Multifunctional barrier coating systems created by multilayer curtain coating

DON VENTRESCA, BENJAMIN BENZ, DAVID EISENHAUER, GREG WELSCH, AND DUSTIN BURTON

ABSTRACT: Functional coatings are applied to paper and paperboard substrates to provide resistance, or a barrier, against media such as oil and grease, water, water vapor, and oxygen, for applications such as food packaging, food service, and other non-food packaging. Today, there is increasing interest in developing recyclable and more sustainable approaches for producing these types of packages.

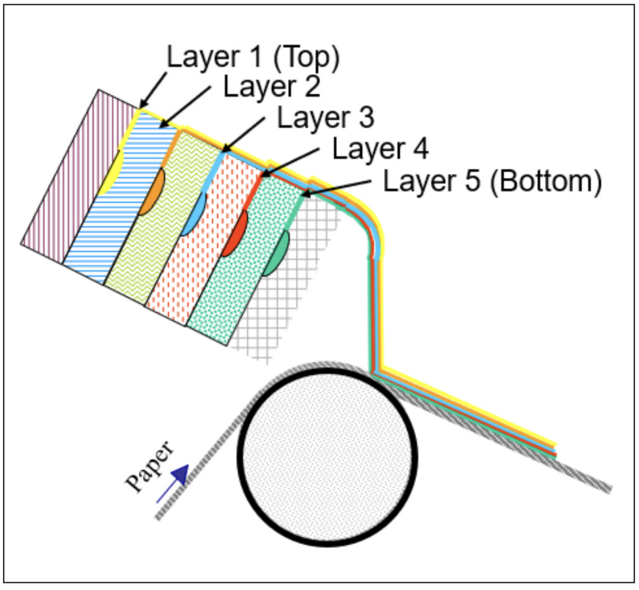
This paper focuses on water-based barrier coatings (WBBC) for oil and grease resistance (OGR), water, moisture vapor transmission rate (MVTR), and oxygen barrier performance. The main goal is to create coated systems that can achieve more than one barrier property using multilayer curtain coating (MLCC) in a single application step. One advantage is in optimizing coating material cost with the use of functional chemistry in confined layers where performance is balanced within the coating layered structure. This allows simultaneous application of layers of different polymer types in one step to achieve the appropriate performance needs for a given barrier application.

This paper provides working examples of using MLCC to create coating structures with multiple barrier properties in a single application pass. Barrier polymers studied include styrene butadiene, styrene acrylate, starch-containing emulsions, and polyvinyl alcohol. The paper also shows the effect of increasing the pigment volume concentration with platy clay or fine ground calcium carbonate on MVTR and OGR barrier properties.

Application: For those contemplating a new coater for their mill, a multilayer curtain coater offers a cost-effective and technically advantageous option for the production of barrier coated paper and paperboard grades. Also, for companies that already have multilayer curtain coaters, this paper demonstrates how to create multilayered coatings for producing multifunctional barrier performance.

