Potential Use of Nanofibrillated Cellulose-loaded Cationic Starch Solutions as Coating Formulation for Recycled Fluting Papers

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Effects of cellulose nanofibers (CNF) and cationic starch (CS) were evaluated as coating components relative to the physical and mechanical properties of fluting papersheets fabricated from recycled corrugated cardboard fibers. Fabricated fluting papers were subjected to size press applications by three different coating blends. Coating suspensions were prepared at various concentrations of CNF (0.5%, 1%, 2%, 3%, and 4%) and 4 wt% CS, and the same amounts of CS/CNF. The paper sheets were fabricated using size press machine as three-time repetitive applications, followed by one-time drying section, and compared to uncoated, CS-coated, and CNF-coated papers. The application of CNF suspensions increased tensile indices up to 11.7%. Moreover, CS/CNF suspensions resulted in a 67.2% increase in tensile index values. The coating of CS/CNF suspensions increased the burst index values by 163% at the CS+1%CNF concentration when compared to the control pulp. Surface application of prepared suspensions reduced the porosity of the samples under all conditions. The highest reduction in the air permeability was observed in the CS+4%CNF-coated samples as 91.5%. It can be concluded that the superficial applications of CNF on the physical and mechanical properties of recycled fluting paper was more effective in the presence of CS.

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INTRODUCTION

The increasing demand of paper products in recent years has led the paper industry to use recycled secondary fibers as an alternative source of virgin fibers (Pathak et al. 2015). Due to both economic and environmental concerns, the use of cellulose derived from recycled fibers has increased in the last decade. Furthermore, the use of recycled secondary fibers protects forest resources and reduces the amount of waste material discarded in sanitary landfills. In contrast, the use of secondary fibers to produce paper has some disadvantages. For instance, mechanical properties of papers produced with recycled fibers are lower when compared to paper with virgin fibers. Because of harsh chemical and mechanical processes occurring during the formation of paper sheets, the quality of fibers decreases. Moreover, as the number of recycling cycles increases, irreversible changes called hornification occur in the fiber structure and affect its properties (Hubbe et al. 2007). The hornification of cellulose fibers decreases the bonding potential of recycled fibers by restricting the fiber-fiber interactions, hence decreasing the mechanical strength of the resulting paper (Nazhad 2005; Wan et al. 2011; Balea et al. 2016). Consequently, to
maintain the quality of paper produced by using recycled fibers is one of the main challenges in the industry.

To decrease the diminishing effect of previous production cycles on new paper products, various approaches are proposed to enhance the quality of papers fabricated from recycled fibers. These approaches include employing refining techniques and incorporating wet-end chemicals (Wistara and Young 1999; Zhang et al. 2002; Manfredi et al. 2013). In the latter case, the use of natural polymer or green polymers is a preferable way to reduce the amount of harmful toxic substances used every day. Today, the valorization effect of cellulose nanofibers (CNF) has been investigated as a potential alternative as strengthen agents in the papermaking industry in order to enhance physical and mechanical properties of paper, because of its ability to form an entangled network amongst the fibers that increases the overall strength features (Taipale et al. 2010; Bharimalla et al. 2017; Campano et al. 2018). CNF has unique properties such as high specific surface area, high aspect ratio, and high mechanical strength. Its renewability and sustainability make CNF a better candidate for evaluation in papermaking (Xhanari et al. 2011). The CNF not only demonstrates an intense entangled network but also singular physical and mechanical strength. Therefore, it is an attractive material for various fields of application in papermaking, such as additive, strength enhancement agent, and coating substrate; also, it could improve mechanical properties including tensile, burst, tear, and internal bond strengths (Henriksson et al. 2008; Siró and Plackett 2010; Jonoobi et al. 2012; He et al. 2016). The effect of CNF addition to recycled pulps to improve final paper and board properties was investigated by several authors (Tarrés et al. 2020). For instance, the addition of CNF to old corrugated container (OCC) pulps showed increases in properties such as tensile index (TI), burst index (BI), short compression span (SCT), and significant decreases in porosity (Sanchez-Salvador et al. 2020). Despite numerous studies on the effect of CNF on paper properties, reference studies that increase the addition of CNF to the surface of paper are limited. Due to the strong contact between the surface hydroxyls and the solvent molecules, nanocellulose can be dispersed in some strongly polar solvents (particularly water). However, at the micro level, hydrogen bonding between nanofibers causes aggregation even in low concentrations as 0.5%. In coating applications, its tendency to aggregate and flocculate hinders its homogeneous dispersion and uniform spreading on to paper surface (Mazhari Mousavi et al. 2017). The main challenges in CNF coating applications are to overcome this drawback and obtain uniform coating layer over the paper surface.

