# The influence of precoating layers on the performance of water-based barrier coatings

KRITEE POKHAREL, DOUGLAS W. BOUSFIELD, AND JINWU WANG

**ABSTRACT:** Cellulose nanofibrils (CNF) on paper have been demonstrated to be an effective barrier against oxygen and grease and have been shown to improve the barrier performance of dispersion-based barrier coatings. The potential to produce paper grades that have good oxygen, grease, and moisture barrier properties is clear, but a better understanding of the synergies between CNF, other coating layers, and water-based barrier coatings (WBBC) is needed to optimize these systems.

Different coat weights of a commercial WBBC were applied to papers that have a range of different qualities and thicknesses of CNF precoating layers. The same WBBC was also applied to pigmented coated paper, with various types of pigments and latex levels. Samples were characterized in terms of grease resistance, water vapor transmission rate (WVTR), and oxygen transmission rate (OTR) before and after folding. The results were contrasted to cases where the WBBC was applied to the paper with no precoating layer.

When the WBBC is applied on a CNF layer or the pigmented coating layer, the performance of the WBBC for the water vapor barrier improves a significant amount compared to when the WBBC is applied to the base paper with no precoating layer. This improvement likely comes from these precoating layers filling in the large paper pores, which leads to the WBBC forming a continuous layer at low coat weights. Folding decreases the moisture barrier performance to some degree, but the grease resistance is not influenced by folding when a CNF precoating layer is involved. Oxygen barrier properties are moderate for the CNF layer alone and are less than 5 $cm^3/m^2$/day when WBBC is coated on the CNF layer. This result likely comes from the barrier coating's ability to repair defects in the CNF layer to stop the easy passage of oxygen in defect regions of the sample.

***Application:*** Understanding of a precoating layer on the barrier performance of dispersion barrier coatings should give rise to new markets for paper in packaging. Using a highly refined cellulose layer as the precoating layer results in good oil/grease resistance and oxygen barrier, even after folding.

Glass, metal, and fossil-derived synthetic plastics are currently used in many food packaging applications, but these materials are often difficult to recycle and do not break down in the environment if littered [1]. Most plastics can be recycled, but due to technological and economic barriers, this is not done routinely in many countries. In the last 50 years, there has been a 20-fold increase in the amount of plastic waste, and less than 6.2% of the plastic produced is recycled [2]. There is an increasing demand for packaging solutions that are made from sustainable materials, can be recycled, and degrade to harmless materials in the environment if littered.

Paper-based packaging meets the long-term need of our society in terms of these issues. In many applications, however, paper lacks the barrier properties needed to keep the product fresh. Many different approaches have been used to achieve the barrier properties, such as impregnating the paper substrate with some material or extrusion coating of a polymer film onto the paper surface [3]. Barrier-coated papers are widely used in the food packaging industry due to their ability to act as barriers against water, water vapor, aroma compounds, and gases like oxygen and carbon dioxide [4].

Water-based barrier coatings (WBBC) are viewed as a preferred method to obtain these barrier properties compared to extrusion coating, as they can be applied at high speeds and lead to good recycling [5–7]. However, their performance is often inferior to extrusion coated polyethylene (PE). These WBBC face difficulties due to the possibility of pinholes or defects during drying that reduce their effectiveness. Although barrier pigments enhance the barrier characteristics, the extent of improvement is frequently restricted and might not meet expectations [8].

The use of precoating layers to enhance the performance of WBBC has been reported in the literature [9]: a 4 $g/m^2$ coating of cellulose nanofibers (CNF) on the paper caused various types of WBBC to decrease the water vapor transmission rate by over 50% compared to paper without the CNF layer. Precoating layers also can improve the moisture, oxygen, and grease barrier properties of paper, as reviewed by Wang et al. [10].

Cellulose nanofibrils (CNF) are emerging as a promising

alternative to plastic due to their abundant and renewable supply, as well as their excellent barrier and mechanical properties, as reported by Lavoine et al. [11]. These layers have attracted considerable attention because of their affordability, potential for recycling with paper, capacity to sequester carbon when disposed of in a landfill, and biodegradability in the environment [12,13]. These CNF represent an additional category of biodegradable polymers that are applicable for coating paper. Recently, layers of CNF have emerged as a pathway to a paper-based system that has good oxygen and grease barrier performance and were also found to retain their barrier properties, even after folding [14,15]. Others have demonstrated that CNF may be successfully used as a barrier on paper or as a single layer [16,17]. Kumar et al. [18] compared various kinds of CNF layers with regards to oxygen transmission rate (OTR); at low humidity, even low-quality CNF manufactured using a refiner had a low oxygen permeability of 2 $cm^3/m^2$/day. A review of the water and oxygen barrier properties of CNF films has been conducted by Wang et al. [10]. A review of the barrier properties of CNF films and other polymers indicates that CNF films can offer oxygen barrier capabilities up to 100 times better than standard polymers [10]. On the other hand, compared to standard polymer films, the water vapor barrier properties of CNF films are poor.

Biopolymers have received attention as a sustainable alternative to traditional plastics made from petroleum because they biodegrade, can be made from biological sources, and have a small carbon footprint. The utilization of biopolymers in packaging is an area of high interest; however, these materials have difficulties in terms of mechanical properties, recycling, costs, and the ability to process. A general overview of biologically sourced materials and biopolymers used in packaging has been provided by various groups [19, 20]. Various biopolymers have been employed in the form of coatings for paper and paperboard, including, but not limited to, polysaccharides (derivatives of starch and cellulose, chitosan, and alginates); proteins (e.g., casein, whey, collagen, soya, and gluten); lipids (such as beeswax, carnauba wax, and free fatty acids); and polyesters (polyhydroxyalkanoate [PHA] and polylactic acid [PLA]) as reviewed by Rastogi and Samyn [20]. The PLA has superior characteristics compared to other biopolymers. However, the material's usefulness is constrained by its brittleness and a low heat deflection temperature (HDT) of only 64.5°C in its pure form, as noted by Huda et al. [21]. This low HDT restricts the processing conditions of the material and can render it unsuitable for certain applications. The PLA also has great potential for long-term food packaging applications, but it does not decompose easily in natural environments and necessitates specialized composting facilities for proper disposal [22]. In addition, PLA and PHA do not have a good resistance to gas permeation [10].

The potential to produce paper grades that have good oxygen, grease, and moisture barrier properties is clear from recent work. However, a good understanding of the interactions of a precoating layer and the WBBC is lacking in the literature. The hypothesis is that the roughness and pores of a paper substrate will affect uniformity of the coating and the presence of stress concentrations; a precoating layer of finer materials adds new functionalities, fills the pores, smooths the substrate, and holds out the barrier coating, thus reducing the amount of the barrier coating needed. Formability is an important property of paperboard to withstand folding, creasing, and deforming without compromising its structural and functional integrity during converting flat sheets into functional 3D packages and subsequent handling. Barrier coated paperboard tends to perform well in flat sheets but often experiences damage under stressful events. The folding resistance of CNF containing materials is also not widely investigated. A recent review of coating cracking and barrier integrity after high deformation of paperboard highlights the need for more research on the mechanisms that cause damage and the approaches to preserve the barrier [23]. Here, papers that have either been coated with a precoating layer of pigments or a layer of CNF are additionally coated with a commercial WBBC. The water vapor, oil/grease, and oxygen barrier properties are characterized before and after folding.

