A Statistically Designed Evaluation of Nanocellulose, Refining and Cationic Starch on the Properties of Linerboard from Recycled Old Corrugated Containers (OCC)

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Methods to improve the physical properties of recycled paper can greatly enhance its potential applications, especially for packaging. This study aimed to understand the effect of refining, cationic starch addition, and cellulosic nanofibers (CNF) generated from old corrugated containers (OCC) addition with recycled OCC on tensile index (TI) and ring crush index (RCI). Linerboard from OCC made on an industrial paper machine was compared with the lab prepared handsheets, and the results indicated that the lab procedure including the refining step produced board reflective of the industrially made linerboard. CNF addition was observed to decrease the drainage rate of the unrefined OCC pulp stock but not significantly when the OCC pulp stock was refined to a freeness of 300 mL CSF. The results of a statistically designed experiment showed that cationic starch, refining, and the interaction between cationic starch and CNF were significant parameters that improve TI. Through experiments that measured the retention of the pulp stock, it was determined that CNF retention was only 44.8% without cationic starch and increased to 90.0% with cationic starch present, thus explaining their interaction. This study indicates that CNF from OCC can be combined with cationic starch at appropriate levels to improve properties of the resulting board without critically decreasing the drainage rate.

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Keywords: Recycled OCC pulps; Cationic starch; Refining; Cellulosic nanofibrils (CNF); Retention

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INTRODUCTION

Corrugated paperboard is one of the most popular resources in modern life. It is widely used in daily activities related to businesses and households. It is utilized not only as containers for goods and foods delivery, but also it occasionally functions as a supporter of packaged goods as well. This type of packaging is selected by users because it is bio-renewable, sustainable, and composed of environmental-friendly resources. Cellulosic fibers are a main component that are used to manufacture those products, and they are a biodegradable or recyclable material. Even though they are reusable sources for the manufacturing process, repeated re-processing for several cycles makes the fibers stiffer and less conformable, which adversely affects the physical properties of paper (Minor 1994).

For the corrugated paperboard, the linerboard and corrugated medium paper are joined together in various patterns using adhesive agents. The box compression (BC) strength is a test that measures the strength of boxes under compression force. This test is related to the condition of boxes when placing them in a stack. However, when conducting the BC, those boxes no longer can be used, because this is a destructive test. Hence, there is another way to predict the BC, if the mechanical property of paper is known, which is edgewise compression test (ECT). The McKee's equation is used to estimate the BC (TAPPI TIP 0304-09 2003).

Edgewise compression strength or edge crush is a mechanical strength under compression load of sheetboards before they are formed into boxes. In order to get this information, sheetboards are damaged and not able to create boxes the same as the conducting BC test. However, there are other strength properties that can be used to predict the edgewise compression strength mentioned in the TAPPI's guideline, which is using the ring crush test (RCT) or short span compression (STFI). These methods are widely used in some areas, and there is a linear relationship between RC and STFI (Dimitrov 2010). The ring crush test (RCT) or short span compression test (STFI) are used to determine the edgewise compression test (ECT) (TAPPI 818 cm-97 1997). In the paper production process, the paper properties, such as ring crush (RC), concora corrugating medium (CM), water drop or Cobb, and others, are tested before delivering to a box plant for converting to finished goods. Once the containers are used for protecting other finished goods in a warehouse, a stacking pattern is a common way to save storage space.

Hornification is a technical term to describe what happens when water is removed from the fibers by both heating in the dryer section of the papermaking process or when using other methods to make paper dried, such as butanol; these drying methods cause a reduction of water retainability within their cell wall (Hubbe *et al*. 2007). The hornified fibers have a decreased chance to create inter-fiber bonding (Minor 1994). When the low fiber bonding exists, it also provides low mechanical strength as well.

The most common way to improve paper strength is refining the fibers. The refining effect creates delamination and fibrillation on the cell wall structure of fibers. These increase the wet fiber flexibility (Hubbe *et al*. 2007), which enhances the strength properties of the paper product. An experiment of refining effects with typical Australian mixed brown wastepaper by Ghosh (2006) shows that increasing the specific refining energy results in a direct proportional increase in the RC. However, this method only has a limitation to improve the strength properties because of the fiber's nature.

The addition of various chemicals also helps to improve the strength properties. This includes wet-end chemicals, as well as surface sizing at size press section. A handsheet study by Ghasemian *et al.* (2012) focuses on the effect of cationic starch addition to the mixed furnish consisting of OCC and virgin neutral sulfite semi-chemical (NSSC) pulp with various ratio and doses. The study shows that the RC and CM of the paper are reduced significantly when reducing the amount of virgin pulp in the furnish, whereas, adding the cationic starch at the same ratio led to an enhancement by up to 2.5% of CM and 7% of RC at the 3.0% wt. dosing rate. Nevertheless, this study did not consider specimens with 100% OCC content. Another study by Dölle *et al.* (2020) about the effect when applying cationic tapioca starch to 100% recycled paper shows that the tensile index increases up to 44% at dosage of 4 lbs/ton of paper. However, there is no improvement data for the RC in this study.

Another method that is used in a lab scale is utilizing cellulosic nanofibers (CNF), which are mixed with the stock before forming a sheet. One experiment by Ehman *et al*. (2020), with the addition of 3 wt% of CNF to chemimechanical pulp (CMP), showed an improvement in the RC and CM by up to 27% and 28%, respectively. However, the freeness in Schopper-Riegler (°SR) of the material increased by 70% from 41 to 70 °SR. Recently, Hu *et al*. (2021) studied the production of CNF by different mechanical methods from bleached softwood kraft pulp (BSKP) and adding them into the recycled pulp. The results show that adding 5.0 wt% of the microfluidic homogenization and suitable PFI milling conditions (RM-CNF1) improved the tensile index and burst index by 35.5% and 49.4%, respectively. Nevertheless, the total drainage time of the material increased by 110% from 31 to 65 seconds. Both of these studies show increases in properties but at the expense of impractical drainage rates on the paper machine from using CNF. This leads to the question of whether it is compatible with a real papermaking process and how to reduce this effect when forming a sheet, especially in the forming section. Another interesting point is what is the effect of CNF to the RC and CM of the recycled paper when adding CNF. Such issues are not covered in the study of Hu *et al*. (2021).

Yousefhashemi *et al*. (2019) studied the use of OCC recycled boards treated with cationic tapioca starch and lignocellulose nanofiber (LCNF) that was made from OCC as well. Furthermore, anionic nanosilica was utilized to improve drainage ability due to the drainage reduction effect from LCNF. As a result, those treatments were able to recover the freeness level and achieved the improvement of tensile strength up to 54%. However, they focused on the condition of freeness at 300 mL CSF, and the result of RC or STFI strength were not reported.

Starkey *et al*. (2021) reported the improvement of STFI of OCC treated with lignin-containing micro- and nano-fibrillated cellulosic (LMNFCs), which was prepared from virgin unbleached softwood kraft pulp with a Masuko Super Mass Colloider. They reported the possibility of basis weight reduction and the elimination of refining by adding LMNFCs to the fibers. This work provided a new approach to recover STFI, and also to lightweight packaging paper in the future based on LMNFC from virgin pulp.

This study focused on the methods to improve physical properties of the paperboard, especially tensile and RC strength, with recycled content (OCC based CNF). Various methods were used to enhance those properties. Nevertheless, this is not the first time that efforts have been made to improve them. There are many groups of people studying in this area, but those studies included the virgin fiber being a part of the paper or no report of RC strength when using recycled materials. This research aims to use the recycled material as both the fibers and the reinforcing nano materials, without any virgin fiber present. In addition, the additives, such as cationic starch and cellulosic nanofibers (CNF), are evaluated separately and in conjunction to improve the tensile and RC properties that the previous studies do not focus on. Moreover, the CNF in this study were produced with 100% OCC, which is a different approach from some previous studies, which have used unbleached virgin pulps as the source for making CNF.

EXPERIMENTAL

Materials

Recycled pulp from OCC was obtained from Greif Industrial Company, USA, before and after refining with 4000 DD, 42” model at 4.5% consistency with 2.1 HPdays/ton. The freeness of the pulp was reduced from 530 to 376 mL CSF. After being centrifuged and fluffed, the pulps with 30% moisture were used to study the existing paper properties as well as strengthen them with various additives and treatment. They were used to produce CNF prepared according to the procedure in following section to study the effects of paper properties after adding to the paper. During the thickening process prior to PFI refining, fines and ash content may be lost. These losses can impact the average fiber length and fines percent observations.

CATO® 237 Modified (cationic) starch (Ingredion Incorporated, Westchester IL, USA) was used as an additive to the sheet for enhancing physical properties. It was prepared by mixing starch power with deionized water to achieve 1% solids. Then, the solution was heated until 93 to 96 °C and kept at constant temperature with continuous stirring for 30 min. It was cooled to room temperature before mixing with the pulps. The charge of the solution after cooking was measured at 0.1% solids, and it was positive, 252.8 ± 35.6 µeq/L or was 252.8 ± 35.6 µeq/OD g starch. This corresponds to a degree of substitution (DS) of 0.041 (charges per repeat unit) for the starch. Deionized (DI) water was used to mix with the pulps throughout the experiment to ensure that there is no effect from contaminants in tap water impacting the sheet properties as well as charge demand measurement.

Preparation of Recycled Paperboards

The overall process for this experiment is depicted in Fig. 1, which consists of preparation of handsheets, cooking of cationic starch, and CNF production.

