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A Novel Cellulose Nanocrystals-Based Approach To Improve the Mechanical Properties of Recycled Paper

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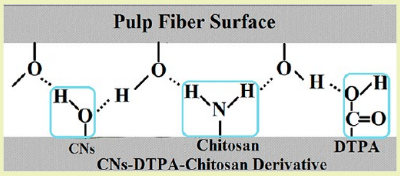

ABSTRACT: The ability to introduce cellulose nanocrystals (CNs) into any of a number of single-component or composite applications is currently limited because they are difficult to efficiently isolate and in certain cases difficult to maintain homogeneously disperse. The current research introduces a novel purification technique and composite application for modified cellulose nanocrystal derivatives by using them as an additive for dry strength in recycled paper OCC (old corrugated containerboard). More specifically, the present work illustrates a way to easily isolate CNs by extracting them through a traditional mineral acid hydrolysis followed up by washing them several times with ethanol. The extracted cellulose nanocrystals did not flocculate and were completely homogeneously dispersed in water. Additionally, it was found that the incorporation of carboxylic acid functionalities onto the CNs by reaction with diethylenetriamine pentaacetic acid (DTPA) followed by cross-linking with chitosan and introduction into the OCC greatly improved its tensile and other mechanical properties. The tensile and burst strength of the modified OCC pulp sheet increased 40.3% and 46%, respectively, with significantly increased gloss and decreased roughness and tear strength as compared to the control sample. Spectral characterization of the CNs and their derivatives was accomplished using TGA, DSC, FT-IR, and SEM.

KEYWORDS: *Cellulose nanocrystals (CNs), Chitosan, Cross-linking, OCC pulp, Mechanical properties*

■ INTRODUCTION

Cellulose is arguably the most important biopolymer on the planet because not only is it the most abundant biomaterial available (as produced by all plants and many microorganisms including algae, plankton, and bacteria), it is renewable, biodegradable, biocompatible, nonhypoallergenic, readily derivatived, extremely strong, and eco-friendly. No other natural or synthetic polymer comes close to matching its highly functional mechanical and chemical properties. It is a carbohydrate polymer made up of repeating β-D-glucopyranose units that is characterized by three hydroxyl groups per anhydroglucose unit that are able to impart a high degree of functionality to the biomacromolecule.[1]

The materials based on cellulose and its derivatives have been used for more than 150 years in a wide variety of applications, such as food, paper, biomaterials, and pharmaceuticals.[2] Typically, printing and writing grade papers are prime examples; starch is used for its surface fluid resistance characteristics (sizing) with the main goal of improving paper surface resistance and printability.[3] In recycled paper applications, the primary concern is addressing low mechanical properties (e.g., bonding, because of the strength losses occurring after one or more uses). Research has shown that strength loss is more important in the case of refined pulp for papermaking, compared to the production of dry-lap pulp, which is unrefined.[4]

The utilization rate of waste fiber for recycled containerboard (old corrugated containerboard or OCC) in 1963 was reported to be 21.1% in the United States, whereas in 2001, it was 67% with a concomitant recovery rate of approximately 70%.[4] In 2011, the American Forest & Paper Association (AF&PA) released a recovery rate for OCC that reached a high of 91.2%. Therefore, any further research in this area must focus on improvements in the strength of OCC to validate current and future recovery rates. Early research identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled paper.[5,6] A few innovative studies have shown that chemical derivatization or the appropriate chemical treatment of fiber surfaces may prevent strength losses from occurring.[7,8] The papermaking industry is currently using commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide as the primary agents to improve the mechanical properties of recycled OCC, but strength improvements are still low relative to that of virgin pulp (original, nonrecycled paper).[9,10]

Meanwhile, numerous advancements in materials science and engineering research have targeted the use of nanomaterials to offer heretofore unattainable benefits. Nanomaterials offer a promising alternative to tackling the issue of low OCC strength because of a concept known as the nanometric size effect as it relates to conventional bulk fillers even at low filler content. Nanometric materials have quite high reinforcing effects, and studies have also shown their positive impact in barrier packaging. However, for decades, studies have been conducted with nonrenewable inorganic fillers and a petroleum-based matrix for a number of applications including packaging, a high

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Figure 1. Photographic images of water-washed cellulose nanocrystals (left), alcohol-washed cellulose nanocrystals (center, and alcohol-washed cellulose nanocrystals dispersed in water (right).

value sector of the pulp market. Increasing environmental concerns have led to, for example, developing new flexible barrier biobased packaging materials and investigating the potential uses of renewable resources for such applications.[10] Recently, nanoparticles made of cellulose (cellulose nanocrystals, CNs) have become an extremely important class of nanomaterials because of their strength-reinforcing effects.

