

# Cellulose Nanofibers with Higher Solid Content as a Coating Material to Improve the Structure and Barrier Properties of Paperboard

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## Summary

In this study the potential of using cellulose nanofibers (CNF) as a coating to improve the structure and barrier properties of paperboard was investigated. Two kinds of CNF were studied including refiner CNF (rCNF) and grinder CNF (gCNF) with and without carboxymethyl cellulose (CMC). These materials were applied onto the surface of paperboard using a rod coater. Although CNF at 2% solid content could not be spread out onto the surface of paper uniformly, 3% CNF along with CMC was successfully coated on the surface of paper. The scanning electron microscope (SEM) images reveal that a full coverage of the paper surface was achieved. The results show that the structure and barrier properties of coated paperboards improved significantly by the application of CNF coatings.

## Introduction

Paper is widely used as a packaging material for its biodegradability and its eco-efficiency. Nevertheless, because of its nature and depending on the application, it usually needs to be coated with other materials to obtain good barrier properties. Currently, these materials are largely produced from fossil-derived synthetic plastics which are not necessarily environmentally friendly. With increasing environmental concerns and the need for sustainable development in the future, the use of renewable materials is expected to grow.

Recently, the development of cellulose nanofiber (CNF) has offered a new alternative to the polymer coating to form a barrier layer. Its ability to form a nanoporous network and once dried, to form a dense network held together by strong inter/intra fibrillar hydrogen bonds, suggest that these films could potentially have barrier properties and be an interesting alternative to, for instance, plastics. In addition, the enhancement of mechanical properties and their use as aqueous suspensions provides opportunities for CNF application as coating for cellulosic substrates. A recent review of this potential is given by Lavoine et al. (2012). Syverud and Stenius (2009) reported that applying a CNF layer lowered sheet porosity and resulted in a denser structure which decreased air permeability. Kumar et al. (2014) report quite good oxygen permeability results for CNF films. Lavoine et al. (2014) show some improvements in mechanical properties of board samples coated with CNF. Despite this promise, CNF suspensions have to be applied at a low solid content (lower than 1%) because of extremely high viscosities at higher solid contents. This means that in practice a large amount of water must be evaporated in the drying section of coating machine that gives rise to high drying costs. When the solid content of CNF is increased, the entanglement of fibers result in high flocculation and the coating cannot be spread out on the base paper evenly.

To address this problem, carboxymethyl cellulose (CMC) was studied here because of its ability to disperse fibers and reduce their flocculation (Liimatainen et al. 2009); CMC can improve the uniformity of fiber suspension (Nazari, 2015). In addition, two kinds of CNF, refiner and grinder produced CNF were used to see whether the type of CNF can affect the coating properties particularly when it is used in a blend with CMC.

Therefore, the goals of this study are: 1) to investigate the effect of CMC on the dispersion properties of CNF and 2: to study the effect of different CNF types with and without CMC on structure and barrier properties of paperboards.

## Material and Methods

Refiner CNF (rCNF) was prepared at the University of Maine Process Development Center from bleached softwood kraft pulp as described by others (Richmond et al. 2013). The ground CNF (gCNF) was produced by taking the refiner CNF and circulating in a bench scale ultra fine grinder (Masuko Sangyo, MKCA6-2, Japan) for 120 min. The consistency of produced CNF was 3% which was diluted to obtain different solid contents. Carboxymethyl cellulose (CMC) with molecular weight of 450000 g/mol and degree of substitution of 0.7 was purchased from CPKelco (Finnfix 4000 G). The solution of CMC was prepared by dispersing an appropriate amount of CMC powder in deionized water at a concentration of 1.5% by stirring for 3 hours at 600 rpm at room temperature. The CMC solution was added to the CNF suspensions after they were prepared.

Morphology of CNF material was examined using transmission electron microscope (TEM) (Philips CM10). The surface structure of uncoated and coated papers was observed by scanning electron microscopy (SEM) (HITACHI TM 3000).

