Test method and coating composition impact on measured moisture vapor transmission rate for waterborne coatings on paper

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ABSTRACT: Moisture vapor barrier is one of the necessary performance attributes for paper packages. Two methods are typically employed to assess the moisture vapor transmission rate (MVTR): the gravimetric cup method (ASTM E96) and the MOCON method (ASTM F1249). While those tests have been compared for free standing polymeric films, less is understood about their application in coated paper.

Our results show that, despite a general agreement between the two methods, discrepancies exist where test protocols and material properties of coated paper impact the MVTR measurement. The measurement discrepancies can be explained by differences in local moisture concentration. Our study provides new insights on moisture vapor barrier assessment of waterborne coatings on paper and implications for achieving paper packages with improved barrier performance.

Application: Evaluation of moisture vapor barrier performance is critical for development and application of barrier coatings for paper packages. Understanding the impact of testing method and coating material on MVTR guides the assessment and implementation of waterborne coatings for different applications.

Barrier coating for paper is a growing area of interest with increasing sustainability demands [1]. One important barrier performance is against moisture vapor. The typical way of assessing moisture vapor barrier is by measuring the moisture vapor transition rate (MVTR) through the coated sample. The standard ways of measuring MVTR include gravimetric cup method (ASTM E96 "Standard test methods for water vapor transmission of materials") and the MOCON method (ASTM F1249 "Standard test method for water vapor transmission rate through plastic film and sheeting using a modulated infrared sensor"). Previous studies confirmed the consistency between those two test methods for polymeric films [2].

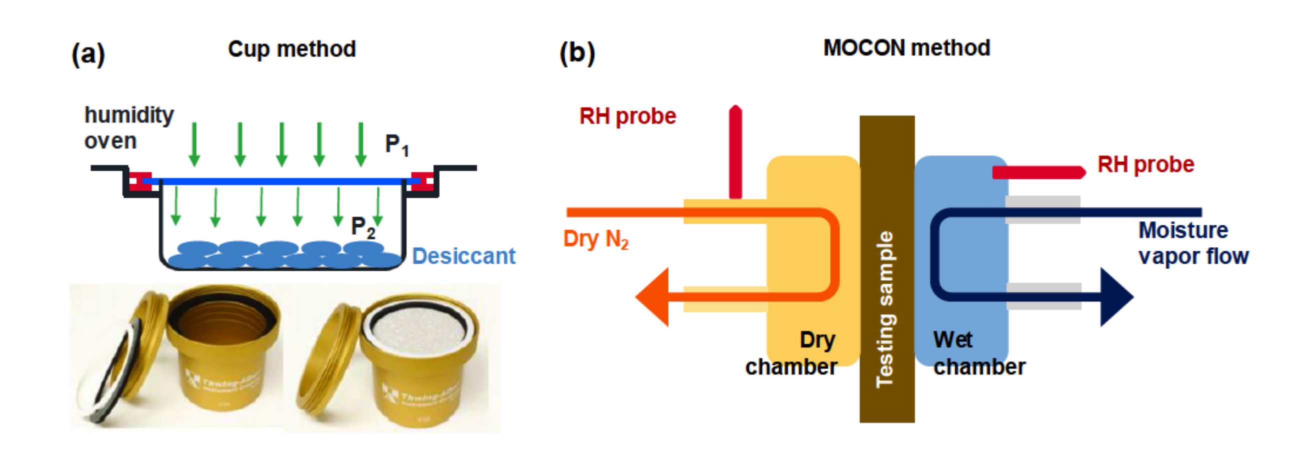
However, those two test methods have largely not been compared for barrier coatings on paper. In particular, little attention has been paid to the moisture transport differences between a free polymeric film and a barrier film coated on paper via waterborne dispersions. Understanding the impact of test method and coating material on MVTR for waterborne coatings on paper provides important information to assess the real barrier performance, and therefore performance, in packaging applications.

The goal of this study is to provide understanding of the measured MVTR for coated paper samples prepared from waterborne coatings. We want to highlight the MVTR dependence of coated paper on both moisture absorption and diffusion. In particular, moisture absorption of the paper substrate itself and the presence of hydrophilic components common in waterborne dispersions change the local moisture concentration and impact moisture transport. The dependence of MVTR on the testing method and the coating material properties needs to be considered to assess the true moisture barrier of paper coated with waterborne dispersions. Our understanding of the previously mentioned impacts also has implications for implementing waterborne coatings for barrier applications.