## METHODS AND MATERIALS

Paper and paper with a CNF layer were made at the Process Development Center at the University of Maine (Orono, ME, USA). The base paper was 80 $g/m^2$ basis weight and had a top layer of CNF films with different coat weights (4 $g/m^2$, 8 $g/m^2$, and 12 $g/m^2$). The basis sheet was 80:20 hardwood/softwood blend. The paper was manufactured on a pilot paper machine, which consists of a Fourdrinier forming section, press section, and drying section.

The CNF used in this experiment was prepared mechanically by using a pilot scale refiner with specialized plates to break down the wood fibers. The wood fibers were bleached softwood kraft pulp. The suspensions were produced at around 3.5% solids. The degree of fibrillation of the CNF was characterized by a MorFi fiber quality analyzer (MorFI; Gières, France). The percent of the fibers less than 200 mm in length are characterized as "fines" in this test. While this test does not measure the nanoscale properties of the fibers, it gives an indication about how fibrillated the fibers are. Fines levels of 70% and 90% were used. Images of the material have been reported in other publications such as Moon et al. [12]. Transmission electron microscope (TEM) and atomic force microscope (AFM) images of the material show a large number of fibrils with diameters on the order of 50 nm often connected to other fibers and cell wall fragments that are in the order of a couple of microns.

The surface application of the CNF was achieved via an in-house built secondary headbox, whereby a diluted suspension with a weight concentration of 0.5% was allowed

to flow from the headbox and form a curtain on the wet paper web. The paper was then processed through the standard pressing and drying sections of the machine. In comparison to the uncoated paper, the CNF-coated paper demonstrated a low air permeability, with permeability coefficients of approximately 10–18 $m^2$ and 10–16 $m^2$, respectively, for the coated and uncoated papers. Furthermore, the coated paper exhibited a significantly slower rate of water uptake — over ten times slower than the uncoated paper. For a more detailed description of the paper production technique with the CNF layer, refer to Johnson et al. [24]. The amount of CNF applied to the paper was 4, 8, and 12 $g/m^2$.

Three different types of kaolin clay were used in this work: 1) Capim RG platy kaolin (Imerys; Paris), a coarse, high-brightness, moderate aspect ratio coating kaolin with size ranges from 2–10 µm; 2) Capim DG fine kaolin (Imerys), a high brightness kaolin with steep particle size distribution of around 2 µm and low aspect ratio; and 3) Capim NP delaminated kaolin (Imerys), a delaminated high brightness kaolin clay with a high aspect ratio and particle size of around 2–10 µm. Genflow 5086 styrene butadiene (SB) latex (Synthomer; London) was used as a binder supplied at a solids content of 50 wt% and has a glass transition temperature of -5°C. The latex content was 20 and 40 parts per hundred parts (pph) pigment. The latex and a kaolin pigment were blended with steady mixing for 1 h using distilled water to adjust the total solids to 60%. The pigmented coating layer was dried at 105°C. The target coat weight for the pigmented precoating was 12 $g/m^2$.

The WBBC was a Joncryl HPB 4030 acrylic emulsion latex (BASF; Ludwigshafen, Germany) that is water resistant, heat sealable, and should give a good water vapor barrier. According to third-party industrial testing, it has been confirmed that this coating creates repulpable and recyclable packaging. It is a translucent emulsion supplied at 40 wt% solid content.

A laboratory bench-size automatic rod coater (Model 21001, BYC Gardner USA; Columbia, MD) equipped with standard Mayer rods was used to perform the coating processes. Varying rod sizes and pressures were utilized to achieve different levels of coat weight. The speed of the coater was set at a fixed rate of 6.1 m/min.

The barrier coating was applied on the CNF side of the paper or on the pigment coating layer. The WBBC was dried at 60°C for 10 min. For each paper with either a CNF precoating layer or a pigmented precoating layer, a range of coat weights was applied, and at least three repeats were generated for each condition.

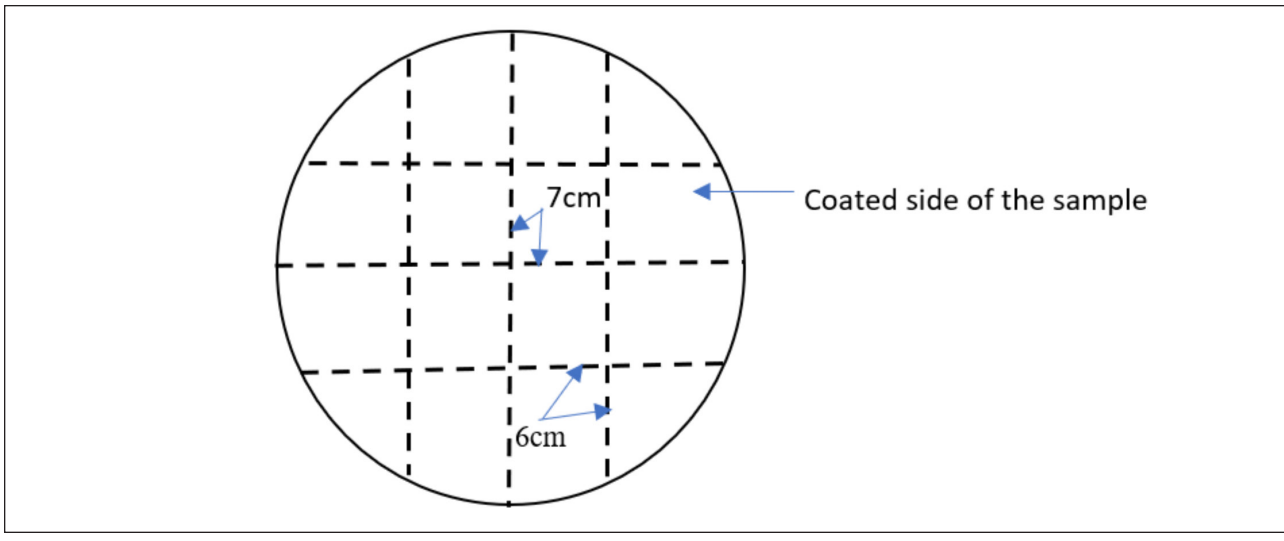
The water vapor barrier property of the coating for both of the above samples was measured according to ASTM 96/E96M-16 "Standard test methods for water vapor transmission of materials." In a controlled temperature and humidity room (23°C and 50% relative humidity [RH]), glass jars were filled with 25 mL of distilled water. To ensure the proper seal ability of the sample to the jar, silicone grease from Dow Corning (Midland, MI, USA) was applied on the edge of the glass jar (Rubbermaid; Atlanta, GA, USA). The jar was then closed with the sample of interest, which had been cut in a circular shape with diameter of 65 mm, as the lid. Next, the sample was held against the jar with a silicone gasket and a metal screw top rim. The weight of the whole jar with the film was recorded before placing it in a conditioned room, and after 24 h the weight of the jar was recorded again. The difference in the weight before and after 24 h is the amount of water vapor transmitted through the sample. The WVTR can be calculated by dividing the change in mass by the area and the time. The results are expressed in $g/m^2$/day.

