Spring 5-2019

Parameters that Influence the Performance of Dispersion Barrier Coatings

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Recommended Citation

Raditya, Randy, "Parameters that Influence the Performance of Dispersion Barrier Coatings" (2019). *Electronic Theses and Dissertations*. 2990.
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PARAMETERS THAT INFLUENCE THE PERFORMANCE OF DISPERSION BARRIER COATINGS

By

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B.S. University of Akron, 2012

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

May 2019

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By Randy Raditya

Thesis Advisor: Dr. Douglas W. Bousfield

An Abstract of the Thesis Presented
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Barrier coating layers are important in many paper grades used in food packaging and have the potential to help reduce our use of plastics in some situations. Barrier layers to produce water proof packaging such as milk or juice cartons or coffee cups are common. Water based dispersion barrier coatings have the potential to be a low-cost alternative to extrusion coated layers. Water borne coatings are reported to be easy to recycle and break down in the environment. However, barrier properties are often less than what is desired and expected for these water borne coatings. The reason for this poor performance is not well understood.

Various papers are coated with a latex intended for barrier properties as well as the latex combined with plate-like pigments with various coating methods. The laboratory coated samples are also compared to a high speed blade coater. The water vapor transmission rate (WVTR) of these samples is measured. A novel method, using cellophane, is proposed to isolate the behavior of the coating layer independent of the paper properties. Latex was also stained before coating; these samples were imaged with a confocal laser scanning microscope (CLSM). The results are compared and normalized in terms of water vapor permeability.

When coated at low speed, different application methods were found to give similar barrier performance. The effect of base substrate was found to be prominent. Coatings on cellophane yield superior barrier performance when compared to coatings on regular copy paper. The absence of pores and roughness on the surface of cellophane promote the formation of continuous uniform coating layer with little defects, important for moisture barrier performance. When typical porous paper is used, the addition of pigments was proven to not only to provide tortuous path of diffusion but also to help prevent the coating to sink into the pores.   Image from the CLSM verify this mechanism.

The high speed blade coating resulted in barrier properties that were better than the low speed laboratory coating samples, especially when the pigment is used. The reason for this result may link back to the alignment that takes place in the high speed shear field under the blade.

ACKNOWLEDGEMENTS

I would like to especially thank Dr. Bousfield for his guidance, support, expertise, inspiration, and patience throughout the whole process of finishing this important step in my life. I am also grateful to all the sponsors and mentors of Paper Surface Science Program who have made this program possible. I thank Jerker Jäder for his guidance and suggestions to get me started with this research. I thank Peter Hayes for his guidance and for providing the important materials used in this research. I would like to also acknowledge my colleagues including Emilia Purington for helping with the CLSM images, Lisa Weeks for the guidance on various subjects, as well as Greg Yum, Yaping Zhu, and Mohammed Al-Gharrawi for their share of this journey. Finally, many thanks to Dr. van Heiningen and Dr. Tajvidi for their time, effort, and expertise that made the completion of this thesis possible.

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CHAPTER 1: INTRODUCTION

1.1 Motivation of Research

More than ever, the need for sustainably sourced biodegradable paper and board is increasing to accommodate the shift away from plastics, glass, and metal in our packaging systems. The demand for food products and other consumer staples packaging and containers is only going to keep rising with the growth of world population, the middle class and the increasing trends towards door to door last-mile deliveries of goods. This is happening on top of the on-going demand for better quality packaging for fast-moving consumer goods (FMCG). Paper has many key attributes in that it can be sustainable, recycled, is light weight to transport, and will break down in the environment.

Global packaging is already a US$400B industry according to a report by Ernst & Young in 2012. Food and beverage packaging comprise of 70% of the end markets. Paper and board category make up the biggest portion of all packaging materials at 34%, followed by rigid plastics at 27%. One of the key success factors for packaging manufacturers is the ability to reduce material and waste. Nowadays more customers put pressure on producers to cut basis weight of packaging or “down-gauging”. Another condition unique to packaging manufacturers or converters is that at times they are stuck in a position where large raw material suppliers could increase price when there is a shift in market price but could not pass the burden to consumer goods companies which have more negotiating power. Being heavily competitive and produce high quality products with optimized cost of goods manufacturing (COGM) is important for packaging companies.

The end-of-use result of paper compared to plastic is quite different. According to data from U.S. Environmental Protection Agency, 77 million tons of container and packaging wastes were generated in 2005, representing 32% of all municipal solid waste (MSW). Of all packaging waste, 39 million tons consist of paper and paperboard packaging such as corrugated boxes, milk cartons, bags, and wrapping papers.

14 million tons were made of plastic packaging such as bottles, bags, and wraps. The percentage of recovery by recycling and composting was 59% for paper-based packaging while only 9% for plastics. The low percent recovery of plastics may be attributed to the economics and market availability of recycled plastics. For example, recycled plastics are usually not suitable for food contact applications due to carryover contaminants. Neither are plastics compostable (Marsh and Bugusu, 2007). A key issue in the media over the last year was the millions of tons of plastic which end up in the ocean and cannot degrade for hundreds of years (Parker, 2018). Not only plastics have lower recovery rate than paper-based packaging, it is also sourced from non-renewable fossil fuels. A move towards more forest-product based packaging is clearly desirable.

In other words, with the increasing trend of packaging demands and the needs for the industry to innovate towards lower cost and more environmentally friendly products, any effort to contribute to the development of cost effective and biodegradable paper-based packaging products is imperative and could have a big impact for the future of the industry.

Packaging, whether made of paper, paperboard, plastics, glass, or metals typically serve the following purposes: protection/preservation, containment and food waste reduction, convenience, marketing, and traceability (Marsh and Bugusu, 2007). Thus, the ability to prevent transport of moisture or gases is one of the most important quality of packaging products. Other requirements include structural integrity and appearance. Since paper and paperboards naturally have pores and rough surfaces, a coating layer is usually added to provide barrier against mass transport of moisture, gases, or grease, and to provide surface smoothness for better printability.

The methods available for production of barrier coating on paper substrates include extrusion, lamination and dispersion coating. Currently, the most common method to produce packaging with reliable quality is by extrusion of polymers such as polyethylene (PE) and poly(ethylene-terephthalate) (PET) or natural wax, which is then applied on paper substrate (Gaikwad and Ko, 2015). This method is well established and is used to make milk and juice cartons as well as paper cups. Lamination also uses polymers but involves bonding and adhesion of the polymer film onto paper substrate. With dispersion coating, aqueous dispersion of polymer particles is applied onto paper substrate. Typical barrier dispersion coatings consist of polymer particles dispersed in water, commonly called latex. Most common polymers used include polyacrylates, polystyrene, polybutadiene, and polyolefins. Beside water and polymer, formulations usually also contain fillers or pigments and additives (Kimpimaki et al, 1997).

In the last few years only, the interest towards dispersion barrier coating has hiked. There are a couple reasons for this. First, dispersion coated papers can be easily recycled through repulping, composting, and incineration. On the other hand, plastic extruded or laminated coated papers especially those with multilayers of polymers do not meet the requirements for biodegradability and composting (Miettinen et al, 2016). They are costly to recycle and involve processes like delamination or selective dissolution-precipitation (Kaiser et al, 2018). Some even have to go as far as adding bio-based interlayer which then can be decomposed by enzymatic treatment (Cinelli et al, 2016). Figure 1.1.1 below describe the huge discrepancy between latex and PE coated paper in terms of compostability.

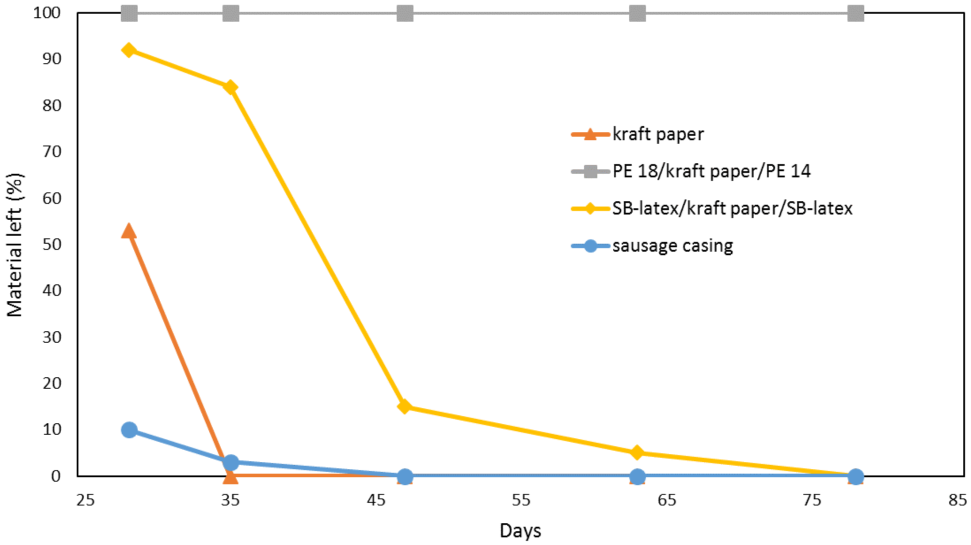


Figure 1.1.1 Compostability of PE and SB-latex coated kraft paper. Degradation was estimated as percentage loss of the surface area. Based on Kimpimaki et al (1997).

Another great advantage is that paper manufacturers have the option to utilize their existing equipment and processes that had normally been used for paper coating for printing and writing purposes. Latex is already a very common substance used in paper coating which acts as binder for the pigments used in coating colors. Pigments is a very important material in paper coatings to improve print quality, gloss, brightness, and opacity (Bollström et al, 2013). The only adjustment needed is the ratio of latex to pigments. With barrier coatings, latex is the main substance while pigments are added to lower cost and improve barrier performance. Dispersion barrier coating can be applied using most current paper coating technologies such as roll coaters with rod (Mayer bar), blade coaters, air knife, dip or spray coaters, and rotogravure (Kimpimaki et al, 1997). On top of the ability to use conventional coating equipment, when compared to extrusion coating, barrier dispersion coating involves fewer processing steps and can be produced at higher application speeds (Gaikwad and Ko, 2015). Transforming these machines into barrier coaters rather than purchasing new equipment can provide manufacturers business advantages.

All these advantages have triggered many research on dispersion barrier coatings in the last decade as water based barrier coatings (WBBC) is projected grow around 6% annually in terms of market share (Miettinen et al, 2016). Many research focused more on the development of the coating formulation chemistry. Some also have developed barrier coating with bio-based polymers or combined with thin inorganic layer. Most aimed to produce barrier coatings that are competitive to polymer extrusion coating. Typical water vapor transmission rate (WVTR) of LDPE film is 1 g-mil/100in^{2}day or to 15.5 g/m^{2}day for a 0.0254 mm film (Frey, 2009). With average density of 0.93 g/cm^3, this film thickness equates to 24 g/m^2 of coat weight. According to Andersson (2002), typically a minimum of 3-5 g/m^2 coat weight is necessary for satisfactory water vapor barrier. Developing comparable or better barrier properties has been the focus for many. In general, the performance of dispersion barrier coatings is still inferior compared to extruded polymer coatings at the same coat weights.

Several have observed the effect of latex, pigments, and base substrates properties to barrier performance as will be discussed more in Section 1.2. A systematic study that looks at the general parameters associated with dispersion barrier coatings in a more fundamental way seems to be lacking. In this thesis, the role of coating methods, coating formulation, base substrate, and machine speed are analyzed and compared. The goal is to understand the parameters and their importance to help develop superior dispersion barrier coatings.

1.2 Past Studies

Studies on dispersion barrier coating gained traction in the last couple of decades and has been accelerating in the last several years. Many research used specific dispersion coating materials and substrates of interests and aimed to create barrier system that could compete or replace traditional methods. Many others focused specifically on understanding the effect of pigments (typically clay or kaolin) or latex properties to the barrier performance, contributing to the development of coating formulations. Only a handful have systematically attempted to understand the importance of different parameters involved in dispersion barrier coatings.

Some research focused on trialing different methods to develop competitive barrier coatings and not so much on analyzing the fundamentals. Kugge and Johnson (2008) developed barrier coatings using styrene-butadiene (SB) latex and clay on linerboard. The water vapor transmission rate (WVTR) obtained was 40 g/m^{2}day for a single coat at low humidity (50% R.H, 23°C). With double coat the WVTR can be cut into half with coat weight of 12 g/m^2. Vähä-Nissi et al (1999) did research on polymer dispersion on high density (HD) paper. Low WVTR below 10 g/m^{2}day at coat weight of 5-20 g/m^2 was achieved using wax modified SB-latex. Ryan et al (2004) used aqueous-based emulsion polymers that include PET, PVDC, and styrene-based emulsions coated on paper carton board. Low WVTR of 6.3 g/m^{2}day for 100µm coating was obtained with 40% solids of PET aqueous emulsion. Further improvement obtained by applying primer coat as pre-coating, yielding WVTR of 3.1 g/m^{2}day. The addition of wax appears to improve barrier to moisture, as shown on Figure 1.2.1.