EXPERIMENTAL METHODS

Sample preparation

Paper substrates used in this study are low porosity, supercalendered paper substrates (62 g/m²). Barrier coatings and their blends were applied by hand to paper substrates at room temperature using a metal Mayer rod drawdown rod and dried in a forced air oven (IsoTemp 180L, Fisher Scientific; Waltham, MA, USA) for 2 min at 100°C prior to application testing. Waterborne coatings used in this study include aqueous polymer solutions, polymeric emulsion blends via traditional latex emulsion processes, and barrier dispersions prepared using the trademarked BLUEWAVE Mechanical Dispersion Process from Dow (Midland, MI, USA) [3]. The ethylene acid ionomer dispersions are made with ionomer or ethylene acid copolymer from Dow. The polyvinyl alcohol (PVOH) and ethylene vinyl alcohol (EVOH), both from Kuraray America (Houston, TX, USA), and the bentonite (Sigma-Aldrich; St. Louis, MO, USA) were post added into dispersions and the mixtures were stirred



1. (a) Illustration of the Cup method, and (b) illustration of the MOCON method (RH: relative humidity; N_2: nitrogen gas). The MOCON method is adapted from MOCON AMETEK website [4].

overnight with a dry weight ratio described in the context. Coat weight was determined by measuring a predefined area of coated paper and comparing it to the weight of an equally sized piece of uncoated paper under the same humidity and temperature. Coat weight for tested samples was carefully controlled and recorded to compare the measured MVTR.

Performance testing

Two testing methods, a Cup method based on ASTM E96 and a MOCON method based on ASTM F1249, were employed and are illustrated in **Fig. 1**. Due to the impacts of coating quality on MVTR, samples were inspected before testing to eliminate those with visible defects. Coat weight was also carefully tracked to ensure consistent comparisons.

Cup method

The Permeability Cup (Perm Cup) method follows ASTM E96 and involves sealing a coated paper sample to the open end of a cup. Desiccant is used to maintain relative humidity (RH) of zero inside the cup and create the vapor pressure difference imposed on the sample from the RH difference between inside and outside of the cup. The samples are exposed to a controlled temperature and a humidity environment, typically using a humidity chamber under tropical conditions of 38°C and 90% RH and a controlled lab under 23°C and 50% RH. Unless specified, the sample direction is coated film to the humidity environment (film to RH) to avoid weight increases due to wet paper. The MVTR is determined based on mass uptake for the perm cup apparatus as a function of time. The cups used were purchased from Thwing-Albert Instrument Co. (West Berlin, NJ, USA) with a sample area of 31.2 cm².