The present study aimed to assess the influence of CNF (with and without CS) as coating substrate on physical and mechanical properties of fluting papersheets fabricated from various secondary fiber sources. Coating suspensions were prepared using various proportions (0.5%, 1%, 2%, 3%, and 4%) of CNF (with and without 4 wt% cationic starch) and applied via a size press. The physical and mechanical properties of the base paper (uncoated control), CNF-coated, CS-coated, and CS/CNF-coated papersheets were evaluated, and the results were compared.

**EXPERIMENTAL**

**Materials**

Recycled OCC (old corrugated cardboard) were kindly provided from KMK Paper Co. (Kütahya, Turkey). CNF (2% w/w) was supplied from Nanografi Nanotechnology Co.
According to the supplier, CNF was produced from cotton fibers and CNF suspensions obtained by super mass colloid refining, followed by a five-times homogenization process as gel form at 2% concentration.

Methods

**Handsheet preparation**

Recycled OCC fibers were used as primary raw material for base fluting paper production in this study. Handsheets were prepared with a basis weight of 130 g/m² using a Rapid Köthen handsheet former (PTI, Vorchdord, Austria) according to TS EN ISO 5269-2 (2006), then conditioned according to TAPPI T402 sp-13 (2013).

**Surface sizing**

Coating application was conducted by employing a self-designed size-press machine using three-times repetitive application of coating suspensions and one drying section. Prior to that, 9% wt. gelatinized corn starch suspension (13 cP) was prepared as coating mixture. Subsequently, different concentrations of CNF (0.5, 1, 2, 3 and 4% wt. to o.d. pulp) were added to the CS mixture suspension completed as total volume of 100 mL (total starch ratio 4%). Later on, fabricated fluting papersheets were pressed between rolls at 5 bar at a speed of 5 cm·s⁻¹ three times for each substrate equally until no suspension was left in the tank and dried with a contact drying system under 6 bar at 93 °C for 10 min. Mechanical (tensile index, TAPPI T494 om-01 (2006); burst index, TAPPI T403 om-15 (2015); internal bond, TAPPI T569 pm-00 (2000); short-span compression test (SCT), TAPPI T826 om-08 (2013); concora medium test (CMT), ISO 7263-1 (2018); ring crush test (RCT), TAPPI T822 om-16 (2016); and concora crush test (CCT), TAPPI T824 cm-14 (2014)) and physical (porosity, ISO 5636-3 (2013)) properties of the handsheets were determined employing respective standard methods.

All the data were statistically analyzed via analysis of variance (ANOVA) and Duncan’s mean separation tests.

RESULTS AND DISCUSSION

**Mechanical Properties**

In general, size-press applications of CNF suspensions did not have a significant impact on the mechanical properties of paper. However, the application of CS/CNF suspensions positively influenced the paper properties. The tensile index values of the fabricated control recycled fluting paper samples, with a weight of 130 g/m², were determined as 18 Nm/g. Subsequently, the fabricated paper samples underwent surface applications in three different forms: CS application, CNF application, and CS/CNF application. The application of 4 wt% of CS to the base paper resulted in a remarkable 83.3% increase in tensile index values, reaching 33 Nm/g (Fig. 1). In contrast, the application of CNF suspensions at different concentrations (0.5% to 4%) resulted in increased values in the range of 18.1 to 20.3 Nm/g. However, when the designed amounts of CNF were mixed with CS to create another coating suspension and applied to the paper surface, tensile index values increased in the range of 29.1 to 30.1 Nm/g.
Fig. 1. Effect of size press application of CS, CNF, and CS/CNF suspensions on the tensile indices of recycled fluting papers (Duncan test at p < 0.05)