Acid hydrolysis of cellulose is an effective method to remove the amorphous regions of cellulose fibers and obtain CNs. Sulfuric acid and mineral (hydrochloric) acid have been the chief methods used to produce cellulose nanocrystals from cellulosic biopolymers.[12]

The present study focuses on the characterization and application of novel cellulose-based nanomaterials for improving the mechanical properties of OCC; more specifically, cellulose nanocrystals have been modified with diethylenetriamine pentaacetic acid DTPA in the presence of sodium hypophosphate (SHP) and later cross-linked with chitosan and applied to an OCC recylcled paper stock for the express purpose of improving its mechanical properties by taking advantage of both chemical cross-linking and hydrogen bonding to the OCC fiber surface. The present research will focus on CNs' characterization and provide a review of their application in OCC strength improvement.

■ EXPERIMENTAL SECTION

Materials. The OCC pulp was furnished by AzkoNobel Pulp and Performance Chemicals, Marietta, GA. Whatman filter paper was from Whatman International, Ltd., Maidstone, England. Chitosan (Ch) CAS no. 9012-76-4 was purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, and diethylenetriamine pentaacetic acid (DTPA), CAS no. 67-43-6. Ethyl alcohol (denatured) and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

Preparation of Cellulose Nanocrystals (CNs). The cellulose nanocrystals (CNs) were prepared from pure cellulose (Whatman paper #4) by acid hydrolysis using HCl (3 N) at 90 °C for 2 h under continuous agitation to obtain cellulosic nanocrystals. The suspension was centrifuged at 5300 rpm for 15 min to concentrate the CNs and remove the excess aqueous acid. The resultant precipitate was rinsed and recentrifuged until a constant neutral pH was achieved. After a neutral pH was achieved, the solid aggregate was washed with ethanol two times and recentrifuged. The CN suspension was dried in air under a hood and then stored under a vacuum desiccator until required for further application.[13] In addition, it was found that water-washed and subsequently dried CNs readily flocculated into aggregates, but upon using an alcohol wash with subsequent drying, they did not aggregate and were easily dispersible in water (Figure 1).

Chemical Modifications of CNs. Approximately 5 g of diethylenetriamine pentaacetic acid (DTPA) and 1 g of SHP were dissolved in 20 mL NaOH solution (pH 12) in a 50 mL Petri dish. Five grams of CNs were combined in a DTPA solution and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 130 °C for 4 h. Reaction products were washed with distilled water and filtered several times to remove unreacted materials. The product referred to as CNs−DTPA was air-dried at 50 °C in an air oven overnight.[14] The proposed reaction scheme is shown in Figure 2.

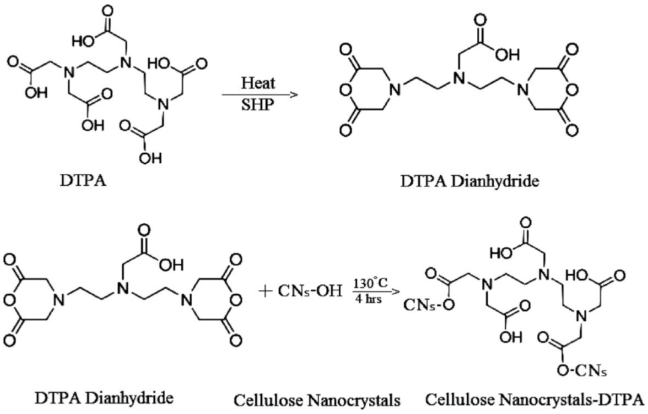

Figure 2. Esterification reaction of CNs with DTPA.

Polyelectrolyte Complexation Reaction. Chitosan (Ch, 1 g) was dissolved into 50 mL of 1.5% acetic acid solution. DTPA-modified cellulose nanocrystals (CNs−DTPA, 1 g) were also dispersed with 50 mL of water and then added to a 50 mL chitosan solution in a 250 mL round-bottomed flask. The reaction mixture was stirred using a magnetic stirrer at 80 °C for 90 min.[13] The proposed reaction scheme based on a literature precedent is shown in Figure 3.

Preparation of OCC Paper Stock. The stock was prepared using a 600 mL pulp slurry (1.8 g OCC having a freeness of 400 CSF) in a sheet molder machine. The pulp slurry was also diluted with 10 L of white water into the sheet molder to produce a uniform sheet. The sheet was dried in a conditioning room and thereafter cured at 105 °C for 1.0 h.

Testing Methods. *Determination of Carboxyl Content.* A known amount of the CNs derivative was dispersed in 0.1 N NaOH and neutralized for 1 h. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator,[15] and the carboxyl content in milliequivalents of acidity per 100 g was calculated as follows

$$\text{Carboxyl Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

where N = normality of HCl; V_2 = volume of HCl without sample; V_1 = volume of HCl with sample; and W = weight of sample.