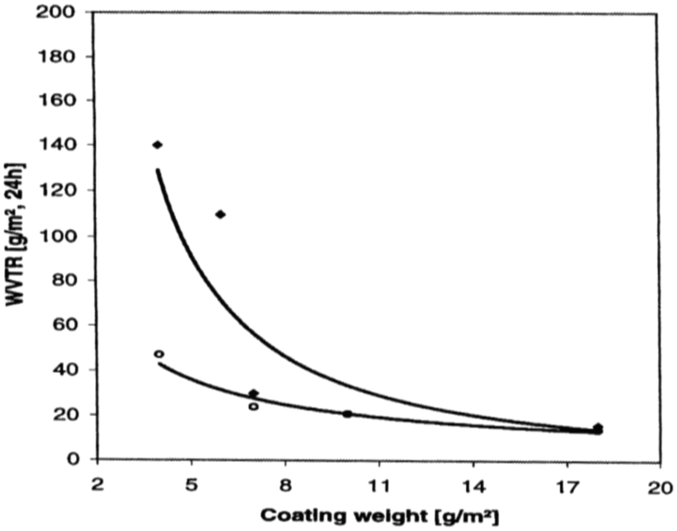


Figure 1.2.1 Typical WVTR for filler modified and wax modified polymer dispersion coating. Single coating on paper board at 75% R.H. and 25°C. Wax modified dispersion gives lower WVTR. From Kimpimaki et al (1997).

The fundamentals of latex film formation have been studied for many years. In general, the process of generating a continuous layer of material on substrate from aqueous dispersion of polymer particles can be broken down into three stages: evaporative drying of water, particle deformation where polymer particles form denser pack, and polymer interdiffusion where the individual particles become indistinguishable. By experiments, factors such as the ambient conditions, the presence of surfactants, plasticizers and pigments, and latex particle structure were found to affect film formation (Keddie, 1997). The presence of surfactants between polymer spheres remains in the structure and may influence the water vapor transmission rates of these films.

Schuman et al (2004) analyzed the influence of SB-latex characteristics such as the degree of cross-linking, glass transition temperature (Tg) and degree of carboxylation on the mechanical properties and water vapor permeability (WVP). It was found that the coating with high degree of cross-linking (high gel content) and low degree of carboxylation exhibited the lowest WVTR at 4.9 g/m^{2}day or 6.8 g/Pa.s.m x 10^{-12} in terms of WVP.

Khosravi et al (2014) have studied latex film formation on substrate with various porosity and hydrophobicity. Polymers PTFE, PFA, PVDC, and Hypod were casted on both nonporous and porous substrates; these results do not involve paper-based substrates. Latex solid concentration in the casting solution was found to be the most important parameter in determining film thickness. Major conditions needed for latex film formation include sufficient exposure time for particle deformation and the use of deformable polymers. Using soft latexes and lowering drying rate facilitate film formation even when the solvent is rapidly drawn into the pores of substrate. However, defect-free films are harder to obtain with increasing substrate pore size.

The influence of pigments, mainly clays and nanoclays to barrier properties have been studied quite extensively. Models have been developed to predict the performance based on pigments properties such as size distribution, aspect ratio, and pigment volume concentrations. Critical pigment volume concentrations (CPVC) for different pigment/latex systems have been studied. More pigments in coatings is generally beneficial up to a point where any more addition of pigment would only deteriorate the coating surface.

Vähä-Nissi et al (1999) studied the effect of pigment factors. Lower WVTR can be achieved more significantly by increasing amount of pigments up to the CPVC at around 40-50% volume. Talc is the best when both grease and water vapor barrier properties are needed. Vähä-Nissi et al also studied the effect of drying power and pigments properties on barrier clay coatings using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Three commercial grades of clay with varying particle sizes were used. Again, the main conclusion is that adding platy fillers improves barrier properties up to CPVC.

A research by Zhu et al (2013) focused heavily on analyzing the effect of kaolin particle size distribution (PSD), aspect ratio (AR) and the particle orientation and location to barrier performance. Models to predict relative permeability based on these factors were developed. It was found that barrier properties do not depend on PSD but heavily correlated with AR distribution and orientation of flakes. Large flakes with high AR provide largest improvement in barrier property.

Kugge et al (2011) explored pigments with different shape factors and aspect ratio and correlated these properties with the rheological properties of the barrier coatings. The barrier performance in terms of WVTR was checked. It was concluded that WVTR performance correlate with shape factor, confirming the belief that formulations containing very platy clay provide more tortuous path for diffusion of water vapor and thus lower WVTR. Gittins et al (2008) reiterated the importance of selecting platy pigments such as kaolin and talc to provide tortuous path for moisture barrier. Styrene-butadiene and styrene-acrylic latexes were used. The effect of aspect ratio and pigment loading was summarized. Greater aspect ratio and greater pigment loading (up to CPVC) improve moisture barrier.

Bollström et al (2013) experimented different size, shape, and shape factor pigments blended with different amounts of styrene-acrylate, styrene-butadiene, or ethylene-acrylate latex for barrier against water vapor and organic solvents. It was found that platy kaolin pigment with highest shape factor improved barrier against water vapor and solvent due to increased distance of pathway for liquid to penetrate the coating layer. However, the improvement was greatest when styrene acrylate latex used. Pure ethylene acrylic latex generates very good barrier properties with WVTR lower than 40 g/m^{2}day for all coat weight range and the addition of kaolin did not provide further improvement. Thus, the choice of latex can be considered the most important factor per this research. Regarding the amount of pigments, it should not exceed the critical pigment volume concentration (CPVC) as more pigments can create pores on the coating surface.

Nyflött et al (2016) also concluded that kaolin concentration above 5% in formulation decreases oxygen permeability by increasing tortuosity for gas diffusion. Kaolin orientation must be parallel to the base plane for greater tortuosity. Kaolin orientation is influenced by drying temperature, thickness of sample, and kaolin concentration.

Sun et al (2007) focused on the development of water-based polymer/clay nanocomposite (PCNC) that would yield the best barrier properties on linerboard. The concept is by increasing specific surface area of clay particles, the tortuous length of diffusion path of water vapor can be increased. It is important that nanoclay is fully exfoliated and dispersed in the polymer matrix. The best PCNC system containing clay called Sap-CTAB with acrylic resin emulsion was found to yield the best WVTR at 70-120 g/m^{2}day, an improvement from pure polymer coating at 275-320 g/m^{2}day.

Gaikwad and Seonghyuk (2015) studied the importance of nanoclay versus regular clay for coating for packaging application. Typical clay pigments have aspect ratio of 10-30 while commercial nanoclays 50-1000. The most important factors concerning filler addition to barrier dispersions are the adhesion of the binder to the pigment particles, the particle shape, and the chemical nature of the pigments. The CPVC value of a polymer/pigment system depends on the latex particle size and its size distribution.

Due to the number of studies that have been done regarding influence of platy clay particles to barrier coating performance, articles that serve more as a literature review summary on this topic can be found. Tan and Thomas (2016) have reviewed and summarized all literatures regarding effect of nanofillers in reducing water vapor permeability (WVP) of polymer/clay and polymer/graphene barrier coatings. Models for predicting WVP barrier performance based on factors such as tortuosity, geometry, platelet stacking, orientation, polymer chain confinement and plasticization have been established. It is said that the model by Nielsen is the most often fitted to others' polymer/clay data.

The author of this thesis observed from the literatures reviewed that most agree the reason pigments improve barrier performance is because the platy particles materials provide long and tortuous diffusion path for water or gases through the coating layer. Figure 1.2.2 shows typical analogy of the tortuous path concept.

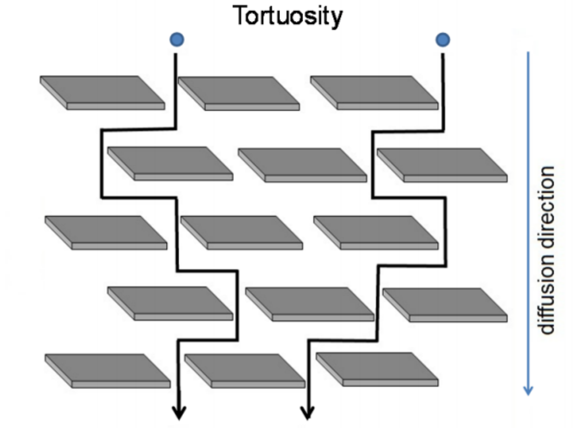


Figure 1.2.2 Typical visual explanation of path of tortuosity for diffusion through pigmented layer. From Tan (2016).

Besides studies on the effect of pigments, others have found the importance of base substrates and pre-treatment to create more homogeneous coating layer. According to Schuman et al (2005), water vapor barrier properties is impacted by the smoothness of substrate. Surface pre-treatment such as hot calendaring and precoating on substrate can give more homogeneous coating film. WVTR results of all samples are all below 41 g/m^{2}day (normalized to a film thickness of 10µm). The best samples consist of 60 wt.% kaolin clay and 5 wt.% wax additive, yielded WVTR of 6 g/m^{2}day, regardless whether hot calendaring was done prior or after coating. Without wax addition, best performance comes from 60 wt.% kaolin clay with hot calendaring at 15 g/m^{2}day (normalized), about 100% improvement from pure latex at 28 g/m^{2}day. Schuman et al also suggests that more parallel orientation of pigment particles in respect to substrate surface improves barrier properties because it increases the degree of diffusion path tortuosity.

In another experiment, Schuman et al (2004) specifically analyzed the impact of paper substrate properties. It is stated that reducing surface roughness of paper substrates by calendaring or corona treatment can improve homogeneity of coating and barrier properties. Calendaring reduces porosity and pore size of the paper and lower liquid absorption and air permeability. It can be seen, however, from the data presented that hot calendaring improves WVTR only slightly, by about 5%. The effect on air permeability (ml/min) was greater at around 25% reduction. The study was done on PVA-film coated on white top liner (WTL) and two-ply sack paper (SP).

Similarly, on another experiment of carboxylated and cross-linked SB latex, Schuman et al (2004) emphasized the effect of hot calendaring or pre-coating to create more homogenous layer on white top kraftliner (WTL) paperboard substrate. Without the addition of wax, the best WVTR obtained was 41 g/m^{2}day with the substrate pre-coated before the dispersion coating. With calendaring and no pre-coating, the best WVTR obtained was 71 g/m^{2}day. Also noted that intense drying promotes film formation and thus homogeneity of coating film and lower WVTR. However, too high of web temperature during drying may also defect the polymer film.

Kendel et al (2008) investigated the effect of pre-coat containing starch, AKD, and kaolin clay and substrates of different porosity. All coatings were applied to an internally sized commercial kraft linerboard (basis weight 200 g/m^2). Uncoated linerboard has a WVTR of 2365 g/m^{2}day at 38°C and 90% R.H. The addition of hydrophobic AKD to the starch improves WVTR by up to 8% only due to the presence of pinholes. Conventional barrier coating gives a WVTR of 203 g/m^{2}day at a coat weight of 21 g/m^2. With this high coat weight, the application of pre-coat of hydrophobic AKD and starch did not improve WVTR, but the addition of 10% kaolin clay improved WVTR by 10%. Another major observation is that increased refining of pulp decreased sheet porosity and thus lower WVTR by up to 22%. Interestingly, in this case adding 20 g/m^2 of conventional barrier coating did not add any more benefit.

In addition, barrier properties involve other sought-after quality than just moisture or grease permeability. Miettinen et al (2016) dispersion coating on various base boards and analyze the barrier properties in terms of grease-resistance, heat sealibility, creasability, tray forming, and blocking tendency and developed barrier coatings with sufficient creasability that can be used for example in disposable packages and plates. This signifies the importance of the choice of base substrate.

A couple more studies seem to have involved multiple parameters associated with barrier coatings altogether and not only focused on certain parameter such as pigments, latex, or substrate. Pal *et al.* (2008) analyzed the effects of pigment shape, baseboard, coat weight, calendaring and RH and temperature on barrier properties through factorial design of experiment. Modified high shaped factor engineered (HSFE) clays were used. The high shape factor and thinner platelet pigment on non-precoated baseboard gave the lowest WVTR with the best value of around 180 g/m^2day for 7 g/m^2 coat weight. Calendaring slightly improved the BP. Relative humidity and temperature had a detrimental effect on barrier properties.

Kimpimaki et al (1997) provides an overview of water based barrier coatings (WBBC). Being emphasized is the importance of even coating thickness as opposed to even surface (see Figure 1.2.3) and it can be achieved more by utilizing air doctor, rod, or bar coaters instead of blade coaters. Also mentioned is the importance of film formation, which is promoted by multiple forces present during the process such as interfacial tension, capillary forces, Van der Waals attraction forces, gravity, thermodynamic, potential energy to surpass maximum repulsion energy. On the other hand, forces such as electrostatic repulsion between polymer particles and particle resistance towards deformation could prevent coalescence during film formation.

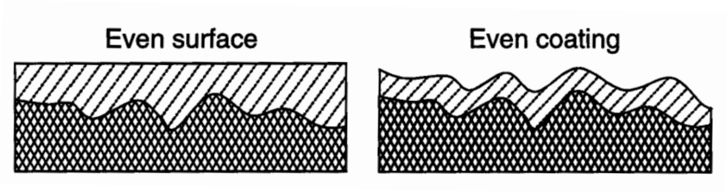


Figure 1.2.3 Even coating thickness illustration. From Kimpimaki et al (1997).

Similar to statement from Kimpimaki et al (1997) regarding the importance of even coating thickness, Tripathi et al (2006) has suggested that curtain coating would be the solution to incomplete coverage, pinholes, base sheet penetration, and non-uniform coating layers issues, especially at low coat weights. Unlike blade or rod coaters which operate under large hydrostatic pressure that often leads to penetration of coating into the base sheet, curtain coating is a non-contact metering method which provides excellent 100% coverage at any coat weight. Although no data was presented, this would theoretically reduce coat weight applications, which is typically 40-60% more than required.