It could be concluded that the presence of cationic starch in the CNF suspensions had a greater impact on the tensile index of 130 g/m² papers compared to only CNF-treated samples. The relatively lower results of CS+CNF suspensions in the current study may be attributed to the physico-chemical and rheological properties of the used CNF and the viscosity characteristics of the obtained coating suspension. The rheological properties of the evaluated commercial CNF were compared with wheat straw CNF (Ref-CNF) obtained in a previous study (Tozluoğlu et al. 2021). Commercially available CNF showed nearly similar viscosity values as periodate-treated wheat straw CNF. However, the incremental effect of commercial CNF added cationic starch suspensions on tensile indices was not determined to be the same (Fig. 2).

Fig. 2. Viscosity as a function of the shear rate of CNF samples
According to the previous study, the higher viscosity of the coating suspensions limits the better distribution of the slurries on the surface during size press application, thus restricting the formation of a homogeneous layer. The impact of CNF coating on the mechanical properties of paper sheets is a subject of debate in the literature (Brodin et al. 2014), with several studies suggesting that the introduction of CNF may result in only minor increases in the tensile index or even slight decreases. Syverud and Stenius (2009) reported slight increases in the tensile indices of paper sheets made from unrefined softwood pulp, which were coated with varying amounts of CNF. The observed increases in tensile indices were 5 Nm/g at an 8 wt% coat weight. In another study, Liu et al. (2014) noted only a 2 Nm/g increase in the tensile index of paper sheets coated with TEMPO-oxidized CNF. Conversely, Hult et al. (2010) indicated a decrease in the tensile strength of coated paperboards when microfibrillated cellulose was blended with shellac. The low increases or even slight decreases can be attributed to wetting/drying cycles, which adversely affect inter-fiber bonding. Given that CNF suspension is predominantly composed of water (98%), and coating applications involve repeated cycles, water exposure may disrupt the hydrogen bonds within the core of the paper sheet (Lavoine et al. 2014a).

Conversely, CNF is commonly recognized for its positive impact on the tensile indices of paper sheets when added in bulk suspensions during the fabrication stage. As tensile indices are significantly influenced by the ratio of fiber-fiber bonding, the addition of CNF to bulk suspensions enhances the tensile indices of the produced papers. This enhancement is achieved by increasing bonding ratios due to the high specific surface areas and smaller particle size of CNF (Eriksen et al. 2008; Henriksson et al. 2008; Hassan et al. 2011). Moreover, CNF concentrations directly influence the paper strength, where higher concentrations of CNF increase bonding ratio between fibers, and thus paper strength (Djafari Petroud et al. 2014). In a study conducted by Sanchez-Salvador et al. (2020), notable increases of 6.6%, 19.2%, 24.2%, and 34.6% were observed in the tensile indices of paper sheets by the addition of 1.5%, 3%, 4.5%, and 6% of CNF obtained from bleached softwood kraft pulp to bulk suspensions of recycled OCC fibers, respectively. Furthermore, González et al. (2012) reported substantial increases of 25%, 67%, and 100% in the tensile indices of paper sheets fabricated from bleached eucalyptus pulps with the addition of 3%, 6%, and 9% of CNF, respectively. Nevertheless, the authors noted that the retention of CNF to the fibers could not be determined. Additionally, higher concentrations led to increased water retention and extended dewatering times, suggesting that superficial applications might be the optimal choice for enhancing tensile indices without effecting the fabrication parameters. Mazhari Mousavi et al. (2017) formulated a coating suspension comprising CNF and CMC (carboxymethyl cellulose) and applied it as double layers to 200 g/m² paper using bar-coating techniques. The authors observed a maximum increase of 10% and 20% in the tensile index when 4% CNF was loaded in the machine direction and cross direction, respectively. The authors attributed this modest improvement to the surface properties of the paperboard, suggesting that the presence of pores and holes on the surface may cause discontinuity and disorder in the CNF layers. In contrast, Kumar et al. (2018) reported a 10% increase in the tensile index of 170 g/m² paperboard at coat weights exceeding 10 g/m². Meanwhile, Mirmehdi et al. (2018) demonstrated a more substantial 41% increase in the tensile index of 75 g/m² paper through the application of 1.4% CNF via spray coating. Notably, these studies predominantly focused on virgin pulp-based paper. The gradual increases in the present study could be attributed to the evaluated
recycled fiber sources. As shown in Fig. 1, coating application of CS/CNF suspensions significantly increased the tensile indices of recycled fluting paper sheets (p < 0.001).