Determination of Degree of Esterification and Degree of Substitution. The CNs derivative was dispersed in DMSO in a conical flask for 10 h, and then excess 0.1N NaOH was added to the solution to saponify the ester over 2 h. The excess NaOH was determined by titration with 0.1N HCl[16,17] to determine the percent esterification and the degree of substitution

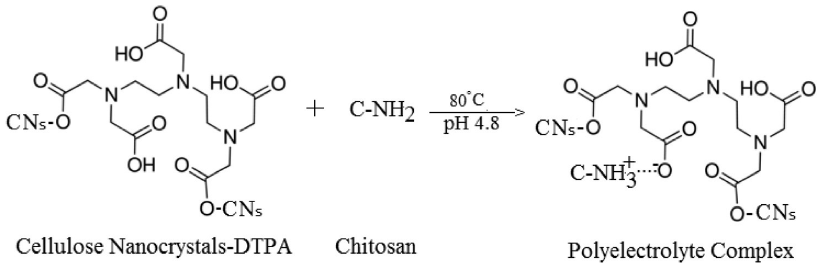

Figure 3. Polyelectrolyte complexation of cellulose nanocrystal DTPA with chitosan.

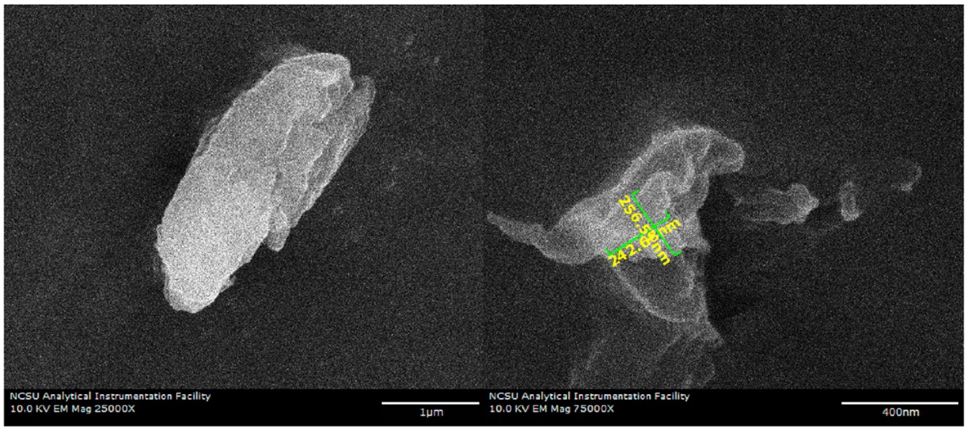

Figure 4. SEM photomicrographs of flocculated (aggregated) CNs. The images have length scales of 1 μm (left) and 400 nm (right), respectively.

$$\text{Degree of Esterification (\%)} = \frac{6.005(V_2 - V_1) \times \text{N}}{W}$$

where N = normality of HCl; V_2 = volume of HCl without sample; and V_1 = volume of HCl with sample.

$$\text{Degree of Substitution} = \frac{162 \times A\%}{100M - (m - 1)A\%}$$

where $A\%$ = degree of esterification; W = weight of sample; and M = molecular weight of cross-linking agent.

Gloss Testing. The gloss of OCC pulp hand sheet was tested with a GLOSSMETER tester according to TAPPI T 480 method.

Roughness Testing. The roughness of OCC pulp hand sheet was tested with an L&W roughness tester according to TAPPI T 538 method.

Tensile Index. The tensile Index of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to TAPPI T 220 method. Tensile index is defined as the quotient of the tensile strength (N/m) and the basis weight (g/m^2) of the paper. For example, the tensile index of paper is determined in units of (N/m)/(g/m^2) = Nm/g, whereas tensile strength is defined as the breaking force (load) per standard width of paper.

Burst Strength. The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to TAPPI T 810 method.

Tear Strength. The tear strength of OCC pulp hand sheet was tested with an L& W tester according to ASTM D 689 method.

Characterization. *FTIR Analysis.* The FTIR spectra were recorded on a NEXUS 670 FTIR spectrophotometer using a KBr disc containing 2% finely ground samples. All the spectra were obtained by accumulation of 64 scans at a resolution of 4 cm^{-1} over a range of 400−4000 cm^{-1}.[18]

Thermal Gravimetric Analysis (TGA). The thermogravimetric analyzer used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were 30−600 and 5 °C/min, respectively, followed by isothermal heating at 600 °C.[19]

Differential Scanning Calorimeter (DSC). A differential scanning calorimeter DSC Q100 was used with a Hermetic pan (T 090127). Samples were subjected to a 2 °C/min temperature ramp from 30−200 °C followed by isothermal heating at 200 °C for 15 min. An empty pan was used as the reference.[20]

Scanning Electron Microscope (SEM). Morphological characterization of modified CNs−DTPA−chitosan derivative-treated OCC pulp hand sheets was obtained using a scanning electron microscope (SEM), Hitachi S-3200N.[14]

Contact Angle. Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea) on CNs−DTPA−chitosan-treated OCC pulp hand sheets. Deionized water was used as the probe fluid.[15]

RESULTS AND DISCUSSION

Characterization of Cellulose Nanocrystals (CNs). *Morphology and Surface Chemical Changes.* The SEM image of water-washed extracted CNs displayed a coagulated-like distribution with nanoparticles having a length and width of 256.5 and 242.6 nm, respectively (Figure 4). In general, CNs possess a surface covered with reactive hydroxyl groups that allow for facile surface decoration for a specific end use via the appropriate chemical reaction strategy. The reaction pathways that were chosen for the particular surface functionalization in this work are shown in Figures 2 and 3.