As an addition, the use of hydrophobic polymers to further provide moisture barrier properties by the nature of the polymer itself has also been explored (Vaha-Nissi, 2006). Hydrophobic polymers such as lauryl methacrylate (LMA) styrene-maleic anhydride (SMA) and provide improved water barrier properties of coatings on folding boxboard. Low WVTR of below 50 g/m^{2}day (normalized for thickness of 25µm) could be obtained. Other observations worth noting include the effect of speed during pilot trial. For some samples, it was observed that the number of pinholes decreased as the line speed increased, which lower penetration into the substrate and more optimal drying. For samples with platy clay and talc it was suggested that the pigment particles were better oriented at higher speeds and improve barrier.

In conclusion, numerous studies have been done on the topic of dispersion barrier coatings, especially within the past 15 years. The majority of established fundamental knowledge are related to the influence of pigments to moisture barrier coatings. Of those studies, most agree that the concept of tortuous path of diffusion explains the improvement in barrier performance. Some have tried to understand the role of latex properties and film formation phenomena on the barrier performance. Others have observed the importance of surface smoothness by calendaring or pre-coating of substrate. In total, the number of systematic studies to clearly understand the fundamentals of dispersion barrier coatings still seem to be rather limited. In this thesis, the influence of process parameters such as coating method and coating speed are characterized as well as comparing the latex only coating with a formulation that contains barrier pigments. A novel method is proposed to measure the barrier properties of just the coating layer using cellophane.

1.3 Structure of Thesis

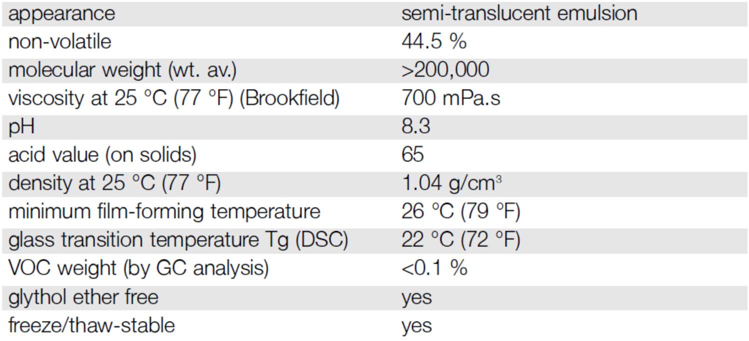
Chapter 2 contains explanation on experimental methodologies of this research, which can be grouped into two low speed experiments and high speed experiments. Chapter 3 includes the results and discussions for low speed experiments which consists of the effect of coating application methods, base substrate, and pigments to water vapor transmission rates (WVTR) and water vapor permeability (WVP) of just the coating. Chapter 4 discusses the results for high speed experiments and how they compare with low speed experiments. In addition to the effect of speed, more discussions on the impact of pigments and base substrates are also included. Chapter 5 summarizes and concludes the thesis with key findings and further recommendations. Additional results of coatings on sized paper and linerboard are also available in the Appendix.

CHAPTER 2: EXPERIMENTAL METHODOLOGY

2.1 Low Speed Experiments Procedures

For all experiments, either pure latex or generic formulation was used. The formulation contains pigments and other additives so by experimenting both pure latex and formulation, the effect pigments can be analyzed. The latex Joncryl DFC 3040-E is provided by BASF and is a film-forming styrene-acrylic for use in water-based inks and overprint varnishes. This latex is suitable for use in paper and film coatings applications requiring food contacts (packaging). Table 2.1.1 below shows the typical physical characteristics.

Table 2.1.1 Physical characteristics of SB-latex from BASF used in this study.



appearance	semi-translucent emulsion
non-volatile	44.5 %
molecular weight (wt. av.)	>200,000
viscosity at 25 °C (77 °F) (Brookfield)	700 mPa.s
pH	8.3
acid value (on solids)	65
density at 25 °C (77 °F)	1.04 g/cm^3
minimum film-forming temperature	26 °C (79 °F)
glass transition temperature Tg (DSC)	22 °C (72 °F)
VOC weight (by GC analysis)	<0.1 %
glythol ether free	yes
freeze/thaw-stable	yes

The "formulation" contains pigments and other additives such as dispersant and thickener, which are also provided by BASF. The pigments material is called Nuclay which is delaminated grade kaolin mineral clay slurry with 67.5% solids. The pigment particles have aspect ratio of 25, while the pigment size distribution is 80% <2µm. The formulation is essentially made of 75% Joncryl latex and 25% Nuclay in terms of solid percentages, plus trace amounts of the other additives. To prepare the formulation, Nuclay must first be agitated to obtain good consistency of the clay slurry. The latex along with additives are then added with good mixing. Ideal pH is 8.5 which can be adjusted with 10% NaOH. After mixing, the formulation should be left to sit for a few hours to allow some entrained air to dissipate. This formulation contains around 53% solid and has Brookfield viscosity of approximately 1500-2000 cP.

Regular copy paper, which is a wood free bleach paper is used as a model substrate to represent common surface used in paper coating. It has a basis weight of 78 g/m^2, 36% porosity and absorption coefficient of 50 cm^3/m^2. The non-coated regular copy paper has a measured water vapor transmission rate (WVTR) of 290 g/m2.

Cellophane is also used in this study, which can be considered a novel method to analyze the effect of paper characteristics to barrier properties. Cellophane allows water vapor to diffuse through it, but it has no pores and is completely smooth. Thus, coating on both regular paper and cellophane allows for analysis of the impact of paper surface characteristics. Cellophane has a basis weight of 46 g/m^2, has no measurable pore volume and without any coating has a WVTR of 223 g/m^2. On a side note, some “cellophane” that can be purchased on the internet is actually not cellophane, but some type of plastic: this plastic has very low WVTR and is not helpful for this type of experiment.

Low speed experiments were conducted using bench scale laboratory coaters, including rod draw down coaters (both grooved and smooth), blade coaters (both stiff and flexible). The use of multiple coating techniques allows comparison of the methods to barrier properties.

Samples were prepared in a uniform manner, in which 4mL of coating of either the pure latex or formulation was applied at the top of the substrate using a 5mL syringe as uniformly and similarly as possible. The motor speed at which the rod or blade was drawn was also kept the same, at 0.07 m/s, except for stiff coater which had to be drawn manually by hand. For rod coater samples, coat weight can be adjusted by changing the gap distance between the plane and the rod, using the built-in micrometer. The same applies for the stiff blade coater. For the flexible coater samples, coat weights were adjusted by changing the position of the blade attachment to vary the angle and thus the force onto the substrate. Figure 2.1.1 shows the different draw-down coating methods.

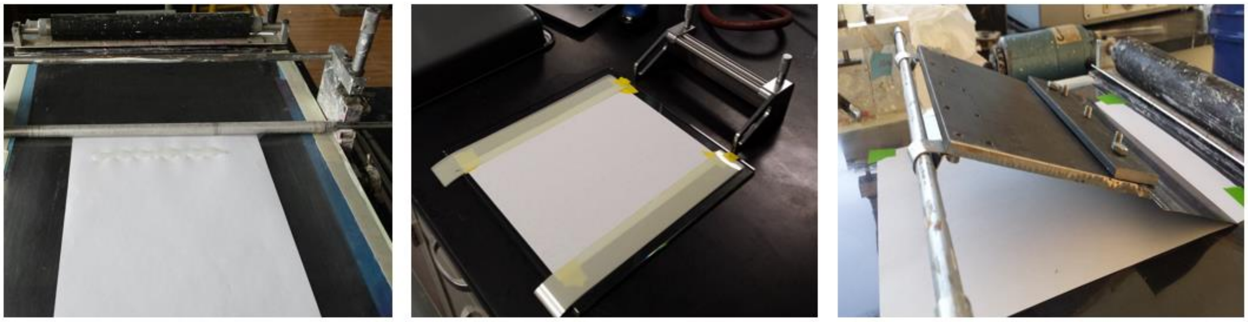


Figure 2.1.1 Different laboratory draw down coating methods. From left to right: rod coater, stiff blade coater, and flexible blade coater.

Once coating layers of the different samples were generated on the substrate, they were immediately put in an oven at 105°C for 5 minutes. The resulting dried films on substrates were then let sit overnight.

To measure the WVTR, samples in the form of 2.7-inches diameter circles were obtained so they fit on jars with custom-made lid. Using this apparatus, the sample is exposed to the atmosphere but at the same time seals the content in the jars, which is water in this case. Figure 2.1.2 shows this set up. The space inside the jars represents 100% relative humidity, while the space outside the jars represents 50% relative humidity, as the jar was placed in a controlled humidity and temperature room (TAPPI room at 25°C and 50% R.H.). By letting the apparatus sit in this condition for a period of time, the difference between the weight of water in the jar after a period of time could be measured using a weight scale, enabling the measurement of WVTR in g/m^{2}day. Based on experiments, the period of time in which the apparatus is left in the TAPPI room does not impact the results, as long as enough time is given to saturate the moisture in the samples. For all experiments, at least 24 hours was used before the second weight measurement is taken. The rate of water diffusion through the substrates and the coated papers is calculated. This method of measuring WVTR mimics the standard method ASTM E96/E96M-10. The repeatability of results has been confirmed. This method has also been compared with WVTR measurement method that uses dry desiccant (DRIERITE anhydrous calcium sulfate) and results showed no major discrepancy. Permeability of just the barrier coating without the substrate is also calculated as described in more details in Chapter 3.

Figure 2.1.2 Procedure for sample forming and WVTR measurement apparatus.

Confocal laser scanning microscope (CLSM) images were obtained using a method similar to that described by Ozaki (2006). The excitation laser was 514 nm. The acceptance window for florescence was 585 to 630 nm. The total z scan dimension was 120 m at 25 m steps. A small amount of Rhodamine-B was added to the latex (0.03 wt. percent based on latex) to cause the latex to be florescent.

2.2 High Speed Experiments Procedures

Cylindrical Laboratory Coater (CLC) model CLC-6000 manufactured by Sensor & Simulation Products was used to produce samples of coated papers at high speed. The speed was set at 1000 fpm (5.08 m/s) for generating all coatings. The pilot scale coater uses IR lamps for pre-drying and post-drying. Pre-drying time was set at 5 seconds while post-drying time 15 seconds, both at 50% power. The distance between the coating blade and the paper on the cylinder can be adjusted with the micrometer. This distance can be varied to generate a range coat weight. For this experiment, the gap distance was set between 0.19" to 0.20" to generate the desired coat weights of around 5 to 30 g/m^2.

Prior to running the coater paper was secured on the cylinder using tapes. The coating material, either pure latex or formulation, is filled into the coating pond of the coater. Once the substrate, coating material, and coater settings are in place, the coating process could be started. The cylinder reaches the desired speed and the slice of the coating pond opened to coat the paper. This process was repeated multiple times with the micrometer setting being the only parameter adjusted to vary the gap distance between blade and substrate, to obtain a range of coat weight. For the pure latex samples, coat weights generated range from 4.8 to 29.4 g/m^2.

For making the "formulation" samples 75% latex and 25% clay as described in Chapter 2 was used. Similar CLC coating procedure for was used and a coat weight range between 4.5 and 27.3 g/m^2 was obtained.

Figure 2.2.1 Picture of cylindrical laboratory coater CLC-6000.

For all experiments in this high-speed trial, a paper that is less absorbent than regular copy paper was used, called Low Absorbency (LA) paper. It has a porosity of 28% as opposed to copy paper at 36%. Bristow wheel absorption test clearly indicates that it is much less absorbent and more hydrophobic. Figure 2.2.2 below compare the absorptivity of both papers.

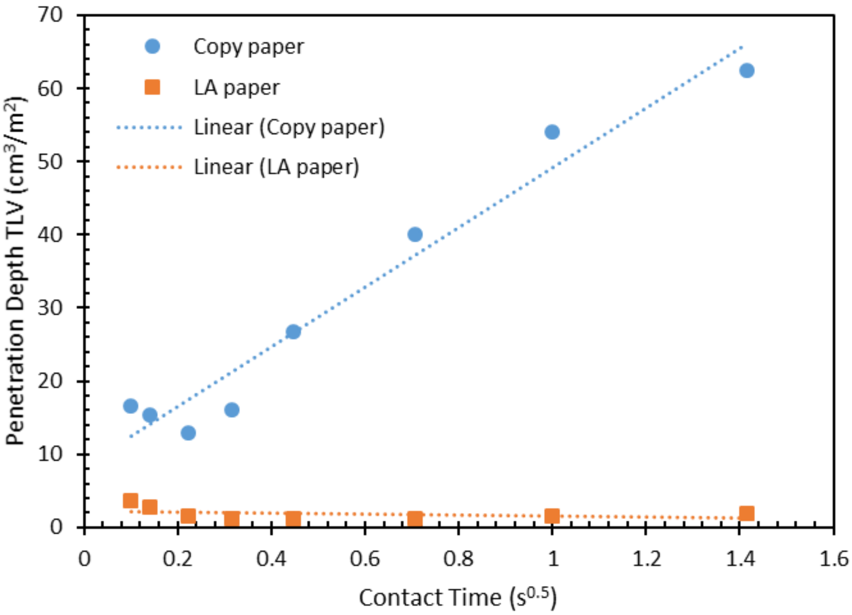


Figure 2.2.2 Bristow wheel absorption test of regular copy paper and low absorbent paper.