It is known that the bonding ratio and individual fiber strength can directly influence the burst strength of fabricated paper sheets. In addition, evaluated fiber source also affects the burst strength whether it is virgin fiber or secondary pulp (Hubbe et al. 2007; Hassan et al. 2011). Generally, recycled fibers show lower mechanical properties when compared to virgin pulp due to the filler content and the hornification of fibers, and it is expected that the application of surface sizing would increase burst strength by incorporating fibers via cationic starch (Sanchez-Salvador et al. 2020). Different amounts of CS, CNF, and CS/CNF suspensions applied on 130 g/m² recycled fluting papersheets and results are demonstrated and compared in Fig. 3. As can be seen from the results, the CS applications increased burst indices up to 145% when compared to the control samples. Interestingly, similar results were not observed on CNF-treated samples. It is reported that the CS incorporation on the CNF suspensions elevate the mechanical properties in a positive manner. Tozluoğlu et al. (2021) reported up to 173% increase in burst indices after size press application of CS/CNF suspensions to fabricated 90 g/m² recycled fluting paper sheets. Similar increases were observed in the present study (up to 163%), after the superficial application of CS+1% CNF to recycled paper sheets. As expected, size press applications of different amounts of CNF suspensions increased the burst strength and with the incorporation of CS to CNF suspensions, the alteration effect increased to even higher levels. This phenomenon could be explained by the particle size distribution of coating suspensions. Starch molecules are relatively smaller than CNF fiber, so CS incorporation on to coating suspensions could facilitate the penetration of suspension beneath the surface; thus, higher increases were observed in burst indices. Because inter-fiber bond strength significantly influenced the burst strength, it can be concluded that coating suspension penetrated under the paper surface and contributed to increase fiber interactions of paper web. Cuong et al. (2021) observed 5.8% and 8.8% increase in burst strength after the bulk addition of 2% and 5% CNF to 125 g/m³ paper, respectively. Similarly, Tajik et al. (2018) reported only 18% increase in the burst index of 60 g/m³ bagasse paper by the bulk addition of 2% CNF. However, better results were obtained through size press coating application. It is commonly asserted that surface applications of CNF can yield better burst strength compared to bulk additions (Adel et al. 2016; Fathi et al. 2019). This is primarily due to the precision in adjusting CNF concentrations in surface applications, minimizing retention issues in post-fabrication applications. Fidan et al. (2021) demonstrated significant improvements in burst strength following the size press application of CS/CNF suspension to 90 g/m² recycled fluting papers. The authors noted a remarkable 124% increase in burst strength with a 1.0 wt% CS/NFC suspension and up to 173% at 4% CNF concentrations. This suggests that the use of starch enhanced fiber bonding, and the gradual size press application contributed to an increased burst index in the paper samples.

In contrast, it was observed by Lavoine et al. (2014b) that the burst index of papersheets was decreased when it was coated with CMF-based coating suspensions. Despite the expectation that cellulose microfibrils should enhance the paper surface, this unexpected decrease in the burst index was attributed to the heterogeneity of the CMF layers. Similarly, Pego et al. (2020) observed lower burst index values on specimens coated with a slurry of 10 wt% CNF. In contrast, Kumar et al. (2016) employed roll-to-roll coating on 178 g/m² kraft paper with 2% CNF/CMC suspensions, reporting a burst strength increase of up to 50%. Likewise, in a study by Lavoine et al. (2014a), the burst index of CMF-coated paper samples was higher than that of uncoated samples. It can be concluded
that the incremental effect depends on the CNF sources, properties, and the application methodology. As shown in Fig. 3, coating application of CS/CNF suspensions significantly increased the burst indices of recycled fluting papersheets (p < 0.001).