The grease barrier properties of samples were evaluated using the TAPPI Standard Test Method T 559 cm-22 "Grease resistance test for paper and paperboard," which is based on 12 distinct solutions numbered from 1 to 12 and designated as Kit test numbers. This test was originally designed to evaluate the performance of papers treated with fluorochemicals, but it is now frequently used as an initial indicator of a sample's resistance to grease or oil penetration for food packaging. These solutions contain castor oil, n-heptane, and toluene in varying proportions. The mixture with the lowest ability to penetrate a sample is solution number one, while solution number 12 is the most aggressive. The solutions were dropped from a height of 40 mm onto the sample. They were removed using tissue paper after 15 s, and each sample was analyzed at least five times. Penetration of the grease through the film was determined by looking for a visible gloss change of the back side of the sample under low-angle light after the grease was wiped from the top side.

Oxygen transmission rate (OTR) was measured following ASTM D3985-17 "Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor," with an oxygen permeability analyzer (OX-TRAN 2/22 OTR Analyzer, Ametek Mocon; Brooklyn Park, MN, USA). The film was placed in a designated cell and conditioned for 6 h with a carrier gas mixture of 96% nitrogen gas ($N_2$) and 4% hydrogen gas ($H_2$) containing water vapor to make the RH at 50%. The testing area of each film was 5.64 $cm^2$. The test was terminated when the difference between the last measurement and the one from five cycles before was less than 1%. The results are expressed in $cm^3/m^2$/day.

To observe the surface and cross section of the coated sample, a tabletop TM 3000 scanning electron microscope (SEM) from Hitachi High-Technologies (Tokyo, Japan) was used. Samples were inserted into the device with no surface preparation. To obtain a cross-section image, the samples were obtained by cutting out the piece of sample with the help of a razor blade and made free of any paper fibers.

For the crack resistance test, the samples were folded as six orthogonal and evenly spaced folding lines that were




*1. Schematic of orthogonal folds made in a coated sample. The arrow indicates the length of folded lines.*

made on each coated sample corresponding to lengths of 6 and 7 cm as shown in **Fig. 1** and described by Zhu et al. [8]. Six folding lines were made with coating placed inwards to the fold. For each fold, the paper was held at 180°, and 4200 Pa pressure was applied for 5 min.

Assuming Fick's law of diffusion and steady-state conditions, WVTR through the paper and coating layers should follow the expression given in Al-Gharrawi et al. [9]:

$$WVTR = \frac{M_W (C_i - C_o)}{\left(\frac{H_P}{D_P} + \frac{H_C}{D_C}\right)} \quad (1)$$

where $M_W$ is the molecular weight of water; $C_i$ and $C_o$ are the concentration of water vapor inside and outside of the jar, respectively; $H_P$ and $H_C$ are the thickness of the paper and coating layer, respectively; and $D_P$ and $D_C$ are the effective diffusion coefficient of the paper and the coating, respectively. The WBBC/CNF partition coefficient of water and gases is assumed to be constant and becomes included in the diffusion coefficient, $D_C$. Equation 1 predicts the same behavior, where the coating is considered as a single layer whose thickness is the sum of the thicknesses of the WBBC coating layer and the precoated CNF layer. In the controlled temperature and humidity room (23°C and 50% RH) in which the tests were conducted, the concentration of saturated water vapor above the water surface inside the jar was 1.1 mole/m³. The 50% RH would have a concentration of half of this value outside of the jar. The WVTR of the uncoated paper was around 400 g/m²/day. The thickness of the paper was 0.098 mm. This thickness gives a diffusion coefficient for the paper of $4 \times 10^{-8}$ m²/s by Eq. 1.

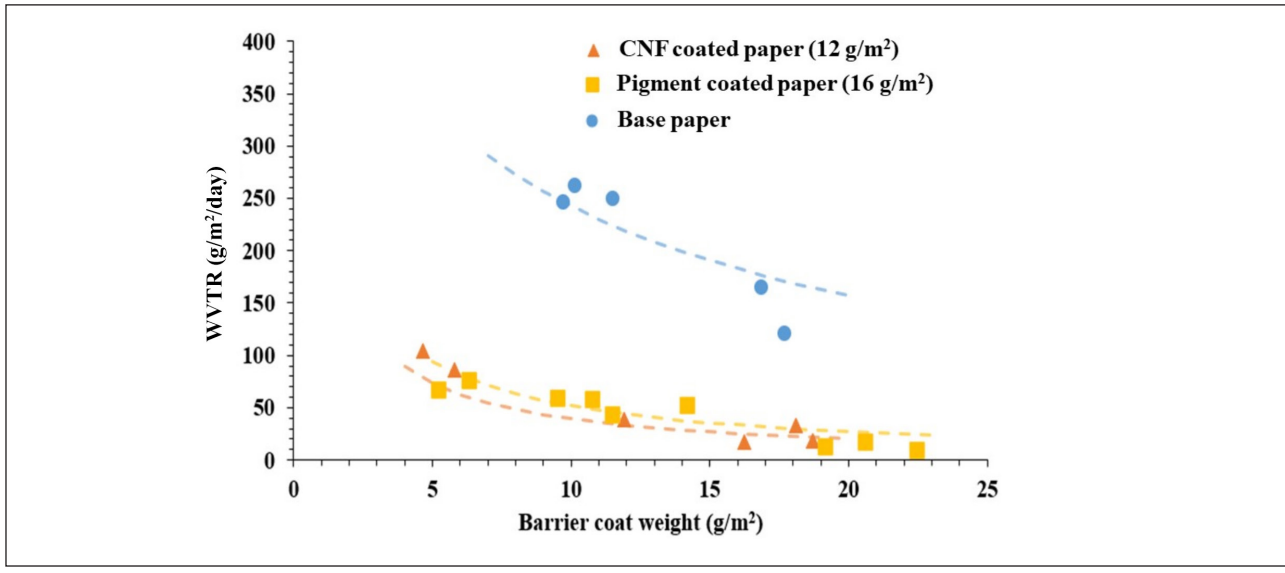
The experiments involve the use of various coat weights of the barrier coating that lead to known values of coating thickness, assuming a dry density of the barrier layer of 1 gm/cm³. Equation 1 is used to analyze the data by tuning the diffusion coefficient of the coating layer $D_C$ to minimize the root mean square error between the equation and the data.