As can be seen from the figures above, regular copy paper behaves like most papers with some porosity and absorptivity. From Figure 2.2.2, absorption coefficient of copy paper can be estimated to be at least 50 cm^3/m^2, indicated by the inclination of the curve. The chart also can be used to indicate the surface roughness coefficient, which is the intersection on the ordinate. In this case of copy paper, it is around 12 cm^3/m^2. The idea is that even if there is no absorption, some liquid could settle on the cavities on the surface of paper that is rough. On the other hand, LA paper has very low absorption coefficient of around 2 cm^3/m^2. The chart also show that surface roughness coefficient is really small, even though its porosity is not much lower than porosity of copy paper. The most plausible explanation is that the fiber surface has been treated with substances that makes it hydrophobic.

For good comparison between low and high-speed coatings, the same LA paper was used to produce coatings at the low speed. Laboratory draw down coater was used, following the same coating procedure as described in Section 2.1. This time only smooth rod was used since it has been concluded that for low speed applications, the coating method has no impact to the performance barrier properties. Similar to the high-speed experiment, two sets of data were obtained, one with pure latex and another with the formulation. For the pure latex coatings, coat weights generated range from 5.3 to 48.4 g/m^2. For the coatings made of formulation, coat weights generated range from 4.3 to 53.0 g/m^2. WVTR is measured using the method described in Section 2.1.

CHAPTER 3: RESULTS FROM LOW SPEED EXPERIMENTS

The WVTR of the latex only coating on the copy paper is shown in Figure 3.1 for various coating methods. The different methods do cover various coat weight ranges, but when compared to each other, there was no clear difference or trend. It was expected that the grooved rod may give poor results compared to the other coating elements that are smooth, but it gave just as good or even better results. The grooved or wire wound rods deposit a slight pattern in the machine direction, but this pattern seems to level quite well by the time the coating is dried.

Figure 3.2 compares the WVTR for the data in Fig. 3.1, with the results with the latex is coated onto cellophane with different coating methods. Two results are quite interesting: 1) the coating method again had little effect on the trend of the curve for cellophane and 2) the latex on cellophane performed much better than that on paper at low coat weights. This later result is strong evidence that the absorption of the coating into the pores of the paper or the filling in of irregularities makes that barrier less effective. Other aspects of the paper surface may also play a role such as the swelling of fibers when wet or the surface roughness of the paper.

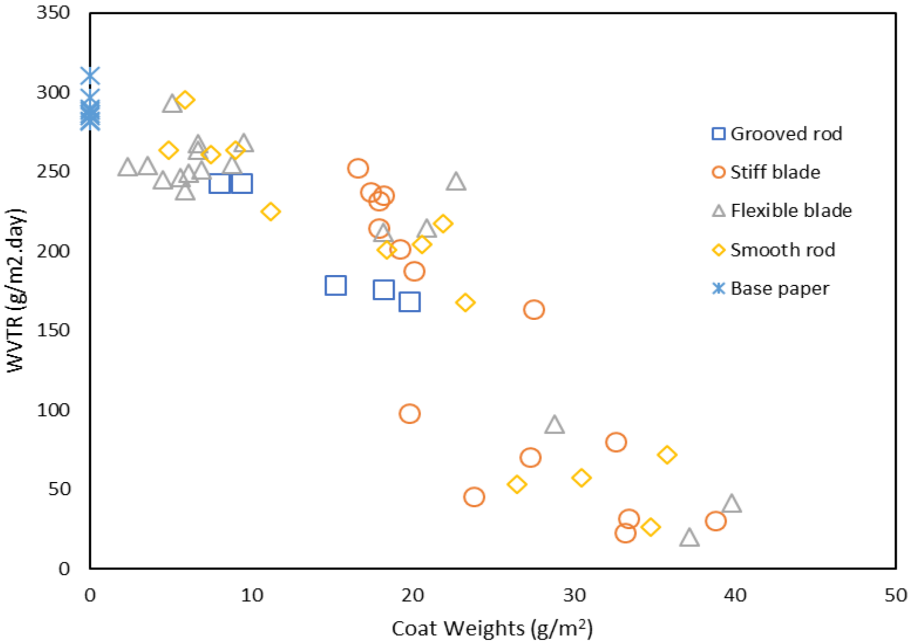


Figure 3.1 WVTR for pure latex system on copy paper with different bench coating methods.

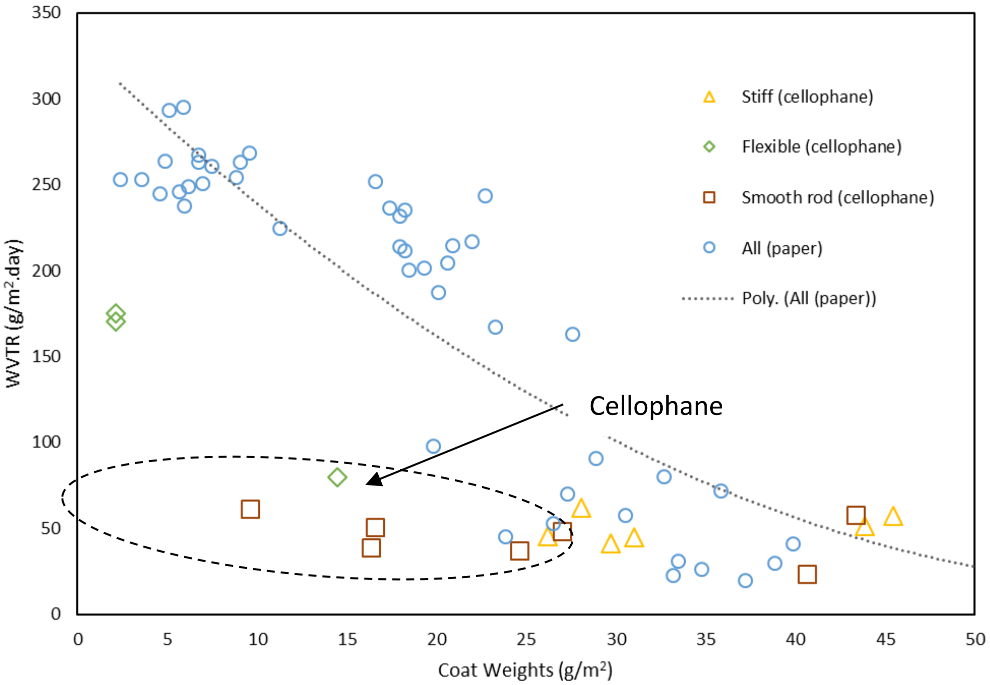


Figure 3.2 WVTR of pure latex coatings on cellophane compared to copy paper.

The comparison between the latex-only results with the formulations are given in Figure 3.3. It is quite clear that the formulation performs significantly better than the latex only cases, especially at low coat weights. This could be caused by the tortuous path concept, where water vapor would have to diffuse a larger distance through the layer, or it could be related to how the pigments in the formulation help hold the coating at the top surface. It should be noted that at the same coat weight, the formulation uses less polymer than the pure latex case.

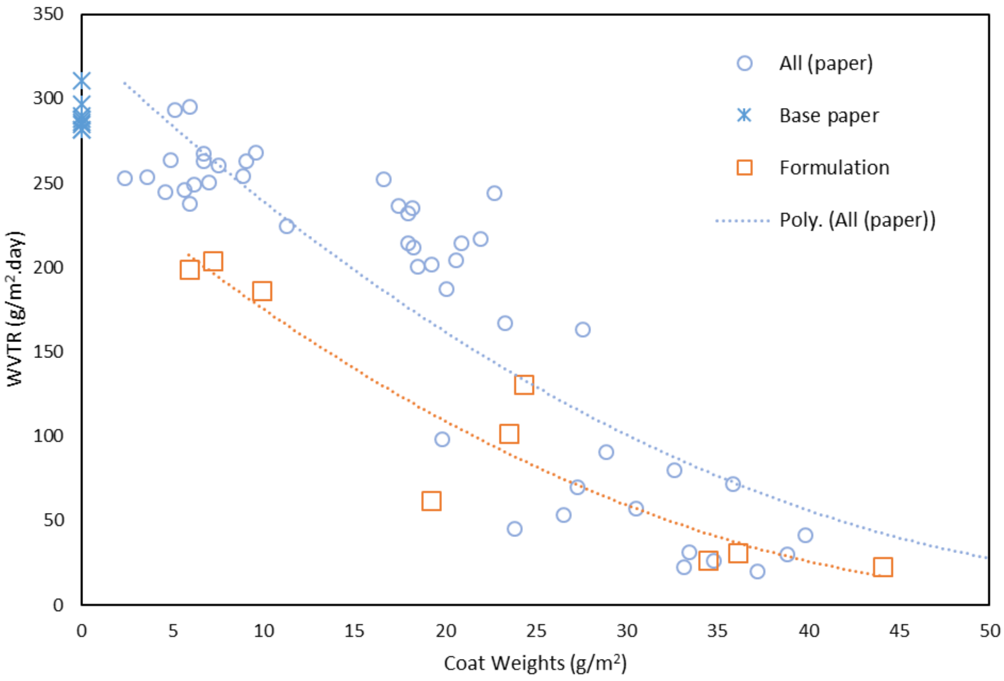


Figure 3.3 WVTR of formulation on copy paper compared to pure latex on copy paper. Lines are polynomial fits to help see the trends of the data.

The flux of a gas through a membrane can be represented in terms of permeability coefficient P as

$$J = \frac{P(p_1 - p_2)}{\delta} \tag{3.1}$$

where J is the flux of molecules in moles per area time, P is the permeability coefficient, p_1 and p_2 are the partial pressures of water vapor and δ is the thickness of the layer. Since the flux rate through the barrier layer has to equal the flux rate through the paper or cellophane, the expression becomes

$$J = \frac{\Delta h}{(\frac{\delta_p}{P_p} + \frac{\delta_c}{P_c})} \tag{3.2}$$

where Δh is the difference of humidity over the entire sample, δ_p and δ_c are the thicknesses of the paper and coating layer, respectively, and P_p and P_c are the permeabilities of the paper and coating layer respectively. These permeabilities are modified to be in terms of relative humidity expressed in terms of partial pressure of water. The molar flux is proportional to the WVTR in terms of mass per area and time. The permeability of the coating layer can be found in terms of the other quantities and has units of g/(m.Pa.day). The permeability of the paper or cellophane is known from tests without coating layers. In theory, a certain material should have a certain permeability to water vapor: this value should not be a function of thickness. The advantage of this expression is that the permeability of just the coating layer can be extracted from the experimental results.

As can be seen in Equation 3.2, only permeabilities of substrate layer and barrier coating layer are included. In theory, with the current method of flux (WVTR) measurement, there exists also a resistance to diffusion due to the air space in between water surface and sample in the testing jar. However, this factor can be neglected as the air gap alone causes much smaller resistance to diffusion than the substrate and coating layers. Average WVTR of uncoated copy paper samples is 290 g/m^2day or 248 x 10^{-7} g/m.day.Pa in terms of permeability, calculated using Eq. 3.1. In terms of resistance to diffusion (δ/D), this is equal to 3.4×10^{-12} s/m. On the other hand, resistance to diffusion due to air gap is only 2.2×10^{-5} s/m, which is smaller by a factor of thousands.

The results of Fig. 3.2 in terms of the water vapor permeability of the coating layer are shown in Figure 3.4. The purpose of plotting the results in this manner is that the contribution of the barrier behavior from just the coating layer is seen. The key point from Fig. 3.4 is that the results for the paper are quite scattered until the coat weights are high, then the results are similar to that of the results on cellophane. High values of permeability likely come not from poor barrier properties of the coating, but an incomplete coating layer or cracks; the large and scattered values from the paper are a clear sign that the barrier layer is not continuous and that water vapor is finding easy paths through the sample, until the coating layer is thick enough to overcome the porosity of the paper. The coating layers on cellophane give a consistent result and a small value.

Figure 3.5 shows the results of the formulation and the pure latex on cellophane. For both, the value is much smaller than the results on paper and show an upward trend with coat weight. Again, the permeability coefficient should not be a function of thickness and the upward trend may indicate the formation of cracks in the coating layer, as is typical of drying of colloidal systems.

The formulation does include a plate like particle: the classic picture of a tortuous path to decrease water vapor transmission rate does seem to explain this result. However, when comparing the difference between the formulation and the pure latex on paper, the difference is much larger than on cellophane. This suggests that the platy particles in the formulation help to hold the coating into a continuous layer. In addition, these particles may block larger pores, improving the barrier properties. The formulation has a clear advantage over using the pure latex in that at a given coat weight, the amount of polymer used is lower for the formulation compared to the pure latex.