Pulp dryness

Approximately 1 g of each pulp was sampled to determine the dryness by a Sartorius IR Moisture Analyzer (Gottingen, Germany). The result is used to calculate the amount of DI water addition in order to get the desired consistency for conducting other experimental steps.

Disintegration

Pulp was prepared with about 24 oven-dried (OD) grams diluted to 1.2% consistency with DI water in the standard disintegrator for 5 min in accordance with TAPPI 205 sp-02 (2002). The pulps were disintegrated another 5 min if there was an addition of starch or CNF added to the pulp stock. If samples were treated with 2 additives, the cationic starch was added first and the CNF was added second, both before the additional 5 min of disintegration.

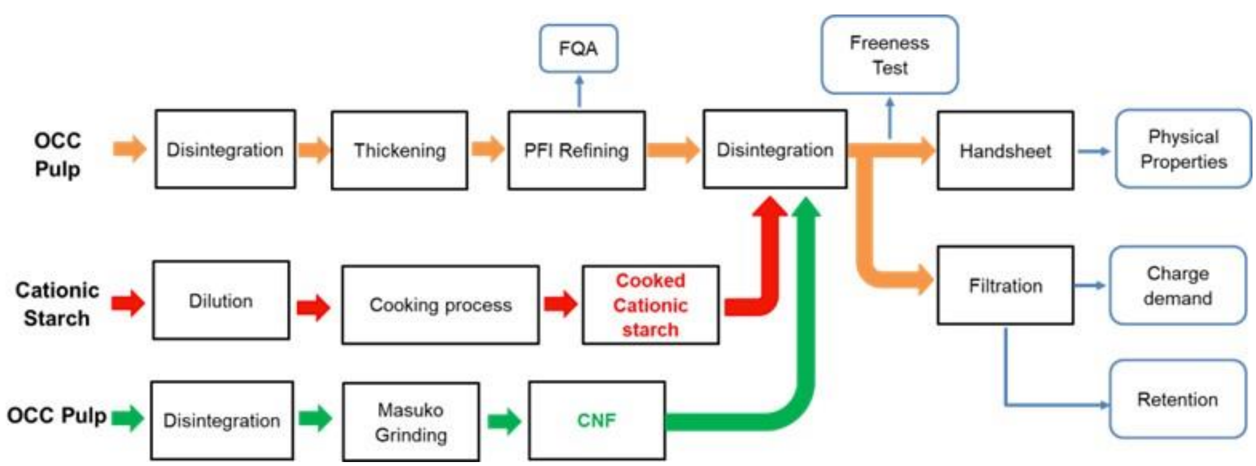


Fig. 1. Flowsheet of the preparation of recycled pulp, cooked cationic starch, and CNF for making handsheets to conduct physical properties testing

Fiber quality analysis

The OpTest Laboratory Fiber Quality Analyzer (FQA; Hawkesbury, Canada) was used to determine the physical characteristics of recycled pulps and unbleached softwood pulps, such as fiber length, fiber width, fine content, coarseness, fiber curl, fiber kink, and shive count. Approximately 1 g of pulp after disintegration or refining was mixed with 600 mL of DI water to determine fiber characteristics in accordance with TAPPI 271 om-98 (1998).

Thickening and filtration

The paper machine wire fabric in Fig. S1 was used to represent the wire fourdrinier section in the paper machine. The square opening size is approximately 0.3 mm x 0.3 mm. It was used to filtrate water from prepared pulps in order to increase the consistency to 10% and to collect the filtrate to conduct the charge demand measurement.

Charge demand measurement

Filtrated water (using the paper machine wire) after completion of treatment processes was sampled and used for a charge demand measurement. The amount of each sample of the filtrate was 10 mL, which was added to the sample container of a CAS touch charge analyzer (Emtec, Tegernsee, Germany) to obtain the charge demand. The cationic titrant was 0.001N Poly-DADMAC, and the anionic titrant was 0.001N PVS-K.

PFI refining

Pulps after thickening to 10% consistency were refined in the PFI mill for each condition (1,500 and 3,000 revolutions) in accordance with TAPPI 248 sp-00 (2000).

Handsheet making and freeness measurement

Unrefined, refined, and additives-added pulps were diluted with DI water to 0.3% consistency. Then, 1,000 mL of diluted pulp was used to determine the Canadian Standard Freeness (CSF) in accordance with TAPPI 227 om-99 (1999). Subsequently, 998 mL of diluted pulp was used to form 161 gsm handsheets in a handsheet mold. After forming handsheets, they were pressed with the standard press and then left to dry in contact on one side with polished steel plates within the drying rings under the condition of 50% RH, 23 °C, and atmospheric pressure (TAPPI 402 sp-98 1998).

Preparation of CNF

The method to produce CNF is based on the study by Starkey *et al*. (2021) with the total energy consumption at 5,600 kWh/OD ton of pulp. The OCC pulp was diluted with DI water to obtain a 1.2% consistency stock and processed using a Masuko Super Mass Colloider (Model No. MKCA6-5J, with 6” diameter stones, Masuko Sangyo Co. Ltd., Kawaguchi, Japan) with silicon carbonate grinding stones (E6-46 DD) to produce CNF. The number of passes was 22.

Characterization of the Paperboards

Physical properties

After handsheets were dried for at least 24 h under standard conditions, basic properties such as basis weight and caliper were evaluated at standard weight scale (TAPPI 410 om-98 1998) and LandW micrometer (TAPPI 411 om-97 1997) before cutting the handsheets for testing physical properties in accordance with TAPPI 205 sp-02 (2002). The density of handsheets was calculated by dividing the basis weight by the measured thickness.

Mechanical properties

The tensile strength (TAPPI 494 om-01 2001), and RC strength (TAPPI 818 cm-97 1997) were tested with five specimens per sample. The measured values were normalized with basis weight of each sample to obtain the index values.

Scanning electron microscope (SEM) imaging

Surfaces and cross sections of handsheets were observed by scanning electron microscope (Model JCM-6000PLUS, JEOL Ltd., Tokyo, Japan). Because the samples were non-conductive, a JEOL smart coater was used to coat the samples with a gold layer for 3.5 min. The magnification level of 200x was applied for surface images, and 100x was applied for cross section images. Both imaging processes used the voltage of 15 kV and high vacuum level.

Statistical analysis

The factorial design of experiment with stepwise regression analysis was applied to all experimental data for tensile index and ring crush index to determine main effects and interactions between each factor, which are refining levels, cationic starch, and CNF, by using the Minitab software. The test method was performed under the confidence level of 95%.

RESULTS AND DISCUSSION

Freeness and Charge Demand

The refining effect is important for the physical structure and chemical behavior of fibers. It creates delamination and fibrillation on the cell wall structure of fibers. These increase the wet fiber flexibility (Paavilainen 1993), which enhances the strength properties of the paper product. The fiber properties of the OCC pulp before and after refining are shown in Table 1. As expected, there was a decrease in the fiber length with the industrial disk refining, indicating some cutting of the fibers. Interestingly the mill refining was not observed to increase the amount of fines. The lab refining did not result in a decrease in fiber length, presumably due to the more efficient PFI refining process relative to industrial disk refining. The lab and industrial refining processes resulted in similar fines contents.

Table 1. Fiber Properties of OCC Pulp With and Without Refining

Description	Before Refining	After Refining at Mill	PFI Refining at 1,500 rev	PFI Refining at 3,000 rev
Fiber length[1] (mm)	1.455	1.357	1.635	1.495
Mean width[2](µm)	21.6	22.2	23.2	23.3
Mean Curl Index[1]	0.09	0.08	0.06	0.05
Kinks (1/mm)	0.7	0.7	0.4	0.4
Fines Content[1] (%)	10.68	10.59	7.33	8.84
Fines Content[2] (%)	48.12	46.35	39.22	42.76
Ash content (%)	8.10	6.85	5.67	5.65
[1] Length Weighted, [2] Arithmetic				

As illustrated in Fig. 2, the refining changed both an ability to drain water during forming a mat in Canadian standard freeness (CSF) and the charge demand of the filtrate of the fiber suspension. When the energy is applied to the fibers by refining, the drainage ability decreases significantly (Hubbe *et al*. 2007). More refining creates internal fibrillation and external fibrillation onto the fiber surfaces. The primary cell wall is delaminated and releases small fibers of this layer into the fiber suspension. Once the suspension is enriched by small fibers, they can obstruct flow channel during forming a mat when conducting freeness measurement. Thus, this effect results in a reduction of freeness. As shown in Fig. 2, the freeness starts from 515 mL CSF and it declined to 400 mL CSF at the medium refining level and continued down to 300 mL CSF at the highest refining level.

Another result that is affected by refining level is the charge demand of the suspension. As mentioned earlier, refining effect creates fines (<200 microns) in fiber suspension. This directly affects the charge demand which has an increased trend when applying higher energy to the fibers (Bhardwaj *et al*. 2004) and creating higher specific surface area.