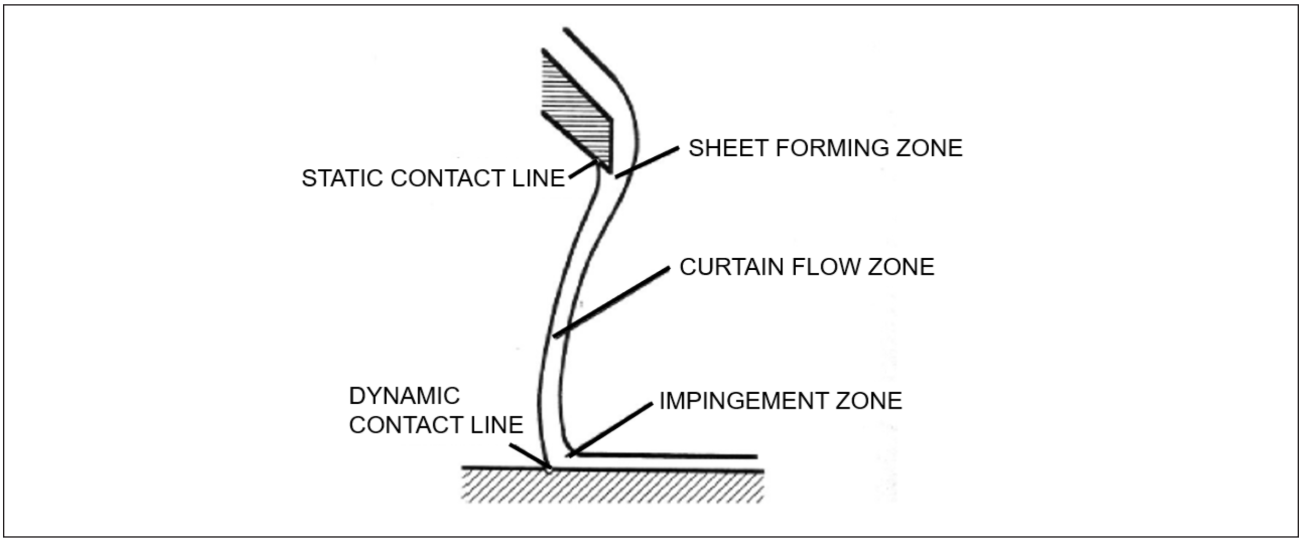
Functional coatings are applied to paper and paperboard substrates to provide resistance, or a barrier, against media such as oil and grease, water, water vapor, and oxygen, for applications such as food packaging, food service, and other non-food packaging. Typical functional barrier coatings can be created by applying a solid coating or extruded film, a solvent based-coating, or a water-based coating to the paper substrate using various means of coating applicators.

This paper focuses on water-based barrier coatings (WBBC) for oil and grease resistance (OGR), water, water vapor transmission rate (MVTR), and oxygen transmission rate (OTR). The main goal was to create coated systems that can achieve more than one barrier property using multilayer curtain coating (MLCC). Curtain coating has emerged as the premier low-impact application method for coated paper and paperboard. As indicated in **Fig. 1** [1], coating color is first distributed in cross-machine direction in a cavity. A uniform pressure distribution is built up until the coating color exits the nozzle. Here, the flow is equalized, and a thin liquid film is formed. After flowing over the slide die lip, the film detaches and creates a curtain, as shown in **Fig. 2** [2], as it falls. The flow is accelerated by gravity forces, resulting in a thinner curtain as it falls and stretches towards the paper surface.



1. Principle of multilayer curtain coating.

Significant research work to date and production experience on coated specialty papers and paperboard has focused on conventional coating techniques or single layer curtain coating [3,4]. However, MLCC has many advantages over these other methods. One advantage is in optimizing



2. Multilayer curtain coater (MLCC) flow zones.

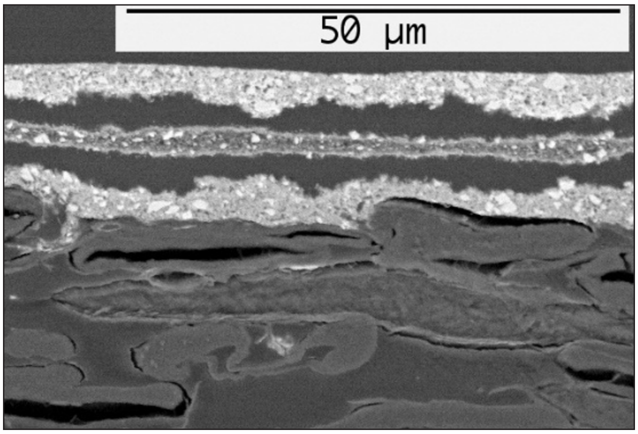
coating material cost through use of functional chemistry in confined layers where performance is balanced within the coating layered structure. This allows applying simultaneously consecutive layers of different polymer types to achieve the appropriate performance. The MLCC also allows the application of such coatings in one coating operation step, minimizing capital investment and machine footprint. Another advantage is the ability to generate thin "contour" layers that are more economically feasible than what is applicable for common coating technologies where excess material is applied in some regions to get the minimum coverage in the areas where the base sheet is thinner. The latter is even more critical when base sheet roughness is not well controlled or is inherent to the substrate available on the given machine where the paper is produced.