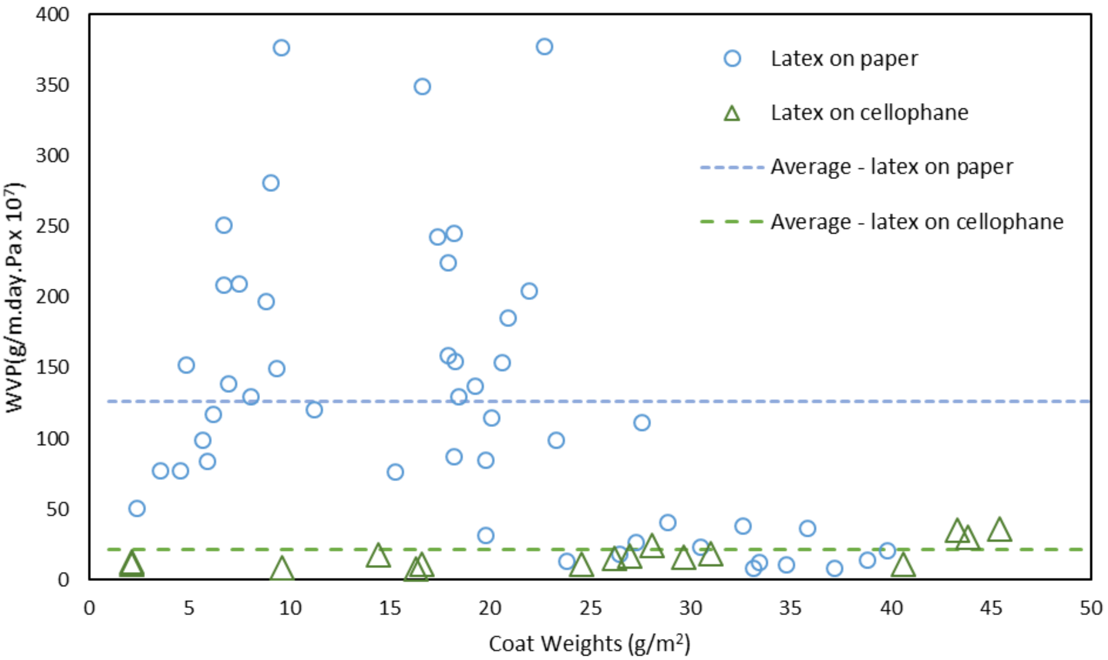


Figure 3.4 The results of Fig. 3.2 in terms of water vapor permeability (WVP). It is shown that WVP is much improved when cellophane is used, from 126 to 21 g/m.day.Pa x 10^{-7}.

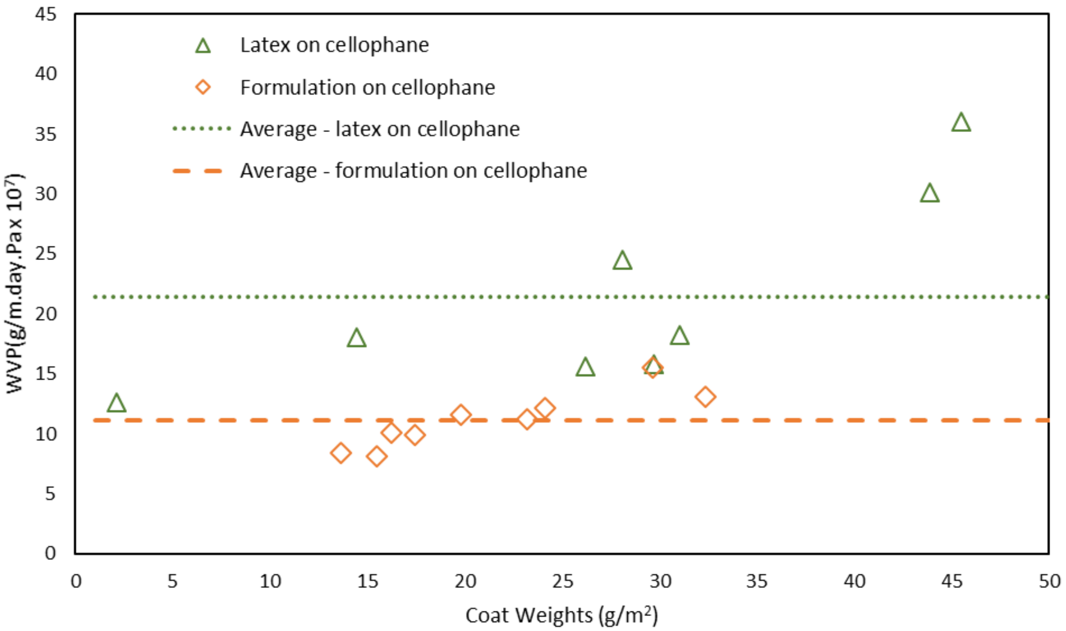


Figure 3.5 Comparison of WVP for pure latex and formulation on cellophane.

The behavior of the pure latex and the formulation are compared in Figure 3.6 on paper in terms of water vapor permeabilities. The formulation gives quite a small and consistent value compared to the results of the pure latex on paper. The average value of the permeability of the formulation is around 5x10^{-7} g/(m^2 day Pa). This result suggests that the role of the plate like pigments is more than just providing a tortuous path for water transmission, but the pigments must help block open paths and keep the coating layer continuous. This concept is important to understand in generating these barrier layers.

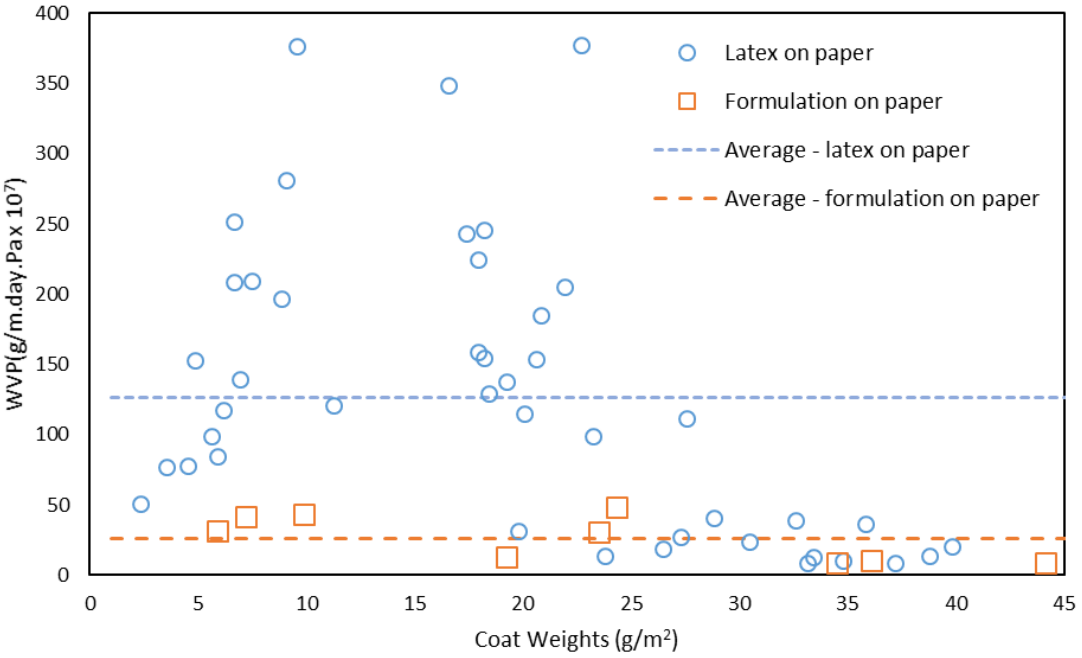


Figure 3.6 Comparison of WVP for pure latex and formulation on paper. The average WVP is improved from 126 to 21 g/m.day.Pa x 10^{-7}.

Figure 3.7 compares the CLSM images of the formulation and the latex-only on cellophane. Both samples have some faint ridges that are likely from the rod draw down coating. The formulation has a few pores that are visible from the top view but no cracks are visible. From the cross-section view, that has some distortion due to some scattering in the microscope, the coating layer is compact with a thickness of around 22 m; this measurement is an average of measuring five different locations, ignoring the scatter in the image. The latex only also has a few pores, but fewer than the formulation. The thickness of the latex only sample 8 m. These thicknesses make sense for a concentrated layer of material.

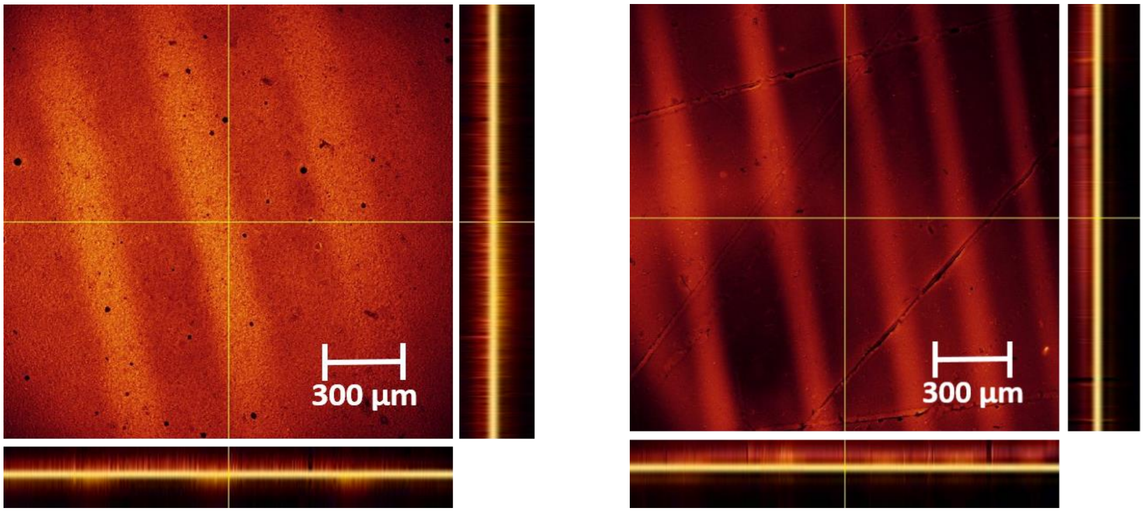


Figure 3.7 CLSM comparison of formulation (left) and latex-only (right) coated on cellophane. The image in bars on the bottom and side of each image are the cross-sectional view along the line drawn in the main image; the total distance in the thickness direction in these side bars is 120 μm. The coat weights for the formulation and latex-only were 24 and 7 g/m^2, respectively.

The comparison of the formulation and the latex only samples are quite different on paper, as shown in Figure 3.8. The coat weights of these are similar, around 18 g/m^2. One key issue that is clear is that the latex-only case has a number of cracks. It is hard to tell if these cracks in some way correlate with fibers or other features of the paper. Another important contrast is that the latex-only case shows material all through the sample, around 60 μm deep, while the formulation cross sections show the material right at the top of the paper, with a thickness of around 20 μm. There are still defects in the formulation layer, but at this coat weight, the formulation forms a clear layer on the top of the paper while the latex only case tends to soak into the full thickness of the paper.

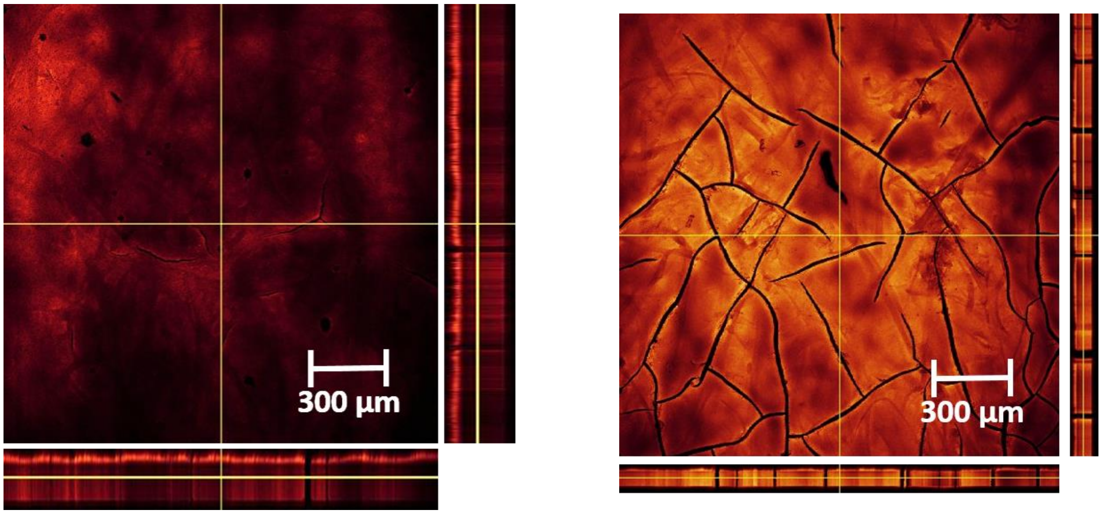


Figure 3.8 CLSM comparison of formulation (left) and latex only (right) coated on paper. The images in bars on the bottom and side of each image are the cross-sectional view along the line drawn in the main image; the total distance in the thickness direction in these bars is 120 m. The coat weights for the formulation and latex only were 24 and 23 g/m^2, respectively.

These images help explain the results of the permeability results above and point out an important aspect of the formulation. The plate like particles in the formulation not only act to increase the tortuous path for water vapor diffusion, but they also help keep the latex from soaking into the paper; the large plates much fill in the pores causing the latex to stay in a layer at the top of the paper. In addition, the plate like particle seem to help stop crack formation.

In conclusion, the influence of coating application method and substrate properties were compared for a barrier formulation and a latex intended for barrier applications. The results are compared in terms of water vapor transmission rate and the water permeability of the coating layer. The laboratory coating method did not have a clear influence on the results. However, the barrier formulation that contained a platy pigment had a significant influence. The use of cellophane as a substrate demonstrated the influence of paper pores on the result: pore significantly reduce the effectiveness of the barrier coating. The use of cellophane is a nice method to obtain the water vapor permeability of the coating layer itself. The formulation had lower permeabilities on both cellophane and paper compared to the pure latex coating: this indicates that the platy particles help block pores and helps keep the barrier layer as a continuous film.

CHAPTER 4: RESULTS FROM HIGH SPEED EXPERIMENTS

In the previous chapter, the influence of coating method, base sheet, and pigment particles have been covered. All those samples were prepared using laboratory coaters, with coating speed of 0.2 m/s at the highest. This chapter will discuss the influence of higher machine speed to the performance of barrier coatings. A different substrate was also used for this set of experiments and was found to have a major impact on the results.

Figure 4.1 below shows the results of the high vs. low speed coatings experiment in terms of WVTR. These data show that coatings produced at high speed generally perform better at any given coat weight, except for pure latex samples at coat weights above 15 g/m^2.