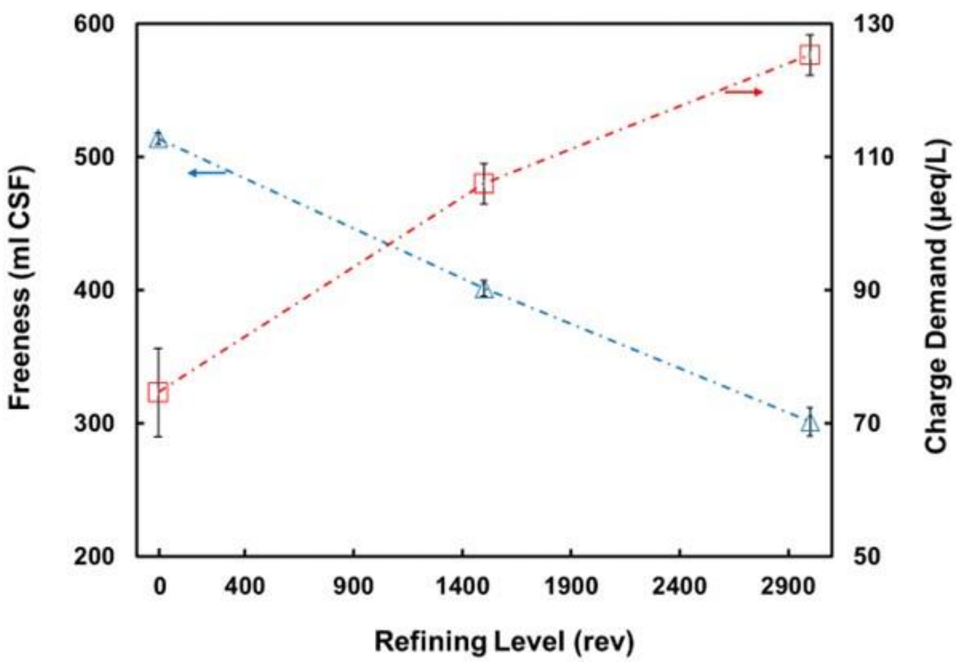
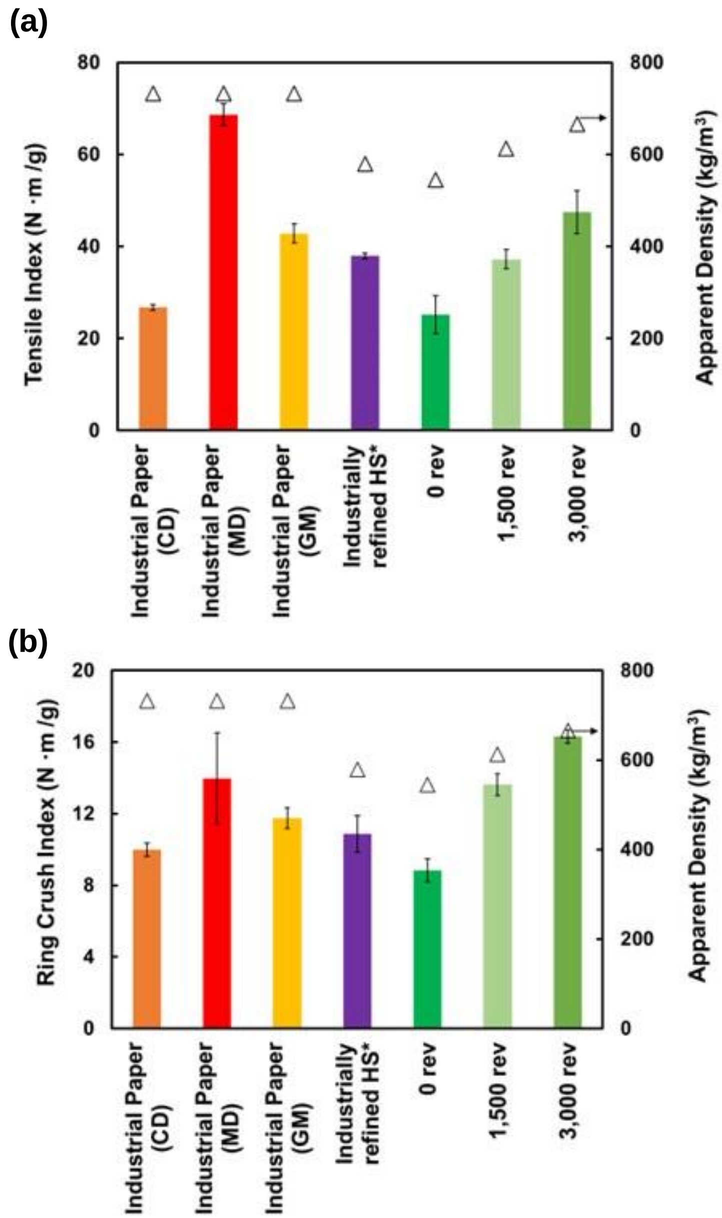


Fig. 2. The effects of PFI refining on OCC pulp on the freeness and charge demand

Comparison of Laboratory and Mill Scale Paper Products

It is of interest to evaluate whether the lab refining produced paper of similar characteristics as the industrial refining for the OCC. The tensile strength, ring crush, and density of the sheet made on an industrial linerboard machine are shown in Fig. 3 along with some lab prepared handsheets. For the industrial linerboard, tensile index, and ring crush index in MD were 2.5 and 1.4 times that in the CD, respectively. Due to the nature of fiber orientations and drying under constraint in the MD, the higher strength of paper in MD is normally higher than in CD.



Notes: CD = Cross machine direction, MD = Machine direction, GM = Geometric mean, and * = lab-made handsheets with industrially refined pulp. Samples labelled 0, 1,500 and 3,000 rev are unrefined OCC from mill that was PFI refined with those revolutions and then lab handsheets made.

Fig. 3. Comparison of (a) tensile index and (b) ring crush index between sheets made on industrial machine and lab-scale handsheets. Open triangles correspond to the apparent density.

In lab-scale work, handsheets were made using the same industrially refined pulp and TAPPI Standard handsheet making methods, and the results are also shown in Fig. 3. The lab handsheets are non-directional with random fiber orientation and are dried in drying rings with no directional differences in restraint. Thus, the strength generated in a lab handsheet is expected to be near the geometric mean of the MD and CD values of the machine-made paper (Wahlström 2013). The results of the lab produced paper using the industrially refined pulp were between the MD and CD values of the industrial paper and were approximately 11% and 8% different than the geometric mean of the MD and CD values in tensile index and ring crush index, respectively.

Also shown in Fig. 2 is the effect of PFI refining in the lab on the strength and density. Approximately 1,500 revolutions in the PFI mill approximately matches the industrially refined pulp that was made into handsheets in the lab tensile and ring crush. This indicates that the range of lab refining of zero, 1,500 and 3,000 revolutions encompassed values for the industrial refined and manufactured paper and was an appropriate range to investigate.

Figure 3 shows the density of the industrially made paper and the lab prepared papers. The density of the industrial paper was higher than the lab papers. The high nip impression load, web tension, and surface sizing in the industrial condition are expected to increase the compaction of the sheet. Also, some differences in refining between industry and lab (such as relative amounts of brushing versus cutting) also may impact the differences in apparent sheet density. In general, these results indicate that paper produced in the lab was reasonably similar to the industrially made paper.

These results are expected based on what is known about industrial paper manufacturing and lab handsheet making (Table 2). Recycled paper production in an industrial-scale and lab-scale have some significant differences. In industry, various processes are involved, such as fiber dispersion process in the pulper and removal of contaminants out of raw materials by hydro-cyclones and pressure screens (Grossmann *et al*. 2014). When making handsheets in the laboratory, normally pulps are already cleaned and maybe in fluffed form that is ready to prepare the handsheet. In terms of fiber modifications, such as adding process and functional additives, process conditions such as the hydrodynamic shear level can affect the efficiency of additives (Hubbe 2014).

Furthermore, the water quality/condition in industrial setting can be very different than in a lab. Various recirculating and recycling times are used due to the efforts to minimize environmental issues and product cost (Han *et al*. 2021). Water condition directly affects the amounts of chemical dosing needed. In the presence of ionic species and contaminants in water, different results from adding chemicals to the process might be expected in industrial practice relative to the lab.

Paper made on industrial paper machine generally provide differences in strength properties between the machine direction (MD) and cross machine direction (CD) (Kröling *et al*. 2014). Paper tension in the MD of the paper machine affects the strength properties of the sheet. Due to applying forces to pull the sheet in the drying process, it enhances the strength properties in the direction that is under the tension (Jentzen 1964).

Table 2. Comparison between Paper Making Conditions at Lab-Scale and Industrial-Scale

Aspect	Industrial Scale	Lab-scale
Screening and Cleaning process	Needed to protect some equipment	With or without depending on interests
Nature of adding additives	Limited and cost needed to change	Free to select conditions
Water condition	Recycled water	Clean water
Production Direction	Machine direction (MD) and Cross direction (CD)	No direction
Paper tension	Between section to section	No tension
Screening and Cleaning process	Needed to protect some equipment	With or without depending on interests

Effects of CNF and Cationic Starch and their Interactions on Paper Properties

In order to enhance recycled pulps properties relative to virgin fibers, cationic starch, CNF and increased refining and their interactions were studied on industrially prepared OCC but with lab PFI refining and handsheet making. The effect of cationic starch and refining levels to the handsheets are plotted in Fig. 4, and the data appear in Table S1 in the appendix.