## RESULTS AND DISCUSSION

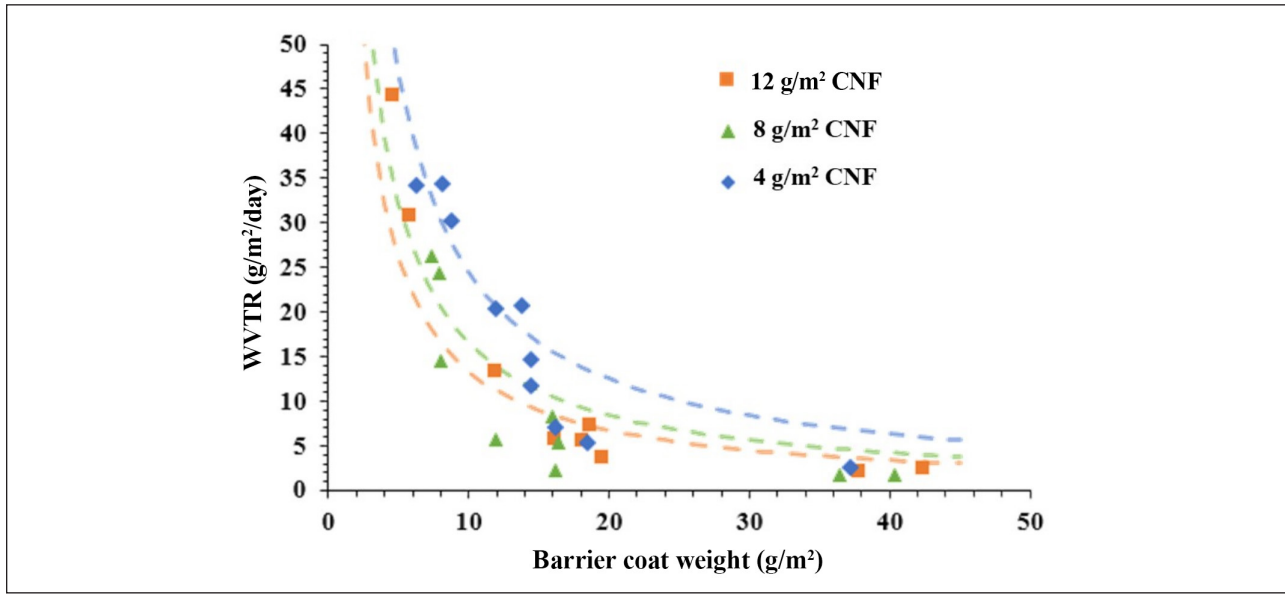
**Figure 2** compares the WVTR obtained for the following: 1) WBBC applied on a paper precoated with 90% fines CNF at 12 g/m²; 2) WBBC applied on a paper precoated with 16 g/m² delaminated kaolin at 40 pph latex; and 3) barrier coating applied on an uncoated base paper (80 g/m²). The results were clear in that a precoating layer makes the WBBC much more effective. For example, at around 10 g/m² of the barrier coatings, we see the WVTR come down from around 200 g/m²/day to 30 g/m²/day and 60 g/m²/day for the CNF and pigment layers, respectively. Similar results have been reported, but the results are limited to 4 g/m² CNF precoating layers and the WBBC was applied to both sides of the sample, as by Al-Gharrawi et al. [9]. For all substrates without the WBBC, the WVTR was on the order of 400 g/m²/day.

The reason for this result is likely caused by the precoating layer "holding up" the barrier coating into a continuous layer as it dries. Without the precoating layer, some amount of the WBBC likely penetrates the paper sheet, leaving pin holes or defects in these regions that allow for the passage of water vapor. At high coat weights of the WBBC, the results may converge, as these defects are filled by an excess of the polymer in the barrier coating.

**Figure 3** compares the WVTR behavior when the barrier coating is applied on different coat weights of the 90% fines CNF precoating layer; as the precoat weight increased, the WVTR decreased for various coat weights of the WBBC. The data exhibited a scattered pattern that is likely attributed to multiple factors, such as random coating defects, the quality of the sealing of the sample against the jar, and other random errors. However, by fitting Eq. 1 through the data, the trends become clear for the different CNF coat




*2. Water vapor transmission rate (WVTR) as a function of water-based barrier coating (WBBC) coat weight applied on: 1) a paper precoated with 90% fines CNF at 12 g/m²; 2) a paper precoated with 16 g/m² delaminated kaolin at 40 pph latex; and 3) an uncoated base paper (80 g/m²). Lines are fit to Eq. 1.*

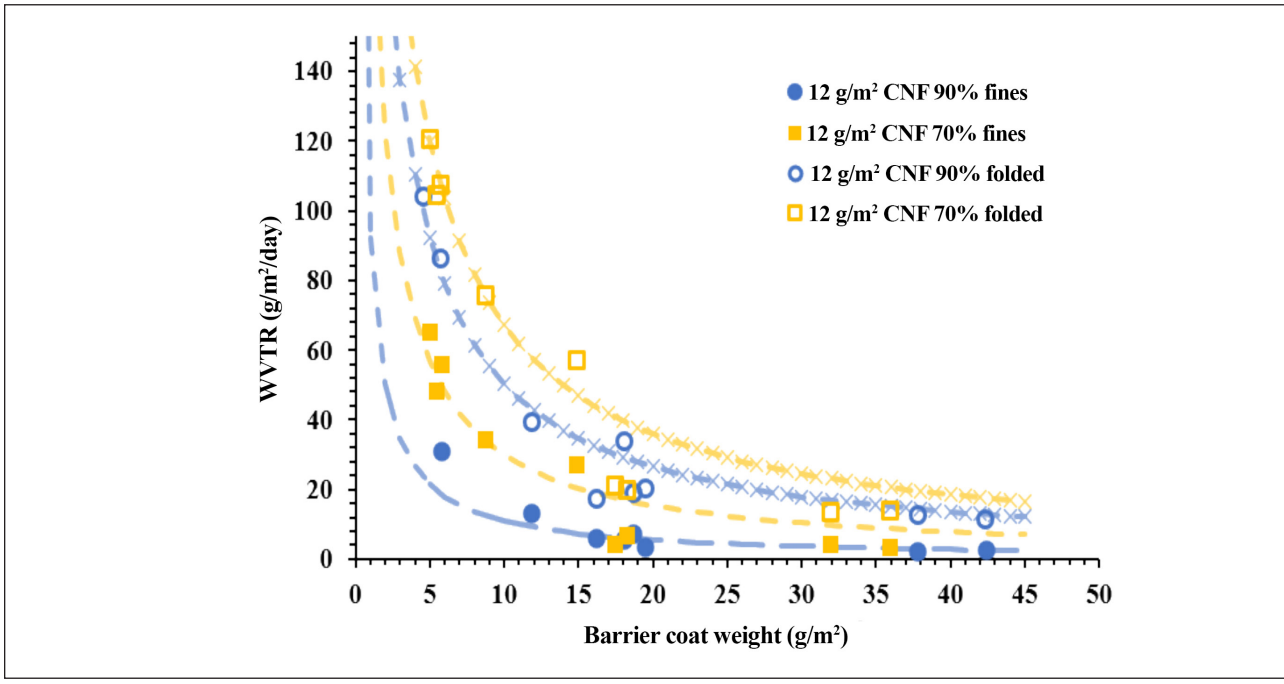



*3. Influence of different coat weights of CNF film as a precoating layer on WBBC layer performance. The CNF quality was 90% fines. Lines are fit to Eq. 1.*