A wood free bleached base paper with grammage of 200g/m<sup>2</sup> was selected for coating experiments. CNF suspensions with different solid content from 1 to 4 wt% to achieve different coating weights with and without CMC (4wt% based on dry weight of CNF) were prepared and applied on the surface of paper using a draw-down rod coater (BYC-Gardner, 2101, USA) in two layers. Coating speed was 50 mm/s and wire-wound rod #52 was used. The coated papers were dried in oven at 105 °C for 5 min. After determining the coat weight, the samples were conditioned at 50% RH and temperature of 23 °C for barrier and structure properties tests according to TAPPI Standard (T460 om-02, T530 om-96 and T 559 pm-96 for air resistance, aqueous resistance and grease resistance, respectively). Water vapor transmission rate (WVTR) was characterized according to ASTM E 96-95 using the water method.

## Results and Discussion

TEM images of rCNF and gCNF are shown in Fig. 1. They reveal that a finer size distribution of CNF was achieved after grinding compared to the refiner produced material. While the refiner produced CNF had a significant number of fibrils less than 100 nm, it also had large fiber fragments on the order of 1 – 10 μm that seem to connect the fine scale fibers. For the grinder produced material, the number of these large scale fiber fragments is reduced and there is a wide range of fiber sizes. A number of the fibers appear to have a morphology more similar to a ribbon: the fiber appears to be the flat remains of the cell wall. These images are quite similar to what others have reported for mechanically produced material.

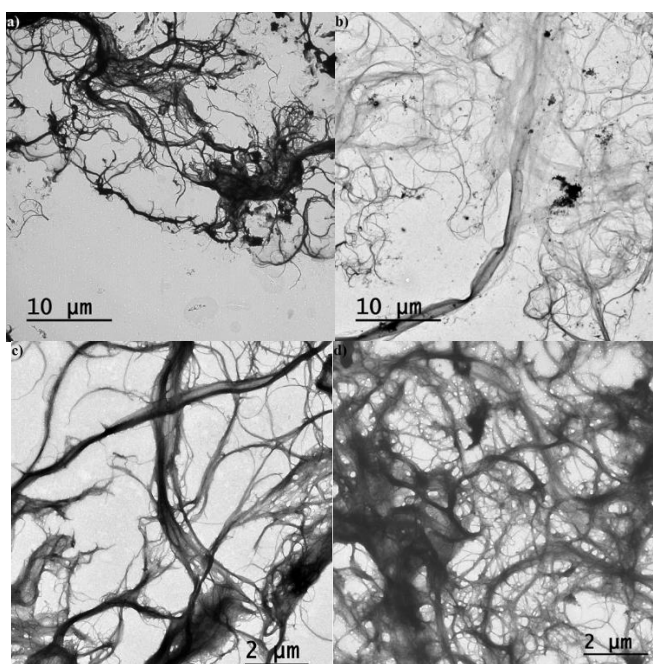


Fig. 1. TEM images of CNF; rCNF (a,c) and gCNF (b,d) at two magnifications

With increasing the solid content of CNF suspension, the coat weight increased as shown in Fig. 2. The highest coat weight was achieved with 3% CNF. This is expected because the rod coater is a volume controlled coating method. Higher coat weight can affect paper properties especially barrier properties provided that a full coverage is achieved. At higher solids (4 %), even with CMC addition, defects in the coating layer are easily observed and because of lots of chunks, CNF cannot be spread out evenly.

The SEM micrograph of the surface of coated papers are shown in Fig. 3. For the rCNF case in Fig. 3b, regions of the base paper are seen that prove that a complete coverage is not obtained. For the gCNF in Fig. 3c, good coverage seems to be obtained. For the 3% rCNF and gCNF, mixed with CMC, good coverage is noted in Fig 3e. CMC addition does generate a suspension that is more uniform than the suspensions without CMC; these suspensions flow in a uniform manner in the rod coater.