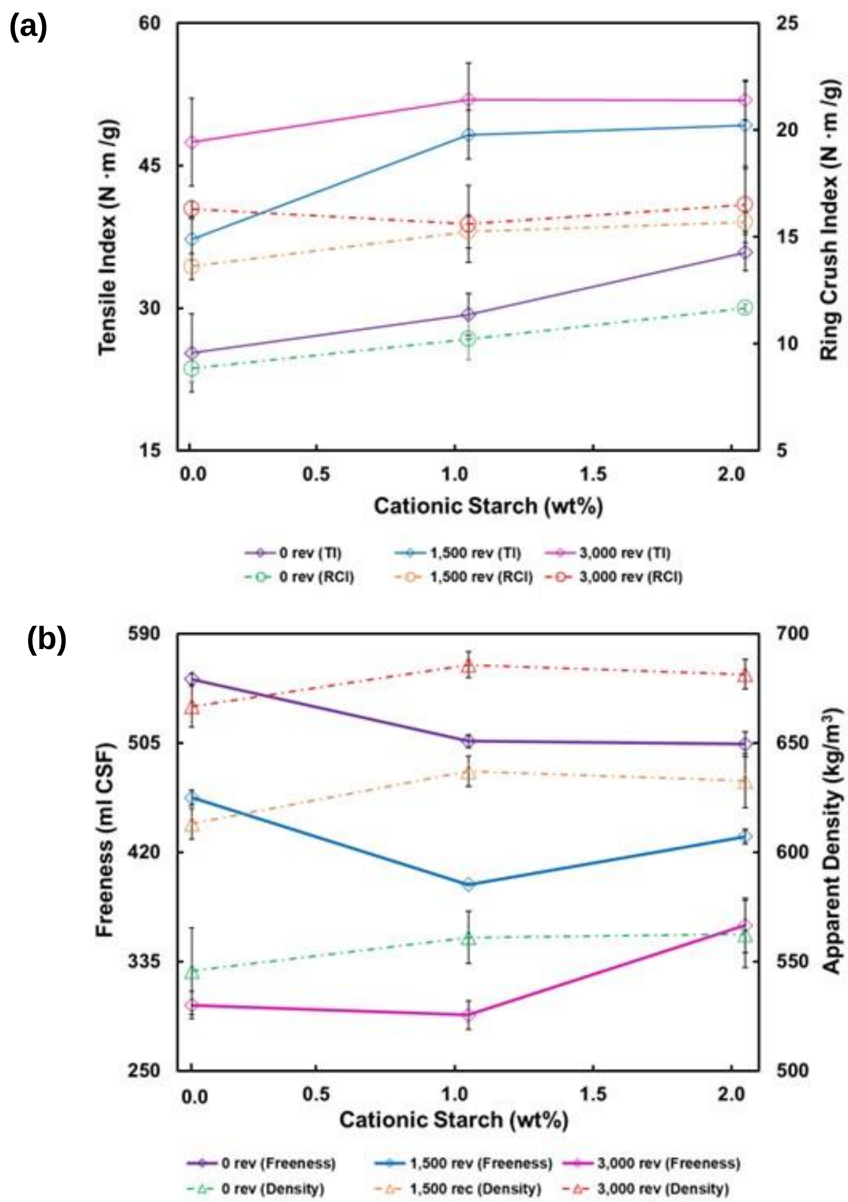


Fig. 4. The effect of cationic starch and refining level on the handsheet (a) tensile index and ring crush index and (b) freeness and apparent density

With an increase in refining level from 0 to 3,000 revolutions, both tensile index (TI) and ring crush index (RCI) were improved from 25.27 to 47.48 N·m/g and 8.84 to 16.32 N·m/g, respectively. This is due to the fact that refining effect delaminates fiber layers, making them more flexible and fibrillating fibers to be able to make more bonding with other adjacent fibers (Hubbe *et al*. 2007) both enhancing the fiber bonding between fibers. As illustrated by Fig. 5b, there were fibrillated fibers after refining at 3,000 rev. Unrefined fibers (Fig. 5a) were smoother and rarely exhibited fibrillation of their surfaces.

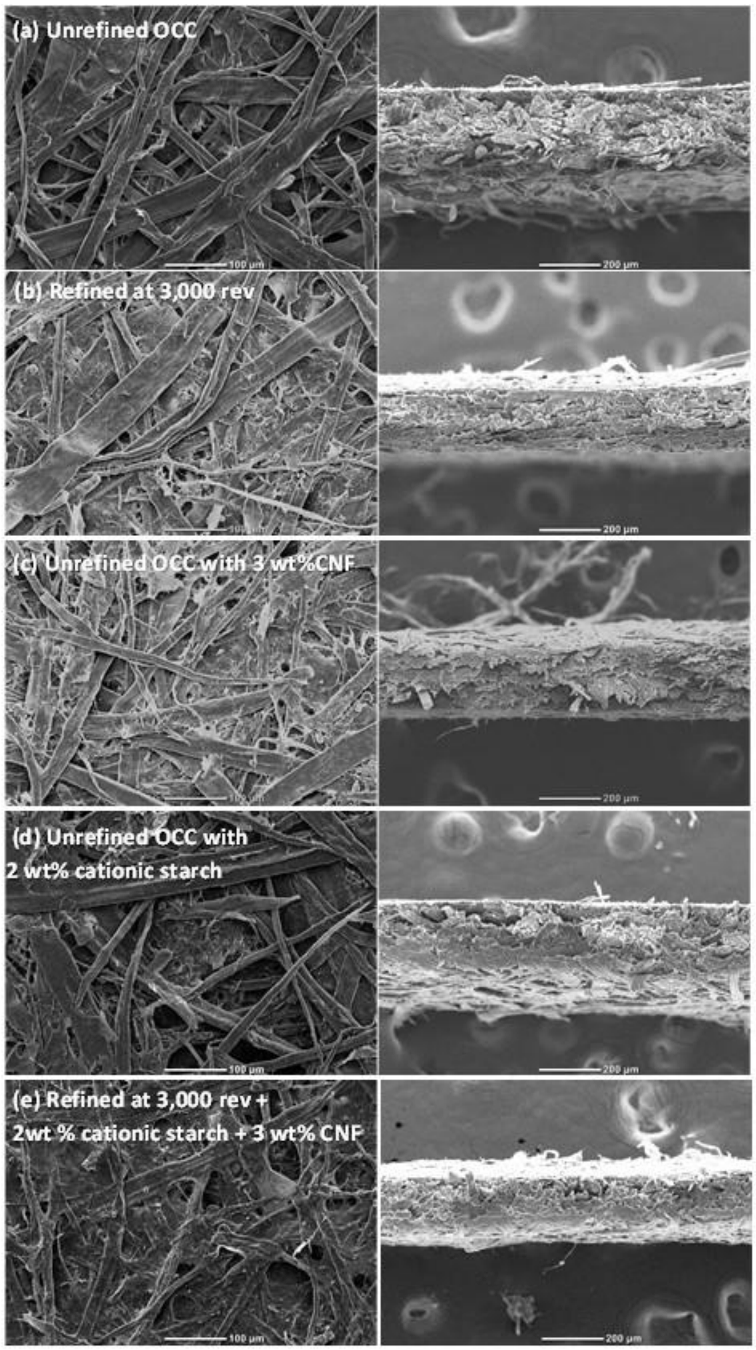
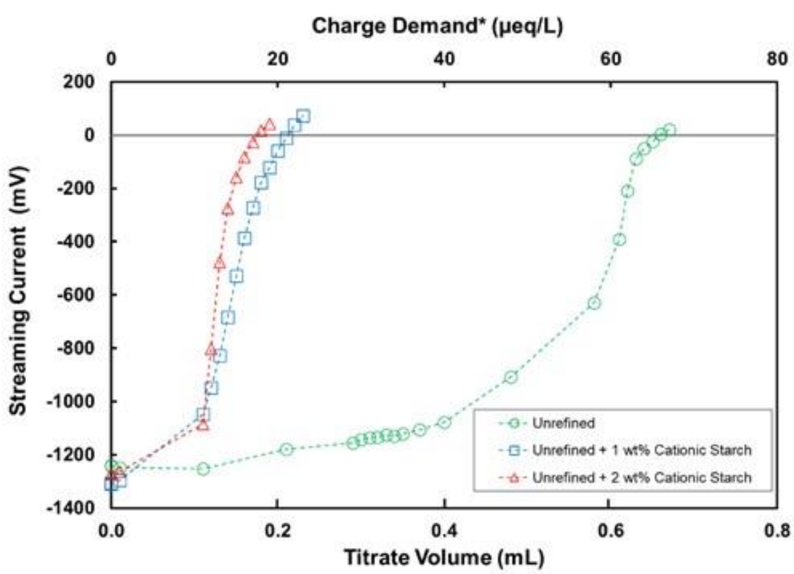


Fig. 5. Images of the surface (left) and cross section (right) handsheets by Scanning Electron Microscopy (SEM) of (a) unrefined OCC, (b) refined OCC at 3,000 rev, (c) unrefined OCC treated with 3wt.% CNF, (d) unrefined OCC treated with 2 wt.% cationic starch, and (e) refined OCC at 3,000 rev treated with 2 wt.% cationic starch and 3wt.% CNF

This also caused an increase of the apparent density of handsheets from 546 to 667 kg/m^3, which reflects increased bonding in the fiber matrix (Fig 4b.). However, refining also produces fines mainly generated from the primary layer of fiber structure, which reduces the dewatering rate from 555 to 301 mL CSF, shown in Fig. 4b. Fines may block drainage channels during forming mat and cause drops of flow, known as a "choke-point mechanism" (Hubbe and Heitmann 2007). After adding cationic starch to pulps at each refining level, both tensile and ring crush properties were significantly improved (Fig. 4). At 2 wt.% of cationic starch and refining level of 3,000 rev, TI and RCI were raised 105% and 87%, respectively, compared to the blank condition of no refining or starch. At the same time, sheet density slightly increases when the dosage of cationic starch increases. Cationic starch can improve bonding between fibers.

Figure 5 shows images of unrefined and refined fibers alone and with CNF, with starch and with CNF+starch. As expected, refining produces flatter fibers with more fibrillation than the unrefined fibers. The CNF deposited onto the fiber surfaces and created surface structures (highly bonded with nano and micro fibrils) similar to the refined fibers and higher density sheets.

