Spring 5-5-2023

The Influence of Pre Coating Layers On Barrier Coatings

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Recommended Citation

Pokharel, Kritee, "The Influence of Pre Coating Layers On Barrier Coatings" (2023). *Electronic Theses and Dissertations*. 3771.
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THE INFLUENCE OF PRE-COATING LAYERS ON BARRIER COATINGS

By

Kritee Pokharel

B.S. Kathmandu University, Nepal, 2020

A THESIS

Submitted in Partial Fulfillment of the

Requirement of the degree of

Master of Science

(In Chemical Engineering)

The Graduate School

University of Maine

May 2023

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THE INFLUENCE OF PRE-COATING LAYERS ON BARRIER COATINGS

By Kritee Pokharel

Thesis Advisor: Dr. Douglas Bousfield and Dr. Jinwu Wang

An Abstract of THESIS Presented
In Partial Fulfillment of the Requirements for the
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ABSTRACT

Layers of 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 good understanding of the synergies between CNF, other coating layers, and water-borne barrier coatings (WBBC) is not clear. Different coat weights of a WBBC were applied to papers that have a range of different qualities and amounts of the CNF layer on them. The same WBBC was also applied to conventionally pigmented coated paper, with various types of pigments and latex levels. Samples are characterized in terms of grease resistance, water vapor transmission rate (WVTR), and oxygen transmission rate before and after folding. When WBBC is applied on a CNF layer, the WVTR improves by more than a factor of ten compared to when a WBBC is applied to the base paper with no CNF layer. Similar improvement is also seen when the WBBC is applied to the pigmented coating layer. Folding decreases, the moisture barrier performance to some degree, but not grease when CNF is used.

DEDICATION

- I would like to dedicate this thesis to my parents – Krishna Prasad Pokharel and Parbati Pokharel, who taught me the value of hard work and perseverance.

- I would like to dedicate this thesis to my sister and brother-in-law – Kripa Pokharel and Achyut Timilsina, who gave me strength and motivation to keep striving for excellence. It would not have been possible without them.

- And dedication to my mentors from Kathmandu University, Nepal whose guidance and support helped shape my academic and personal growth.

ACKNOWLEDGEMENT

I would like to express my gratitude to several individuals who have supported me throughout the course of this project.

First and foremost, I would like to thank my advisors Dr. Douglas Bousfield and Dr. Jinwu Wang for their guidance, expertise, and encouragement throughout the course of my thesis. Additionally, I appreciate their patience and commitment to helping me achieve my academic goals, and I am deeply grateful for their ongoing support. Their mentorship has had a significant impact on my academic career, and I am honored to have had the opportunity to work with such an exceptional advisor. I would also like to acknowledge the third member of my thesis committee, Dr. William J. DeSisto, I am grateful for his time and commitment, and willingness to serve on my committee and I appreciate his effort to ensure the success of my academic endeavors.

I would also like to extend my gratitude to Dr. Mehdi Tajvedi, Dr. Emma Perry, and Dr. Colleen Walker for permitting me to utilize their laboratory resources during my research. Their gracious assistance and readiness to offer access to equipment and materials have played a key role in the accomplishment of my work. Their expertise and advice were priceless.

Thank you to project sponsors Forest Product Laboratory, Madison MI, and Paper Science Surface Program (PSSP) at University of Maine. I would like to express my gratitude to the members of PPSP for generously dedicating their time to provide feedback that contributed to the development of this project. It was a pleasure to engage with such a highly motivated group of individuals who share admirable goals.

I am very thankful to my lab partners in Dr. Douglas Bousefield's group, namely Mubarak Khlewee, Chidubem Uchefuna, Aysan Najd Mazhar, Amenah Khalaf, and Bright Appiah. Their

invaluable assistance made working in the lab much more efficient and enjoyable. Their support and guidance were greatly appreciated, and I am grateful for their willingness to help in every possible way.

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1. INTRODUCTION

1.1.Background

Plastic packaging is a rapidly expanding market segment, which is especially true of flexible packaging. Plastic's growth is mostly attributable to its low price, ease of use, chemical resistance, processing capability, and transparency (Khosravi-Darani & Bucci, 2015); (Nurul Fazita, et al., 2016). Concerns about the world's environment have been sparked by the widespread adoption of plastic packaging (Greene & Tonjes, 2014). Glass, aluminum, tin, and fossil-derived synthetic plastics are currently used in packaging, which raises concerns from both an environmental and economic standpoint (Azerdo, et al., 2017). Most of these plastics can be recycled, but due to technological and economic barriers, this is not done routinely in many countries. (Anon., 2022) reports that the world today generates two times as much waste made of plastic as it did two decades ago, with the majority of this waste being dumped in landfills, burned, or released into the environment, and just 9% of this waste being properly recycled. 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.

These requirements are well met by paper-based packaging. 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 or laminating a metal foil or plastic film onto the paper surface (Mcculloch, et al., 2018). Barrier coatings are one of the approaches that is required to create paper-based systems that meet the packaging requirements as it could enhance the quality and shelf- life of the packaged product. 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 (Tyagi, et al., 2021). They are used to make cartons for frozen food, single-use items, packages for dry foods, and wrappings that don't stick to grease. They are also used in industrial wrappings, including copy paper. The coating layer of these papers provides protection against strong odors and prevents the leakage of harmful substances. Generally, the barrier properties of paper are regulated by using conventional petroleum-based materials like PVC (polyvinyl chloride), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene, polypropylene, polyethylene terephthalate (PET), and waxes. Apart from these, non-conventional coating materials such as lignin-based coatings, polyvinyl alcohol (PVA), alkene ketene dimer (AKD), and a combination of PVA and AKD are also utilized for regulating the barrier properties of paper. (Kuman, et al., 2022). However, these materials are less recyclable and might take more than 500 years for very slow biodegradation. Polyfluorinated materials (PFAS) are also extensively used to create paper coatings that provide superior resistance to water and oil. However, these coatings have been found to release toxic substances into the water during the repulping process, making them detrimental to the environment and are now discontinued. (Schaider, et al., 2017). Barrier dispersion coated papers are also eco-friendly since they are compostable and recyclable, making them a sustainable alternative to conventional coatings like polyethylene (Kimpimaki & Savolainen, 1997)

Water borne barrier coatings (WBBC) are viewed as a preferred method to obtain these barrier properties compared to extrusion coating, they can be applied at high speeds and lead to good recycling (Bollström, et al., 2013), (Vähä-Nissi, et al., 2006). WBBC have been the subject of extensive study in recent years, and it has been discovered that they can be used as alternatives to traditional barrier materials like polyethylene (PE), fluorochemicals, and waxes; however, they require a two-layer coating process and a specific coating technology (Miettien, et al., 2017).

Water-based barrier coatings face difficulties due to the possibility of pinholes and the incidence of blocking after manufacturing. Although barrier pigments enhance the barrier characteristics, the extent of improvement is frequently restricted and might not meet expectations (Al-Gharrawi, et al., 2022). The use of precoating layers to enhance the performance of barrier coatings has been highly studied and reported in the literature. Using biodegradable materials for pre coatings is becoming an increasingly popular choice due to their environmental benefits. Biodegradable materials such as chitosan, alginate and cellulose nanofibrils derived from natural resources such as shellfish, seaweed and plant fibers respectively show a potential characteristic of a barrier layer. (Kopacic, et al., 2018) shows that uncoated paper having a WVTR of 690 g/m^2 × 24 h was decreased by more than 60% when coated with chitosan and alginate. Such materials are not only sustainable but also biocompatible and biodegradable, which can be broken down by microorganisms into the environment. Along with that they can also improve the moisture, oxygen, and grease barrier properties of paper (Wang, et al., 2018) (Hamadi, et al., 2020). Most packaging materials used today are made from fossil-derived plastics. Even fiber-based packaging solutions typically include one or more layers of synthetic polymers to achieve the necessary barrier properties of the package (Rodionova, et al., 2012).

Cellulose can be found in a wide range of organisms, from plants and animals to fungi and bacteria, making it the most common renewable natural biopolymer on Earth. As the primary component of plant structures, it is garnering attention as a potential renewable chemical resource to displace petroleum-based products. (Abdul Khalil, et al., 2014). Cellulose nanofibers (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 (Oksman, et al., 2016). These layers have attracted considerable attention because of their affordability, potential for recycling with paper, capability to sequester carbon when disposed of in a landfill, and biodegradability in the environment (Moon, et al., 2011) (Moon, et al., 2016). CNF represents an additional category of biodegradable polymers that are applicable for coating paper. Recently, layers of CNF have emerged as pathway to forming paper-based system that has good oxygen and grease barrier performance and also were found to retain their barrier properties even after folding (Ferrer, et al., 2017), (Österberg, et al., 2013), (Fein, et al., 2021). Several additional studies (Aulin, et al., 2010); (Syverud & Stenius, 2008) have demonstrated that CNF may be successfully used as a barrier in paper coating or as a single monolayer. By applying a coating weight of 10 g/m^2 CNF to paper, the resulting product can effectively achieve the required level of water and oxygen barrier (Yook, et al., 2020). A review of the water and oxygen barrier properties of CNF films have been conducted by (Lavoine, et al., 2012), (Wang, et al., 2018), and (Nair, et al., 2019). (Wang, et al., 2018) found that CNF films can offer oxygen barrier capabilities up to 100 times better than standard polymers, such as polyethylene (PE). On the other hand, compared to standard polymer films like PE, the water vapor barrier properties of CNF films are relatively poor.