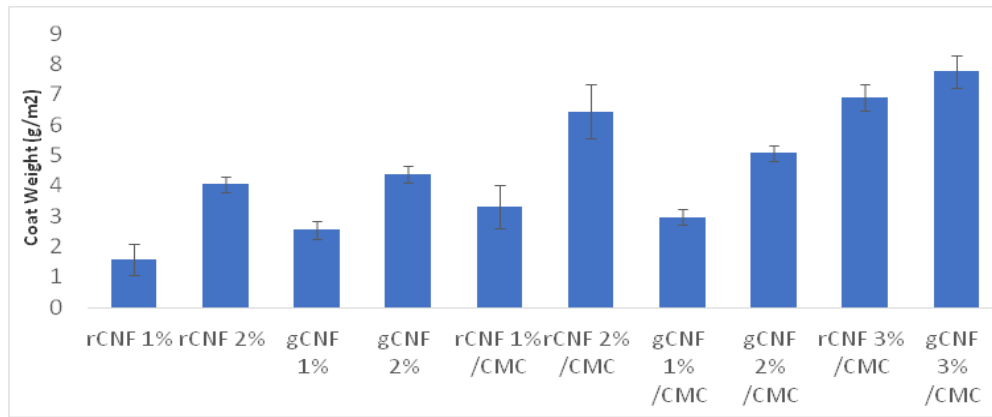


Fig.2. The coat weight of papers coated with CNF and CNF/CMC at different solid contents

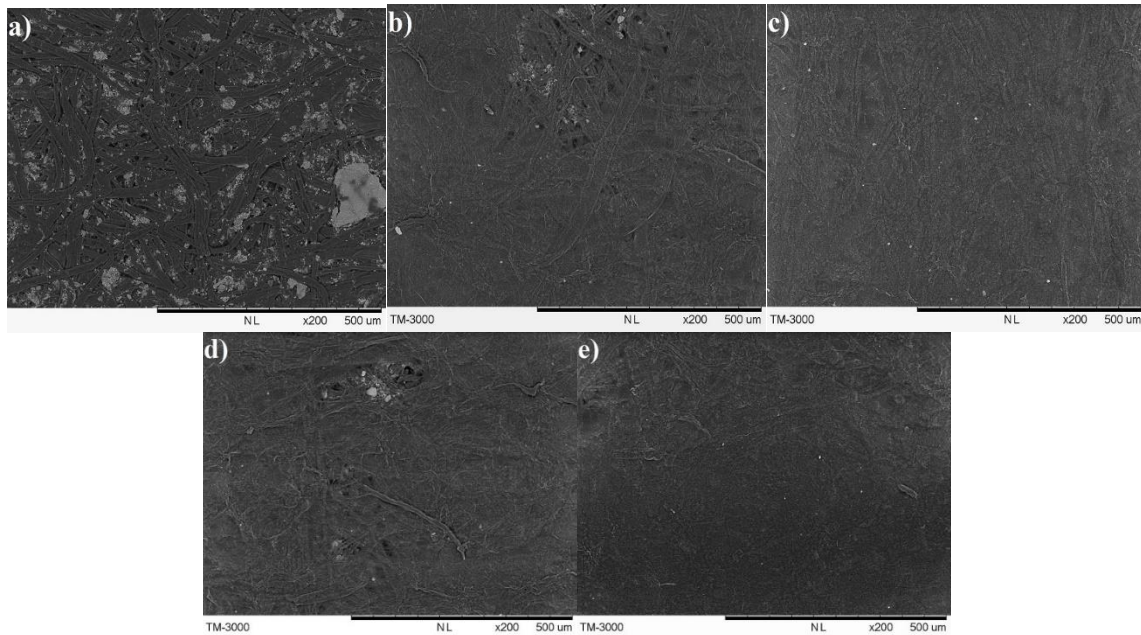


Fig. 3. SEM micrographs of the surface of paperboard; a) uncoated base paper; b,c) coated paper with 2% rCNF and gCNF along with CMC, respectively; d,e) coated paper with 3% rCNF and gCNF along with CMC, respectively.

The air resistance of uncoated and coated paper and its relationship with coat weight is presented in Fig. 4. A significant improvement in the air barrier property was achieved especially when gCNF together with CMC was applied. As mentioned above, using grinder CNF with finer size distribution together with CMC resulted in a much better spread out and full coverage of paper surface which means that the pores on the surface of paper are blocked. It is well known that the connected pores on the surface of paper have an important effect on air permeability. These results are determined by the ability of the coating to spread in a uniform manner, not the inherent properties of the coatings.