The cationic starch also plays a role in flocculation because it is positively charged. The charge demand of the system filtrate is shown in Fig. 6. The negative charge of the system decreased with increased cationic starch but always was less than zero for the additions of cationic starch used in this study. The charge demand of the system was 64, 21, and 17 μeq/L for 0, 1, and 2% cationic charge additions, respectively. The cationic starch interacts with negative fines particles in the solution by charge interaction (Bhardwaj *et al*. 2005). They form larger particle sizes and adhere to fiber surfaces, which increases bonding and contributes to paper strength (Bhardwaj *et al*. 2005). Cationic starch increased the drainage for the 3,000-rev refined material by about 10% but for the lower refining levels the drainage either decreased or stayed about the same (Fig. 4).

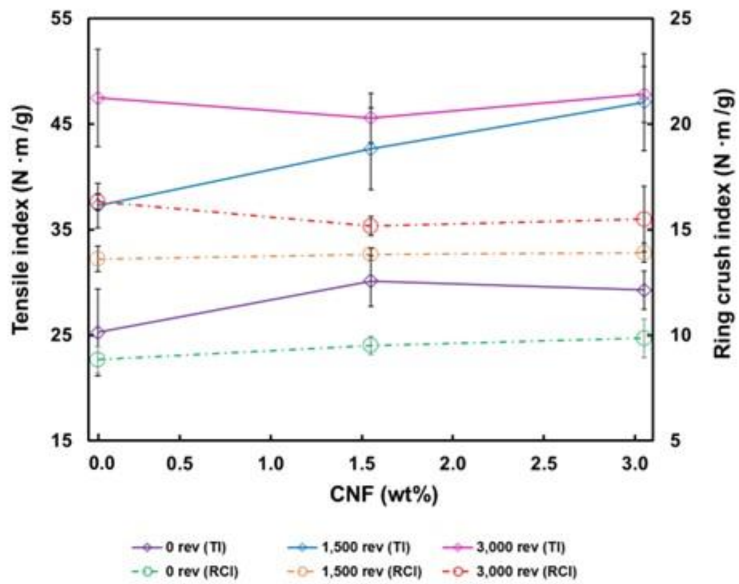


Remark: * = Reading charge demand at neutral point or streaming current = 0 mV

Fig. 6. Streaming current of the OCC fiber suspension filtrate after treatment with 0, 1 and 2 % cationic starch. The filtrate was obtained during a thickening process in which 0.3% OCC pulp was filtered with a paper machine wire (0.3x0.3 mm^2 openings).

Figure 7 depicts the effects of CNF and refining levels on mechanical properties of the handsheets as well as the density and freeness results. The data appear in Table S1 in the Appendix. When adding CNF before forming handsheets, the dewatering rate (freeness) decreased from 555 to 483 mL CSF for the non-refined pulp. This is mainly due to the CNF acting like fines and participating in the choke point mechanism. Slight increases of apparent density of the handsheets were observed due to the CNF contributing to more bonding area during mat forming, as well as reducing the porosity of the sheet (Ehman *et al*. 2020). Interestingly, addition of 3% CNF to the 3000 rev PFI refined pulp (heavily refined) only marginally decreased the freeness from to 301 to 297 mL CSF.

(a)



(b)

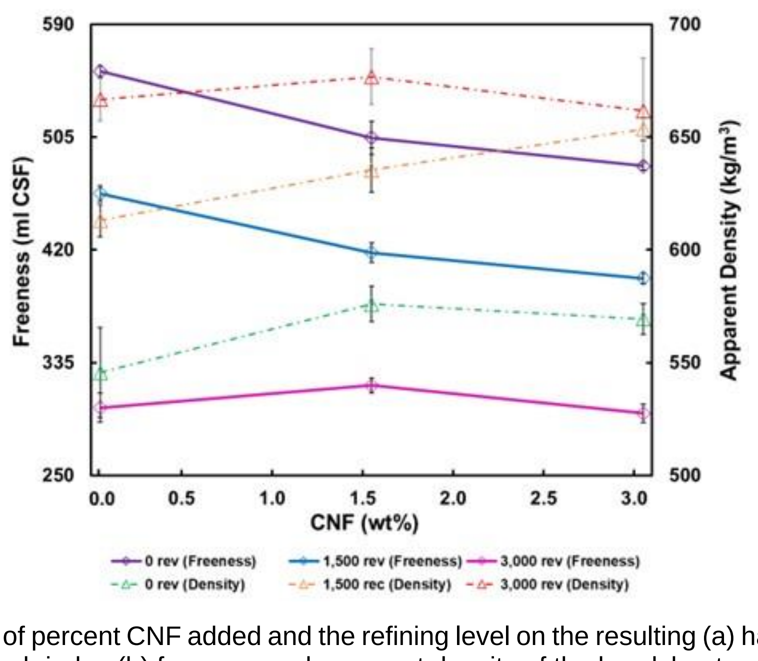


Fig. 7. The effect of percent CNF added and the refining level on the resulting (a) handsheet tensile index and ring crush index (b) freeness and apparent density of the handsheets

Moreover, higher tensile index and ring crush index were observed with higher dosing rate of the CNF in Fig. 7, as expected from higher density and more bonding. This is in agreement with research reporting that TI increases with CNF content (González *et* *al*. 2012; Kajanto and Kosonen 2012; Balea *et al*. 2016, 2019; Vallejos *et al.* 2016; Barbash and Yashchenko 2020; Ehman *et al*. 2016, 2020; Yousefhashemi *et al*. 2019; Hu *et al*. 2021; Zambrano *et al*. 2021).

All of the tensile index and ring crush index experimental results are plotted versus density in Fig. 8. As expected, an increase in apparent density was correlated to improved mechanical properties of the handsheets, in this case, including tensile and ring crush (Hu *et al.* 2021).

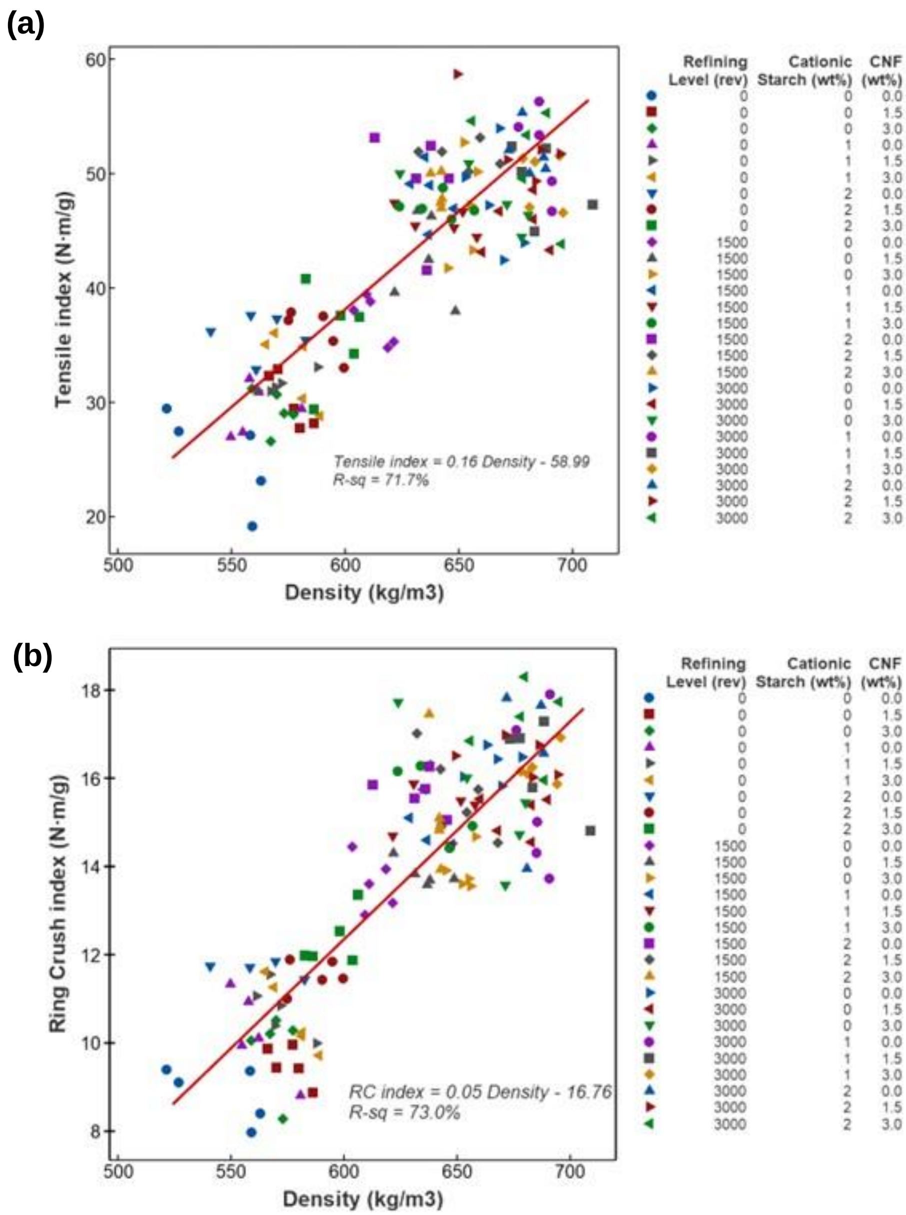


Fig. 8. Scatter plots of all experimental results showing the distribution of (a) tensile index (b) ring crush index with sheet density

In general, the sheets with different refining level, cationic starch, and CNF exhibited a somewhat positive linear relationship between paper strength and sheet density. Similar plots of TI and RCI with respect to freeness are shown in Fig. S2.