Table 1. Thermal Analyses of CNs and CNs Derivatives

sample	TGA maximum (DTG) degradation temp. (°C)	residual char at 600 °C (%)	DSC melting point (°C)
DTPA salt	280	25.10	199.2
CNs	334	7.0	94.0
CNs−DTPA	320	14.0	98.5
CNs−DTPA−Ch	325	30.0	113.0
Ch	290	26.0	269.0

The carboxyl content of the CNs increased from a minimal 62 meq/100 g in the control to over 6 times (375 meq/100 g)

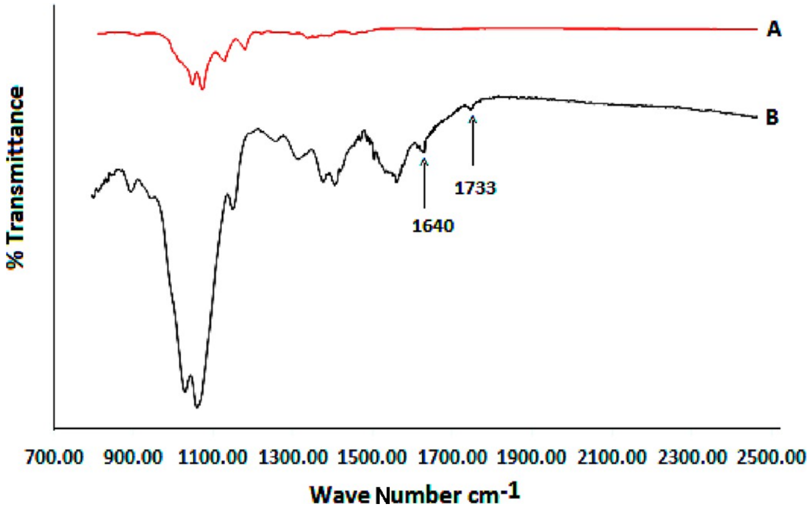

Figure 5. FT-IR spectra of CNs (A) and CNs−DTPA−chitosan. The 1733 cm^{-1} band can be attributed to the ester carbonyl stretch (from the DTPA attachment), whereas the 1640 cm^{-1} band of carbonyl groups in an amide bond of CNs−DTPA derivatives.

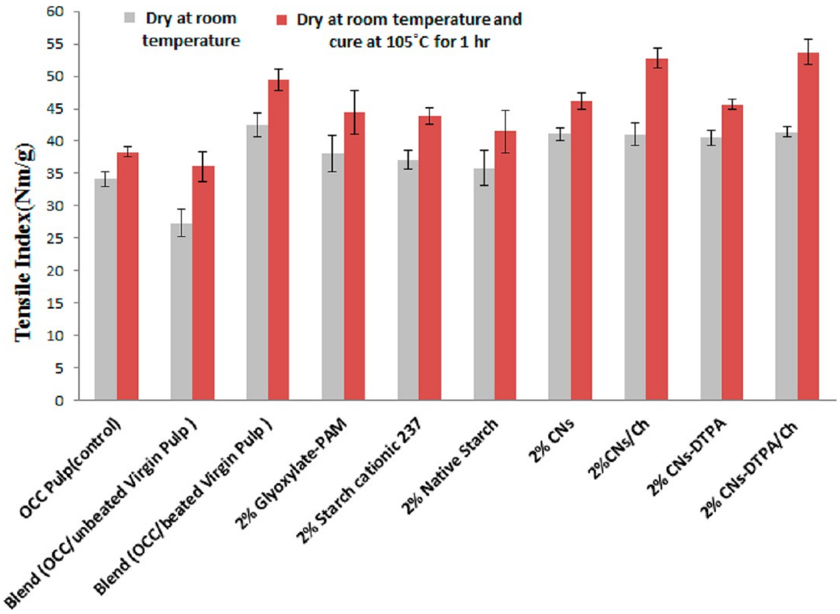

Figure 6. Tensile strength of CNs derivative-treated OCC recycled pulp hand sheets.

in the test sample. To further clarify the changes that occurred after the surface modification, the DS (degree of substitution) and percent esterification were explicitly investigated and determined by titration. For this study, the monomer formula weight and number of hydroxyls per starch monomer unit that were used in the calculations were 162 Da and 3, respectively. Thus, the degree of substitution and percent esterification were calculated to be 0.25% and 37.2%. The intrinsic viscosities of 1 M CED-dissolved CNs and CNs−DTPA systems were determined at 25 °C with an Ubbelohde-type viscometer to determine molecular weight.[15] Depending on the specific viscosity measured, typical molecular weights of CNs and CNs−DTPA were found to be 19,200 Da and 22,800 Da, respectively.