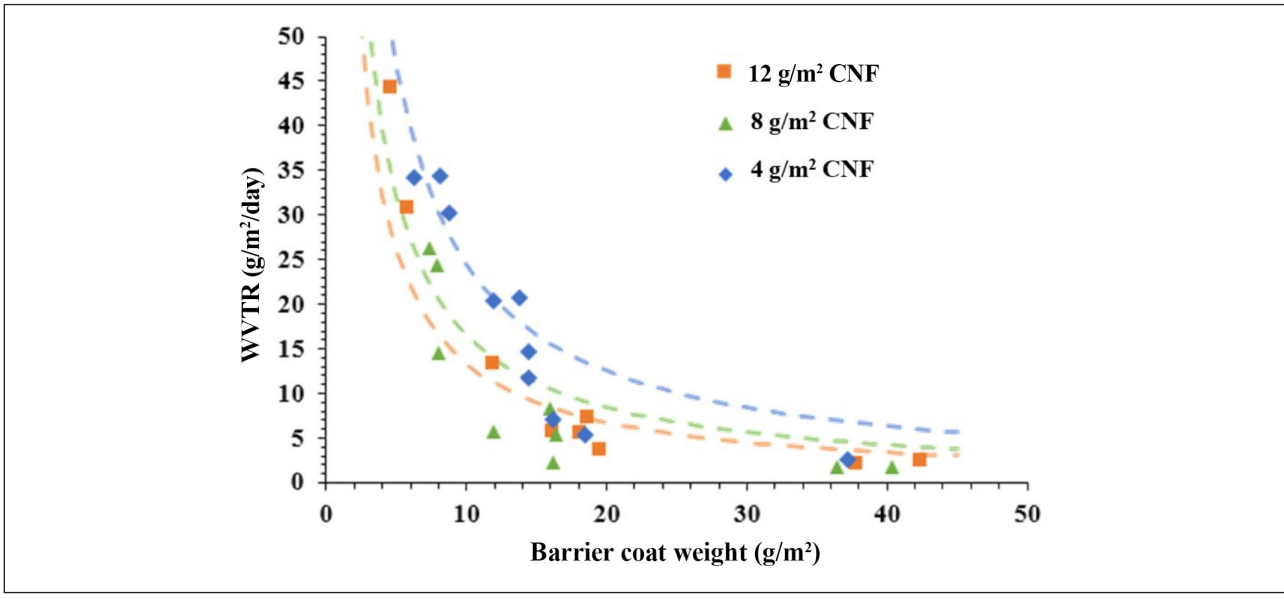
weights. The 8 and the 12 g/m² CNF layers tend to give similar results, and after coating with the WBBC, give WVTR under 10 g/m²/day for barrier coat weights of less than 20 g/m². Even with the lowest level of CNF (4 g/m²) with 11 g/m² of the WBBC, a WVTR of 20 g/m²/day was obtained, which is still lower than many different commercial packaging requirements [10].

The influence of the quality of the CNF used is shown in **Fig. 4**. The 70% fines CNF as a precoating layer is compared to the 90% fines CNF, both at 12 g/m² as the precoat weight. At low values of the barrier coat weight, there was a significant difference between the two fines levels, but this difference is small as the barrier coat weight increases. The reason likely was related to the ability of the CNF to fill up pores in the paper substrate, and the high fines content CNF seems to fill these pores more completely than the 70% fines CNF.

Also shown in Fig. 4 is the influence of CNF quality and folding of the sample. The finer CNF rendered better water barrier results than the coarse one. In all cases, the WVTR increases with folding, to a limited amount. Others have reported that CNF layers retain their oil/grease barrier properties even after folding [14]. Folding of the sample deformed the precoating layer and the barrier layer, likely leading to cracks. These results indicate that the CNF layer has some ability to withstand folding.



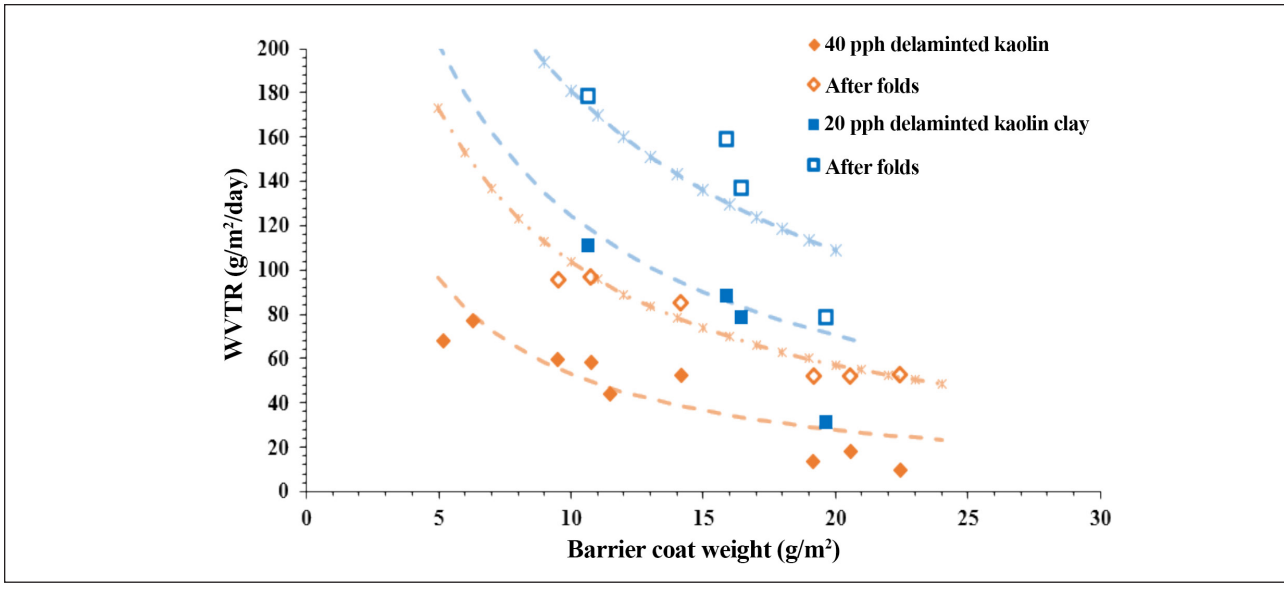

*4. Influence of the quality of CNF (fine v. coarse) as a precoat layer on WBBC layer performance, along with results after six orthogonal folds in the sample. Lines are fit to Eq. 1.*