While CNF films have many desirable qualities and can mask even the largest pores when applied on paper surfaces, the films themselves may be highly porous (Henriksson, et al., 2007); (Henriksson, et al., 2008). (Kumar, et al., 2014) compared various kinds of CNF layers on 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). Increasing the barrier properties of CNF could greatly expand its applications in packaging industry (Fein, 2020). CNF working as a monolayer may have some limitation, but it shows that their barrier properties can be extensively improved once CNF is used as a precoating layer in a multilayer packaging. CNF layers were found to improve the performance of a barrier coating (Kumar, et al., 2014); the exact mechanism for this was not clear out but may be linked to the CNF layer holding the barrier coating in a continuous layer.

1.2.Current Packaging status and its limitations

There are certain specifications required for food packaging, they must have proper barrier properties, heat sealing, convenient storage and disposal, and appealing appearance for effective communication of the product information. The right packaging materials should maintain the quality, freshness, and safety of food product while also being cost effective. Packaging applications often rely on polymer materials sourced from petroleum, including polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyamide (PA), due to their superior mechanical properties, widespread availability, and affordability. These synthetic polymers exhibit excellent performance characteristics such as high tensile and tearing strengths, toughness, and heat-sealing ability. They also offer effective barrier properties against water, oxygen, carbon dioxide, aromas, and anhydrides. (Siracusa, et al., 2008). Other material commonly used for packaging is glass, usually used for packaging food and beverage items, because of its transparency and durability making it an ideal material for displaying contents but as it is heavy and fragile, it is difficult to transport and increases the risk of breakage during shipping (Wang, et al., 2018) (Fein, 2020). Aluminum foil and metallized coatings offer exceptional protection properties due to their metallic crystalline structures and low porosity. Nevertheless, these packaging materials pose recycling challenges and do not biodegrade, leading to environmental concerns. Additionally, the production of materials like aluminum generates a significant environmental impact. (Wang, et al., 2018).

Biopolymer also has gotten a lot of attention as a sustainable alternative to traditional plastics made from petroleum. This is because they biodegrade, can be made from biological sources, and have a smaller carbon footprint. The utilization of biopolymers in packaging is an area of high interest; however, these materials can pose certain difficulties. To provide a general overview of biologically sourced materials and biopolymers used in packaging, (Johansson, et al., 2012) and (Rastogi & Samyn, 2015) have conducted reviews. 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 (polyhydroxyalkanoates (PHA) and polylactic acid (PLA)) (Rastogi

& Samyn, 2015). 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., 2006). This low HDT restricts the processing conditions of the material and can render it unsuitable for certain applications. PLA also has great potential for long-term food packaging applications considering it is difficult for a high molecular weight PLA to be contaminated with fungi or mold even when placed in high humidity conditions, but its non-biodegradable nature makes it an unsuitable substitute for plastic packaging. PLA does not decompose easily in natural environments and necessitates specialized composting facilities for proper disposal. (Gross & Karla, 2002)

Making food safer and better is important for consumers, so we need packaging that protects it from different external factors. These factor include microbes, water vapor, oxygen, light, mechanical contaminants, and other elements that can potentially impact the properties of the product. (Wroblewska Krepsztul, et al., 2018) (Sydow & Bienczak, 2019). Despite the potential benefits of bio-based packaging materials, their widespread use in the food industry is limited due to their inferior properties in most cases. (Pan, et al., 2016). Cellulose-based packaging materials could serve as a viable alternative if they can be directly recycled into the paper-making process (Fein, 2020). In the area of waterborne barrier coatings, many studies have focused on the use of natural polymers, such as starch, pectin, and xylan. These natural polymers are typically used for oxygen barrier and oil and grease barrier applications. However, it should be noted that aluminum sets a high bar for oxygen barrier performance in most applications where true oxygen barrier is required (Zhao, et al., 2008), (Grondahl, et al., 2004) , (Vartiainen, et al., 2010). Several methods have been developed in recent years to permit the use of aqueous barrier coatings on paper and board. Nonetheless, the market for aqueous barrier paper remains a small section of the overall barrier coating market for paper and paperboard. Extruded polyethylene (PE), fluoropolymers, and aluminum foil are the principal barrier materials used in the paper industry (Vyorykka, et al., 2011).

1.3.Motivation and Hypothesis

Plastics have been considered the "bricks" that make up the "foundation" of the modern world. Single-use packaging makes up about half of the plastic waste we produce globally, and these plastics are not easy to recycle (Arvanitoyannis & Bosnea, 2001). The expanding use of single-use plastics in developing nations contributes to a larger waste challenge. (Mari Williams, 2019). Many plastics cannot be broken down in landfills or incinerators, so they add to global warming by releasing greenhouse gases.

The motivation of this study is driven by the increasing demand for sustainable packaging material that can effectively protect food products and preserve their freshness. Barrier coatings on paper can provide an alternative to traditional plastic packaging, but they must be able to provide adequate barrier to moisture, gases, and other contaminants. (Anon., n.d.) in his recent paper discusses that the performance of water-based barrier coating layers can be improved by adding the CNF layer to the paper. This is because the presence of CNF appears to obstruct the penetration of the paper structure by the barrier coating, resulting in a continuous layer of the waterborne coating.

This study utilizes Water Based Barrier Coatings (WBBC), a type of new generation dispersion coatings that incorporate biomaterials. These coatings combine knowledge and expertise in polymer dispersion chemistry and specialized pigment development. The hypothesis of this study is a way to improve the barrier properties of a paper is by incorporating pre coated layers, such as CNF or mixture of clay and latex, as they can form a homogenous coating on the paper surface that will hold the barrier layer keeping its barrier properties consistent.

1.4.Objective

The objective is to substitute conventional snack packaging, including those used for potato chips and candy, with eco-friendly cellulose-based packaging that is both recyclable and biodegradable, reducing the environmental impact if discarded improperly. Further this study is done to comprehend the synergies between various pre-coating layers applied to a barrier layer. Layers of 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 (Al-Gharrawi, 2021).

The potential to produce paper grades that have good oxygen, grease, and moisture barrier properties is clear, but a good understanding of the synergies between CNF, other coating layers, and water-borne barrier coatings (WBBC) is not clear. This study also explores the comparison on the performance of barrier layer with CNF pre coated paper to that with conventionally available pigment coated paper, in terms of their barrier properties, mechanical strength and uniformity. Along with that this study will help to provide insights and recommendations for the design and development of improved packaging materials with enhanced barrier properties.

2. METHODS AND MATERIALS

2.1.Materials

CNF films applied on a paper were made at Process Development Center at University of Maine. The paper is 80g/m^2 basis weight and has a top layer of CNF films with different coat weights (4g/m^2, 8g/m^2 and, 12g/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 to break down the wood fibers. The wood fibers were bleached softwood Kraft pulp. The suspensions were obtained at around 3.5% solid. The solid was increased up to 15% by using a filtration process.

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 lower 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, please refer to (Johnson, et al., 2019)

Three different types of Kaolin clay from IMERYS were used in this work named Capim RG (Platy Kaolin) is a coarse, high-brightness, high aspect ratio coating kaolin and has a long and thin particle size that ranges from 2-10μ, Capim DG (Fine Kaolin) has a high brightness and steep particle size distribution combine to provide optimum brightness and opacity. It consists of a small spherical particle around 2μ and has a low aspect ratio, Capim NP (Delaminated Kaolin) is a delaminated high brightness kaolin clay having a long and thin plate like structure with a particle size of around 2-10μ as a pre coated layer. The low level of ultrafine particles and low surface area of Capim^{TM} clay improve coating strength enabling the binder reduction compared to fine glossing kaolin or giving improved glue ability in board and packaging applications. Styrene Butadiene latex from Synthomer was used with kaolin clay as a binder because of its elastic nature exhibiting excellent stretch and recovery properties, it is also highly adhesive with solid content of 50 wt.% and have a transition temperature of approximately 55°C.

For barrier coating, we used Joncryl HPB 4030 from BASF. This is an RC Acrylic emulsion that is water resistant, heat seal ability binder for replacing extruded wax or polyethylene coatings on paper substrate for cups, boxes, and other types of food packaging. According to the Fiber Box Association (FBA) voluntary standard for corrugated boxes, internal lab testing, and third-party industrial testing it has been confirmed that Joncryl HPB 4030 can be used to create repulp able and recyclable packaging. It is a translucent emulsion of 1.08 g/cm3 density at 25 °C and has a 54 wt.% solid content.

2.2.Methods

The effectiveness of a barrier coating depends on the coating device's ability to apply the coating, distribute the dispersion throughout the web, measure the coating's effectiveness, and dry the coating. Instead of striving for a perfectly smooth surface, dispersion coatings instead aim for uniform coating thickness. This is because, from a barrier point of view, a coating that is even can be better than one that is layered on top of hills of fiber networks and is thinner. Research has shown that blade coaters consistently produce uniform coatings and surfaces (Kimpimaki, et al., 1998). A laboratory bench-size automatic rod coater (model 21001, BYC Gardner USA) equipped with standard Mayer rods was used to perform the coating process as shown in the figure.1 (Alessandro, 2020-2021). Varying rod sizes and pressures were utilized to achieve different levels of coating. For achieving low coat weight, rod size and pressure knobs of 3 and 6.5 were used, while for moderate coat weight, #5 and #7 were utilized. For high coat weights, #7 and #7.5 were used. The speed of the coater was set at a fixed rate of 6.1 m/min.