![Fig. 3. Effect of size press application of CS, CNF, and CS/CNF suspensions on the burst indices of recycled fluting papers (Duncan test at p < 0.05)](image)

Internal bonding plays a significant role in papermaking, particularly in printing and coating processes. Moreover, it is influenced by both pulp properties and applied treatment methods. The internal bond is intricately linked to the quantity of bonds formed between fibers and the strength of these bonds. Because secondary fibers exhibit reduced mechanical strength and paper pulps may contain impurities, the resulting papers typically exhibit lower internal bond strength in comparison to papers made from virgin pulp (Espinosa et al. 2019; Tozluoğlu et al. 2021). As a result of the size press, there has been a tremendous increase in the internal bond strength of recycled papers. Moreover, as increasing CNF concentrations caused more hydrogen bonding between fibers, the internal bond values were further increased.

Internal bond strength is shown in Fig. 4. Internal bond values of control fluting papersheets were observed as 76.3 J/m² and size press application of CS increased internal bond strength up to 203.1 J/m² (166%). After the surface application of different proportions of CNF suspensions, a 21% increase (at 4 wt%) was observed on the internal bond strength. This relatively lower increase could be explained by the viscosity values of coating suspensions. The higher viscosity degree of the CNF suspensions restricts the form of uniform coating layer on the paper surface, therefore limiting the increase of internal bond strength values on lower loadings. In contrast, the addition of different proportions of CNF to the CS suspensions increased the viscosity of the mixture and led to a uniform coating layer on the paper surface. The use of starch along with the CNF helped the CNF to increase the internal bonding ratio more effectively. After the size press application of CS/CNF suspension, remarkable increases were observed (up to 332.4%), and the highest increase was obtained in CS+1% CNF suspensions.
Delgado-Aguilar et al. (2015) investigated the impact of incorporating CNF into a deinked recycled pulp (DIP) suspension derived from the disintegration and flotation of a blend comprising old newspapers (ONP) and old magazines (OMG). These findings revealed a linear increase in the internal bond values as 24.4% with the addition of 1.5 wt% CNF. Furthermore, Tozluoğlu et al. (2021) reported substantial improvement up to 90.1% in the internal bond strength of recycled fluting paper sheets after incorporating 4 wt% periodate-pretreated CNF into the papermaking slurry. In contrast, Tarrés et al. (2016) applied a coating of 0.45 wt% CNF and 2.5 wt% CS to paper sheets, resulting in a remarkable 119.0% increase in internal bond strength. Because recycled paper exhibited porous structure, size press led to penetration of coating suspension into the substrate. Thus, the internal bonding ratio increased drastically. Additionally, Fidan et al. (2021) noted a substantial 110.9% improvement in internal bond strength following the surface sizing of 90 g/m² fluting papers using CS/CNF suspensions. Similarly, Tozluoğlu and Fidan (2023) reported 119.9% increase in internal bond strength of 110 g/m² recycled fluting paper sheets after size press of CS+4% CNF. In comparison to the previous findings, this gradual increase can be explained by the use of untreated control samples rather than CS surface sized samples that were evaluated in the previous study. Lavoine et al. (2014b) reported that size press application leads coating slurries to penetrate beneath the surface by pressure and increases fiber-to-fiber interactions by filling the gaps among the fibers. When considering these situations, an increase in internal bond strength after size press application is inevitable. However, a slight decrease observed in internal bond strength by Beneventi et al. (2014) after spray coating of 6 g/m² CNF onto 35 g/m² kraft paper samples. It was stated that the low grammage and porous structure of evaluated samples might cause a decrease in internal bond strength. In contrast, a 27.8% increase in internal bond strength was reported by Ottesen et al. (2017) after the slot-die application of 0.85 wt% TEMPO-CNFS/5 wt% CMC coating suspension on 255 g/m² recycled paperboards. It was indicated by the authors that the relatively low increase in internal bond strength could be explained by the high grammage of the paper and low solid loadings diminish the incremental effect of coating application. As shown in Fig. 4, coating
application of CS/CNF suspensions significantly increased the internal bond strength of recycled fluting papersheets (p < 0.001).

Crush Tests

The study of the final properties of CNF-coated papers has been discussed in four main crush tests. To the best of the authors’ knowledge, few studies have discussed and compared these results to evaluate end-use properties of fabricated paper sheets. The crush test results (SCT, CCT, CMT, RCT) of recycled fluting paper sheets coated with CS, CNF, and CS/CNF suspensions using size press as a function of different CNF loadings are given in Figs. 5, 6, 7a, and 7b.