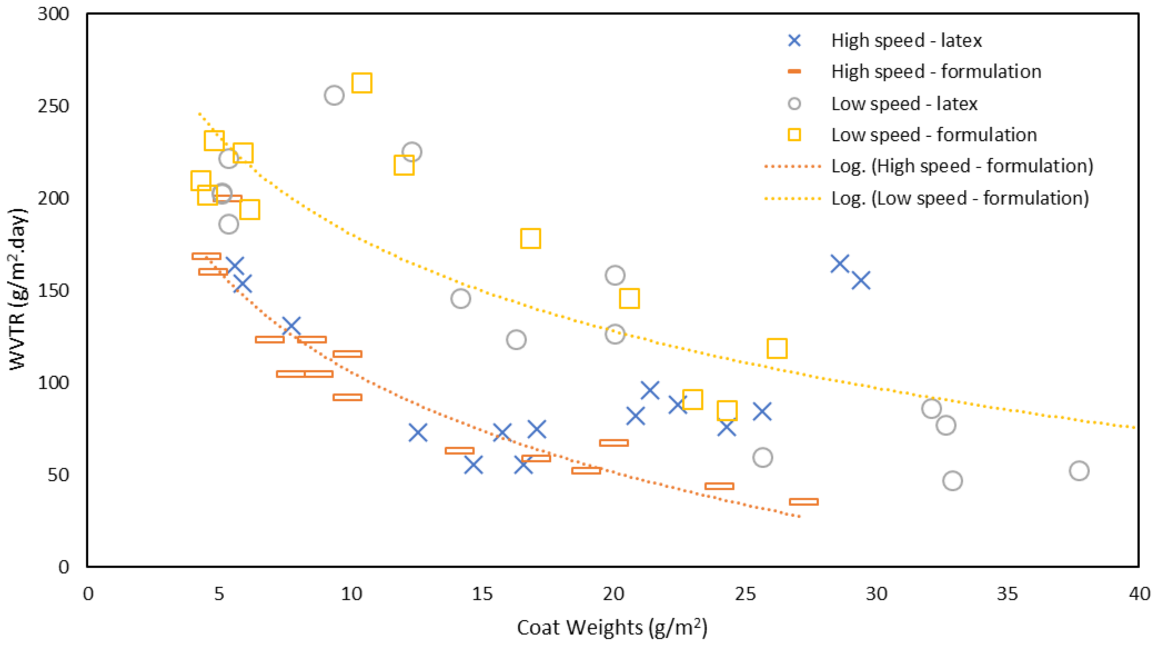


Figure 4.1 WVTR of coating samples made at low and high speeds.

Looking at the samples physically, these higher coat weight pure latex samples have more cracks in the middle of the coat paths. These defects at higher coat weights are more prominent on samples coated using the CLC than on those coated using the low speed draw down coaters. Difference in drying rates between the two methods may affect the latex film formation at higher coating thickness. The high-speed movement of the cylinder may facilitate cracking of the film as well. Some studies have found that excessive drying power using the IR lamp can cause defects.

Defects are not present on formulation samples. The mechanism that causes cracks or defects to be developed only on pure latex samples may need to be understood. In a study of dispersion barrier coatings on pigment-coated kraft paper, Andersson et al (2002) that high IR power for drying could cause more pinholes in certain cases, leading to poor barrier performance, but based on the experiment in most cases low or high IR power do not make much impact. Vähä-Nissi et al also stated that excessive use of IR-dryer at the beginning of drying can increase the number of pinholes. However, 15 seconds of drying time at 50% IR lamp power used in this experiment should not allow the temperature on coating surface to exceed much more than 100°C.

Regardless, the use of pure latex without pigments is not the common way to create barrier coatings. Many studies have concluded that pigments especially those with high aspect ratios contribute to improving barrier properties by providing tortuous path for diffusion. Moreover, in Chapter 2 it has been discussed that pigments do not only provide tortuous path but more importantly aid the coating layer to form on top substrate instead of sinking into paper pores. In addition, manufacturers try to maximize the amount of pigments added to formulation in order to minimize overall cost, without compromising product quality. Thus, focus can be given more in development of good barrier coatings made of formulation and not pure latex. Pure latex samples are incorporated in this study only to help understand the role of pigments in formulation.

Without including the defective pure latex samples at higher coat weights, Figure 4.1 shows that high speed coated samples made of formulation perform better than low speed coated samples throughout most coat weight ranges.

As indicated previously, maximizing pigments concentration in the formulation can reduce the cost to make formulation. The cost of pigments is trivial compared to latex, and thus Figure 4.2 was generated to show the barrier performance as a function of latex coat weights only. As one can see, WVTR of around 50 g/m^{2}day could be achieved at coat weight range around 15 g/m^2, which is not much inferior when compared to LDPE film performance of 15 g/m^{2}day at 24 g/m^2.

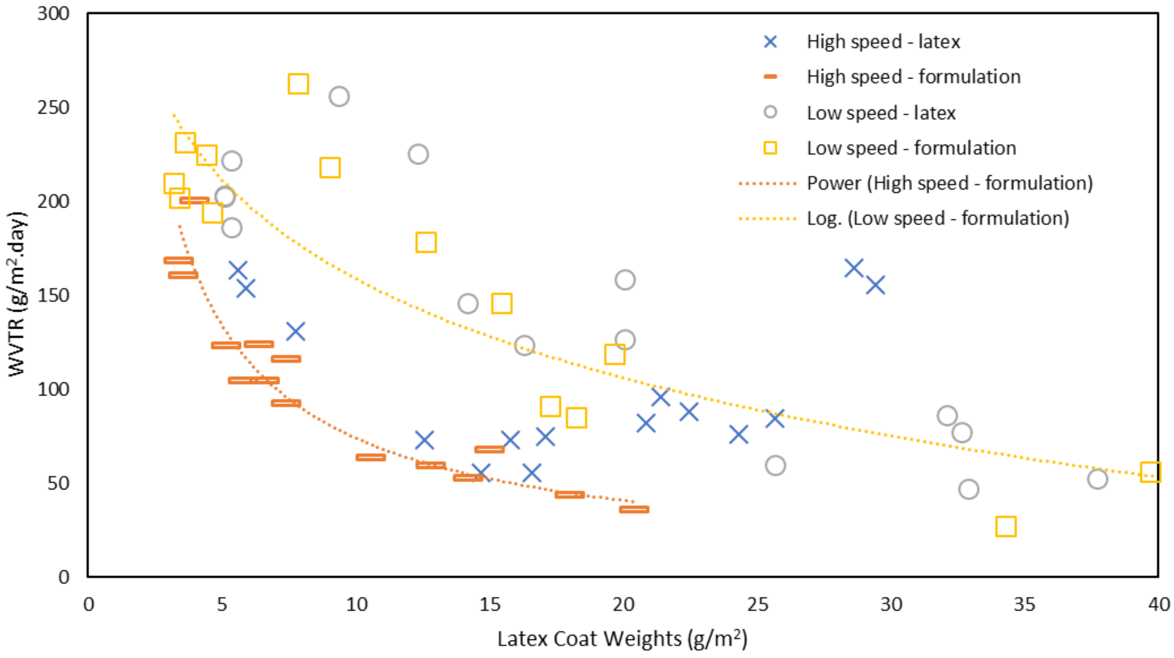


Figure 4.2 WVTR of coating samples made at low and high speeds as a function of latex coat weights.

Figure 4.3 shows the same data as in Figure 4.1 in terms of water vapor permeabilities, focusing more on comparing between low and high-speed samples and less on formulation against pure latex samples. The permeability of high speed samples averages at 21 g/m.day.Pa x 10^{-7} while the permeability of low speed samples is 39 g/m.day.Pa x 10^{-7} on average for the whole coat weight range of 1-50 g/m^2. Permeabilities values of high-speed samples are also more consistent (almost a flat trendline) than low speed coatings, indicating more uniform layers and less defects were formed at higher speed.

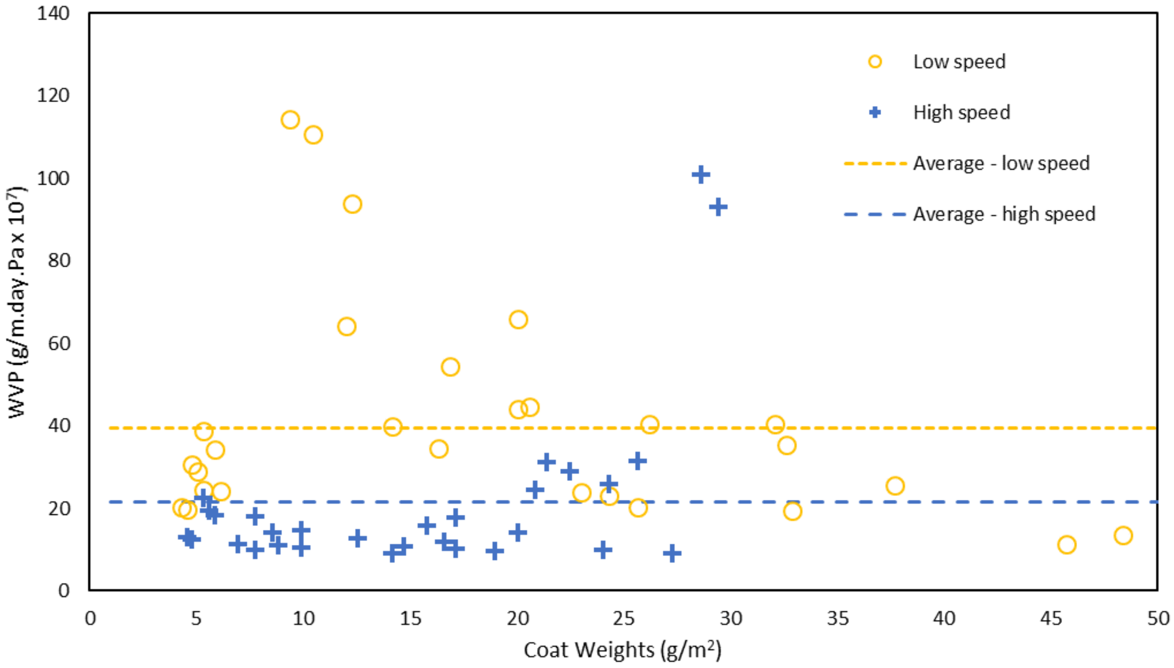


Figure 4.3 WVP of coating samples made at low and high speeds. High speed coatings depict slightly lower WVP at 21 g/m.day.Pa x 10^{-7}.

This finding is in contrary to some unpublished claims that coatings made at higher speeds perform poorer than those prepared with draw downs. These claims partly motivated this research to help understand what are the driving forces that could cause poor barrier performance.

Figure 4.4 shows the same data sets as on Figure 4.3 in terms of permeability and just comparing formulations and not coating speed. It appears that the data are scattered regardless of coating material used. The effect of high speed as shown on Figure 4.3 seems to be more prominent in determining the quality of barrier rather than the involvement of pigments.

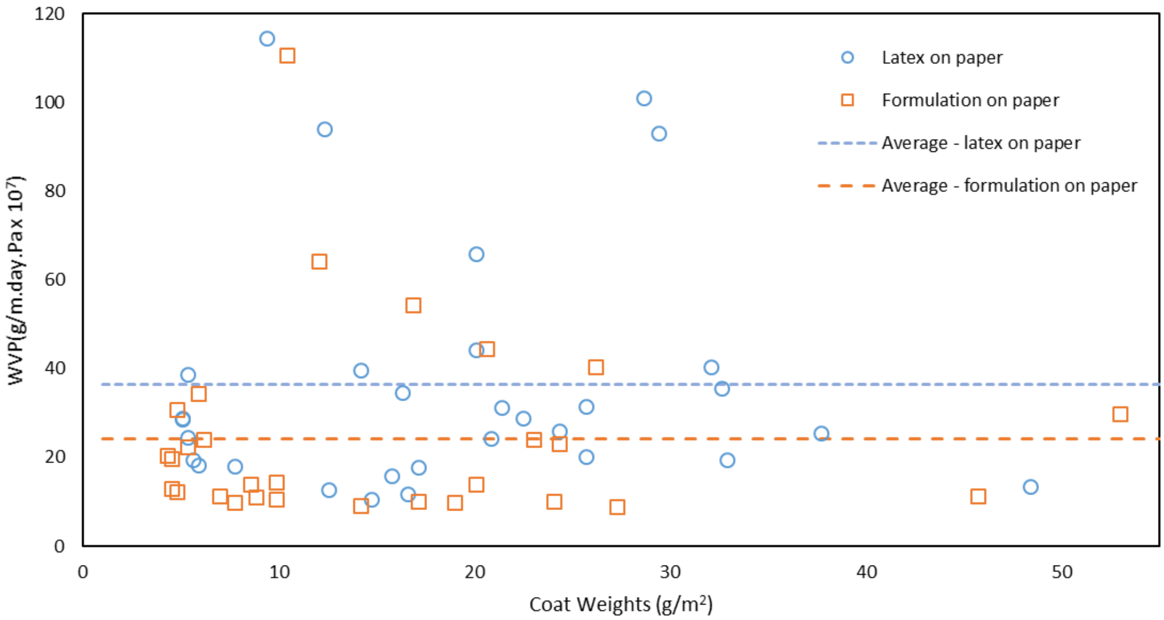


Figure 4.4 WVP of coating samples made of pure latex and formulation at all speeds. Pigments in formulation help improve WVP slightly from 36 to 24 g/m.day.Pa x 10^{-7}.

