and permeability properties. It has also provided a better alternative for a low cost extracting process at a shorter time (against acid hydrolysis, which includes dialysis step that lasts for 3-4 days). Application of this type of bio-coating can lead to reduction of total packaging weight by utilizing thinner and lighter plastics since its barrier properties were already improved. This can eventually provide economic benefit to producers and environmental benefit such as reduced energy use during transport.

It is recommended that more tests related to physical properties (e.g. coefficient of friction, strength testing) and application to other flexible packaging (e.g. PET, PLA, etc.) has to be done to further verify its applicability to more packaging requirements. Given the possibility of bio-coating removal / dissolution when in contact with water (as shown by the decreasing permeability while increasing %RH) the need to protect CNCs after application should also be explored (such as adding another layer of film to sandwich the CNC bio-coating layer, or better adhesion conditions for CNCs on the film) to ensure its long-term usage in humid/ wet conditions.

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