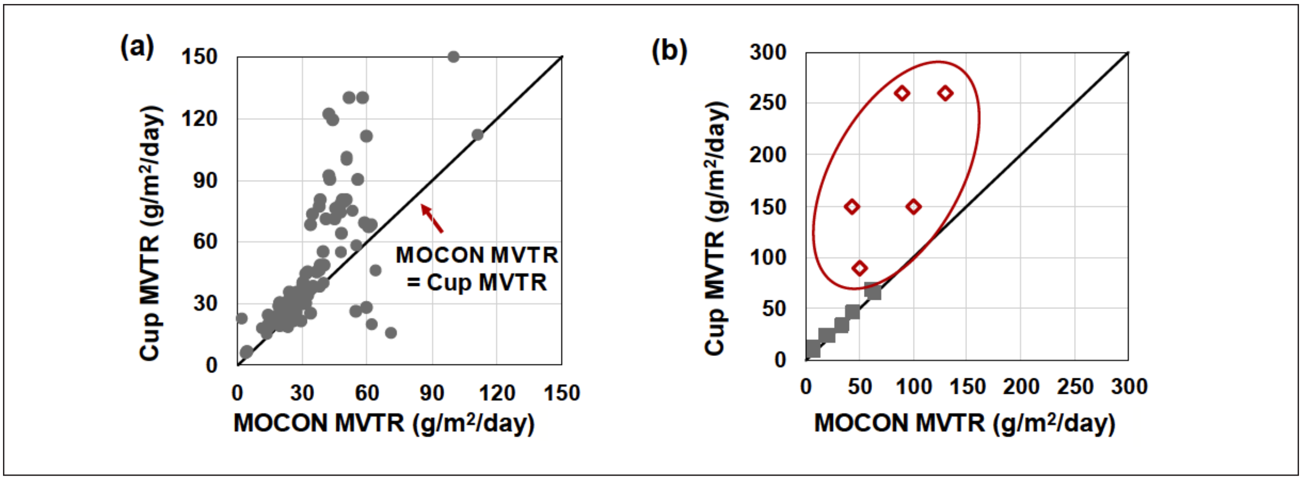
MOCON method

The MVTR performance of the paper coatings was tested at 38°C and 90% RH using MOCON according to ASTM Method F-1249. A MOCON 3/34 module was used to evaluate MVTR for this study. Coated paper specimens were masked and loaded directly in the MOCON unit for measurement. The masking material is 3 mil aluminum with an acrylic adhesive layer to make the seal. The testing sample area is 20.27 cm². The carrier gas (dry nitrogen gas, N_2) circulates the dry chamber to ensure accurate measurement of moisture concentration, while the test gas moisture vapor circulates through the wet chamber to maintain a constant RH level set by the instrument. The samples were tested in two directions: barrier to test gas direction, where the coated film is directly exposed to the wet chamber, and barrier to carrier direction, where coated film is exposed to the dry chamber leaving the paper substrate facing the humidity.

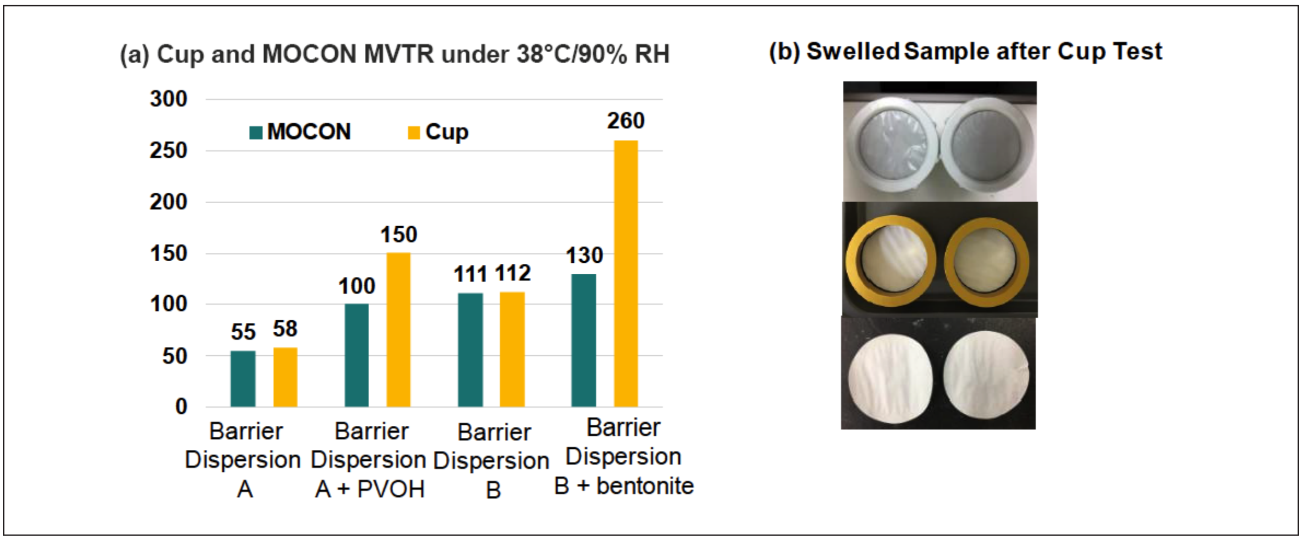
RESULTS AND DISCUSSION

Figure 2a compares the MVTR tested under tropical conditions (38°C/90% RH) with Cup method and with the MOCON method for samples demonstrating MVTR in a range from 0 to 150 g/m²/day. The black line represents the ideal case where Cup MVTR would equal MOCON MVTR. Figure 2a indicates some disagreements between the two test methods. To ensure control of potential variabilities from operator error such as sample damage, coat weight variability, etc., a subset of samples was tested again with careful inspection of sample integrity. These test results are compared in Fig. 2b, which demonstrates both very good agreement (grey squares) and significant deviations (open red diamonds), consistent with the larger data set. The origin of discrepancies is further discussed in the context of material properties for coatings from waterborne dispersions.