Thermal Behavior. The thermogravimetric behaviors of the CNs derivatives was evaluated over a 5 °C/min heating ramp under nitrogen and are shown in Table 1. For several samples, a weight loss below and around 100 °C was attributed to water evaporation.[21] However, the weight loss above 100 °C was due to the thermal decomposition of the CNs/derivatives themselves.[20] DTPA had a single sharp decomposition peak at 280.26 °C, whereas the CNs have a single weight loss peak at 334.56 °C; however, all derivatives of CNs have a decrease in maximum weight loss temperature and concomitant significantly higher residual mass after heating to 600 °C. This may be explained by the fact that the cellulose nanocrystals surface-modifying agents have a lower decomposition temperature. This layer is on the surface of the CNs, and these materials attached via ester bonds have a lower temperature of degradation.[15]

The thermal behavior obtained from a differential scanning calorimetric analysis of the CNs derivatives was evaluated with a 2 °C/min heating ramp up to 200 °C under nitrogen as shown in Table 1. DTPA displays a very sharp melting point at 199.2 °C, whereas an endothermic peak was observed at 94.0 °C for the CNs. The melting points all increased for the reaction products as illustrated in Table 1. The increase in the melting points may be due to the chemical architectural

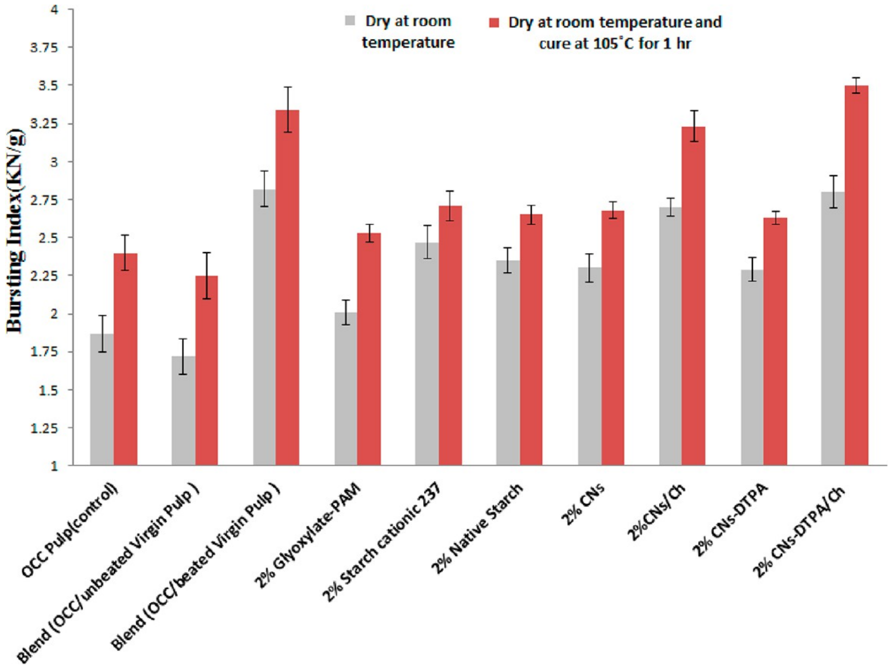

Figure 7. Bursting strength of CNS derivative-treated OCC recycled pulp hand sheets.

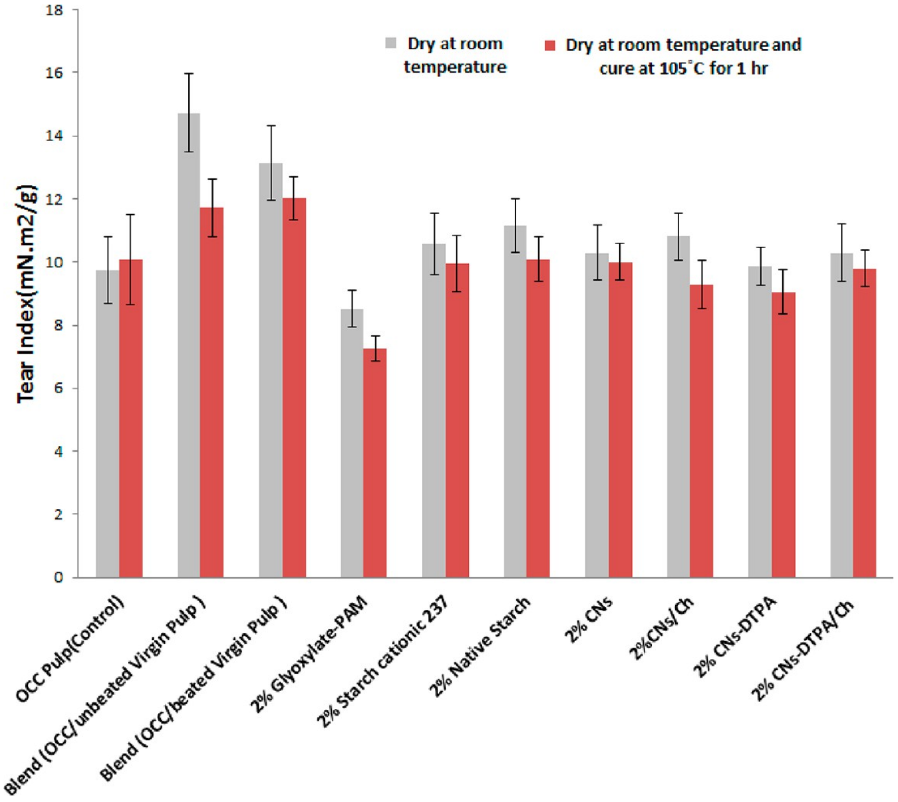

Figure 8. Tear strength of cellulose nanocrystals derivative-treated OCC recycled pulp hand sheets.