Fabricated 130 g/m² control fluting samples demonstrated 11.5 Nm/g SCT values. With the application of CS, the SCT values increased to 18.7 Nm/g (62.9%). When compared to CS suspensions, due to their higher viscosity, size press application of CNF suspensions demonstrated lower increases in SCT values than CS coated samples, up to 57.3% at 2 wt% solid loadings. Furthermore, the application of different proportions of CS/CNF to paper surfaces increased SCT values in the range of 20.8 to 22.3 Nm/g (up to 93.9%).

![Fig. 5. Effect of size press application of CS, CNF, and CS/CNF suspensions on the SCT values of recycled fluting papers (Duncan test at p < 0.05)](image)

The incremental effect of CS/CNF suspensions could be explained by the decreased mechanical strength of recycled fibers. Moreover, the contamination in the secondary fibers led to lower physical and mechanical properties in recycled papers by decreasing the fiber-fiber interactions, when compared to virgin pulp-based samples. Therefore, surface sizing of CS/CNF compensated for the strength losses by increasing hydrogen bonds in the structure. Sanchez-Salvador et al. (2020) reported 12.3%, 16.3%, 19.0%, and 23.4% increases in SCT values of recycled cardboard fibers by the bulk addition of 1.5%, 3%, 4.5%, and 6% CNF, respectively. In the same manner, Balea et al. (2016) reported a 40% increase in SCT values of OCC by the bulk addition of 4.5% CNF obtained from bleached eucalyptus kraft and bleached never-dried northern pine pulps. In contrast, Fidan et al. (2021) indicated that the coating application of CNF provides better SCT values than bulk addition of the same amount of CNF. The authors reported a 133.3% increase in SCT...
values of recycled fluting papersheet after size press application of 4% CNF. As shown in Fig. 5, the SCT of papersheets coated by CS/CNF suspensions was increased significantly (p < 0.001).

![Fig. 6. Effect of size press application of CS, CNF, and CS/CNF suspensions on the CMT values of recycled fluting papers (Duncan test at p < 0.05)](image)

Tensile, burst, and tear tests do not provide enough information about how the corrugated sheet will perform in cardboard production. The CMT test allows the investigation of corrugated sheets before manufacturing them into the final product. Because corrugated boards are often subjected to high compression and excessive loads, the CMT is the fundamental measure of the performance characteristics of corrugated boards (Biricik 2012; Ghasemian et al. 2012). The CMT values of recycled fluting papers were found as 74 N. Because recycled fibers lose their mechanical strength due to harsh chemical processes while recycling, size press application of CS more than doubled CMT values by itself (167.4 N). The superficial application of different proportions of CS/CNF suspensions on to paper surfaces increased the CMT values in the range of 235.8 to 247.8 N (p < 0.001). The highest increase was observed in CS+1% CNF samples as 247.8 N (Fig. 6). The CMT strength is directly correlated with the bonding ratio between the fibers. Because CNF suspension often contains 98% water, water penetrates the papersheet during the coating application and causes ruptures in the bonds. However, due to its specific surface area, CNF penetrates the paper and causes an increase in bonds both on the surface and inner surface. Therefore, size press of CS/CNF suspension increased the CMT values of papersheets despite the expected ruptures of bonds. Tozluoğlu et al. (2021) reported a 50.6% increase in CMT values of paper sheets fabricated from recycled fibers by the addition of 4% CNF to the pulp suspension. Additionally, Ehman et al. (2020) added CNFs obtained from pine kraft pulp fibers by TEMPO oxidation to the chemi-thermomechanical pulp at a rate of 3 wt%. They found that the CMT of the 125 g/m² samples was higher than the CMT of control sample by as much as 27.4%. Furthermore, there are studies in which higher CMT values (145 N) were obtained by using waste paper fibers (Masrol et al. 2016). In contrast to the bulk addition, it is reported that the application of 4% CNF as coating suspension demonstrated remarkable increase as 105.8% when compared to the control samples (Fidan et al. 2021).
The ring crush test (RCT) and Concora crush test (CCT) values are regarded as an effective method to evaluate the contribution of materials to the compressive strengths of corrugated boxes. It was observed that coating application of CS/CNF suspensions increased the RCT and CCT values altogether. Size press coating application of different proportions of CS, CNF, and CS/CNF slurries to the paper sheets increased RCT values from 8.30 Nm/g up to 17.1 Nm/g and CCT values from 8.5 Nm/g up to 26.7 Nm/g. The highest increase in RCT value was obtained after CS+0.5% CNF application as 106% (Fig. 7a). Tozluoğlu et al. (2021) reported a 21.5% increase in RCT values of paper sheet fabricated from recycled fibers by the addition of 4% of CNF to the pulp slurries. Furthermore, Ehman et al. (2020) measured the RCT index of the papers containing 3 wt% CNF and determined an increase of 28.2% compared to the RCT index of the control
samples. However, Fidan et al. (2021) concluded that superficial applications of CNF perform better on RCT, in contrast to bulk additions.