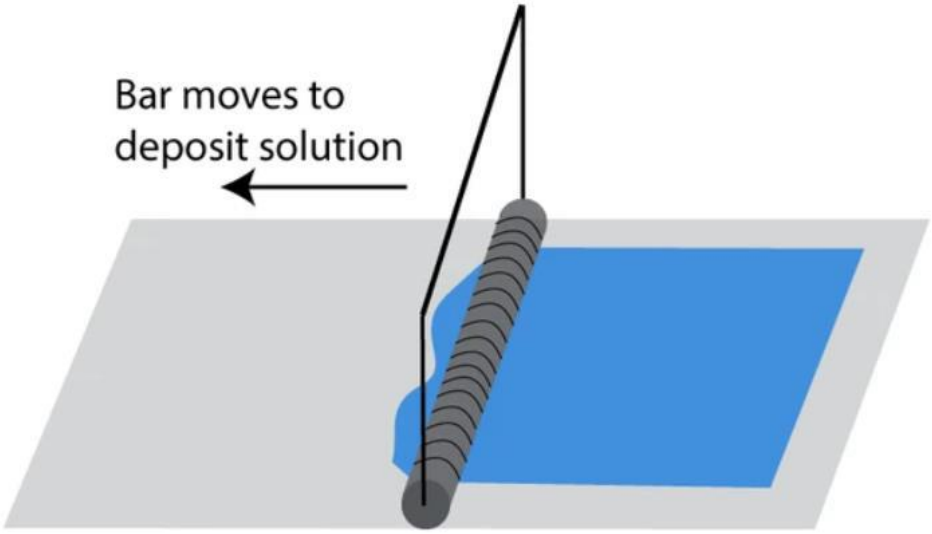


Figure 1: Rod coating method

2.2.1. Cellulose Nanofiber as a precoated layer

The base paper used has a basis weight of 60 to 120 g/m^2 and a CNF top film varies in the coat weight of 4, 8, and 12 g/m^2. The CNF used in this study was made from softwood Kraft pulp that had been bleached. A fiber size analyzer (MorFI, Techpap Inc.) was used to measure the fine content of the suspension, which was found to be between 70% and 90%. The fineness of CNF refers to the diameter or width of the individual fibers, the higher the fineness, the smaller the diameter. The fines content here is a measure of the quality of the CNF, and lower fines content reflects less energy and more large cellulose fibers. The typical material produced at UMaine is 90% fine.

Water Based Barrier Coating (WBBC) were applied on CNF side of the paper. Varying coat weight ranging from small, medium to high were applied with the help of different rod sizes. The coat weight is determined by measuring the weight change after coating the paper. The coating here is dried at 60°C as suggested by the company for 10mins in order to get the best results.

2.2.2. Conventional pigment coating as a base layer

The base paper used here has a basis weight of 80g/m^2, produced in Process Development Center of University of Maine. The base sheet was an 80:20 hardwood: softwood blend. Three different types of kaolin clay (Delaminated Kaolin, Platy Kaolin, and Fine Kaolin) were used, and Styrene Butadiene (SB) latex was added at the ratio of 20pph and 40pph along with distilled water and mixed for an hour with a mechanical stirrer then letting it sit for another hour at room temperature to achieve 60 wt.% solids of the mixture before applying as a coat. The pigment-latex mixture was applied to the base paper using a draw-down coater and dried at 105 °C for 9–10 min. For the water-based barrier coating on the paper, an acrylic emulsion was used, which had a 54% solid weight. The barrier coatings were applied as lower, medium, and high coat weights on the paper.

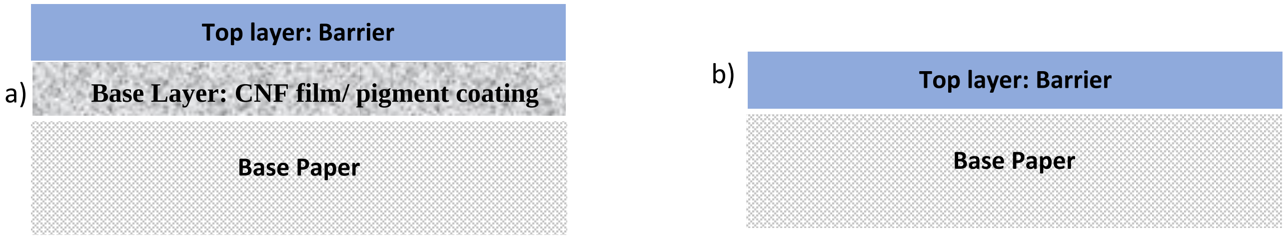


Figure 2: Schematic diagram of coated paper sample (a) showing the base paper is coated with CNF/ pigment layer as Base Layer and further coated with barrier layer as Top Layer on it, coated paper sample (b) showing the base paper is coated with barrier layer as a top layer on it.

The water vapor barrier property of the coating for both the above samples was measured according to ASTM 96/E96M-16. In a controlled temperature and humidity room (23 °C and 50% relative humidity), glass jars were filled up with 25mL of distilled water, to ensure proper seal ability of the sample to the jar silicon grease from (DOW CORNING) was applied on the edge of the mason glass jar (Rubbermaid Incorporated, GA, USA) and closed by the sample of interest that was cut in a circular shape with diameter of 65mm as the lid. Then, the sample were 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, after 24 hours the weight of the jar was recorded again, to avoid any initial changes due to humidity conditions. The difference of the weight before and after conditioning (Δmass) denotes the amount of water vapor transmitted through the film. The water vapor transmission rate can be calculated using,

$$WVTR\ (\frac{g}{m^2.day}) = \frac{\Delta mass}{\pi.r^2.day} \tag{2.1}$$

Where, r indicates the radius of the sample. The test was replicated at least three times at least on each coat weight of the sample. The results are expressed in gm/m^2/day.

The grease barrier properties of samples were evaluated using the TAPPI method (T559 cm-09), which is based on twelve 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 solution with the lowest surface energy, viscosity, and contact angle on the sample paper surface is solution number one, while solution number twelve 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 seconds, 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 with an OX-TRAN 2/22 OTR Analyzer (MOCON, MN). The film was placed in a designated cell and conditioned for 6 hours with a carrier gas mixture of 96% N_2 and 4% H_2 containing water vapor to make the relative humidity at 50%. The testing area of each film was 5.64 cm2. The test was terminated when the difference between the last measurement and the one from 5 cycles before was less than 1%. Oxygen permeability value was obtained by multiplying the OTR value by the thickness. The results are expressed in cc^3/m^2/day. To observe the surface and cross section of the coated sample a tabletop Scanning Electron Microscope (SEM) (TM 3000, Hitachi High-Technologies Corporation, Tokyo, Japan) was used.

2.3.Crack resistance Test

For crack resistance test, the samples were folded as six orthogonal and evenly spaced folding lines were made on each coated sample corresponding to length of 6 and 7 cm as shown in Figure3. Six folding lines were made at the same time with coating placed inwards to the fold to maximize the potential crack damage. For each fold, the paper manually was folded at 180 deg and the 4200 Pa pressure was applied for five minutes to create a fold. (Yaping, et al., 2019)

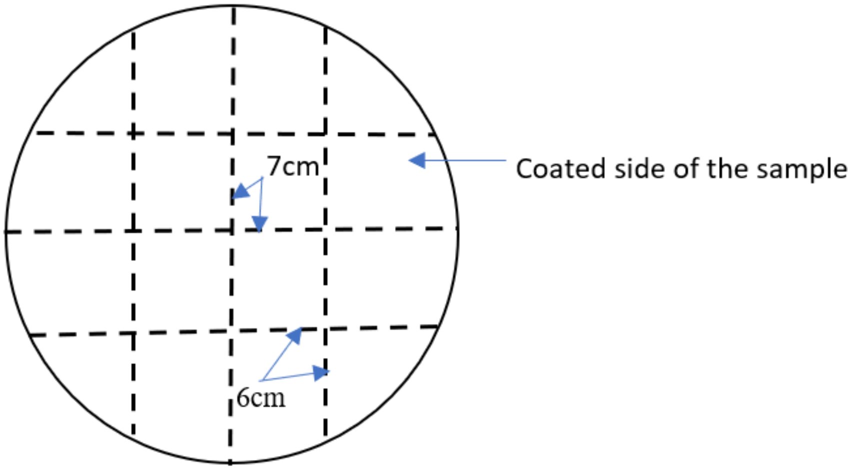


Figure 3: Schematic of orthogonal folds made in a coated sample. The arrow indicates the length of folded lines.