Some representative waterborne coating examples illustrating the test discrepancies between the Cup and MOCON methods are listed in **Fig. 3a**, where hydrophilic components such as PVOH (0.7 wt%) and bentonite (5 wt%) are



2. Comparison of the moisture vapor transmission rate (MVTR; g/m²/day) measured under 38°C/90% relative humidity (RH) with Cup method (y axis) and MOCON (x axis): (a) Data summary from a wide range of samples, and (b) selective data where the exact same sample species were used for MOCON and Cup tests.

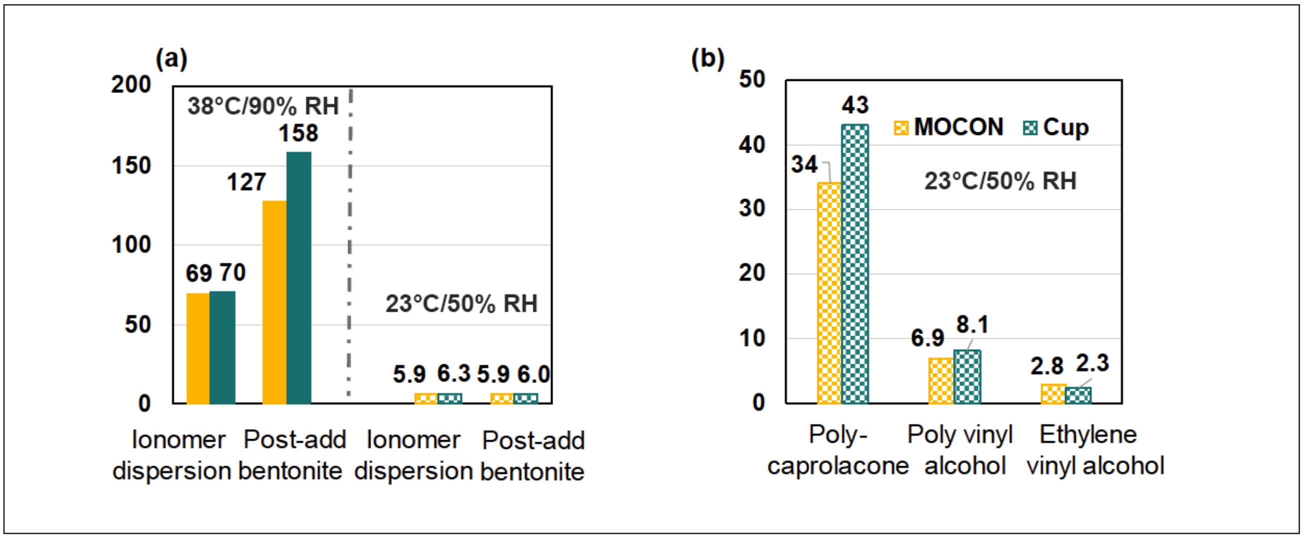


3. (a) Hydrophilic components raise MVTR differences between Cup and MOCON method, and (b) observed sample swelling with the Cup test.