When comparing only samples made at high speed, as displayed by Figure 4.5, no distinction can be gathered between pure latex and formulation, other than the defects on thicker pure latex samples above 20 g/m^{2} as has been discussed before.

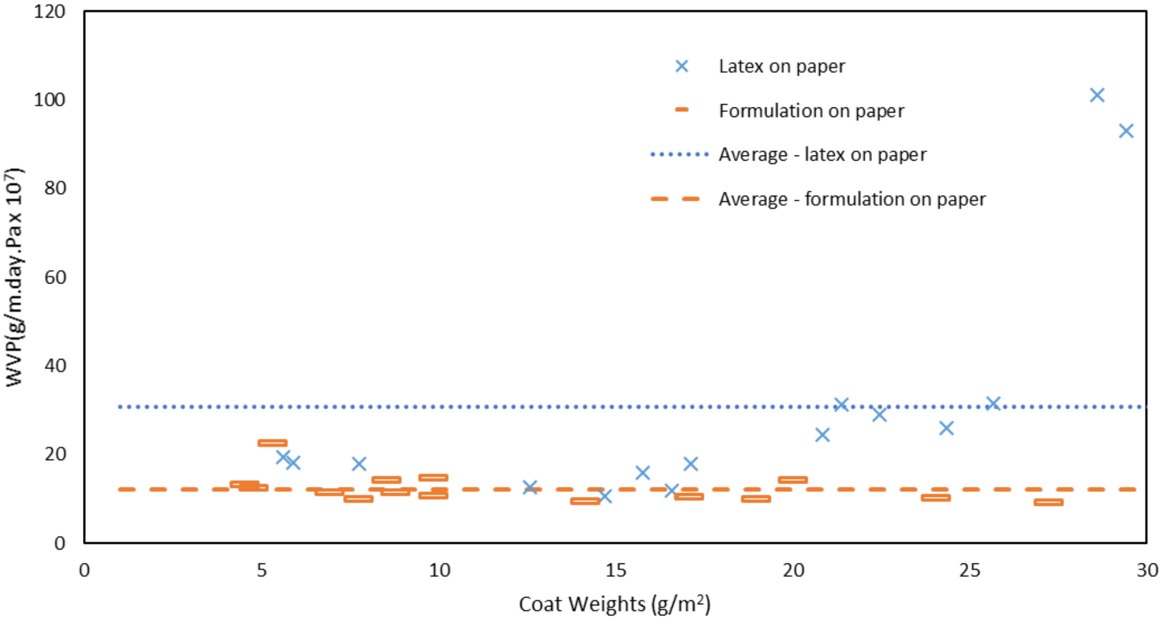


Figure 4.5 Comparison of latex vs. formulation samples made at high speeds only. High coat weights of latex only results are not included.

When comparing only samples made at low speed, as displayed by Figure 4.6, also no distinction can be gathered between pure latex and formulation. This observation is in contrast with the data from Chapter 1 on the effect of formulation to barrier performance. This data does not support the conclusion that formulation improves barrier performance on paper.

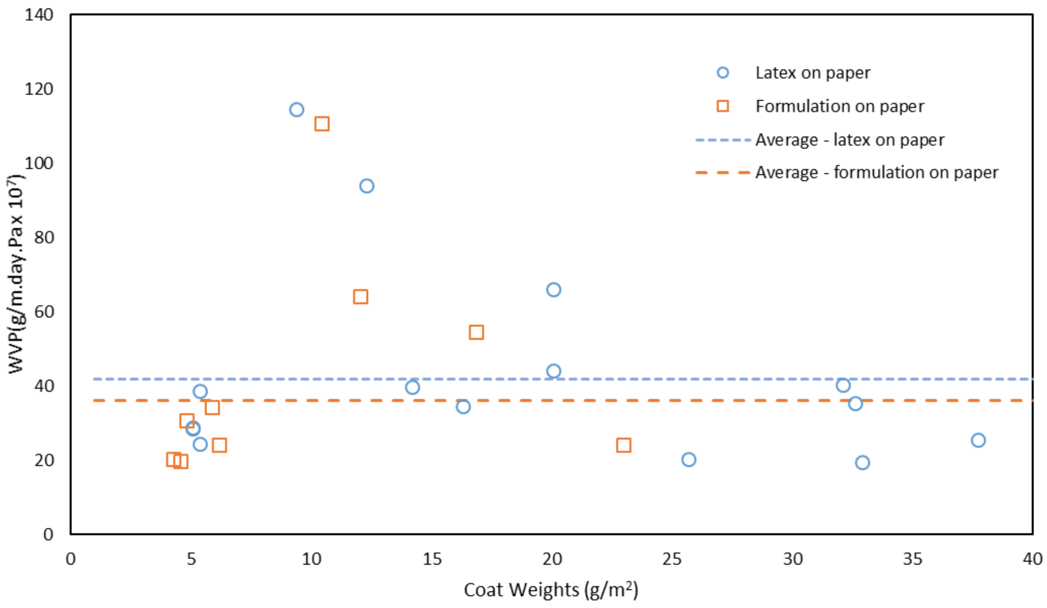


Figure 4.6 Comparison of latex vs. formulation samples made at low speeds only. Pigments do not improve barrier performance significantly.

All these findings as indicated on Figure 4.4 to 4.6 lead to the conclusion that in this series of experiment, pigments in the formulation do not have as much impact to performance unlike the use of pigments on regular copy paper as shown in the previous series of experiments in Chapter 3. More importantly, the highest WVP in this series of experiment is around 115 g/m.day.Pa x 10^{-7} while coatings on regular copy paper permeabilities scattered even as high as in the 200-250 g/m.day.Pa x 10^{-7} ranges (see Figure 3.4 in Chapter 3). The big difference is the base sheet used in the two studies.

This series of experiments use a much less absorbent paper than regular copy paper, as shown by the Bristow wheel test comparisons shown on Figure 2.2.2. This paper, called LA paper in this study, has an absorption coefficient of less than 2 cm^3/m^2 and porosity of 28%. On the other hand, regular copy paper has an absorption coefficient of 50 cm^3/m^2 and porosity of 36%. Even though the porosity of both papers are not that far apart, the hydrophobic nature of LA paper may help eliminate issues with coating layer non-uniformity associated with papers with high porosity. Therefore, it is expected, that less dewatering of coatings during coating film formation leads to a better barrier layer on top of substrate.

For paper with high porosity and high absorbency like the regular copy paper, the addition of pigments in formulations helps with generating more continuous layer and improved barrier performance by preventing the coating from sinking into paper pores. In the case of low absorbent papers, the use of pigments still helps with lowering WVTR and WVP, but its role is less prominent when the coating is on a low absorbent paper. In other words, LA paper behaves similar to cellophane on which coatings do not form much defects. As discussed in Chapter 3, coated cellophane has much better barrier performance than coatings on paper. The use of pigments on cellophane also improved the performance, but only by around 5-10 g/m.day.Pa x 10^{-7}, as shown on Figure 3.5. Table 4.1 and 4.2 below summarizes the results of average WVTR and WVP for the different base substrates used.

	BASE SHEET PROPERTIES				WVTR WITH COATING					WVP WITH COATING			
	Basis weight	Porosity	Absorption coefficient	Base sheet WVTR	Avg. WVTR (<20 gsm)	Avg. WVTR (20-40 gsm)	Stdev (20-40 gsm)	WVTR improvement	Base sheet WVP	Avg. WVP (<20 gsm)	Avg WVP (20-40 gsm)	Stdev (20-40 gsm)	WVP improvement
	g/m^2	%	cm^3/m^2	g/m^{2}day	g/m^{2}day	g/m^{2}day		%	g/m.day.Pa x 10^7	g/m.day.Pa x 10^7	g/m.day.Pa x 10^7		%
Copy paper	78	36	50	290	234	102	76	65%	248	159	76	92	52%
Low Absorbent paper	48	28	2	322	196	87	38	73%	283	50	36	15	29%
Cellophane	46	0	N/A	223	96	47	8	79%	22	12	17	4	-48%

Table 4.1 Comparison of latex only coatings on different substrates applied at low speed.

	BASE SHEET PROPERTIES				WVTR WITH COATING					WVP WITH COATING			
	Basis weight	Porosity	Absorption coefficient	Base sheet WVTR	Avg. WVTR (<20 gsm)	Avg. WVTR (20-40 gsm)	Stdev (20-40 gsm)	WVTR improvement	Base sheet WVP	Avg. WVP (<20 gsm)	Avg WVP (20-40 gsm)	Stdev (20-40 gsm)	WVP improvement
	g/m^2	%	cm^3/m^2	g/m^{2}day	g/m^{2}day	g/m^{2}day		%	g/m.day.Pa x 10^7	g/m.day.Pa x 10^7	g/m.day.Pa x 10^7		%
Copy paper	78	36	50	290	163	73	45	75%	248	32	24	16	24%
Low Absorbent paper	48	28	2	322	215	110	24	66%	283	45	33	10	26%
Cellophane	46	0	N/A	223	55	47	4	79%	22	10	13	2	-35%

Table 4.2 Comparison of formulation samples coated on different substrates applied at low speed.

Both Table 4.1 and 4.2 provide a different way to emphasize the high contribution of parameters to barrier performance. All data presented are from low speed experiments. Average WVTR's and WVP's are calculated for two ranges of coat weights (<20 g/m^2 and between 20-40 g/m^2). WVTR improvements are based on the improvement provided by the coatings at 20-40 g/m^2 in respect to WVTR of the base substrates. WVP improvements are based on the improvement provided by the coatings at 20-40 g/m^2 in respect to WVP of coatings at <20 g/m^2, showing the contribution of additional coating thickness.

As shown on Table 4.1, without the contribution of pigment, the choice of substrate is really important in determining the WVTR and WVP improvements. WVTR improvements increase from 65% to 79% by the use of smoother and less absorbent substrates. Standard deviation, which represents the consistency of coating quality is also greatly improved. By using regular copy paper, lower WVP (76 g/m.day.Pa x 10^{-7}) can be achieved by adding more coat weights, but still much worse than coating on cellophane at lower coat weights. Adding more coat weights is less impactful to performance when LA paper or cellophane is used, as shown by the WVP improvement data. WVP improvement is actually negative on cellophane, possibly due to defects that are only formed when the coating is too thick, affecting film formation.

Looking at Table 4.2, WVTR improvement on regular copy paper is increased by the use of pigments. It now has WVTR improvement of 75% as opposed to 65% without pigment. Standard deviation was also improved, although still higher than those of coatings on other substrates. Interestingly, pigments do not show positive impact to WVTR for coatings on LA paper and cellophane (73% to 66% for LA paper and 79% to 79% for cellophane). Similarly, WVP of LA paper and cellophane only improve slightly with the addition of pigments, whereas the WVP improvement on copy paper is much higher, from 159 to 32 g/m.day.Pa x 10^{-7} for coat weight range <20 g/m^2. This is in contrary to the idea that pigments should improve barrier properties by providing tortuous path, regardless of the substrate used.

All of these results show that base substrate choice has the most significant impact to barrier performance and that pigments can eliminate issues with coating on highly porous and absorbent substrates. The pigments were thought to improve barrier performance by creating path of tortuosity. However, if that is the case, then pigments also would improve performance greatly for coatings on cellophane and low absorbent papers. Pigments improve barrier performance by filling in the pores, facilitating more uniform film formation only when latex tends to sink in into absorbent substrates and form pinholes in the coating layer.

In the study by Weeks and Bousfield (2017), it was found that less filtercake is formed on the less absorbent coated surface when compared with uncoated surface of a substrate. Filtercake is formed when fluid in coating formulation penetrates into the substrate, leaving the solids on top of fibers as filtercake. This finding further supports previous statement about the effectiveness of non-absorbent substrate to hold coating layer on top of fiber surface and thus can improve barrier properties. The fast penetration of fluid into absorbent substrates reduces the uniformity of barrier layers. This explains why barrier properties of coatings on LA paper are much better than barrier properties of regular copy paper.

A study by Johnson et al (2019) on the use of cellulose nanofibrils (CNF) to improve barrier performance shows similar functionalities of the CNF and pigments in barrier formulations. On top of being good oxygen and grease barrier, CNF is coated onto paper to generate continuous layer of barrier coating. The permeability of the paper can be reduced by two orders of magnitude. WVTR as low as 20 g/m^2day was achieved at 6 g/m^2 coat weight when 4 g/m^2 of CNF was on the top layer of the paper: this top layer closes up pores and should keep the barrier layer as a uniform layer.

Many things are quite different between coating utilizing CLC coater and draw down coaters. One of the most important factors is obviously the speed. Referring also to the study by Weeks and Bousfield (2017), when other factors such as particle size variations in formulation and base substrate properties are kept constant, pressure pulse that exists between the substrate and blade was found to increase as speed increases. In consequence, the penetration of liquid into the substrate vary with coating speed. This is also proven by the increase in filtercake formation with increasing speed. In other words, as speed increases, more rapid dewatering occur and create less uniform layer on top of substrate. However, this finding on the effect of speed is also in contrary to the finding on LA paper, where high speed coated samples perform slightly better. The effect of substrate may overcome the effect of speed (higher pressure pulse) when non-absorbent substrate is used.

On the other hand, based on a couple of literatures, higher coating speed is said to help with pigments particles alignment. Vähä-Nissi (2006) observed that for some samples the number of pinholes decreased as the line speed increased, which lower penetration into the substrate and more optimal drying. For samples with platy clay and talc it was suggested that the pigment particles were better oriented at higher speeds and improve barrier. Popil (2006) also indicates that good platelets orientation is parallel to substrate surface, and that it can usually be achieved by coating at high speeds, high solids content, and high viscosity.