robustness arising from increased hydrogen bonding and plasticization as well as the higher molecular organization obtained from cross-linking.[15]

FT-IR Analysis. The FT-IR spectra of the CNs and CNs–DTPA–chitosan are shown in Figure 5. The spectrum of CNs shows a prominent peak at 3400 cm^{-1} that arises from the hydroxyl groups, although the carbonyl region does not clearly show a carbonyl stretch, likely due to its low levels (65 meq./100 g) and being swamped out by the remaining stronger signals in the spectrum. However, when the CNs were reacted with DTPA and were further cross-linked with chitosan, a peak appeared at approximately 1733 cm^{-1} that is attributable to the carbonyl group. In addition, another new peak was observed at 1640 cm^{-1} when chitosan cross-linked with CNs-DTPA derivatives. This peak is attributable to the characteristic stretching band of carbonyl groups in the amide bond of CNs–

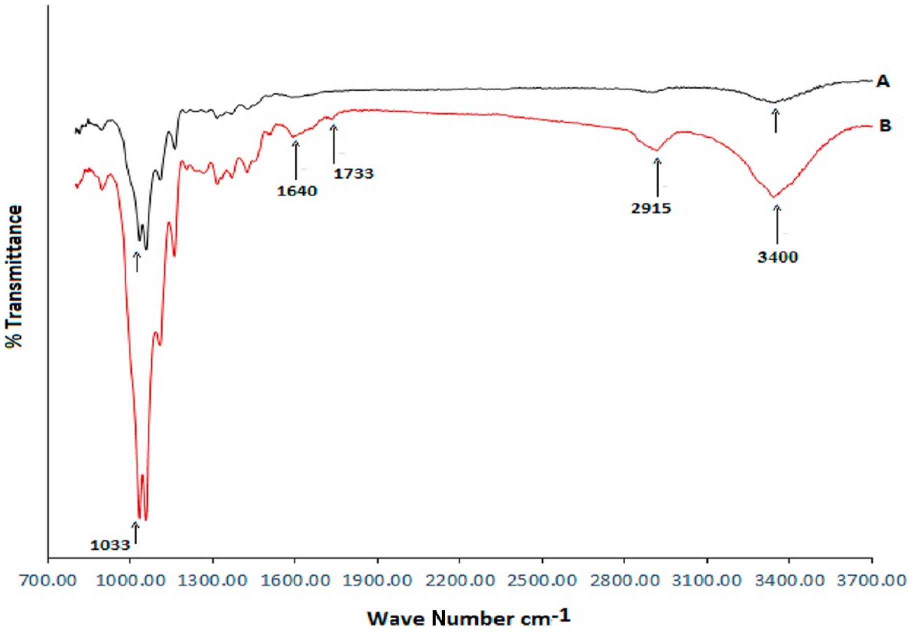

Figure 9. ATR spectra of pulp sheet (A) and cellulose nanocrystals−DTPA−chitosan pulp sheet.

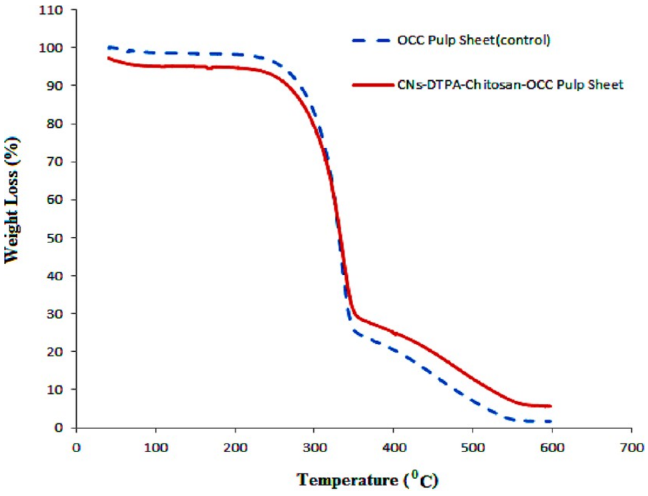

Figure 10. Thermo-gravimetric analysis of OCC pulp sheet and cellulose nanocrystals−DTPA−chitosan-treated OCC pulp sheet.