*5. The WVTR as a function of WBBC barrier coat weight for different types of kaolin pigments. The pigmented precoating layer coat weight was 20 g/m², and the latex content was 40 pph. Lines are fit to Eq. 1.*

The influence of the pigment type used in the pigmented precoating layer is given in **Fig. 5**. The pigmented precoating layer coat weight was constant at around 20 g/m². Though there was even more scatter in the data than using CNF precoating layers, the trend lines show that the type of pigment had little influence on the performance of the WBBC. Because of the high solids of the coating applied and the size of the pigments, the pigmented precoating layers fill up all the surface pores and replace them with a small pore structure. This structure has little ability to block water vapor but is good at holding up the WBBC into a uniform layer.

The effect of folding the samples with the pigmented precoating layer is shown in **Fig. 6**. The increase in WVTR with folding was clear and consistent. The amount of increase was greater than what was observed with the CNF precoating layer. The pigmented layer was expected to be brittle and not able to withstand deformation. Therefore, folding-generated cracks in that layer led to defects in the barrier layer.




*6. The WVTR as a function of barrier coat weight on 20 g/m² pigmented precoating layer that has delaminated kaolin with 20 and 40 pph styrene butadiene (SB) latex, respectively, along with results after six orthogonal folds. Lines are fit to Eq. 1.*

Also, Fig. 6 shows that the 20 pph latex content precoating layer resulted in a higher WVTR at the different barrier coat weights than the 40 pph latex content layer. Increasing the latex content in the pigmented layer led to a decrease in the porosity of that layer. The decrease in porosity helped the barrier layer stay as a uniform layer, and it also decreased the number of paths for diffusion of water vapor in the pigmented layer.

The results of the oil and grease barrier test are presented in **Table I**. The paper without any coatings and with 4 g/m² CNF had no grease resistance and did not pass even Kit test number 1. The paper with 8 g/m² CNF precoating layers had some significant grease resistance. The 12 g/m² CNF precoated paper, for both qualities of CNF, had excellent grease resistance, even after folding. After the WBBC was applied on top of the CNF precoated paper, the Kit test value appeared to be 7 for all the samples, even after folding; the barrier layer was dissolved by the test solutions numbered higher than 7 because they contain mostly organic solvents of toluene and heptane. This resulted in a limiting value for this test method when the barrier layer was present. Other test methods for oil and grease resistance without solvents may not give this type of result.

The pigmented precoating layer showed a significant

| Sample Base | Barrier Coat Weight, g/m² | Grease Barrier Test, Kit number | Grease Barrier Test after Folding, Kit number |
|---|---|---|---|
| Base paper | 0 | < 1 | < 1 |
| | 10 | 7 | 7 |
| 90% fines CNF precoating,12 g/m² | 0 | 11–12 | 11–12 |
| | 6 | 7 | 7 |
| 70% fines CNF precoating,12 g/m² | 0 | 10 | 10 |
| | 5 | 7 | 7 |
| 90% fines CNF precoating, 8 g/m² | 0 | 4 | 4 |
| | 6 | 6–7 | 6–7 |
| 90% fines CNF precoating, 4 g/m² | 0 | < 1 | < 1 |
| | 7 | 7 | 7 |
| Pigment precoated (40 pph delaminated kaolin), 12 g/m² | 0 | 7 | < 1 |
| | 9 | 7 | < 1 |

*I. Oil and grease Kit test (TAPPI T 559) values for different cellulose nanofibrils (CNF) and pigmented precoated papers, before and after water-based barrier coating (WBCC) highlighted in blue.*

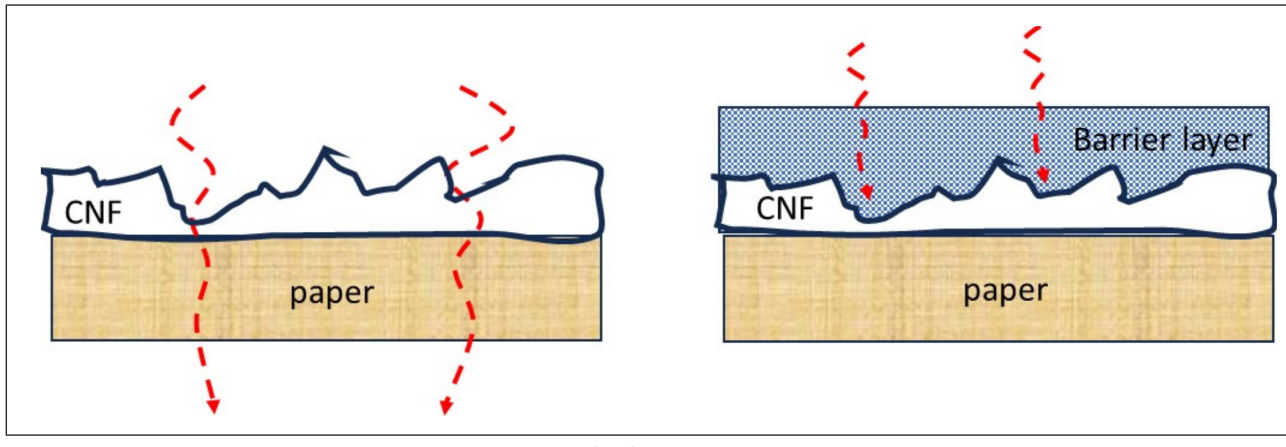
| Sample Base | Barrier Coat Weight, g/m² | OTR, cm³/m²/day | OTR After Folding, cm³/m²/day |
|---|---|---|---|
| Base paper | 0 | > 2000z | - |
| | 15 | 1026 | - |
| 90% fines CNF film on a paper, 8 g/m² | 0 | > 2000 | - |
| | 15 | 5 | 23 |
| 90% fines CNF film on a paper, 12 g/m² | 0 | 1457 | - |
| | 20 | 4 | 15 |
| Pigment coated paper (40 pph delaminated kaolin), 23 g/m² | 0 | > 2000 | - |
| | 16 | 1078 | - |

***II. Oxygen transmission rate (OTR) at 50% relative humidity and 23°C for various samples, before and after WBBC highlighted in blue.***