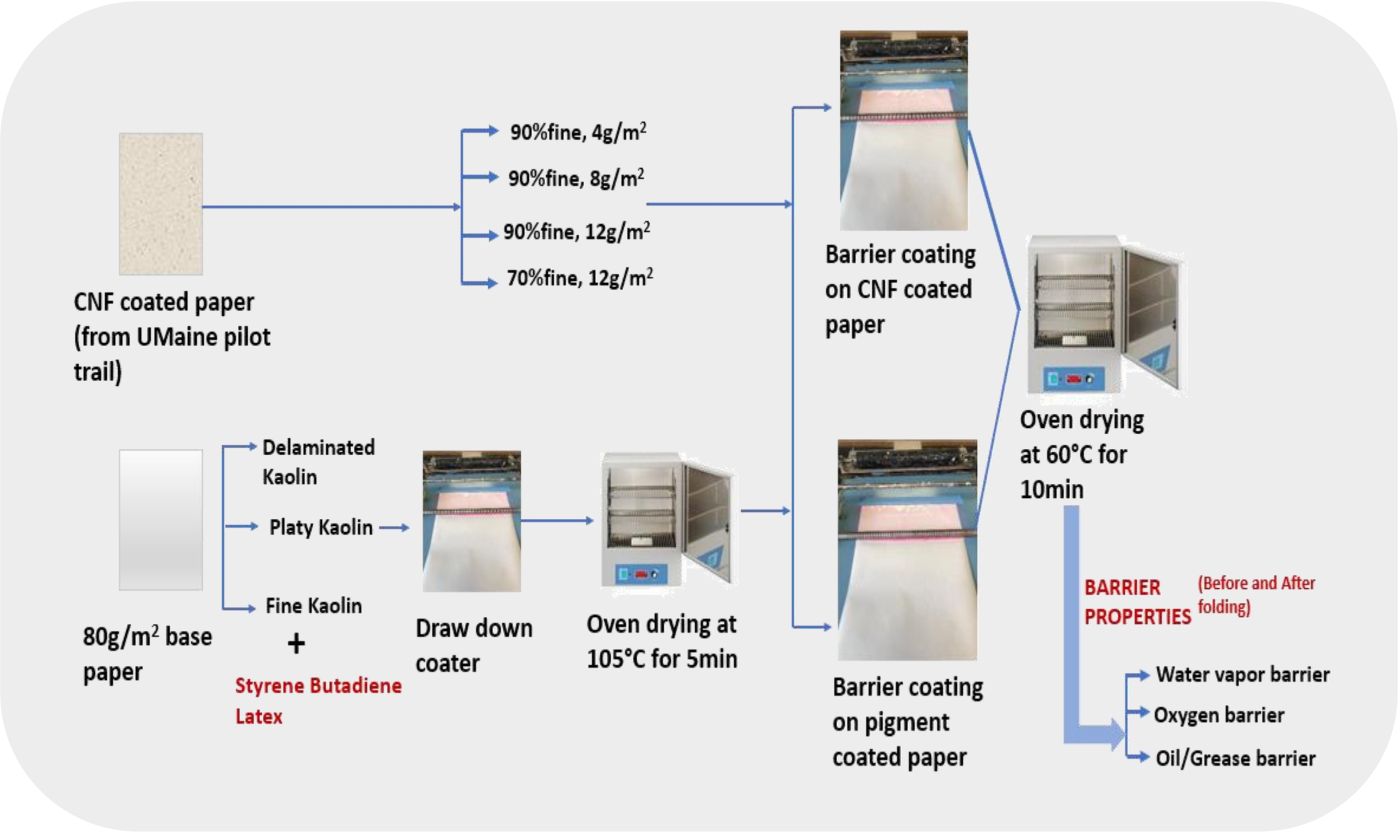


Figure 4: Schematic diagram of coating process for different sample preparation

3. THEORY

Assuming Fick's law and steady-state conditions for water vapor transmission through paper and coatings, we can write the following equation to predict the total flux of water vapor or the WVTR for two layers:

$$\boldsymbol{WVTR = \frac{M_W(C_i - C_f)}{(\frac{H_P}{D_P} + \frac{H_C}{D_C})}} \tag{3.1}$$

where, MW is the molecular weight of water, C_i and C_f 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, D_P and D_C are the effective diffusion coefficient of the paper and the coating respectively. The partition coefficient of water and polymer is assumed to be constant and becomes included with the diffusion coefficient. Eqn (3.1) predicts the same behavior where the coating thickness is the sum of the coating layer thickness and the precoated paper layer are considered as a single layer. Using the vapor pressure of water at room temperature, the concentration of water vapor inside the jar is 1.1 mole/m^3. The 50% relative humidity would have a concentration of half of this value outside of the jar. The WVTR of the uncoated paper is around 400 g/m^2/day. The thickness of the paper was 0.098 mm. This thickness gives a diffusion coefficient for the paper of 4×10^{-8} m^2/s. The experiments involve the use of various coat weights, and Eq. (3.1) is employed to analyze the data by tuning the diffusion coefficient of the coating layer D_C to minimize the root mean square error. The gravimetric measurement of the coat weight of each sample is used to determine the coating thickness, which is then applied in Eq. (3.1).

4. RESULTS AND DISCUSSIONS

4.1.Water Vapor Transmission Rate (WVTR) with different pre coating layer

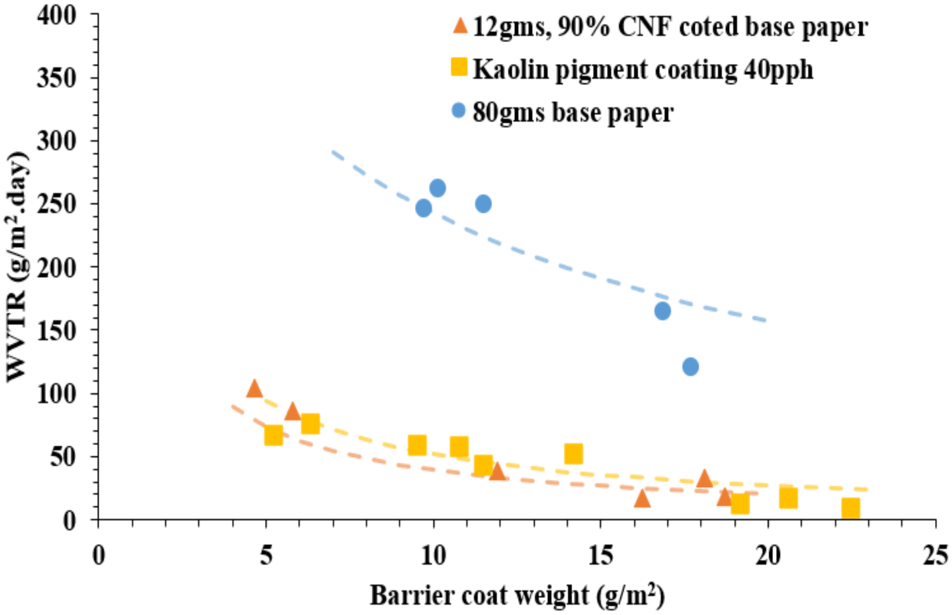


Figure 5: Water Vapor Transmission Rate as a function of barrier coat weight on different pre coat layer; paper coated with 12g/m^2 CNF coated paper, on a paper coated with 16g/m^2 pigment coating that has 40pph SB latex with delaminated kaolin and applied on a base paper. Line is the fit of equation 3.1.

The ability of a coating to act as a barrier against water vapor depends on various factors, such as the substrate's surface properties, film formation properties, and coating technique. A minimum coat weight of 3-5 g/m^2 is necessary to achieve satisfactory barrier properties against both water vapor permeation and absorption. Additionally, a 10 g/m^2 pinhole-free dispersion coating provides the same level of barrier protection as a 10 g/m^2 polyethylene film in terms of water vapor transmission rate (WVTR) properties. (Vaha-Nissi, et al., 1997) When it comes to improving the performance of barrier coatings, precoating layers such as pigment coating or CNF films can make a significant difference. These pre coating layer can help hold the barrier material into a uniform layer, which is a key factor in achieving optimal barrier properties. As we can see the WVTR on the paper with the barrier layer decreases by over a factor of 2 in the presence of pre coated layer. Figure 5 compares the WVTR between barrier coatings on 12 g/m^2 CNF coated paper with 90% fines, barrier coatings on delaminated kaolin coated paper at 40 pph, and barrier coating on a regular base paper (80 g/m^2). Even in a low coat weight CNF film, the pigmented layer makes the WBBC more effective. For example at around 10 g/m^2, we see the WVTR come down from around 200 g/m^2/day to 30 g/m^2/day and 60 g/m^2/day, respectively, for the CNF and pigment layers. Similar results were seen in the work donw by (Al-Gharrawi, et al., 2022)where he had sandwiched the paper with CNF layer between the barrier coatings on both sides of the sample.

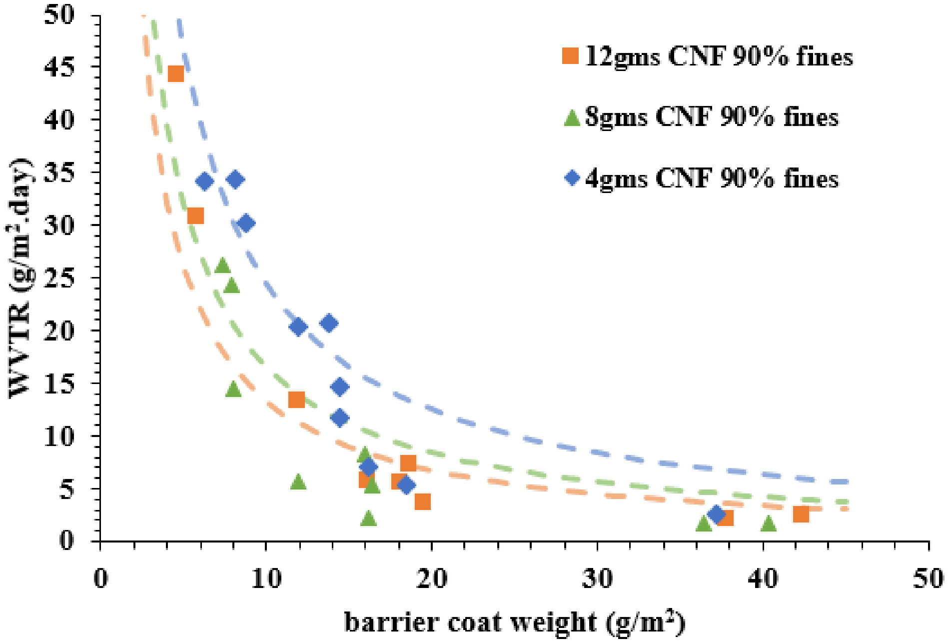


Figure 6: The influence of the thickness of the CNF film as a pre coated layer to different coat weights of barrier layer performance. Lines are fit of Eq. 3.1