(a) (b) (c)

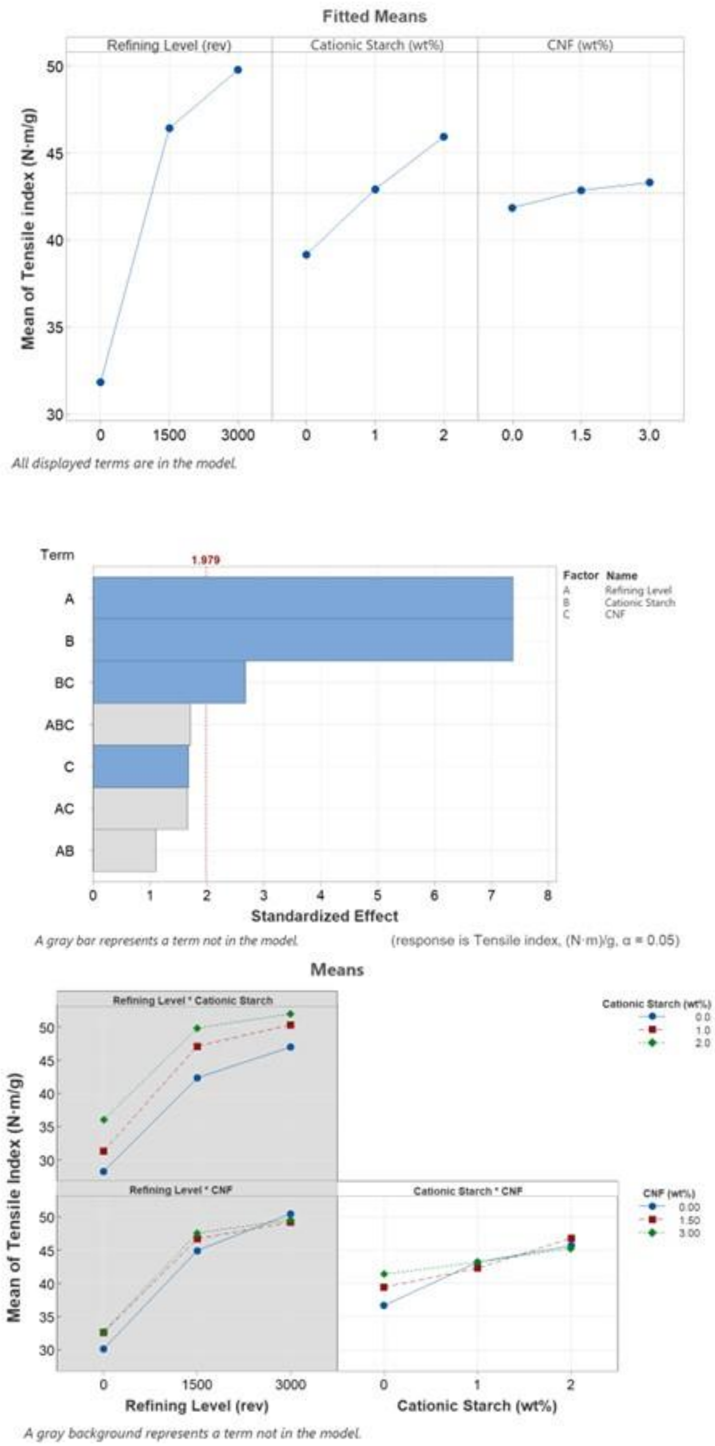


Fig. 9. Results of the factorial design of experiment with stepwise regression by the Minitab software which are (a) Main effect plots for tensile index, (b) Pareto chart of the standardized effects, and (c) Interaction plot for tensile index. Grey indicates no statistical significance at a 95% confidence level. Blue bars in Figure 10b are significant and the white plot in Figure 10c is significant.

There was a negative linear relationship between paper strength versus Canadian standard freeness. With an increase of freeness (or less refining), paper strengths were lower due to the lower conformability of the fibers and the looser structure of the matrix. This unrefined pulp is associated with lower density and drainage channels to allow the water to flow through the fiber mat due to less fibrillation generated.

It was of interest to determine whether there were any interactions between the refining levels, cationic starch, and CNF. To evaluate, the data were processed using a factorial design analysis with stepwise regression. Figure 9a shows the main effects and the interaction effects as well as a Pareto chart in Fig. 9b for tensile index. For the main effects plot, the refining level had the greatest effect on strength, followed by starch and then CNF with the smallest effect.

The Pareto chart in Fig. 9b shows significant factors and interactions when the standardized effect was greater than 1.979. The chart indicates that refining level, cationic starch, and interaction between cationic starch and CNF were significant with 95% confidence level. Even though the CNF only showed a very slight increase in TI when used without cationic starch, the interaction between cationic starch and CNF resulted in significant strength gains. This suggests that retention of the nanocellulose was low when added alone (see later for retention data) because it increased TI only slightly, but the CNF retention was enhanced by cationic starch and thus the retained CNF could contribute to TI increases as shown in Fig. 10.

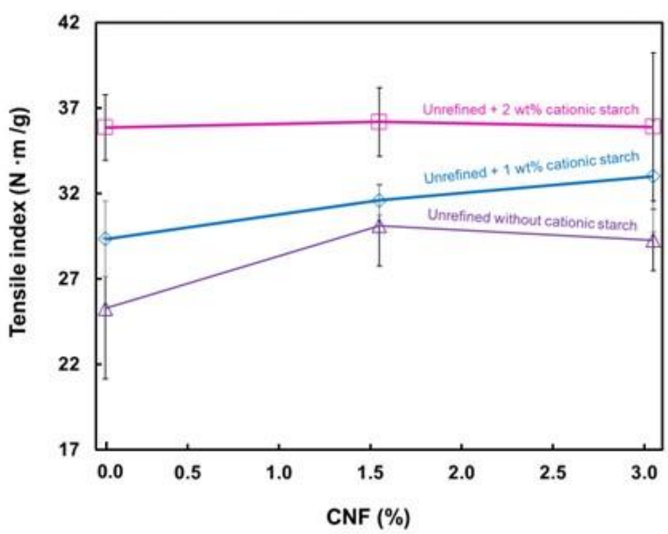


Fig. 10. Tensile Index (TI) versus weight % CNF at different levels of cationic starch weight % addition to OCC pulp

This explanation is consistent with the result of % solids consistency of the filtrate in separate experiments in which the pulp stock (0.3% consistency) was filtered on the paper machine wire and the filtrate carefully collected, as shown in Fig. 11. The consistency of the refined pulp filtrate with dosing of 3 wt% CNF was 0.119%, but this was reduced significantly to 0.044% when adding 2% cationic starch. This result supports the idea of cationic starch enhancing the retention of CNF. Note, from Fig. 6, the pulp system was negatively charged and as such, the cationic starch was expected to improve retention. From these measurements, and by subtracting the appropriate control samples, the percentage retention of the CNF can be calculated as 44.8% without cationic starch and 90.0% with cationic starch. No other studies that we are aware of have reported explicitly the CNF retention; studies report just the overall retention (including fines and CNF) and have not shown the interaction between CNF and cationic starch quantitatively as in this report (González *et al*. 2012; Kajanto and Kosonen 2012; Balea *et al*. 2016; Vallejos *et al*. 2016; Yousefhashemi *et al*. 2019; Zambrano *et al*. 2021).

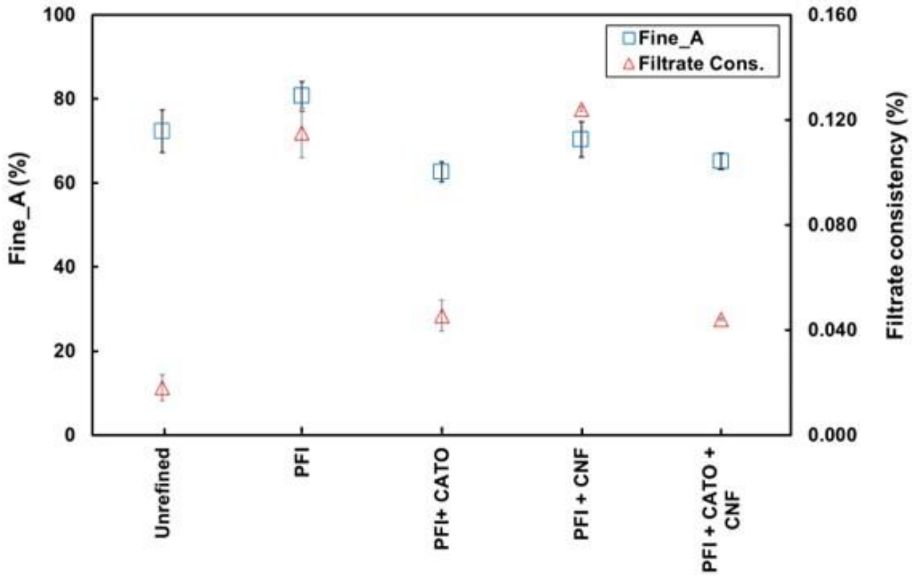


Fig. 11. Arithmetic percentage of fines in the filtrate (Fine_A, %) and filtrate consistency for unrefined pulp, refined pulp (PFI – 3,000 rev), refined pulp (PFI – 3,000 rev) treated with 2% cationic starch, refined pulp (PFI – 3,000 rev) treated with CNF, and refined pulp (PFI – 3,000 rev) treated with cationic starch and CNF. The pulp was 0.3% consistency when filtered with the paper wire.