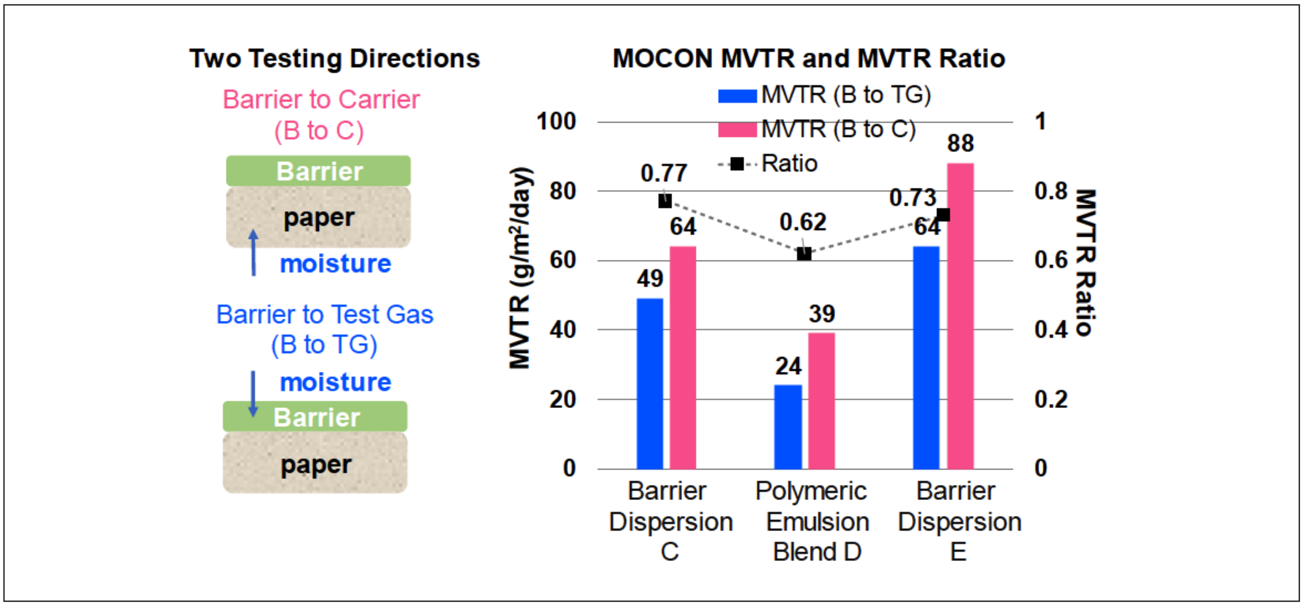
intentionally introduced to increase the coating hydrophilicity. The introduction of hydrophilic components considerably increases the magnitude of the MVTR discrepancies between the two methods as compared with results from the control samples without those additives. In addition, significant sample swelling was observed for those samples containing hydrophilic additives after the Cup measurement, when the samples were exposed to a humidity chamber over 1–3 days. Figure 3b shows a photo for the tested samples where wrinkling of coated paper was found after the cup test. The results demonstrate the impact of moisture absorption on moisture permeation, which will be further elaborated based on transport fundamentals.

To further demonstrate the impacts of hydrophilic components on tested MVTR, **Fig. 4** compares the tested MVTR using both Cup and MOCON methods with different materials and under different testing conditions. In Fig. 4a, two testing conditions, 23°C/50% RH and 38°C/90% RH, are compared with ethylene methacrylic acid ionomer dispersion and its mixture with 18 wt% bentonite. While these coatings show similar MVTR tested under 23°C/50% RH and very good agreement between the Cup and MOCON methods, the MVTR tested with the pigmented sample is approximately twice that of pigment-free sample at 38°C/90% RH. Furthermore, a larger discrepancy between MOCON MVTR and Cup MVTR was observed for the pigmented sample compared to the pigment-free one. Figure 4a indicates that introducing hydrophilic components exacerbates undesirable moisture permeation under the higher humidity condition with Cup method, while such impact is not observed under low humidity.

Usually, the impacts of testing method and material property on MVTR are intertwined and difficult to separate. In **Fig. 4b**, single-component hydrophilic films are tested to



4. Comparing the testing condition and material impact on tested MVTR: (a) Impacts of incorporating bentonite on Cup MVTR and MOCON MVTR under 23°C/50% RH and 38°C/90% RH; and (b) MVTR tested with MOCON and Cup method for solvent cast polycaprolactone (PCL) film, polyvinyl alcohol (PVOH), and ethylene vinyl alcohol (EVOH) film coated on paper under 23°C/50% RH.



5. Sample direction impacts on measured MVTR with MOCON under 38°C/90% RH.

demonstrate how sample hydrophilicity can impact the tested MVTR. The tested coated paper samples included: 1) coated paper using EVOH solution; 2) coated paper using PVOH solution; and 3) solvent cast polycaprolactone (PCL) film on paper. A clear discrepancy between MOCON MVTR and the Cup MVTR is observed, highlighting the impact of testing materials and in particular the hydrophilicity of tested samples with different chemistries. Exposing hydrophilic samples to high humidity can also change material properties such as increased free volume due to plasticization and reduced degree of crystallization. The Cup MVTR at 38°C/90% RH for EVOH, PVOH, and PCL films gives MVTR > 800 g/m²/day, which exceeds the MOCON testing limit.