In the impingement zone, the curtain is deflected to about 90°. Because of velocity differences between the curtain and the moving web, an extreme acceleration of the coating occurs in the impingement zone. Final extension and contraction of the coating occurs on the web surface, where it is applied as an ideal contour coating if no defects are formed [5].

With a slide die coating technique shown in Fig. 1, the simultaneous application of more than 10 layers was the industry standard in the photographic film industry. This suggests the application of up to 5 layers is achievable in these types of applications. The aim of the undermost layer (carrier layer) is, in general, to improve runnability by promoting wetting, preventing air entrainment, and controlling heel formation at the impingement zone. A thin topcoat may provide optical and printability aspects. Layers in between may be functional layers providing barrier properties or acting as spacers between those layers.

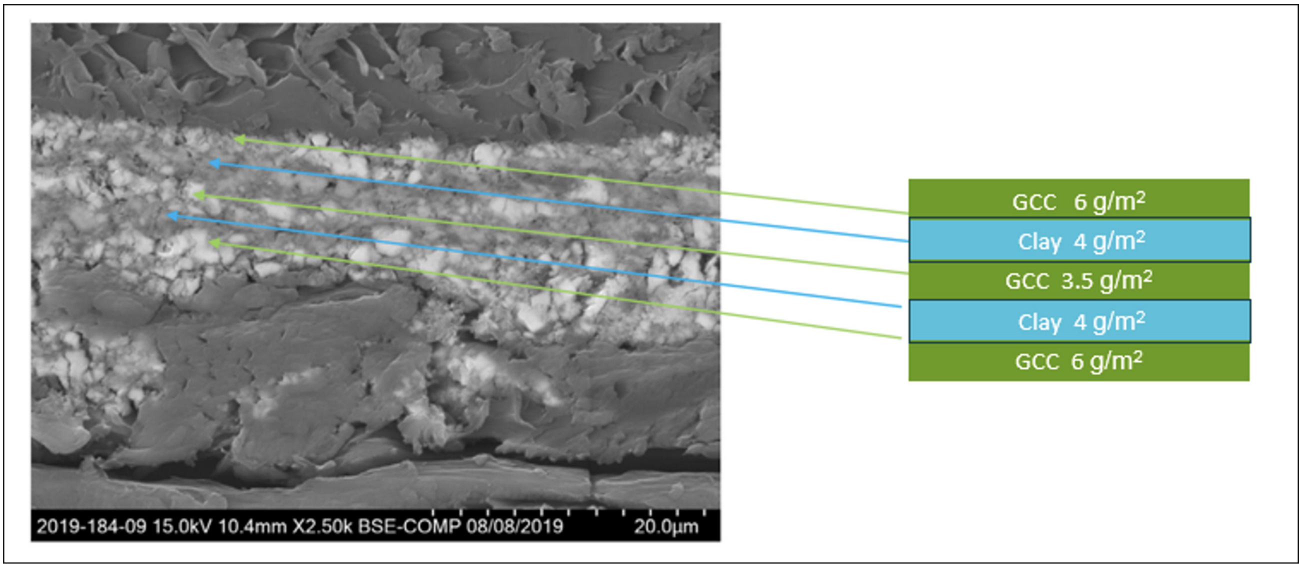
The benefits of MLCC that we intend to demonstrate in this work include:

- Ideal contour coating: uniform and homogeneous coverage of a base stock. This pertains to the ability to generate thin "contour" layers that are more economically feasible than what is applicable for common coating technologies where excess material is applied in some regions in order to get the minimum coverage in the areas where the base sheet is thinner.
- Simultaneous application and drying of several wet layers with different functions.
- Because of laminar flow, no mixing of layers occurs (see **Fig. 3** [6]). MLCC also allows the application of such coatings in one coating operation step, minimizing capital investment and machine footprint.
- MLCC can be used to apply two or more latex-rich barrier coatings with a non-blocking top layer.