Figure 9c is the interaction plot with boxes colored in grey, indicating that there was no interaction between the two factors (refining + cationic starch and refining + CNF) and the box in white indicating significant interaction (cationic starch + CNF). If the curves are parallel, it indicates that there is no interaction between factors. In contrast, if they are unparallel or crossing, this means there are interactions between factors. In Fig. 9c, for the cationic starch and CNF interaction plot, unparallel and crossing curves are observed, reflecting statistical significance for the interaction.

The ring crush data and design of experiment analysis is shown in Fig. S3. The main effects plot is similar to the TI result, with refining having the greatest effect, starch the middle, and CNF the lowest effect on ring crush index (RCI). The standardized effects graph shows with the cut-off value at 1.979 that RC is significantly affected by the refining and the cationic starch and the interaction between them, shown in Fig. S3b in the appendix. Similar to the TI results, the refining level and cationic starch played a major role in an improvement of RCI. In addition, the interaction between refining and cationic starch was found to be significant at the 95% confidential interval but not the interaction between cationic starch and CNF. Nevertheless, the CNF also provided small increases in RCI.

Regarding the analysis of factorial design of experiment, cationic starch impacts both TI and RCI considerably. Due to the nature of negatively charged cellulosic fibers, positively charged starch interacts with electrostatic forces and adsorbs onto fibers and enhances bonding strength between them. As a result, higher fracture forces are required to break, which represents an improvement of TI.

However, CNF were not shown to impart a statistically significant increase in the measured RCI. This may be because CNF improves the relative bonding area between fibers (reflected in higher sheet density), which provides greater TI (Page 1969). However, the sheets made with CNF with higher density at the same basis weight have a lower thickness, which decreases the bending moment of inertia, and thus results in non-statistically significant changes in RCI. Developing methods to maintain sheet thickness while improving bonding with CNF should be further investigated.

CONCLUSIONS

1. With a confidence level of 95%, the findings indicate that refining, cationic starch, cellulose nanofibers (CNF), and the interaction between cationic starch and CNF all played an important role with respect to the tensile index (TI) for old corrugated container (OCC) pulp. A higher level of mechanical treatment and chemical treatment both contribute favorably to increases in the TI and the apparent density of the sheets.
2. The positive interaction between starch and CNF on TI is attributed to higher retention of CNF in the sheets due to the starch in addition to the individual contributions of the CNF and cationic starch on TI.
3. The ring-crush index (RCI), on the other hand, demonstrated a different result than TI. Refining, cationic starch, and the interaction between refining and cationic starch were the significant factors for RCI at a 95% confidence level. CNF addition was not observed to improve RCI, but this may have been an effect of the sheets having higher density and lower thickness, which did not statistically improve the RCI.
4. The addition of cationic starch was able to improve the dewatering rate of the OCC fiber suspension when the highest refining level was applied; however, applying refining alone or adding CNF resulted in a significant decrease in the rate of dewatering of the fiber suspension.
5. The study indicates that the use of OCC derived CNF can be used as a strength additive for linerboard with careful attention to its retention. Developing methods to maintain sheet thickness while improving bonding with CNF should be further investigated.

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APPENDIX

EXPERIMENTAL

Materials

Thickening and filtration

For thickening and filtration of pulp and the retention experiments, an industrial paper machine wire was used as the filtering media. It is constructed out of plastic yarn that has a diameter of 0.3 mm and generates openings that are approximately 0.3 mm x 0.3 mm in size. The number of opening holes is 1936 that can be found in 1 in^2. (This was *not* used as the wire mesh in the handsheet mold.)

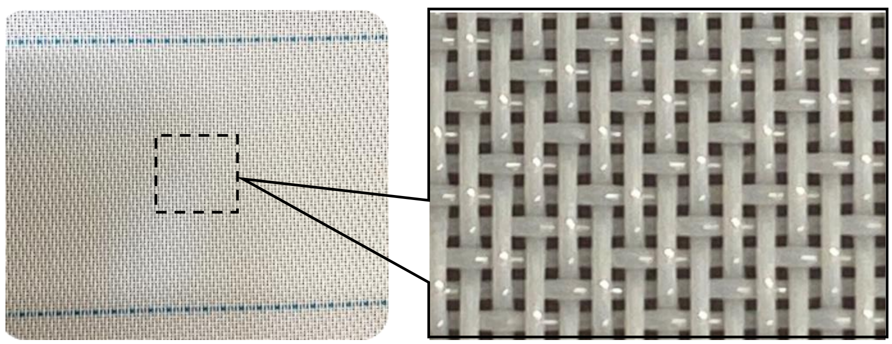

Fig. S1. Wire fabric used for thickening pulps having openings of approximately 0.3 mm x 0.3 mm

RESULTS AND DISCUSSION

Handsheet and Pulp Properties of Handsheet Samples

Table S1 displays all the trial results of the handsheets, including the base weight, apparent density, Canadian standard freeness, tensile index, and ring crush index in accordance with the different refining levels, cationic starch, and CNF. In order to maintain control over the influence that basis weight has on mechanical qualities, the procedure for handsheet preparation was adhered to strictly throughout the whole process of handsheet production. As a consequence of this, it was discovered that the typical basic weight of all handsheets was about 163.54 + 5.31 g/m^2, which is extremely near the target of 161 g/m^2. The apparent sheet density is displayed in Table S1, which is a calculation that is made using the measured basis weight and measured caliper of each sample condition. Increasing the refining levels, using cationic starch, and adding CNF led to an increase in sheet density. Increased refining levels and addition of CNF both contributed to an increase in the fines in the fiber suspension. In addition to this, the cationic starch was responsible for the collection of the fine materials that became adhered to the fiber surfaces, which led to an increase in sheet density.

Table S1. All Experimental Results of Handsheets

Condition	Basis weight (g/m^2)	Tensile Index (N·m/g)	Ring Crush Index (N·m/g)	Apparent Density (kg/m^3)	Caliper (μm)	Freeness (ml CSF)
0-0-0	154.33 ± 5.62	25.27 ± 4.12	8.84 ± 0.63	545.63 ± 19.86	283 ± 7.1	555 ± 4.2
0-0-1.5	164.18 ± 2.25	30.12 ± 2.38	9.51 ± 0.43	575.98 ± 7.88	285 ± 3.4	504 ± 12.4
0-0-3	164.64 ± 1.99	29.28 ± 1.82	9.86 ± 0.90	569.36 ± 6.87	289 ± 4.5	483 ± 3.4
0-1-0	162.59 ± 3.47	29.34 ± 2.21	10.22 ± 0.98	561.04 ± 11.97	290 ± 4.6	506 ± 5.2
0-1-1.5	167.67 ± 2.90	31.60 ± 0.86	10.76 ± 0.61	571.62 ± 9.89	293 ± 6.2	586 ± 17.8
0-1-3	157.23 ± 2.70	33.01 ± 3.24	10.59 ± 0.81	577.02 ± 9.91	272 ± 3.1	460 ± 6.0
0-2-0	163.41 ± 4.47	35.87 ± 1.91	11.67 ± 0.18	562.47 ± 15.37	291 ± 2.5	504 ± 9.6
0-2-1.5	163.46 ± 3.09	36.19 ± 2.01	11.52 ± 0.36	587.13 ± 11.09	278 ± 3.8	468 ± 6.7
0-2-3	167.63 ± 2.95	35.89 ± 4.32	12.34 ± 0.63	595.37 ± 10.49	282 ± 2.9	442 ± 3.9
1,500-0-0	162.30 ± 1.90	37.27 ± 2.12	13.61 ± 0.61	613.00 ± 7.19	265 ± 5.4	462 ± 6.0
1,500-0-1.5	159.82 ± 2.46	42.65 ± 3.90	13.83 ± 0.29	635.40 ± 9.78	252 ± 2.8	418 ± 7.6
1,500-0-3	164.93 ± 1.27	47.06 ± 4.59	13.90 ± 0.46	653.57 ± 5.03	252 ± 3.1	399 ± 4.1
1,500-1-0	160.91 ± 1.73	48.26 ± 2.57	15.26 ± 0.77	637.03 ± 6.86	253 ± 2.4	395 ± 0.9
1,500-1-1.5	178.48 ± 4.23	45.84 ± 1.18	15.19 ± 0.59	642.12 ± 15.24	278 ± 4.4	403 ± 12.8
1,500-1-3	161.69 ± 3.17	47.13 ± 1.01	15.34 ± 0.83	640.83 ± 12.56	252 ± 1.7	371 ± 4.8
1,500-2-0	163.16 ± 3.16	49.27 ± 4.59	15.70 ± 0.44	632.68 ± 12.25	258 ± 2.2	432 ± 5.7
1,500-2-1.5	161.98 ± 3.51	51.62 ± 1.15	15.75 ± 0.95	651.46 ± 14.14	248 ± 3.1	354 ± 1.0
1,500-2-3	159.12 ± 0.42	48.54 ± 1.52	15.25 ± 1.32	641.52 ± 2.15	248 ± 3.4	380 ± 8.1
3,000-0-0	167.74 ± 2.38	47.48 ± 4.63	16.32 ± 0.38	666.68 ± 9.47	252 ± 3.8	301 ± 10.8
3,000-0-1.5	162.82 ± 2.98	45.57 ± 2.33	15.17 ± 0.45	676.73 ± 12.37	241 ± 2.7	318 ± 5.6
3,000-0-3	160.39 ± 5.65	47.80 ± 2.64	15.50 ± 1.54	661.67 ± 23.31	242 ± 3.7	297 ± 7.1
3,000-1-0	169.53 ± 1.49	51.98 ± 3.86	15.61 ± 1.81	685.79 ± 6.03	247 ± 0.9	293 ± 11.1
3,000-1-1.5	163.34 ± 3.31	49.43 ± 3.23	16.34 ± 1.02	686.31 ± 13.89	238 ± 1.3	284 ± 14.1
3,000-1-3	163.39 ± 1.91	49.53 ± 2.48	16.27 ± 0.40	686.73 ± 8.03	238 ± 1.9	282 ± 4.0
3,000-2-0	168.71 ± 1.67	51.92 ± 2.11	16.51 ± 1.79	681.47 ± 6.76	248 ± 1.7	363 ± 21.2
3,000-2-1.5	159.47 ± 4.15	52.63 ± 3.56	16.48 ± 0.42	677.20 ± 17.63	235 ± 1.5	293 ± 5.9
3,000-2-3	162.74 ± 3.57	51.37 ± 4.74	17.26 ± 0.90	679.46 ± 14.90	240 ± 3.0	281 ± 6.6