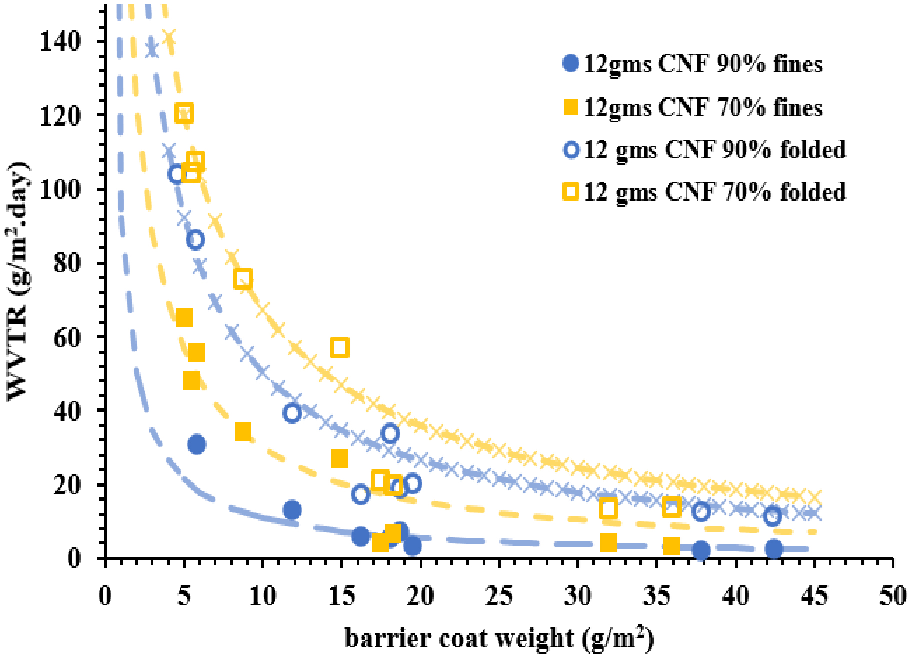


Figure 7: The influence of quality of CNF as a pre coated layer to different coat weights of barrier layer performance and its result after six orthogonal folds in the sample is shown. Lines are fit of Eq. 3.1.

As a hydrophilic substance, CNF has a high affinity for water and cannot solely work as a barrier to water vapor transmission; its barrier qualities also depend on factors such as the coat weight and quality of the CNF employed. Figure 4 compares different coats of 90% fines CNF as a pre coating layer used, as expected when the coat weight increases the WVTR decreases. The data exhibits a scattered pattern that is likely attributed to multiple factors. The scatter may result from various sources, including random incidents of coating defects, fine defects within the CNF layer, and problems with the sample's sealing against the glass jar. Although significant efforts have been made to reduce this scatter, there may still be unforeseeable events occurring in the film that contribute to the wide range of scatter. The lines in the figure represent the fit of Eq. (3.1) to the data by varying D_C to minimize errors. Although, in some instances, the data may not strictly adhere to Eq. (3.1), this method provides a means of capturing the overall results of the examined coatings. Although, the quantity of CNF film used show some difference in the WVTR, but even in lowest level of CNF ($4g/m^2$) with $11g/m^2$ of water-based barrier coating gives a WVTR of 20 g/m^2/day, which is still lower than many different commercial packaging requirements (Wang, et al., 2018). In figure 5 shows different quality of CNF used, two different fine quality of CNF 70% and 90% having the same 12g/m^2 coat weight were used as a pre coating layer for different barrier coatings. Lower coat weight of barrier coating does show some difference in WVTR according to the quality of CNF used. However, when the thickness of barrier layer is increased from 15 g/m^2 we can see similar results. Another factor to keep in mind would be the impact of folding shown, when compared to the folded sample, it was seen that the WVTR went up when the coated paper sample was folded, this increase in WVTR suggests that folding the paper sample has an impact on the properties of the coating, which in turn affects its ability to resist water vapor transmission. One possible explanation for this increase in WVTR is that folding the paper sample causes mechanical stress on the coating, which can result in cracks or defects that allow more water vapor to pass through. Additionally, folding can cause changes in the microstructure of the paper and coating layers, which can also affect their ability to resist water vapor transmission. These results have important implications for the development of coated paper products that need to maintain their barrier properties even after folding.

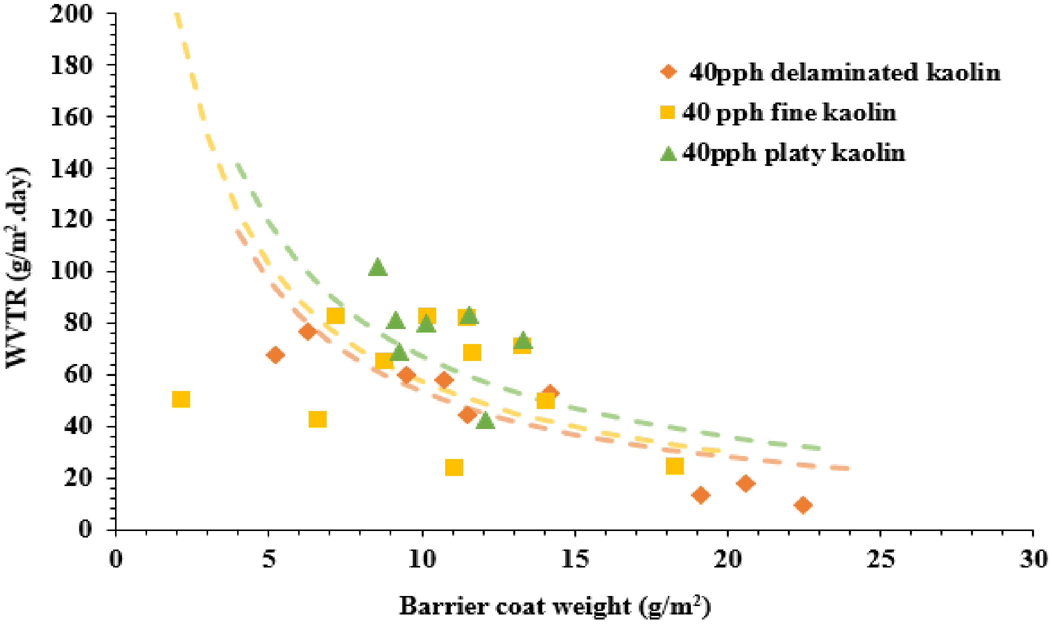


Figure 8: WVTR as a function of barrier coat weight, influence of different types of 40pph kaolin clay mixture used as a base layer at 20g/m^2 to different coat weights of barrier layer performance. Lines are fit to eq. 3.1.

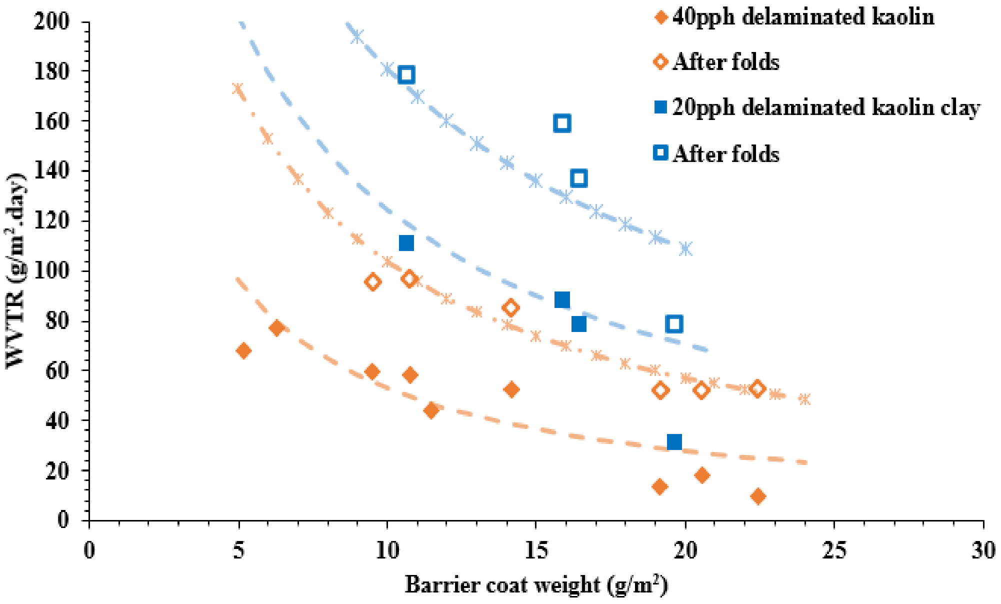


Figure 9: WVTR as a function of barrier coat weight, on different concentration of pigment: latex ratio of delaminated kaolin clay used as a pre coating layer to different coat weights of barrier layer performance at 20g/m^2 on WBBC performance and its results after six orthogonal folds are shown. Lines are fit to eq. 3.1.