Another consideration in evaluation of moisture barrier is the impact of sample direction, because the moisture may go through the paper substrate side first or the coated film side first in real applications. **Figure 5** compares the MOCON MVTR for the exact same coated paper sample tested in two sample directions: 1) having the coated film exposed to high humidity, and 2) having the paper substrate exposed to high humidity. This and previous work have shown that the MVTR tested with the paper to moisture usually gives higher values than the coating to moisture direction under 38°C/90% RH with a single-layer coating. The ratios between the MVTR tested with the same samples but different directions are also compared. The

Samples	MVTR (ΔW) (barrier to humidity)	MVTR (ΔW) (barrier to desiccant)	Weight Gain of Sample
Barrier Dispersion C	49 (0.40)	64 (0.64)	0.032
Polymeric Emulsion Blend D	27 (0.22)	50 (0.41)	0.032
Barrier Dispersion E	61 (0.52)	86 (0.82)	0.033

I. Sample direction impact using cup method: moisture vapor transmission rate (MVTR; g/m²/day) and cup weight gain ΔW (g) under 38°C/90% relative humidity (RH).

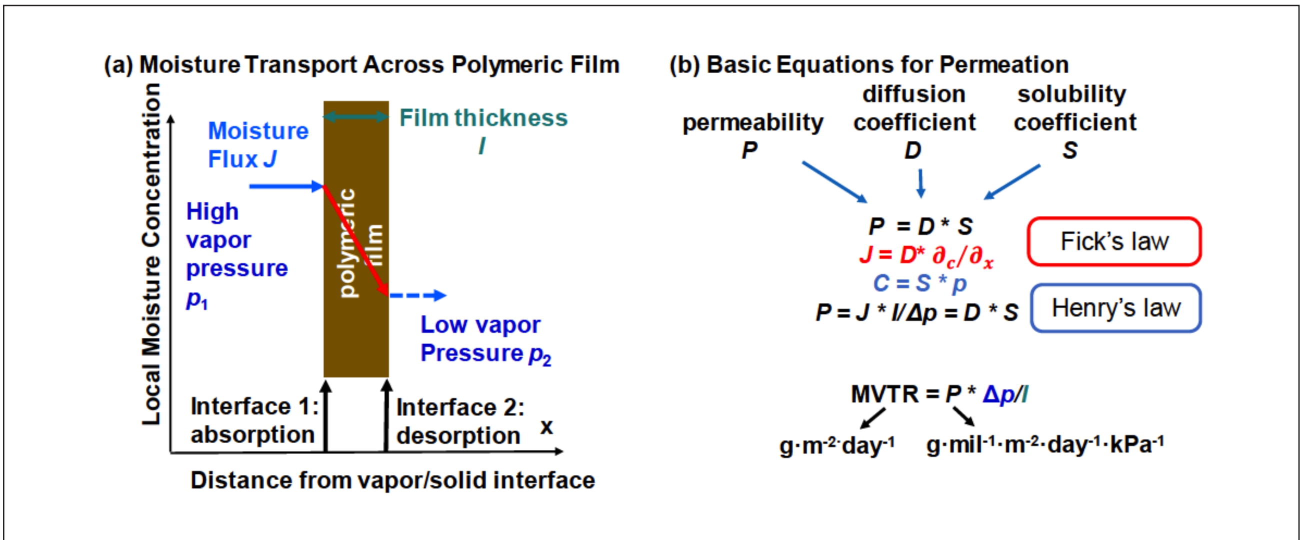
ratio is not constant, but instead is dependent upon the specific coating.

Table I further compares sample direction impacts on cup MVTR using the same coated paper sheet for MOCON. The Cup MVTR values are consistent with the MOCON value shown in Fig. 5. Sample direction has the same impact on Cup MVTR where barrier to humidity (same as barrier to test gas [B to TG] direction for MOCON) gives lower MVTR than barrier to desiccant (same as barrier to carrier [B to C] direction for MOCON). Additionally, the weight gain of tested sample was measured, since the paper substrate can absorb moisture. The weight gain of sample itself is not sufficient to explain the MVTR discrepancies between the two testing directions, which reinforced that such discrepancies are driven by permeation fundamentals rather than experimental artifacts.