Another major difference between CLC and draw down coaters is the mechanical movement of the equipment. With the CLC, there exist centrifugal force associated with the rotation of the cylinder, which may counteract the capillary force and force from the blade, forces that contribute to the penetration of fluid into substrate. Similar phenomenon is utilized by Hwang et al (2011), who found a novel method to control wicking distance in paper by varying rotation speeds of the wheel where the paper is placed. The wicking distance, h, can be calculated by the following equation

$$\Delta P = \Delta P_c - \rho\omega^2 \left(R_0 - \frac{h}{2} \right) h \tag{4.1}$$

where ΔP is the net driving pressure for absorption, ΔPc is the capillary pressure, ρ is density, and ω is the angular velocity of the rotating device.

Besides speed and mechanical forces, drying mechanism is also different. At low speed experiments, once coating is applied on substrate, samples were transferred into oven and left for 5 minutes at 105°C. Average time to transfer samples to the oven was about 20 seconds, when air drying at ambient temperature could happen. With the CLC coater, besides preheating of base substrate prior to coating application, the film that is formed on the substrate is also immediately heated using IR lamps, although with only 15 seconds at 50% power the temperature should not have exceeded much more than 100°C based on the heating curve of 1000T3 lamp. A more thorough study on the difference in mechanism between oven drying or IR lamps drying may help provide some explanation.

Overall, in this chapter the base sheet properties were found to have high contribution to the performance of barrier performance. The effect of pigments is not as prominent when non-absorbent substrate is used. Also, the use of non-absorbent substrate may help overcome any negative impact associated with coating at higher speed such as high pressure pulse, while mechanisms that help with barrier quality such as the centrifugal force and better platelet alignments still exist.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Dispersion barrier coatings can provide a solution to environmental issues associated with plastics. It can also allow papermills to transition from printing to packaging products without requiring high capital expenditures. However, technology for dispersion barrier coatings that can compete with more superior products such as polymer extruded barrier coatings is still in the research and development stages. More studies are still needed to understand the importance of the different parameters associated with the making of dispersion barrier coatings.

In this thesis, the effect of coating methods, pigments, base substrates, and machine speeds to barrier properties, especially water vapor transmission rates are compared. A novel method of using cellophane to analyze coating performance without the disturbance of surface roughness and porosity associated with paper was introduced. The performance of just the coating layer and the role of pigments in barrier coating formulations could be studied with this method.

At low speed, different coating application methods which include various rod and blade coaters do not show any difference in the WVTR curve. Curtain coating method as described in one literature may portray a different curve. The effect of base substrate was found to be prominent, as indicated by the barrier performance of coating on cellophane. The smoothness and non-porous nature of cellophane help in generating more uniform layer of coating. When typical porous substrate such as regular copy paper must be used, however, the addition of pigments was proven to be imperative not only to provide tortuous path of diffusion but more significantly to help preventing the dispersion coating to sink into the pores.

This concept of coating hold-out provided by pigments particles was further proven. When non-absorbent and less porous paper was used for both low and high speed coatings, the contribution of pigments to moisture barrier properties was not as significant as its contribution on regular copy paper. The role of pigments to fill in pores and help creating more complete coverage of substrate is greater than its role to provide tortuous path for diffusion. The importance of base substrate properties thus must be emphasized. The use of low absorbent paper greatly improves barrier performance, whether pigments are used or not in the formulation.

Moreover, when the issue of non-uniform coating layer has been overcome either by using low absorbent substrate or using pigments on porous and absorbent substrates, coating at high speed may slightly improve the barrier quality due to the existence of centrifugal force on most cylindrical coaters and better pigment platelets alignments which increase tortuous path for diffusion. These theories may support the finding that coatings on low absorbent paper made at high speed perform slightly better than the low speed samples.

5.2 Recommendations

Further research on this topic may include analysis on performance of pure latex and formulation coatings at high speed on regular copy paper or any similar substrate with comparable absorbency. Having such data will really complete the analysis on different substrate absorbency, effect of pigments, and machine speed and movement. More substrates with varying surface absorbency can also be used so a model may be developed to predict barrier performance based on substrate properties, with and without pigments. Another aspect that can be investigated further is the difference between drying mechanisms of oven drying and CLC coater IR lamp drying. Determining the most comparable dryer settings could potentially eliminate any effect caused by the difference in drying mechanism between low speed versus high speed experiments.

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APPENDIX I: WVTR MEASUREMENT METHOD

Figure A.1 below shows that different period of time used between first weight measurement of jar and the second measurement do not significantly alter WVTR results after 24 hours. This test was done on six different samples. Thus, in this research samples were conditioned in the TAPPI controlled temperature and humidity room (25°C and 50% R.H.) for at least 24 hours before second weight measurement for WVTR determination.

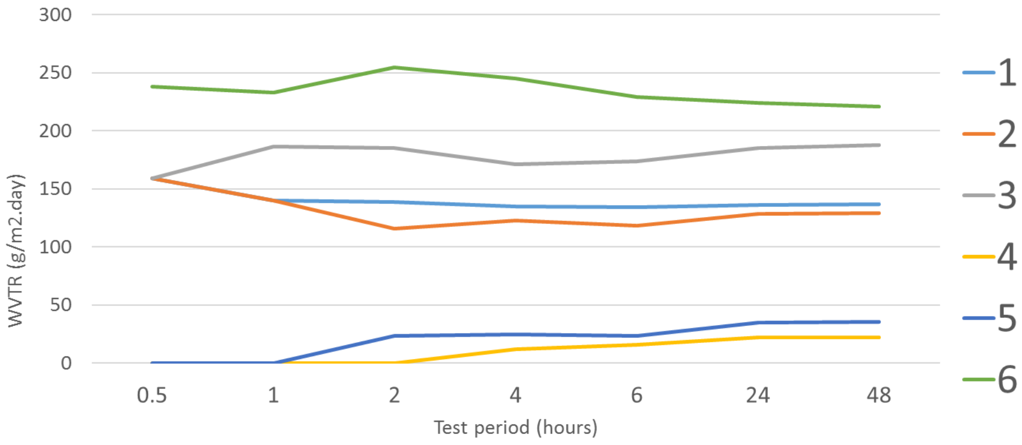

Figure A1.1 WVTR of five different samples measured after different periods of time.

To determine repeatability of WVTR measurement method, multiple samples were measured for WVTR twice. No results of same sample differ more than 10% and the differences of WVTR between the different samples can still clearly be observed, as shown by Figure A1.2.

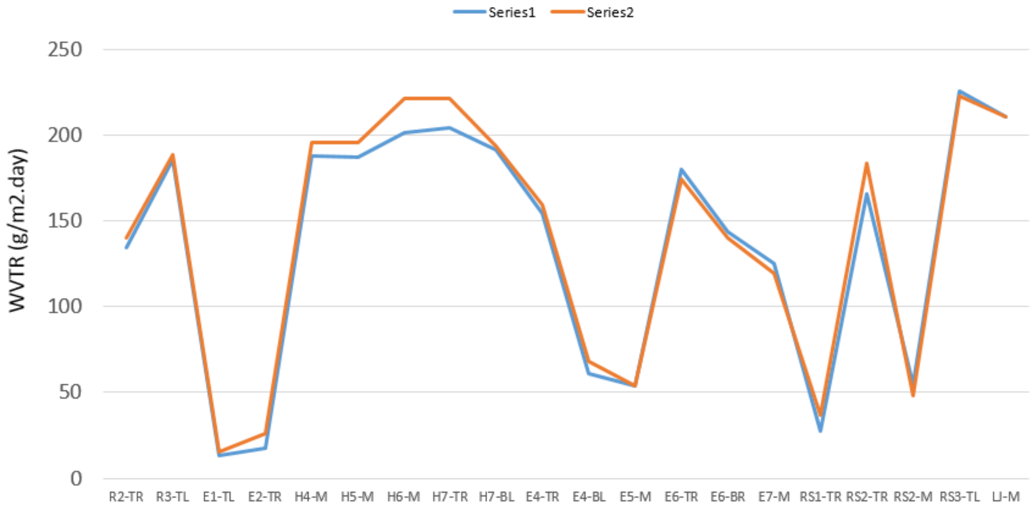

Figure A1.2 Repeatability of WVTR measurement method used in this research.

APPENDIX II: EXPERIMENT ON SIZED PAPER

Another experiment that was done by the author was pure latex coating on sized paper. As shown by Figure A2.1, pure latex coatings on sized paper depicts similar WVP trend as formulation on cellophane coatings. The WVP values are also close and much lower than WVP of pure latex on copy paper. This indicates that sized paper behaves similar to cellophane and even without the addition of pigments can generate comparable barrier performance as formulation on cellophane.

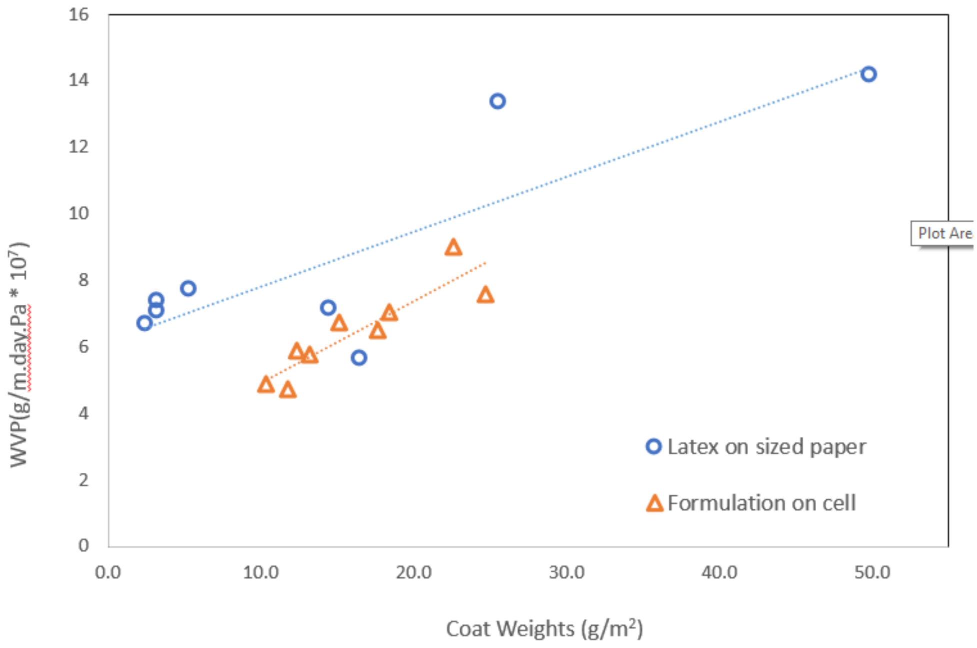

Figure A2.1 Latex on sized paper coatings compared to formulation on cellophane coatings.

APPENDIX III: EXPERIMENT ON LINERBOARD

The author also experimented coatings on linerboard with different calipers. It was expected that higher caliper would generate poorer barrier coating due to lack of surface coverage. However, the data as shown on Figure A3.1 shows the opposite The linerboard with lowest caliper even at much higher coat weight gave the highest WVP. A repeat of this study should be conducted.

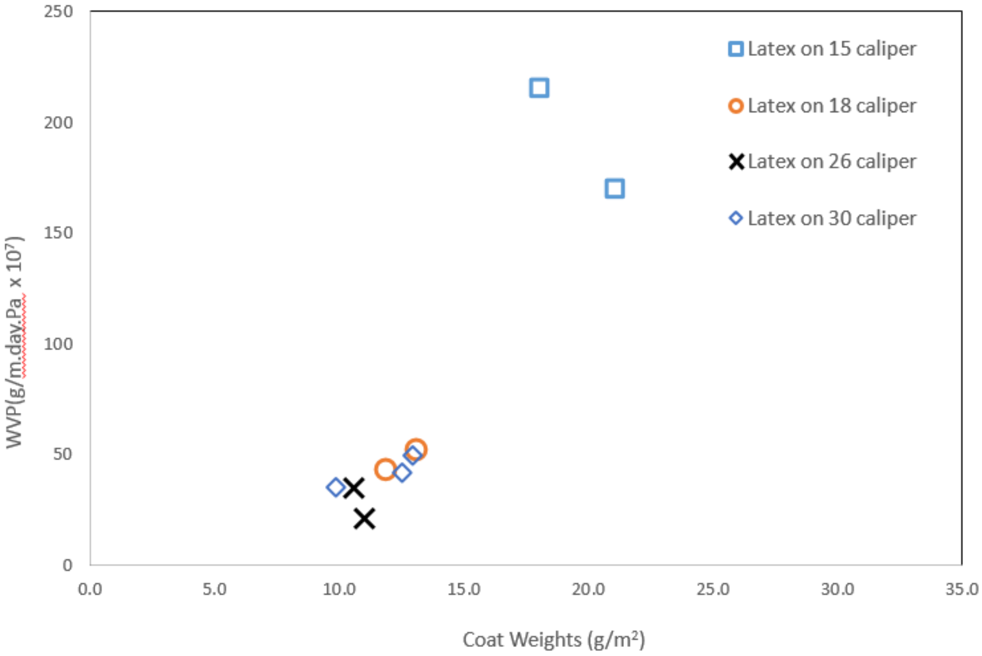

Figure A3.1 WVP of pure latex on linerboards with different calipers.

BIOGRAPHY OF THE AUTHOR

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