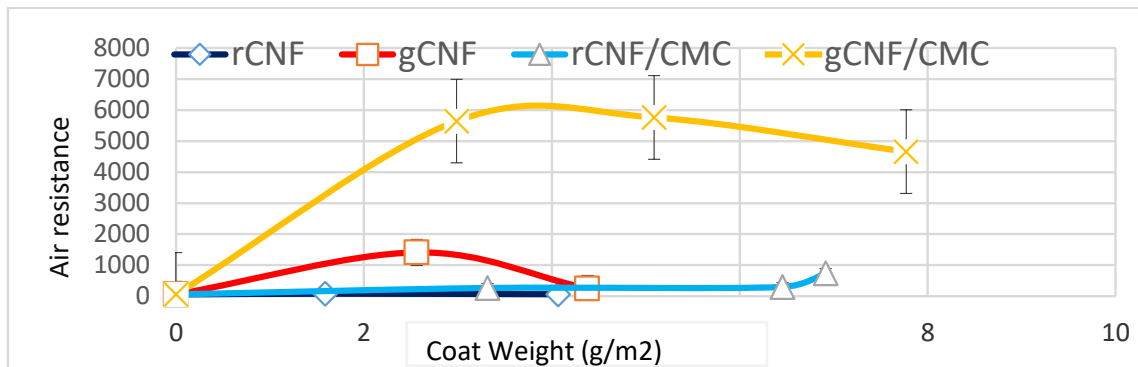


Fig.4. Air resistance of uncoated and coated paperboards as a function of coat weight

Fig. 5 shows the results of aqueous resistance of paperboards as a function of coat weight. It is obvious that coating with CNF improved this characteristic considerably. It should be noted that applying CNF alone did not improve this property compared to uncoated paper. However, when gCNF along with CMC was used the aqueous resistance of coated paperboards increased significantly. The highest resistance was achieved with the 3% gCNF with CMC.

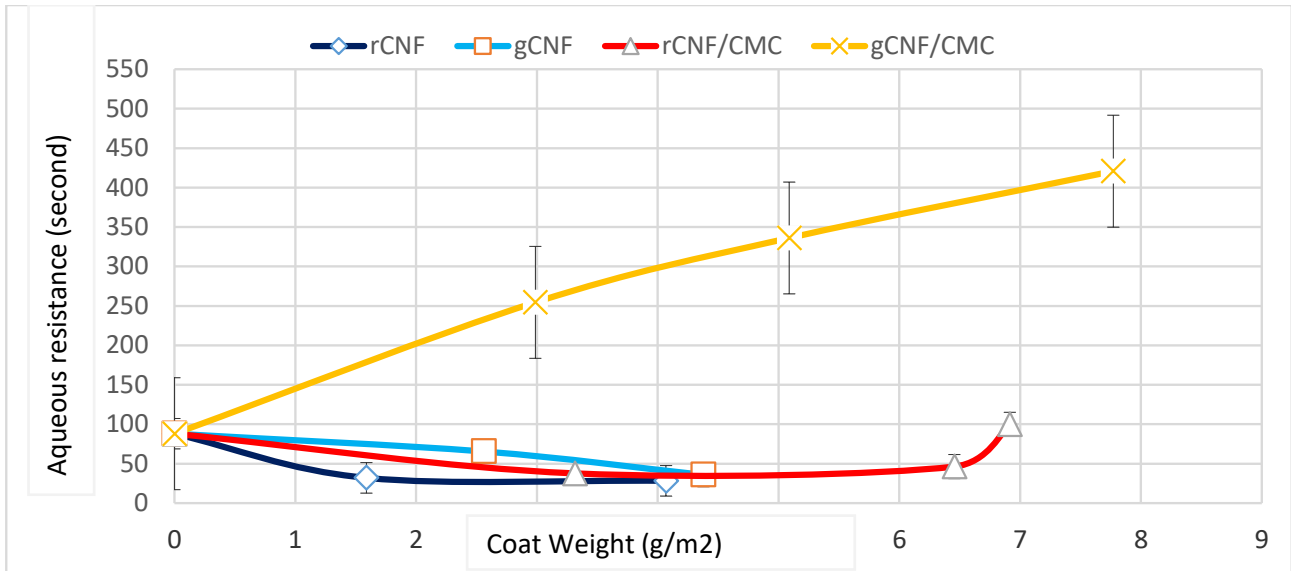


Fig. 5. Aqueous resistance of uncoated and coated paperboards as a function of coat weight.