Using pigment coating as a base layer, three different types of kaolin clay pigment were mixed with a binder namely styrene butadiene later (SB latex) at different pigment volume concentrations. On figure 6 we can see WVTR values being compared as a function of barrier coat weight. The three different types of pigment used show little to no effect at all when it comes to the water vapor transmission rate, although they have different particle size respectively, it is possible that these factors offset any differences in permeability. When the binder level in a coating is higher than the critical pigment volume ratio (CPVR) of 20 parts per hundred (pph), it indicates the presence of many pores in the coating, which results in higher moisture permeability. Conversely, a binder level of 40 pph is lower than the CPVR, leading to a continuous 3D matrix of binder with pigment filler and a reduced water vapor transmission rate, assuming there are no entrained air pores. Figure 4(b) also indicates a slight increase in the water vapor transmission rate after folding, as observed from the increase in WVTR relative to the unfolded sample. For coat weights ranging from 5 to 25 g/m^2, all folded samples exhibit an increase in WVTR of at least 1.5 times.

4.2. Oil and Grease Barrier properties (OGR) with different pre coating layer

The KIT test (T559), which is a TAPPI method, was employed to assess the grease resistance of coatings. To conduct this test, a range of 12 different sample mixtures containing varying ratios of n-heptane, castor oil, and toluene were used. The samples were labeled from 1 to 12, with the highest value indicating the most aggressive grease. To assess the degree of grease penetration, grease was applied to the coating surface using a dropper and then wiped away after 15 seconds. Any samples that appeared translucent indicated that grease had penetrated the sample. After wiping away the grease, the sample was flipped to the uncoated side to see if there were any changes in translucence. The KIT rating was determined by identifying the highest sample number that successfully resisted grease penetration. Additionally, the grease resistance of the folded WVTR samples was evaluated to determine if there were any changes in barrier properties.

The results of the oil and grease barrier test presented in table I shed light on several important aspects related to the grease resistance of coatings. For instance, the impact of the quantity of CNF films applied to paper was examined, and it was found that increasing the quantity led to an improvement in grease resistance, 4 g/m^2 of CNF coated on a paper gives us the KIT value of 1. However, when the test was done on the surface of 12g/m^2 CNF coated paper we could see the KIT number 12. After the barrier is coated on top of the CNF paper, the KIT test appears to be "7" for all the samples, and we could see the barrier layer getting dissolved once we increased the test number from “7”. Furthermore, it was demonstrated that the type of pigment used in the coating has a significant effect on the grease resistance of the resulting layer. This underscores the importance of careful selection of pigments when developing coatings intended to provide resistance against grease and oil. Additionally, it highlights the critical role of the pigment-to-latex ratio in determining the performance of the coating. It was observed that an increase in the latex content resulted in better binding of the pigment and the formation of a more coherent layer, which led to improved grease resistance. However, it is important to note that the folding of coated samples can have a significant impact on the grease resistance, as observed in the test results. Therefore, further research is needed to explore the effects of other factors such as temperature, humidity, and time on the grease resistance of coatings and to develop coatings that provide superior resistance against different types of grease and oil. Overall, the findings presented in this study contribute to the ongoing efforts to develop coatings with enhanced performance and durability in a wide range of applications. OGR did seem to vary depending on the quality and quantity of CNF used as well as the PVC of pigment-to-latex coated on a paper. However, the WBBC on top of these sample doesn’t seem to be affected by its pre coated layer giving us the intact kit number “7”.

Table 1:TAPPI 559 Repellency of Paper and Board to Grease, Oil and Waxes (KIT test) test values for different CNF films and pigment coated sample as a base layer with barrier coatings on it.

Sample base	Barrier coat weight (g/m^2)	Grease barrier test (KIT number)	Grease barrier test after folding (KIT number)
Base paper, 80 g/m^2	0	<1	<1
	10	7	7
90% fines CNF film on paper, 12 g/m^2	0	11-12	11-12
	6	7	7
70% fines CNF film on paper, 12 g/m^2	0	10	10
	5	7	7
90% fines CNF films on paper, 8g/m^2	0	4	4
	6	6-7	6-7
90% fines CNF film on paper, 4g/m^2	0	<1	<1
	7	7	7
Pigment coated paper (40pph delaminated kaolin), 12 g/m^2	0	7	<1
	9	7	<1

4.3.Oxygen Transmission Rate (OTR) properties with different pre coating layers.

In general, it can be stated that CNF films itself demonstrate a commendable capacity to act as oxygen barriers when in a desiccated state and exhibit favorable performance when the relative humidity level is maintained below 65%, as CNF films tend to absorb moisture due to their hydrophilic structure, which can cause swelling of fibers. (Wang, et al., 2018). The oxygen transmission rate of the different samples was measured at 23°C and 50% relative humidity following ASTM D3985-17 standard. Before the test starts, the samples are conditioned inside the machine for 6 hours at the given temperature and humidity. To measure the Oxygen Transmission Rate (OTR), an Mocon Ox-Tran 2/22 OTR analyzer was utilized. After the conditioning process, the analyzer underwent a "rezero" process, which involved purging the sensor and film with a mixture of 98% N_2 and 2% H_2 for 15 minutes. The OTR value was then recorded after exposing the film to 100% oxygen transmission for 15 minutes. The re zero process was repeated after every two tests, and the testing cycle was continued until the OTR values from the last five measurements differed by less than 1%.

As shown in Table 2 the barrier layer itself does not have a great resistance to gas when coated on a base paper. However, when we use a CNF pre coated layer and apply barrier coating on top of it, the transmission results dramatically decrease to 5 cc/m^2/day from 1026 cc/m^2/day, the different quality of CNF used a as pre coating layer did not show any difference in the results. The decrease in OTR could be due to a synergistic effect between the CNF and barrier layers. When the two layers are combined, the CNF may provide a surface for the barrier layer to adhere to, resulting in a more effective barrier. The CNF layer may also serve as a filler, reducing the size of defects or discontinuities in the barrier layer and thus improving performance. In Table 3, folding the samples showed only twice the increase in the results compared to unfolded samples, this could be the result of CNF and barrier layer tightly bounding to the substrate as we can see in fig 10 (c) and (d), giving us more robust coating that was better able to resist cracking and breaking.

The results appear to be similar to those obtained with uncoated base paper, suggesting that the pigment-coated samples lack resistance to oxygen transfer. Figure 11(c) and (d) indicate that, in contrast to the CNF layer shown previously, the pigment coating is less homogeneous, making for a less stable pre-layer for the barrier layer to adhere to.

Table 2: Oxygen Transmission Rate values of different samples according to the ASTM D3985-17 method with a Mocon Ox-Tran 2/22 oxygen permeation analyzer at 50% relative humidity and 23°C, the mixture of 98% N_2 and 2% H_2 as a carrier gas at 24 psig and O_2 at 23.6 psig.

Sample base	Barrier coat weights (g/m^2)	OTR ($cc/m^2/day$)
Base paper (80 g/m^2)	0	>2000
	15	1026
90% fines CNF film on a paper, 8 g/m^2	0	>2000
	15	5
90 % fines CNF film on a paper, 12 g/m^2	0	1457
	20	4
Pigment coated paper (40pph delaminated kaolin), 23 g/m^2	0	>2000
	16	1078

Table 3: Showing the difference between the value of Oxygen Transmission Rate before and after folding.

Sample base	Barrier coatings (g/m^2)	OTR ($cc/m^2/day$)	OTR ($cc/m^2/day$) After folding
90% fines CNF film on a paper, 8 g/m^2	15	5	23
90 % fines CNF film on a paper, 12 g/m^2	20	4	15

4.4.Scanning Electron Microscopy (SEM) Analysis of pre coating layer

To analyze the microstructure and surface morphology of a coated paper a comprehensive understanding of SEM image is required. It allows higher magnification and resolution of paper's surface, providing detailed information about the coating and any defects or irregularities in the layer.