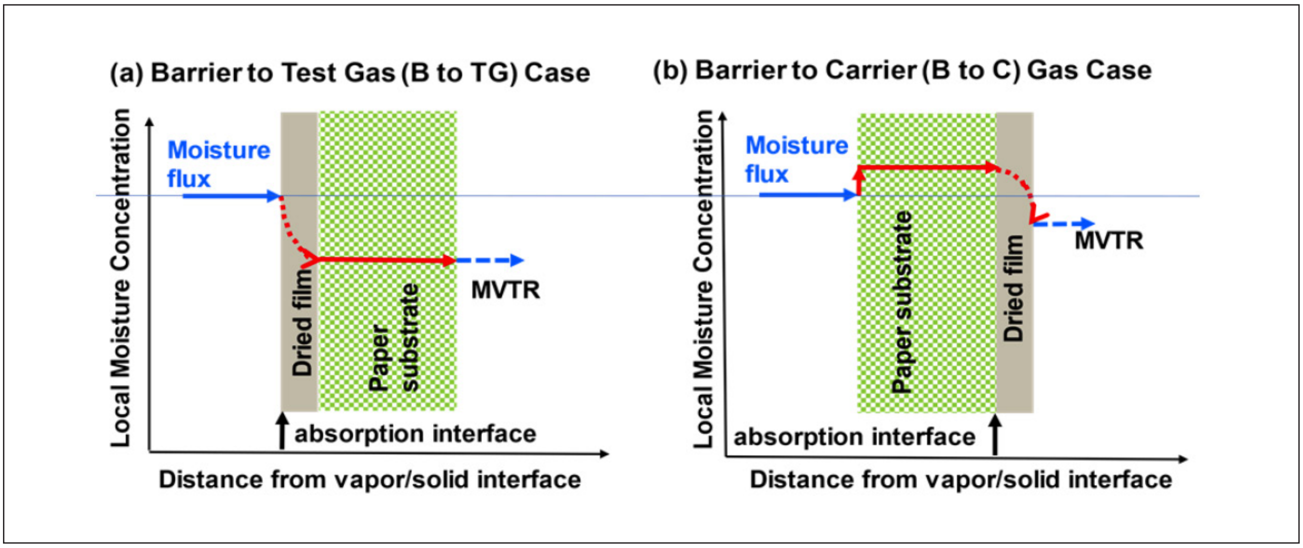
The three examples demonstrate the different moisture transport phenomena for paper coating samples using waterborne coatings. Compared with free standing polymeric films, three characteristics distinctive for coated paper samples compared with extruded single-component hydrophobic polymeric films are highlighted: first, paper with even a single layer coating has a "multilayer" structure if the moisture-absorbing paper is considered one of the layers; second, waterborne coating formulations usually contain hydrophilic components; and third, the dried coating layer itself may have structural heterogeneity due to the presence of two interfaces, substrate/coating and coating/air [5]. Consequently, the transport of water vapor through coated paper or a free standing hydrophobic polymeric film is influenced by different considerations.

Figure 6 illustrates the transport phenomena for a hydrophobic, free standing, rubbery polymeric film: the moisture is first absorbed at the humid air/film interface and then diffuses through the film until the moisture desorbs at the dry air/film interface [6]. The transport phenomena can be described with Henry's law of absorption, which assumes non-concentration dependent moisture absorption, and Fick's law of diffusion, which states that the moisture flux *J* is proportional to concentration gradient times the diffusion coefficient *D*. Because permeability *P* is defined as the product of diffusion coefficient *D* and solution coefficient *S*, a simple linear dependence of permeability on pressure and concentration can be derived based on Henry's law and Fick's law (Fig. 6) [7]. Note that while permeability *P* is a material property, the tested MVTR depends on testing condition and sample thickness.

Figure 7 illustrates two methods for testing of MVTR of coated paper samples. Figure 7a illustrates the barrier to test gas (moisture) method where the moisture goes



6. Schematics illustrating (a) the transport phenomenon, and (b) relevant equations for homogeneous polymeric film [7].



7. Schematics illustrating the transport phenomenon for (a) B to TG direction, and (b) B to C direction.

through the coating first. In the presence of hydrophilic components, the assumption of linear decrease of local moisture concentration vs. the distance from moisture vapor/solid interface becomes questionable. The hydrophilic components absorb moisture and raise local moisture concentration, which enhances moisture permeation. In some cases, humidity induced undesirable changes of samples that can also be observed as shown in Fig. 3. High humidity and increased sample hydrophilicity are expected to exacerbate moisture absorption and non-Fickian diffusion, leading to larger observed differences in MVTR between Cup and MOCON measurements, as illustrated in Fig. 4. The differences in MVTR from Cup method compared with MOCON method are also influenced by test duration. In the Cup method, samples are subjected to humidity over a few days to ensure that equilibrium is reached, while the MOCON method usually takes less than one day. The testing method impact on MVTR has also been reported for self-standing, hydrophilic gelatin films where similar transport physics could apply [8].