Although there is a decrease in water vapor transmission rate (WVTR) of coated paper compared with uncoated paper, a significant difference was not observed. Fig.6 shows the WVTR of uncoated and coated papers as a function of coat weight. This test was performed at 50% RH and 23 °C. The results are in accordance with other reports mentioning that with increasing the relative humidity and temperature, the WVTR of coated paper would increase. The main reason is related to the hydrophilic characteristic of CNF. Although it is well known that crystalline cellulose has good barrier properties, with increase of the humidity, the amorphous cellulose absorbs water resulting in weakening of inter and intra bonding in cellulose chains. This results in higher mobility of cellulose chains and fibril network and as a result more sites for water molecule permeation (Aulin et al.2010).

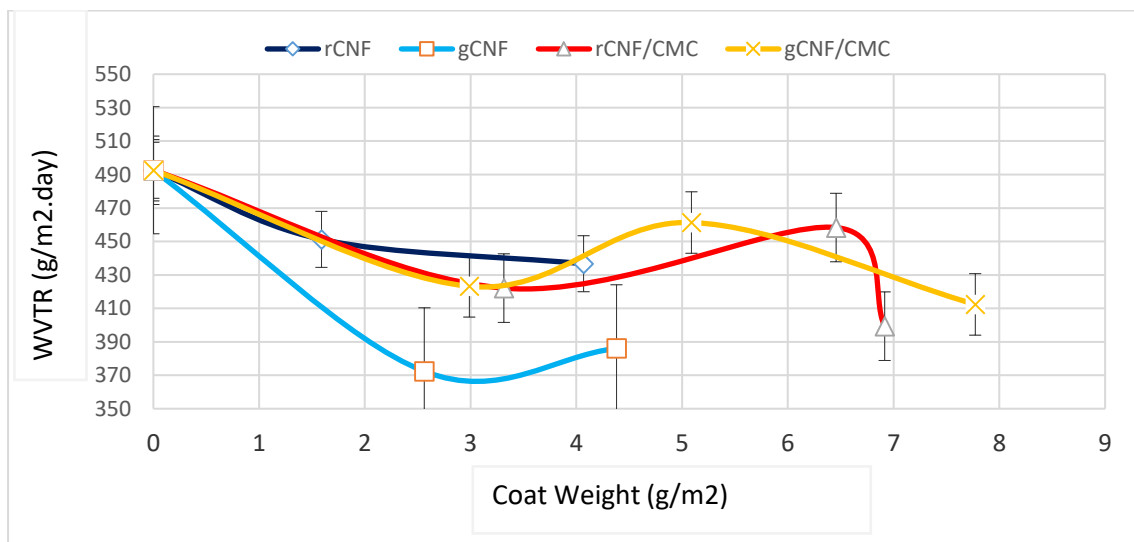


Fig. 6. WVTR of uncoated and coated paperboards as a function of coat weight.

Fig. 7 presents the grease resistance of coated papers as a function of coat weight. This property was evaluated according to the Kit test. The results showed that base paper coated with 2 wt% solids achieved the highest grease resistance compared to the uncoated paper. As mentioned above this sample also showed the highest air resistance. A high coating weight together with a full coverage of paper surface might be the most important reasons. The nano size and web structure of CNF on the surface of

paper decrease the pores and consequently decrease the migration of grease through the paper. Based on the results of air and grease resistance, it seems that 2 wt% compared to 3 wt% CNF resulted in a more homogeneous structure. The results are in agreement with the results presented by Aulin et al. 2010 who showed that when the air permeability decreases, i.e., increased coat weight, the oil resistance increases. Song et al. 2015 reported that the pores coverage of paper surface after coating particularly in higher coat weight is the main reason to decrease the oil penetration.