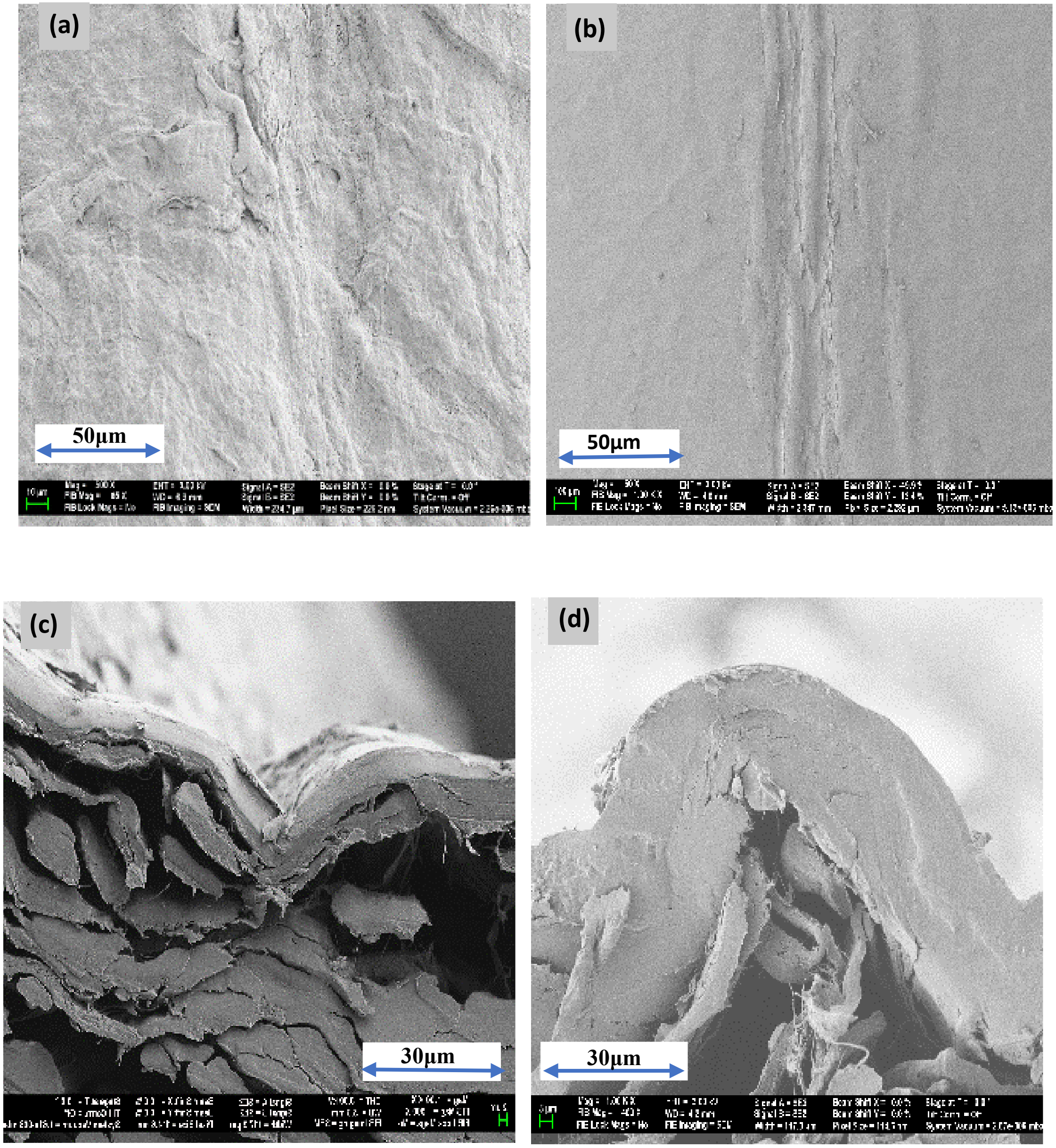
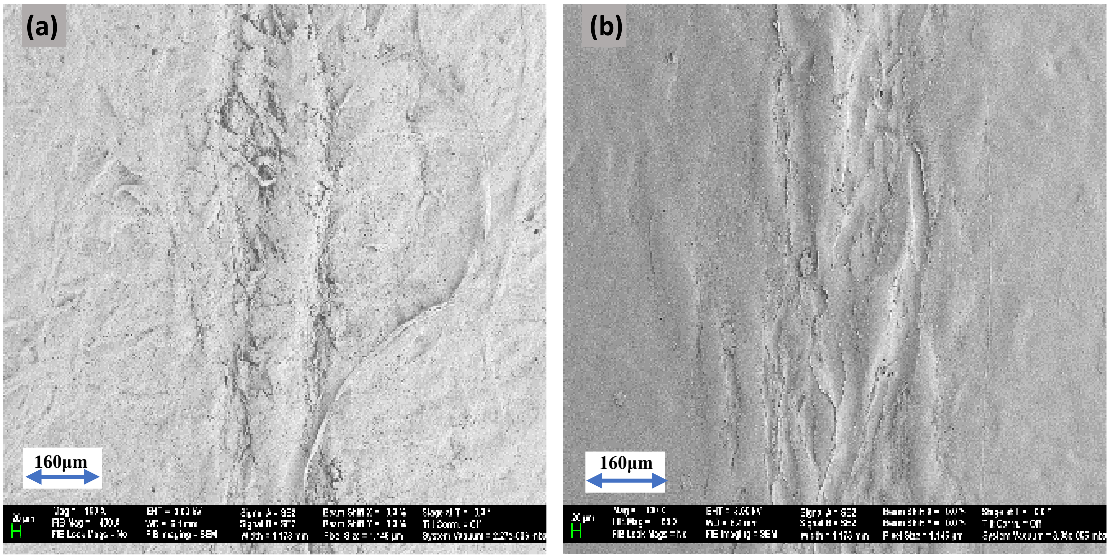


Figure 10: SEM images of CNF coated paper (a) Top surface SEM image at 500× of 8g/m^2, 90% fine CNF coated paper with single fold, (b) Top surface SEM image at 50× of 8g/m^2, 90% fine CNF coated paper with 16g/m^2 of barrier coatings and single fold, (c) cross section SEM image at 1000× of 8g/m^2, 90% fine CNF coated paper with single fold, (d) cross section SEM image at 1000× of 8g/m^2, 90% fine CNF coated paper with 16g/m^2 barrier coatings and single fold.

Figure 8 shows the microstructure of the surfaces and cross section of a CNF precoated paper. To obtain a cross section image, the samples were obtained by cutting out the piece of sample with the help of razor blade and made free of any paper fibers before and after barrier coatings were applied. At magnification of 500x (Figure 3(a)) on surface image of CNF coated paper and 50x (Figure 3(b)) on surface image of CNF precoated with barrier coatings on top of it, the characteristic multiscale fibrous and porous structure was evident. Once the barrier coating is applied on top of the CNF coated paper, we can see the surface is uniform, completely covering up the fibrous CNF layer giving us really good results in water vapor transmission, and oxygen transmission. Figure 3(c) shows the cross section of CNF coated paper at the magnification of 1000x, giving us an image of tightly packed fibers in a uniform layer, which could be because of several reasons including the high surface area of CNF which promotes strong inter-fiber interactions.



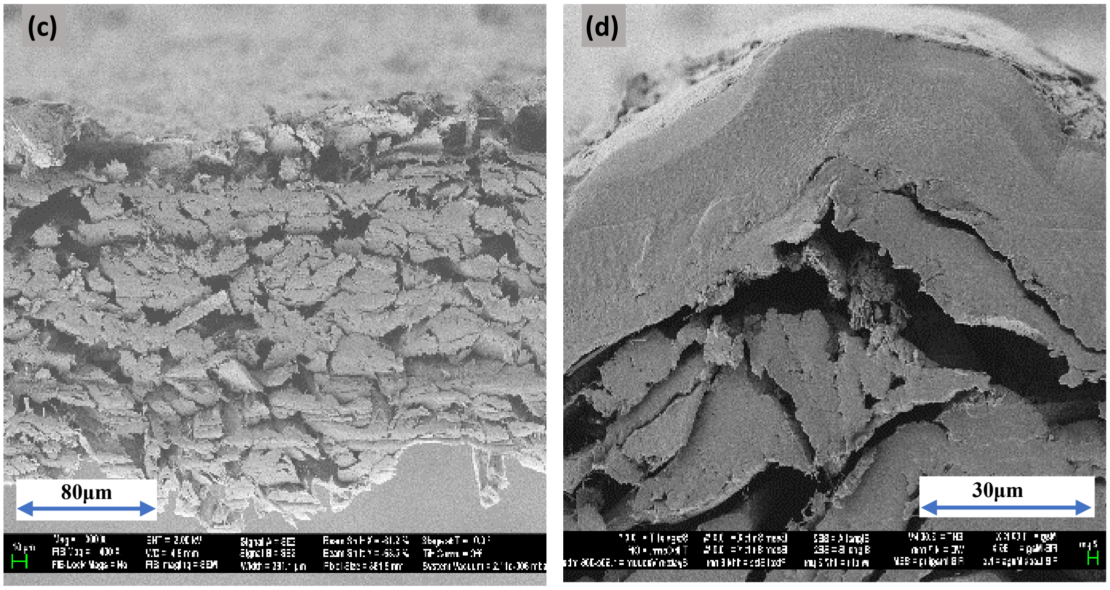


Figure 11: SEM images of pigment coated paper (e)Top surface SEM image at 100× of pigment (delaminated kaolin at 40pph) coated paper with single fold, (f)Top surface SEM image at 50× of pigment (delaminated kaolin at 40pph) with 16g/m^2 barrier coatings and single fold, (g) cross section SEM image at 300× of Pigment (delaminated kaolin at 40pph) coated paper, (h) cross section SEM image at 1000× of Pigment (delaminated kaolin at 40pph) coated paper with 16g/m^2 barrier coatings and single fold.

SEM of pigment coating in figure 11 (a) and (b) shows the crack resistance of the paper before and after barrier coating is applied on top of the pigment layer. In Figure 11(a) at 100x we could see presence of some voids or cracks in coating that indicates poor adhesion in coating layer. The coating layer possibly delaminates in the region of the crack, exposing the paper fiber and creating a larger area and decreasing the barrier resistance whereas, after the application of barrier layer on top, as seen in Figure 11(b) at 100x the cracking effect decreases comparatively. For better understanding of the pre coating layer involved a cross section image of the sample was obtained by cutting out the piece of sample with the help of razor blade and made free of any paper fibers before and after barrier coating was obtained. The cross-section SEM image suggests that the pigment coating does not adhere on top of paper forming a uniform coating base layer as seen with CNF films due to the presence of more crystalline structures.

5. CONCLUSION AND FUTURE RESEARCH

5.1.Conclusion

The general objective of this study was to develop environmentally friendly food packaging with effective barrier properties that could enhance the product's shelf life. To achieve this, the potential choice of paper-based packaging with a CNF film as a preliminary coating, followed by the application of waterborne barrier coatings. The study aimed to investigate two distinct approaches to enhance the barrier properties. The first method entailed utilizing CNF as a pre-coated layer, while the second method involved applying a latex and pigment mixture at different latex concentrations. Although the water borne barrier layer does not exhibit significant resistance to water vapor, it possesses satisfactory barrier properties against oil and grease.

- Although the water borne barrier coating does not exhibit significant resistance to water vapor, it possesses satisfactory barrier properties against oil and grease.

- The performance of the water-based barrier layer can be greatly enhanced by utilizing a CNF layer as an initial coating on paper. The CNF layer creates a uniform surface on the paper that adheres well to the top barrier layer, resulting in an overall improvement in performance.