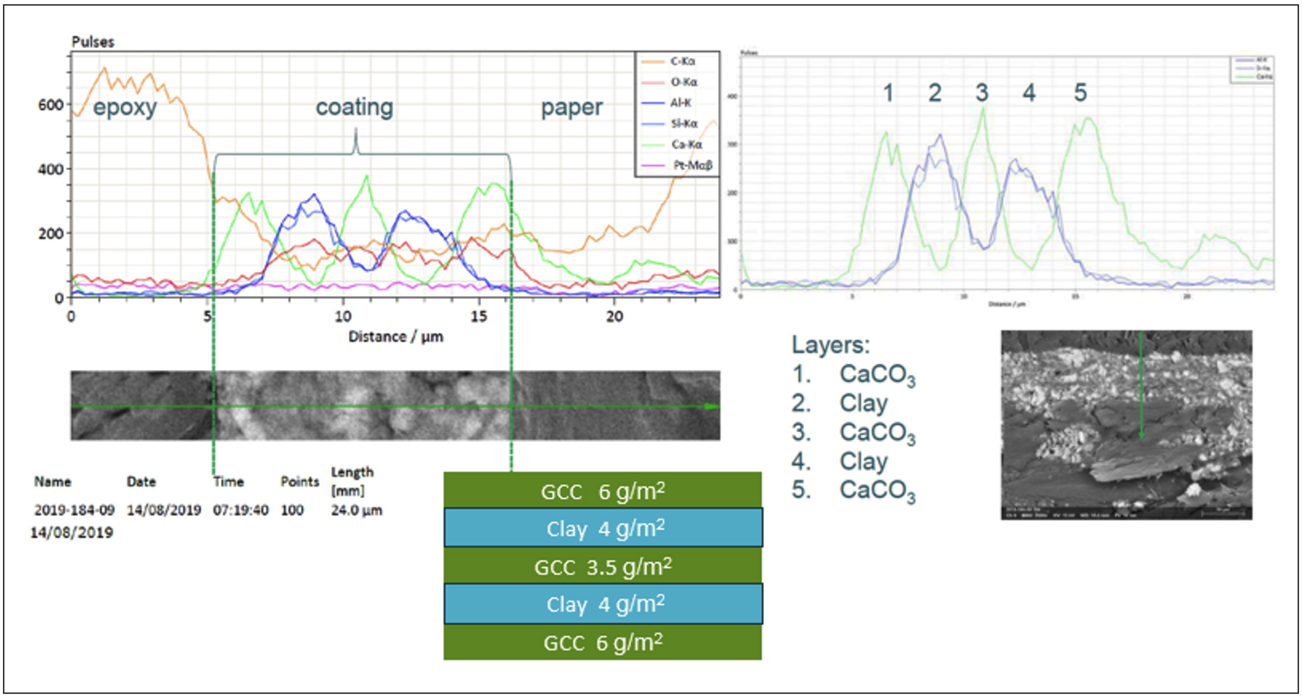


3. Cross section of MLCC example with three layers.

Novel studies conducted by Kilcher and Dahlvik showed, analytically, the clear separation of pigmented layers in an MLCC structure [7]. **Figure 4** shows a scanning electron microscope (SEM) cross-section photomicrograph of a coating structure made of alternating layers of a carbonate-based coating and a clay-based coating that was produced with a slide die curtain coater. The insert next to it indicates



4. Cross section of MLCC example with five layers (GCC: ground calcium carbonate).



5. Scanning electron microscope (SEM) cross section and energy dispersive X-ray (EDX) line scan ($CaCO_3$: calcium carbonate).

the pigment type and coat weight of each layer. In **Fig. 5**, we see the results of an energy dispersive X-ray spectroscopic (EDX) elemental analysis on this cross-section. The EDX analysis clearly shows the differentiation of the layers, matching the key element in each layer (calcium for calcium carbonate and aluminum and silicon for clay) with the expected order of the layer and composition.