Figure 7b illustrates the scenario of testing samples with substrate to test gas (or barrier to carrier gas) where moisture goes through the paper substrate side first. Because paper substrates can easily take up moisture, the local moisture concentration starts to increase at the vapor/paper interface. When the moisture goes through the paper substrate, the paper keeps taking moisture and eventually becomes a "wet sponge" with higher local humidity than that of the vapor phase. When moisture starts to enter the paper/film interface, the local moisture concentration is higher than that of the controlled humidity level, resulting in a higher driving force for diffusion and absorption. Consequently, the tested MVTR is expected to be higher than when the coated film is exposed to the humidity (exemplified by the data from Fig. 5 and Table I). This trend is observed in most cases, based on multiple experiments.

Local moisture concentration is also reasonably expected to be sensitive to structural heterogeneity in the coating. Depending on the formulation used, the composition profile in the thickness direction (e.g., composition difference between paper and air interfaces) from waterborne coatings could have large impacts on directional moisture vapor permeation. If the driving force is solely from the moisture vapor pressure difference due to the raised local moisture concentration from wet paper substrate, a uni-

Example	1st coat	2nd coat	MOCON MVTR (B to TG)	MOCON MVTR (B to C)
1	Barrier Dispersion F	Hydrophilic Barrier Dispersion G	30	33
2	Hydrophilic Barrier Dispersion G	Barrier Dispersion F	22	37
3	Hydrophilic Barrier Emulsion Blends with Pigment	Barrier Emulsion Blend H	26	51

II. The MVTR testing for multilayer coatings reported as g/m²/day (38°C/90% RH).

versal MVTR ratio between MVTR (coating to moisture) and MVTR (paper to moisture) would be expected. However, the non-universal MVTR ratio shown in Fig. 5 suggests that structural heterogeneity in the coating also plays a role in MVTR.

Finally, the impacts of test method and material properties on MVTR are further demonstrated with multilayer coating systems where the composition differences across film depth are accentuated. **Table II** shows three examples on the tested MOCON MVTR with two sample directions. Example 1 has hydrophilic Barrier Dispersion G as the top layer, and the MVTR is similar regardless of the sample direction because either paper substrate or coating from Barrier Dispersion G can absorb moisture and raise the local moisture concentration. If the hydrophilic Barrier Dispersion G layer is the bottom layer (Example 2), the MOCON MVTR with paper to moisture will be like that of Example 1, but the MOCON MVTR with coating to moisture is much lower. Similarly, Example 3 has the hydrophilic pigmented precoat as the bottom layer and does show the enlarged MVTR discrepancy between testing sample directions as that of Example 2. The implication is that having the most moisture resistant coating facing the humidity source is the most efficient to deliver desirable moisture barrier.

CONCLUSIONS

Moisture barrier was evaluated for a range of coated papers using waterborne dispersions coated on low porosity glassine paper substrate. The standard Cup method (ASTM E96) and the MOCON method (ASTM F1249) gave generally consistent trends. However, the measured MVTR is dependent on both test method and material properties of the coating. Discrepancies between the test methods are driven by transport phenomena distinctive to coated paper and are not observed with free standing single-component hydrophobic polymeric films. This exacerbated non-ideal moisture transport due to moisture absorption under high humidity results in higher Cup MVTR than MOCON MVTR, and moisture uptake by paper substrates could increase the MVTR with paper to moisture direction more so than with coating to moisture direction. This strongly suggests that non-ideal moisture transport due to the dependence of local moisture concentration on the test method and the coated sample can explain the observed discrepancies in the Cup and MOCON MVTR results, which impact the assessment of moisture barrier for waterborne coatings on paper. Our study highlights the considerable impacts of test methods and coating composition on MVTR testing for waterborne coatings where moisture absorption and non-Fickian diffusion are common. Furthermore, understanding of the unique moisture transport for paper coating has large implications on the practical implementation of moisture barrier coatings. **TJ**

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In this study, we highlight the test method impacts on moisture barrier performance for coated paper samples, which have not been thoroughly discussed from previous studies. The most difficult aspect of this study was connecting materials with performance to understand both, while minimizing experimental errors. We addressed the issue with good experimental design.

We found that testing method and materials all matter for the testing results. Even standard testing methods may not necessarily give us the consistency to assess the coating performance. The most interesting finding was the testing direction impact, which will have implications due to the use of different paper substrates.

For mills, this study can help with better evaluation of various barrier materials. The next step is to apply this knowledge to better design paper packages for different applications.

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