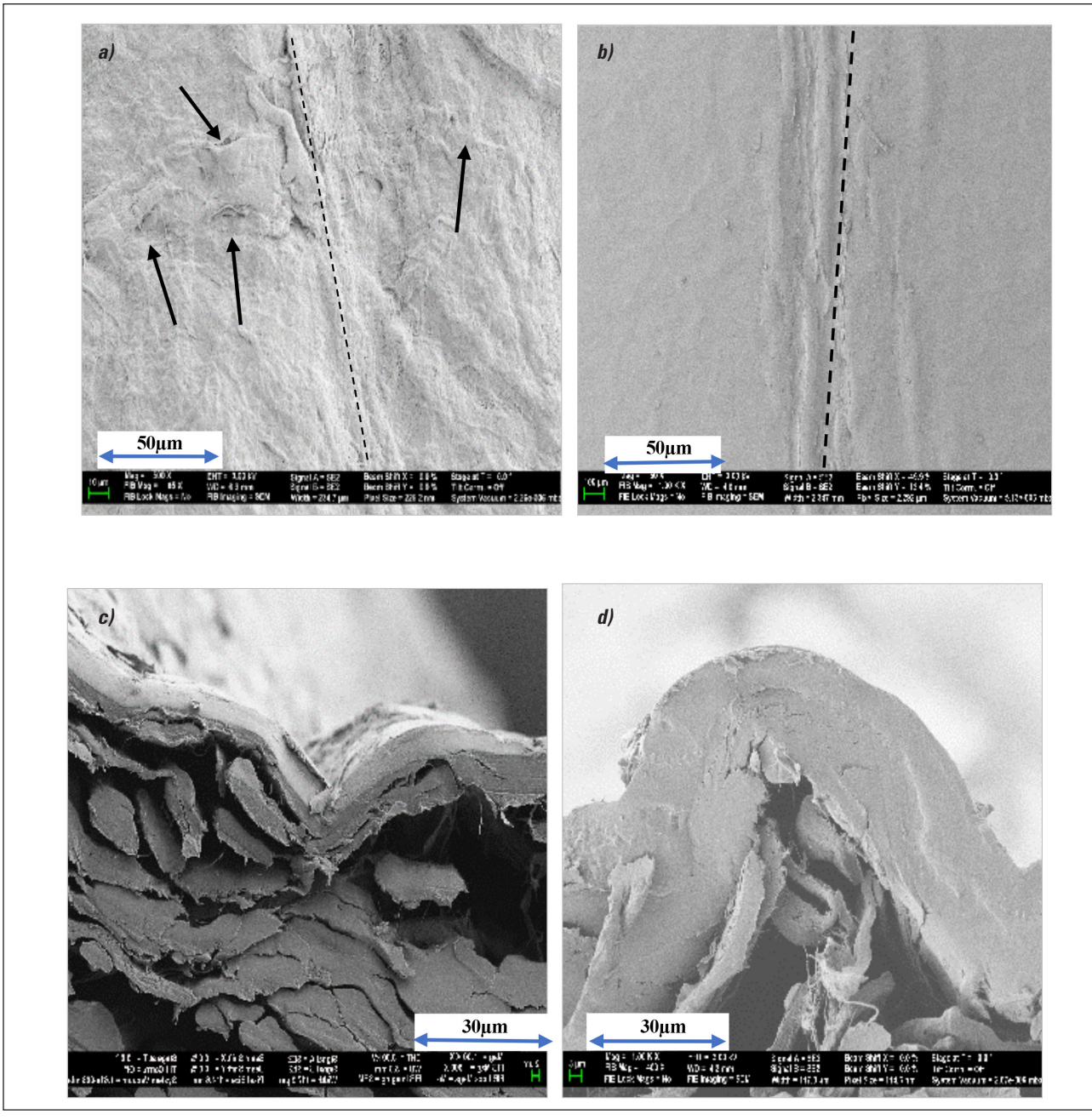
oil and grease resistance, as indicated in Table I. However, after folding, this layer tends to crack, leading to poor grease resistance. The barrier layer added to this pigmented layer also gave a Kit test value of 7, but again, with folding, the oil and grease resistance was lost. These results show how the pigmented layer has the potential to crack upon folding, and even having a barrier layer over it does not help prevent cracking. Others have shown that double coated paper samples may have less propensity to crack when the second layer has a large strain-to-failure behavior [25,26].

**Table II** shows the OTR for the various samples. As expected, the base paper and the pigmented precoated paper had no resistance to oxygen transmission. When the base paper was coated with the barrier coating, some improvement to the oxygen barrier property was observed, but the value was above what is often desired for many food items; many polymers do not have good oxygen barrier properties, as discussed by Wang et al. [10]. Surprisingly, the CNF precoated papers at 8 and 12 g/m² also did not show good oxygen barrier properties. Others have reported low oxygen transmission rates of CNF films that are cast dried [16,18]. However, when the CNF precoated papers with the barrier coating were tested, the transmission results decreased to less than 5 cm³/m²/day. This result was seen for both qualities of CNF used as the precoating layer. This decrease in OTR was likely due to a synergistic effect between the CNF layer and barrier layer. The way that the CNF layer was applied to the paper results in a layer that has some defects and regions that have low amounts of CNF, because the dispersion of CNF was not perfectly uniform when it was applied to the paper web. When the barrier layer was applied to the CNF layer, it could cover these defects and regions that have low amounts of CNF, slowing the oxygen transmission in these regions. The net result was that the whole sample has a good oxygen barrier property. **Figure 7** depicts the situation where oxygen can diffuse through defects in the CNF layer, but once the barrier layer was applied to it, the diffusion through these regions was reduced.

Table II also gives the results of folding properties for the key samples. The OTR increased with folding, but it was a limited change. This result shows the ability of the CNF layer to undergo a folding event and retain its barrier




***7. Diffusion of oxygen through thin regions of the CNF layer (left), along with the blockage of these diffusion paths by the barrier layer (right).***