- Furthermore, the incorporation of a CNF precoat noticeably enhances the water and oxygen barriers of a subsequent water-based barrier coating. However, there appears to be minimal impact on the oil and grease barrier properties.

- The overall performance of the paper can be improved by the application of a CNF layer; this improvement is independent of the amount or quality of the application. Although folding the sample may somewhat lower its moisture and oxygen barrier, the sample's resistance to grease is unaffected by the folding process.

- Although not as effective as CNF, a pigment coating used as the base layer for a barrier coating can still provide some degree of moisture and grease barrier, depending on the pigment to latex ratio in the mixture. However, when it comes to the oxygen barrier, the pigment coating does not help to a large extent.

5.2.Recommendation for future work

- To gain a more comprehensive understanding of the sample's feasibility, various mechanical tests such as tensile strength, flexibility or ductility tests, and tear resistance tests could be conducted. These tests can provide valuable insights into the material's strength, durability, and other related properties, which in turn can aid in identifying potential applications for the material.

- Assessment of environmental impact: While this study focused on developing environmentally friendly packaging materials, future research could investigate the environmental impact of these materials over their entire lifecycle. This could include assessing the environmental impact of raw material extraction, production, transportation, use, and disposal or recycling.

- Investigation of consumer behavior and preferences: Understanding consumer behavior and preferences regarding sustainable packaging is crucial to developing packaging materials that are widely accepted and adopted. Future research could investigate how consumers perceive and respond to different types of sustainable packaging materials and identify factors that influence their purchasing decisions.

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APPENDIX

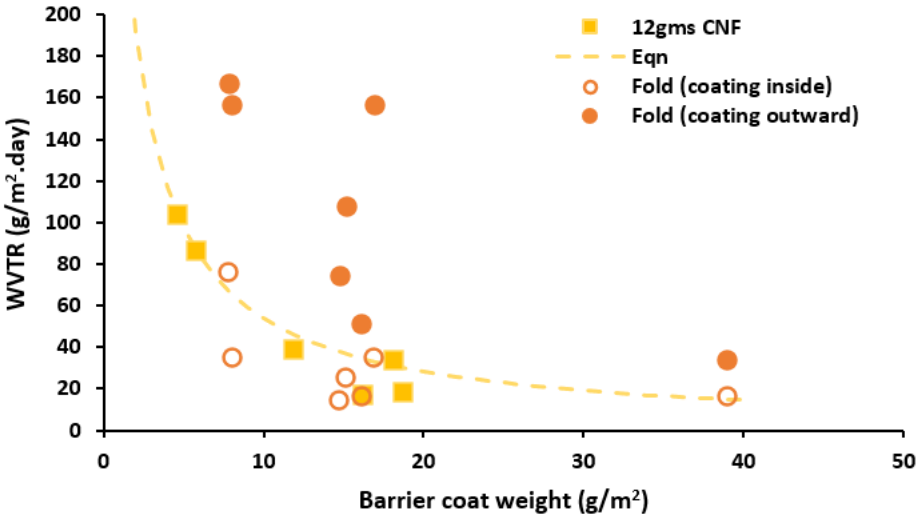

Figure A 1: Graph showing the changes seen in WVTR values after inward and outward folding.

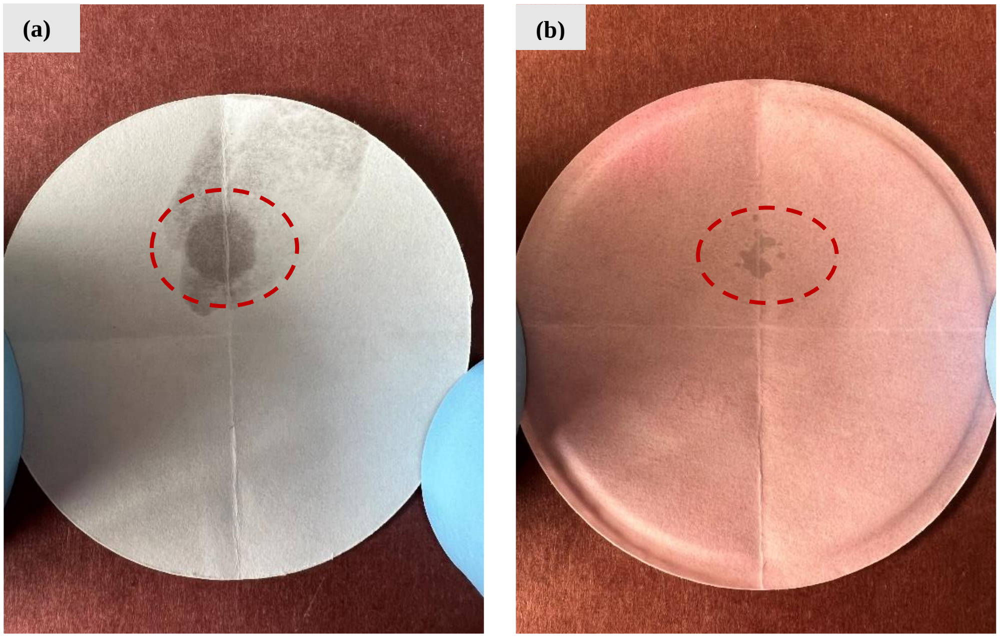

Figure A 2: OGR test on (a) base paper (b) base paper coated with 18g/m^2 WBBC.

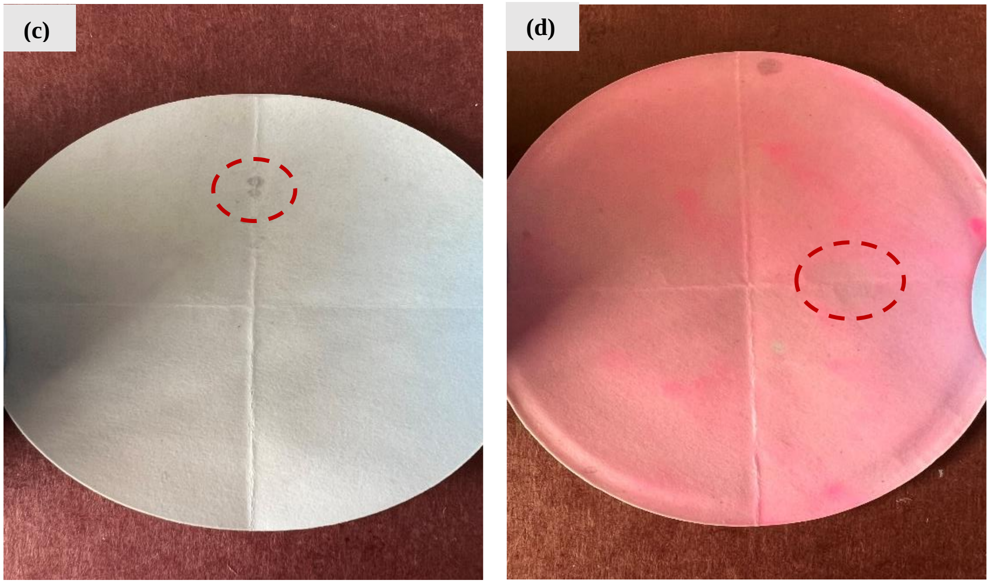

Figure A 3: OGR done on (c) 25g/m^2 pigment coated paper (d) after applying 18g/m^2 WBBC on that pigment coated paper.

Table A 1: Characterization of different base paper used.

SAMPLE BASE	Coat Weight (g/m^2)	Void fraction (silicone oil test)	Gurley time (Gurley's second)	TLV (Total Liquid Volume, contact time: 0.05sec), cm^3/m^2	Air permeability, m^2 (Darcy's Coefficient)
Base paper	**---------**	42.75%	21.52	72.72	1.21E-14
Fine Kaolin	**11g/m^2**	13%	323.18	13.84	2.55E-15
Delaminated Kaolin	**12g/m^2**	14%	784.1	15.62	1.06E-15
Platy Kaolin	**18g/m^2**	39%	332.4	17.62	2.71E-15
90% fines CNF	**12g/m^2**	42.80%	7757.66	12.86	3.90E-17
70% fines CNF	**12g/m^2**	40.95%	6466.03	14.29	4.74E-17
90% fines CNF	**8g/m^2**	33.53%	2372.08	11.66	1.27E-16
90% fines CNF	**4g/m^2**	46.61%	37.57	52.63	7.53E-15

BIOGRAPHY OF THE AUTHOR

Kritee Pokharel is a dedicated student who is working on her master's degree at the University of Maine. She is expected to finish in May 2023. Born and raised in Nepal, she obtained her Bachelor of Science degree from the prestigious Kathmandu University, located in Dhulikhel, Nepal, in 2020. Throughout her undergraduate education, Kritee showcased a robust passion for research, participating in various studies, including the production of biofuel from wastewater through lipid extraction.

Following her undergraduate achievements, Kritee chose to continue her academic journey in the field of chemical engineering, deepening her understanding and honing her skills. Her research primarily investigates the impact of various precoating layers on paper for the creation of eco-friendly snack packaging. She is also an engaged member of both the American Institute of Chemical Engineering (AIChE) and the Technical Association of the Pulp and Paper Industries (TAPPI), contributing to multiple conferences. 2023Upon completing her master's degree, Kritee aspires to embark on a career in research and development, concentrating on renewable energy and sustainability.

Kritee is a candidate for the Master of Science in Chemical and Biomedical Engineering from the University of Maine in May 2023.