DTPA derivatives.[23] However, the intensity of this amide band increased after the CNs−DTPA−Ch derivative was dried at 105 °C after incorporation into an OCC pulp matrix, strongly pointing to the conclusion that at high temperature the polyelectrolyte complex originating from the interaction between the carboxyl group of CNs−DTPA and amino group of chitosan was converted to amide bond (Figure 9).[22]

Cellulose Nanocrystals Derivatives Application for OCC Strength Improvement. *Effect of Cellulose Nanocrystals Derivatives on OCC Pulp Paper Strength Properties.* Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to have sufficient resistance in applications that require packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to the adequate development of hydrogen bonds. Also, it depends on the quantity and area of bonding sites. In recycling, fibers irreversibly damage, and this damage can affect final paper resistance properties. Figure 6 shows the tensile index of OCC recycled pulp hand sheet that results after the addition of either virgin (nonrecycled) pulp or cellulosic nanoparticle derivatives.

Virgin pulp in theory has a much higher mechanical resistance because the fibers have not been damaged from prior use. The control for these studies was the base OCC recycled pulp (CSF = 400, a measure of the adsorption of water, i.e., higher value, less adsorption). Earlier research reported that the range of tensile index (Nm/g) for an OCC pulp sheet is 20−35.[24] Defibrillated or nondefibrillated virgin softwood kraft pulp (revolutions =5000, CSF = 530) was blended with OCC recycled pulp (50:50) to increase the strength properties. In tandem, 2% CNs derivatives (based on the mass of dried pulp) were also mixed with the OCC pulp slurry separately. As a result, the nondefibrillated virgin pulp sample had a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Figure 6). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (to defribillate) introduced to the virgin pulp. The tensile index of 2% CNs and its derivatives-treated OCC pulp samples such as CNs−DTPA, CNs−Ch, and CNs−DTPA−Ch were found to be 20.5, 20.3, 37.6, and 40.3% higher than the control sample. The result was also significantly higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and native cornstarch. This may be because of the very high surface area/volume ratio (very small size) of the CNs and the concomitant stronger bonding that is generated with the OCC pulp fibers through the high quantity of carboxyl and amino groups in the nanoparticles.[25,26] However, the density of CNs−DTPA−Ch treated sample increased about 25% which may also be one of the reasons for the increase in the strength.[27]

In contrast, the tensile index of 2% CN−Ch and CNs−DTPA−Ch derivatives-treated OCC pulp samples was also better than defibrillated virgin pulp blends (Figure 6). Similarly, the burst strength of CNs, CNs−DTPA, CNs−Ch, and CNs−DTPA−Ch-treated samples increased 11, 10.8, 35, and 46%

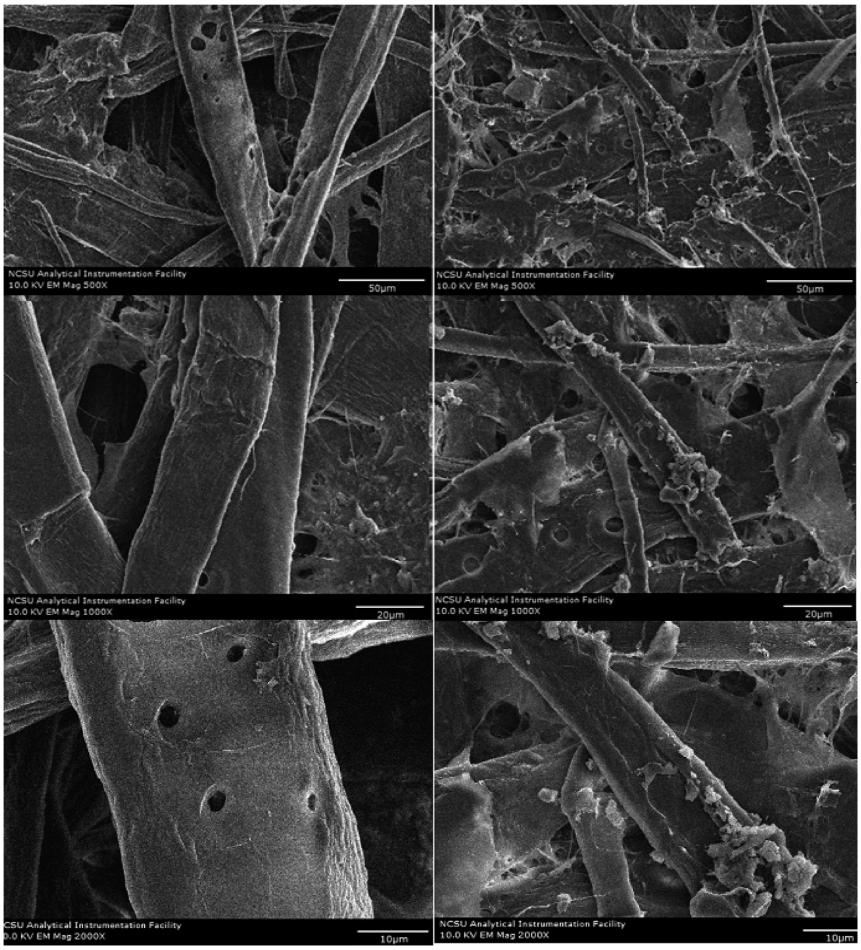

Figure 11. SEM image of OCC recycled pulp hand sheet (three left photomicroimages) and 2% CNs−Ch derivatives-treated OCC pulp hand sheet (three right photomicroimages). Top, middle, and bottom images have length scales of 50, 20, and 10 μm, respectively.