In contrast, the highest CCT value was observed as 212.9% after size press application of 4% CNF. According to Tozluoğlu et al. (2021), maximum 44.1% increase in CCT values were obtained from recycled paper after 4% CNF addition to the bulk suspensions. The highest CCT value was observed as 221.2% after size press application of 4% CNF samples (Fidan et al. 2021). In parallel with the previous studies, current work has shown that higher mechanical strength can be obtained via one-time size press coating application of CS/CNF, rather than repeated coating applications or using CNF as bulk additives. As shown in Figs. 7a and 7b, the RCT and CCT of paper sheets coated by CS/CNF suspensions was improved significantly (p < 0.001).

**Air Permeability**

Air permeability of paper coated with CS/CNF suspensions using the size press as a function of coat weight is given in Fig. 8. As expected, the air permeability significantly decreased as a result of surface sizing of various CS/CNF suspensions onto paper (p < 0.001). Air permeability is defined as the amount of air in cm$^3$ passing through a unit area in a minute in the current study. Air permeability gives comprehensive information about the formation of the paper. Due to the filler content of the recycled pulp and damages occurring the recycling process of the of secondary fibers, fabricated control samples demonstrated porous structure and resulted in 441.3 m$^3$/min air permeability values and with the size press application of CS, air permeability values decreased by 57.4% (188 m$^3$/min). However, superficial applications of different proportions of CNF had a relatively lower decreased effect on air permeability values than CS-treated samples. At maximum solid loading designed in the current study (4%), a maximum 50.8% decrease was observed in the CNF-coated samples.

![Fig. 8. Effect of size press application of CS, CNF, and CS/CNF suspensions on the air permeability of recycled fluting papers (Duncan test at p < 0.05)](image-url)
the air permeability up to 91.5% at higher solid loadings. The main focus of most research on CNFs in the papermaking industry has been using them as a bulk additive for virgin pulp and paper surface applications. For example, Sanchez-Salvador et al. (2020) observed that the bulk addition of CNF to recycled pulp fibers at 1.5%, 3%, 4.5%, and 6% (o.d.) reduced porosity values 55.9%, 64.4%, 75.8%, and 87.7%, respectively. Moreover, substantial decrease in air permeability, up to 75%, in recycled newsprint pulp fibers was reported by Balea et al. (2018) with the addition of CNF in the range of 1% to 5% to the bulk suspension of papermaking slurry. In addition, Balea et al. (2016) observed a decrease in air permeability by almost 90% when 4.5% of CNF was added to recycled OCC paper pulps. Similar results were reported by Fidan et al. (2021). According to that, after size press application of 4% CS/CNF suspension to 90 g/m² fluting papers, 69.8% decrease in air permeability was observed in coated samples. In addition, El-Samahy et al. (2017) reported that bar coating of CNF to 110 g/m² papersheet reduced the air permeability up to 7 times depending on the thickness of the coating. Furthermore, with bar coating process, 100 times reduction in air permeability of CNF-coated papers was observed by Liu et al. (2014). In contrast, 10 times successive coating of CMF suspensions to 300 g/m² cardboard by bar coating process did not affect the air permeability at any significance level (Lavoine et al. 2014b). In contrast, a couple of studies reported that the air permeability of paper was not affected or even increased after the application of CNF/CNC/CMF/CMC coatings (Lavoine et al. 2014a; Pego et al. 2020). In a study conducted by Lavoine et al. (2014a), multiple layers of CMF coating did not significantly change the air permeability, as the number of coating layers increased up to ten. The authors concluded that, due to the fact that the evaluated commercial cardboard was coated only on one surface and a low solid content of CMF suspensions was applied, no significant change detected in the air permeability by the coating application. Furthermore, Pego et al. (2020) reported that the air permeability of coated paper samples was found lower when compared to those subjected to additive method. The result was attributed to the permeable nature of the superficial film layer which forms during the coating method.