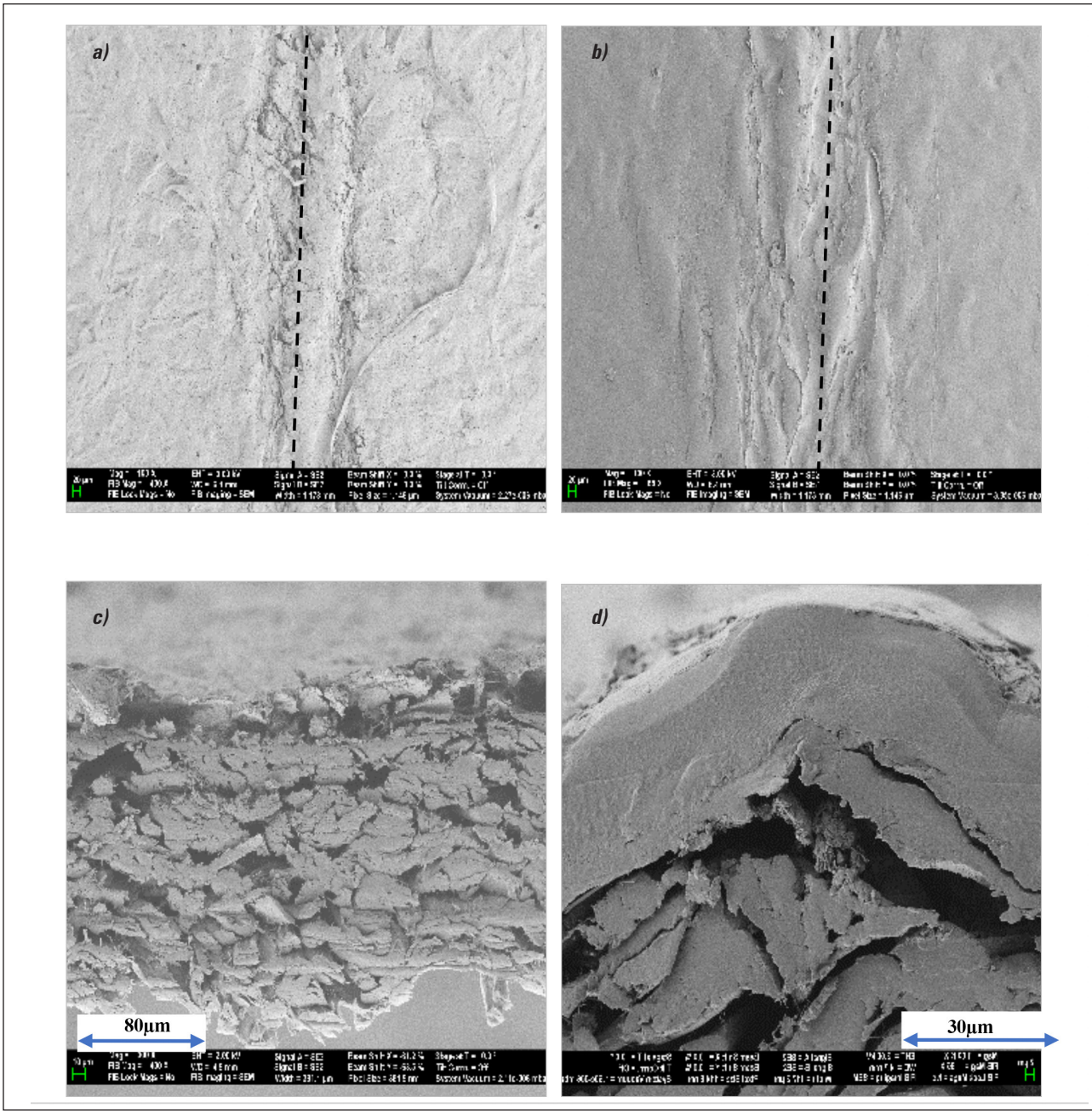



*8. Scanning electron microscope (SEM) images of CNF coated paper at 8 g/m² and 90% fines with a single fold (left images) and the same with a 16 g/m² barrier layer applied near a folding region. (a) Top surface with no barrier layer; (b) top surface with barrier layer near a fold; (c) cross section with no barrier layer at a fold; and (d) cross section with barrier layer at the fold. The fold line is indicated by a broken line. Arrows mark defects in the CNF layer away from the fold line.*

properties, just like the results of the oil and grease resistance in Table I. The increase in OTR is likely caused by defects generated along the fold lines, as shown in Fig. 1. This behavior may be acceptable for the packaging of some food items.

**Figure 8** shows the SEM images of the microstructure of the surfaces and cross section of the 8 g/m² CNF precoated paper with and without 16 g/m² barrier layer near a fold, both the top view and cross sections. For the samples without the barrier layer, away from the fold region, it was evident that there were defects in the CNF layer, marked with a few arrows in the image. Once the barrier layer was applied, there was no evidence of defects or a fibrous structure. The location of the fold was evident in the images, but wide cracks were not evident in the fold line for both samples. The cross sections showed that both the CNF layer and the barrier layer near the fold hold together and do not generate cracks. The images provide evidence for the mechanism depicted in Fig. 7.

For comparison, **Fig. 9** shows similar results for the




***9. Surface (a & b) and cross-sectional (c & d) SEM images of a pigmented precoated paper that has delaminated kaolin pigment with 40 pph latex (a & c), and the same sample coated with 16 g/m² of the barrier coating (b & d) near a fold that is marked by the broken line.***

pigmented precoated paper near a fold, along with the results when this sample was coated with the barrier coating. For the pigmented coating, fine pores were evident throughout the top surface of the coating and near the fold, where damage was clear. Once the barrier coating was applied, the fine pores away from the fold were not visible, but near the fold, cracks were still evident. In the cross section without the barrier layer, the pigmented coating layer was difficult to see. This may be caused by damage during cross sectioning, since the method to obtain the cross section was just simple cutting with a sharp blade. For the sample with the barrier layer, the layer was clear, and its thickness was close to what would be expected based on the coat weight. Damage was not evident in the barrier layer near the fold, but the sample had poor WVTR and OTR performance compared to samples that had the CNF as the precoating layer.

## CONCLUSION

The barrier properties of paper samples that had precoating layers of CNF or pigmented coatings with a top coating layer of a WBBC were evaluated before and after folding.

Both types of precoating layers caused the barrier coating to perform significantly better when evaluating water vapor transmission. Folding of these samples decreased the water vapor barrier properties by a limited amount. For paper with the CNF precoating layers and no barrier coating, the oil and grease resistance was measured as a Kit test value of 12, even after folding. The barrier coating interacted with the oil and grease test solutions, which limited the test results to a moderate level. Moderate oxygen barrier properties were found for the paper with the precoating layers of CNF. However, good oxygen barrier properties of less than 10 $cm^3/m^2$/day were found for the precoating layers of CNF with a barrier coating; the barrier coating healed defects in the CNF layer to generate good oxygen barrier properties. While these barrier properties decreased with folding, the oxygen barrier properties were still significant. **TJ**

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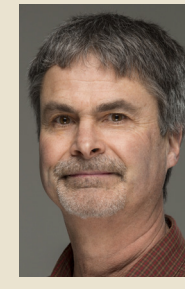
## ABOUT THE AUTHORS

We studied water-based barrier coating (WBBC) to improve the performance of paper-based packaging while displacing use of plastics. The research shows the clear benefits of using a cellulose nanofibrils (CNF) layer in terms of water vapor and oxygen transmission rates in packaging.

Mills may use this information to develop new packaging grades. Our next step is to apply the CNF layer at high speed.

*Pokharel is a graduate student and Bousfield is professor in the Department of Chemical and Biomedical Engineering at the University of Maine in Orono, ME, USA. Wu is scientist at the USDA Forest Products Laboratory in Madison, WI, USA. Email Bousfield at bousfld@maine.edu.*

***Pokharel***



***Bousfield***

***Wu***

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