Condition code: aa-bb-cc; aa = Refining Level (rev), bb = Cationic Starch (wt.%), cc = CNF (wt.%)

Tensile index and ring crush index are plotted against freeness (Fig. S2). It is observed that there was a negative linear relationship between the two strength attributes and freeness.

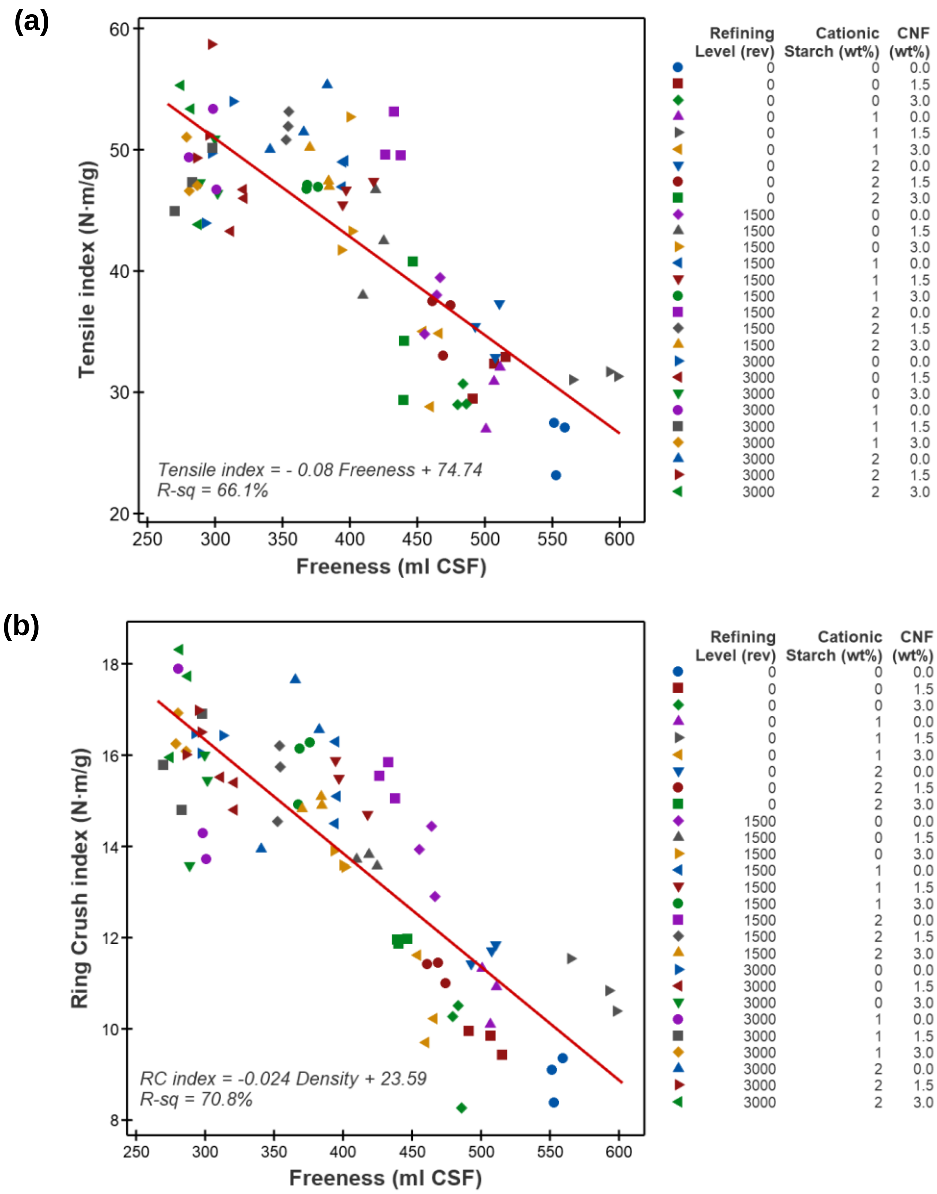

Fig. S2. Scatter plots of all experimental results showing the distribution of (a) tensile index and (b) ring crush index with Canadian standard freeness

Results of the statistical analysis of the factorial design with stepwise regression that was performed for ring crush strength with the use of the Minitab software are displayed in Fig. S3.

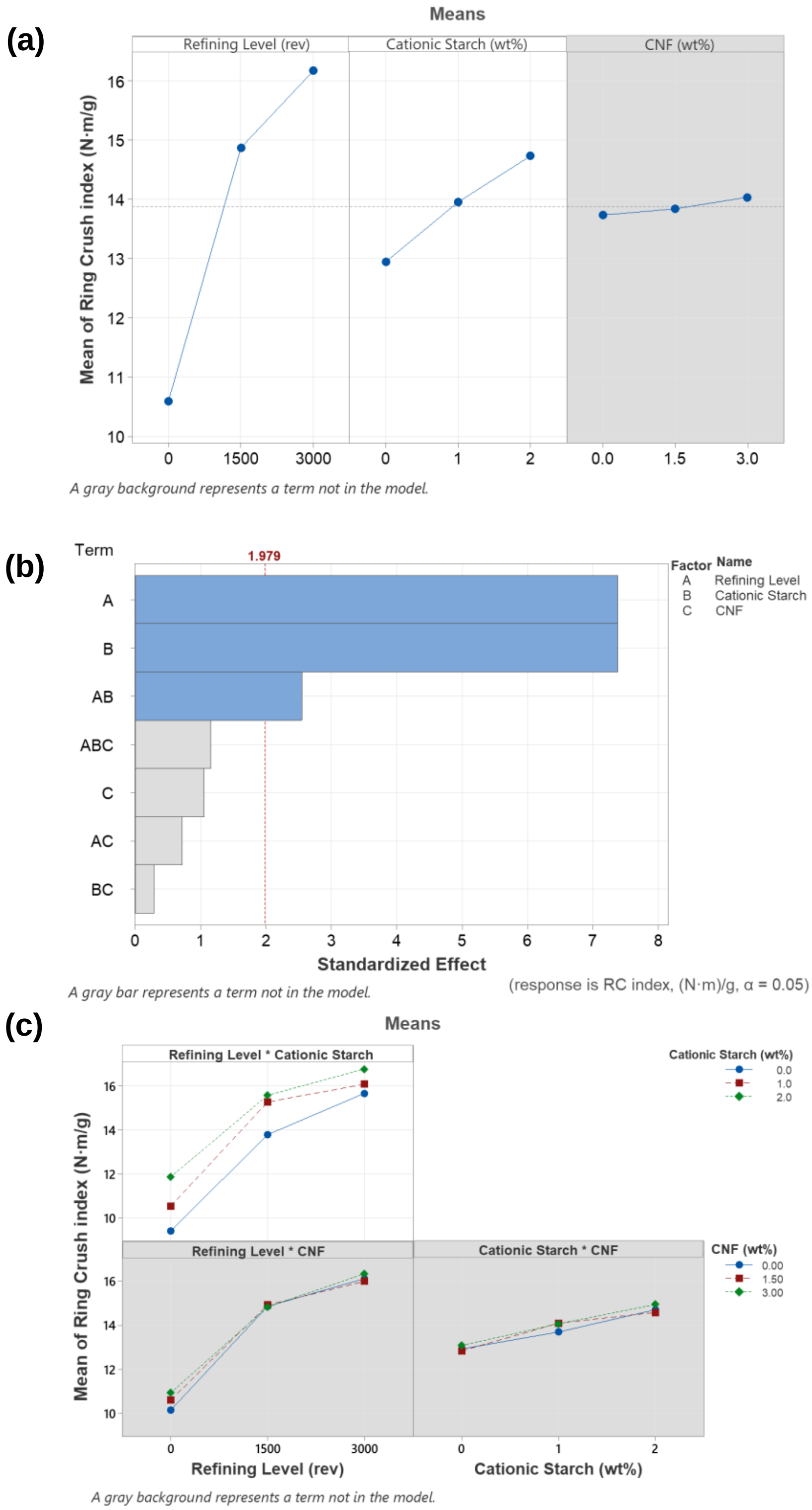

Fig. S3. Results of the factorial design of experiment with stepwise regression by the Minitab software which are (a) Main effect plots for ring crush index, (b) Pareto chart of the standardized, and (c) Interaction plot for ring crush index.