In addition to the concentration of coating suspensions, the amount of the applied layer is influenced the air permeability as well. It was stated by Afra et al. (2016) that 1.5 wt% double-CNFWF-layered paper samples demonstrated lower air permeability than 3 wt% single-CNFWF-layered paper samples. Furthermore, Hult et al. (2010) reported that the application of CMF on paper samples as single and multiple layers decreased the air permeability as more layers of coating were applied. Tyagi et al. (2019) reported a 300 times decrease in air permeability of a double-layer-coated paper samples that consisted of CNF and CNC as individual layers, compared to that of uncoated paper samples. Moreover, it was found that the double-layer coating is more effective in improving the oil and grease resistance and reducing the OTR (oxygen transmission rate). Charani et al. (2013) evaluated CMF in papermaking using coating and bulk addition methods and found that the coating method was more effective at decreasing the air permeability of paper samples when compared to the bulk addition method. Boissard (2017) suggests that, at low solid contents, size press coating method is more effective in the air permeability of substrates than bar coating. This phenomenon revealed that, although size press application does not form a complete layer on the paper surface, the CNF coating still results in a lower overall porosity of the substrate by filling the gaps between fibers. As shown in Fig. 8, the air permeability of papersheets coated by CS/CNF suspensions decreased significantly (p < 0.001).
The influence of size press application of CNF alone and in the presence of cationic starch on the fluting paper was investigated. It can be concluded that coating by CNF alone demonstrated insignificant results due to its high viscosity. However, the presence of CS in the suspension decreased the viscosity values and led it to spread homogeneously. Also, different coating methods could be employed to eliminate these drawbacks such as spray or dip coating. Moreover, one-time deposition of coating suspension also influenced the overall properties by breaking the wetting/drying cycle during coating processes. Thus, in possible future work, it could be better that the coating would be applied to the top of the wet web before the press section to avoid damaging the fiber structure.

CONCLUSIONS

1. Surface application of cationic starch / cellulose nanofiber (CS/CNF) suspensions improved the overall mechanical properties of recycled fluting papers except for tensile index. Furthermore, CNF was more effective in the presence of CS.

2. It was clearly shown that in the most cases superficial application of CNF to the paper surface gave relatively similar results with the bulk addition in the wet-end. On the other hand, bulk addition has some disadvantages such as increasing the Schopper-Riegler degrees value and dewatering time. To avoid these drawbacks, coating applications of CNF is much preferable to obtain similar incremental effects.

3. The viscous nature of CNF suspensions hinders the homogeneous spreading and distribution of suspensions onto paper surface. To eliminate this situation, decreasing the suspension concentrations and preparing mixed suspensions is required.

4. Further investigations should be conducted regarding the surface modifications to increase the layer uniformity and the amount of bonded CNF and CS/CNF suspensions to surface in achieving optimum mechanical and air permeability properties for recycled fluting papers.

REFERENCES CITED


in the presence of cellulose nanofibrils on structural, optical and strength properties of paper from soda bagasse pulp,” *Carbohydrate Polymers* 194, 1-8. DOI: 10.1016/j.carbpol.2018.04.026


TAPPI T569 pm-00 (2000). “Internal bond strength (Scott type),” TAPPI Press, Atlanta, GA, USA.

TAPPI T822 om-16 (2016). “Ring crush of paperboard (rigid support method),” TAPPI Press, Atlanta, GA, USA.

TAPPI T824 cm-14 (2014). “Fluted edge crush of corrugating medium (flexible beam method),” TAPPI Press, Atlanta, GA, USA.


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