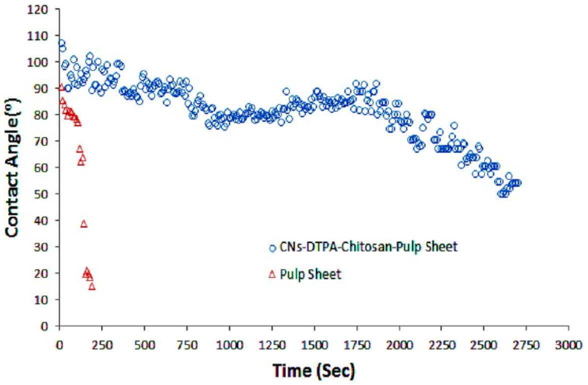

Figure 12. Contact angle of OCC pulp sheet (Δ) and CNs-DTPA/chitosan-treated OCC pulp sheet (O).

compared to the control sample, and all the cases provided better results compared to the commercial dry strength additive (Figure 7). It is also observed from Figure 8 that the tear strength of CNs, CNs−DTPA, CN−-Ch, and CN−DTPA−Ch-treated OCC pulp samples were lower than the control sample, but slightly higher than commercial glyoxylate polyacrylamide-treated sample. However, CNs−DTPA−Ch-treated pulp sheet gloss increased more than two times, and the roughness significantly decreased. This may happen due to the increased density of the CNs−DTPA−Ch-treated pulp sheet compared to the control sample.[27]

Bond Formation with OCC Recycled Pulp. The basic groups ($-NH_2$) on every ring in chitosan−DTPA−CNs derivatives develop positive charges when they are in a sufficiently acidic medium and may thus form ionic or covalent bonds with the negatively charged cellulosics in paper fibers during the paper making process.[28] In addition, the DTPA in chitosan−DTPA−CNs derivatives contains a number of free carboxyl groups that can also engage in ionic bonds with the fiber surface of pulp and also increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxyl and amine groups for increasing bonding between fibers during sheet formation also contributed an increase in tensile strength.[29]

It can also be observed from Figure 9 that the chitosan−DTPA−CNs derivatives-treated pulp sheet has a large band at 3400 cm^{-1} compared to the control pulp sheet. This large band can be attributed to the hydrogen bonding interactions arising among the hydroxyl groups within the chitosan, CNs,[30] and DTPA moieties. However, a large new peak observed at 1640 cm^{-1} is present from the polyelectrolyte complex of chitosan−DTPA−CNs derivatives that has been converted to an amide linkage when the pulp sheet is dried at high temperature.[22] In addition, a high residual char (5.8%) value was observed in the chitosan−DTPA−CNs-treated pulp sheet compared to the control pulp sheet (1.7%) after heating at 600 °C (Figure 10), which is attributed to chitosan−DTPA−CNs cross-links to the pulp fiber.

Scanning electron microscopy of OCC recycled pulp samples and CNsX/C derivatives-treated OCC recycled pulp samples are shown in Figure 11. The OCC pulp sample control shows a continuous irregular pore structure with plate-like solid pore walls, but the CNs−DTPA−Ch-treated OCC pulp sample SEM images reveal a smoother surface with the appearance of depositions on the fibers surface. It may be that the depositions arise from the phenomenon of cross-linking on the OCC pulp fibers.

Contact Angle. The dynamic contact angle with DI water at 9 s was determined to be 90° for OCC pulp sheet (control). The water angle significantly dropped 15° for approximately 180 s (Figure 12). In contrast, the dynamic contact angles with DI water at 9 s for the CNs−DTPA−Ch-treated OCC pulp sheet was 108°, and the contact angle dropped approximately 85° for approximately 1875 s and then finally dropped 50° for approximately 2700 s. This reflects the significantly decreased water absorbency of the CNs−DTPA−Ch-treated OCC pulp sheet relative to the control pulp sheet. This may explain that the OCC furnish has a very irregular surface and is extremely hydrophilic showing nearly no surface contact angle measurement in the typical contact angle time frame. Our additive, chitosan, is strongly hydrophobic and also produces a sticky gel under acidic pH (wet) that adopts a plastic-like character under dry conditions. Thus, when a pulp sheet is generated with the additive, under the pressing time, it spreads very evenly over the rough surface, covering it very uniformly to produce a paper surface that was very smooth and also possessed increased gloss (Figure 11). Thus, because the additive-treated sheet surface was hydrophobic due to the plastic-like chitosan under dry conditions, the contact angle increased somewhat.

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Notes

The authors declare no competing financial interest.

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