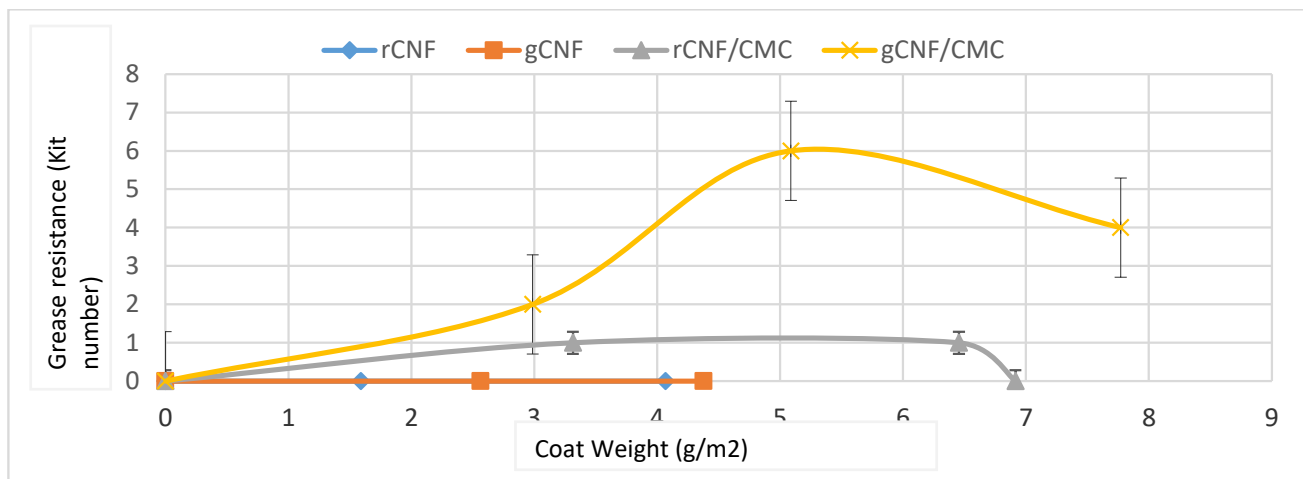


Fig. 7. Grease resistance of uncoated and coated paperboards as a function of coat weight.

## Conclusion

Application of CNF with higher solid content as a coating material was achieved when it was applied with CMC. However, the highest coat weight as well as full surface coverage were achieved with gCNF resulting in a distinct improvement in barrier properties except for WVTR. The hydrophilic characteristic of CNF is probably the main reason for this observation.

## References

- Aulin, C., Gallstedt, M., Lindstrom, T.** (2010): Oxygen and oil barrier properties of microfibrillated cellulose films and coatings, *Cellulose*, 17, 559-574.
- Behzad Nazari** (2015). New applications for cellulose nanofibers: Rheological challenges, PhD Thesis, University of Maine, USA.
- Kristin, S., Stenius, P.** (2009): Strength and barrier properties of MFC films, *Cellulose*, 16, 75-85.
- Kumar, V., Bollstrom, R., Yang, A., Chen, Q., Chen, G., Salminen, P., Bousfield, D.W., Toivakka, M.** (2014): Comparison of nano- and microfibrillated cellulose films, *Cellulose*, 21, 3443-3456.
- Lavoine, N., Bras, J., Desloges, I.** (2014): Mechanical and barrier properties of cardboard and 3d packaging coated with microfibrillated cellulose, *J. Appl. Polym. Sci.*, 131:40106.
- Lavoine, N., Desloges, I., Dufresne, A., Bras, J.** (2012): Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review, *Carbohydr. Polym.*, 90, 735-764.
- Liimatainen, H., Haavisto, S., Haapala, A., Niinimäki, J.** (2009): Influence of adsorbed and dissolved carboxymethyl cellulose on fiber suspension dispersing, dewaterability, and fines retention, *Bioresources*, 4(1), 321-340.
- Richmond, F., Haugwout, C., Bousfield, D.W.** (2014): The Use of Cellulose Nanofibers in Paper Coating Formulation, TAPPI PaperCon.
- Song, Z., Xiao, H., Li, Y.** (2015): Effects of renewable materials coating on oil resistant properties of paper, *Nordic Pulp & Paper Research.*, 30, 344-349.