This paper, which is a continuation of a previous work by Ventresca and Welsch [8], reviews examples of using MLCC to create coating structures with multiple barrier properties in a single pass. Barrier polymers studied include styrene butadiene (SB), styrene acrylate (SA), starch-containing emulsion (SCE), and polyvinyl alcohol (PVOH). The paper also shows the effect of increasing the pigment volume concentration with platy clay or fine ground calcium carbonate on MVTR and OGR barrier properties.

EXPERIMENTAL

A description of the pigments and binders used in this study is found in **Table I**. Binders used included SB, SA, PVOH, and SCE. A description of the barrier coatings and their properties used in this study are summarized in **Table II**.

The barrier formulations were applied onto a mill coated (both sides) folding boxboard (FBB) substrate with a

Ingredient	Description
Fine calcium carbonate	Brightness = 96; Median Diameter = 0.7 um
Platey clay	Brightness = 88.5; 80% <2 um; Shape Factor = 20
SB binder	Styrene Butadiene (SB); Tg = -2°C; PS = 140 nm
SA binder	Styrene Acrylate (SA); Tg = 22°C; PS = 140 nm
PVOH	Degree of Hydrolyzation = 99.0%–99.6 mol%; Degree of Polymerization = 100%
SCE	High Bio-content Starch Containing Emulsion (SCE); Biodegradable per ASTM D 5338.

I. Description of pigments and binders used (Tg: glass transition temperature; PVOH: polyvinyl alcohol).

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F11	F12
Fine calcium carbonate	100	100	100					100			
Platey clay				100	100	100			100		
SB binder	10	25	40	20	35	60	100				
SA binder								25	35		
PVOH										100	
SCE											100
Surfactant	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Pigment volume concentration, %	79.5	60.9	49.3	66.9	53.6	40.2	0	62.0	54.7	0	0
pH	8.71	8.44	8.65	8.78	8.54	8.50	5.49	8.62	8.77	-	6.24
Solid, %	65.0	64.3	65.2	64.79	64.1	61.8	53.8	65.4	63.6	16.1	43.5
Brookfield viscosity at 20 rpm, MPas	640	1240	1800	560	350	385	390	1840	1600	1540	1080
Brookfield viscosity at 100 rpm, MPas	260	430	630	220	160	180	170	620	521	-	360
Density, g/cc	1.605	1.494	1.394	1.485	1.423	1.334	1.032	1.524	1.438	1.038	1.190
SB: styrene butadiene; SA: styrene acrylate; PVOH: polyvinyl alcohol; SCE: starch-containing emulsion.											

II. Description of barrier coatings.

basis weight of 235 g/m². The side that was used for the MLCC layer application was pre-coated and had a Parker print surf (PPS) roughness of 1.10 µm (1000 psi).

The barrier coatings were applied with a multilayered slide die curtain coater at Trinseo's Application Development Center in Rheinmünster, Germany. Each barrier layer was applied at a coat weight of 5.0 g/m² (3.5 lbs/3300 ft²) at a targeted speed of 600–700 m/min (1969–2297 ft/min). The PVOH was studied at 2 g/m² and 4 g/m². The barrier coating systems that were created are summarized in **Table III**.

Barrier testing analysis

A description of the devices and methods used for barrier testing are explained in the following sections.

Defect and pinhole characterization

The defect characterization test [9] is conducted by applying a 1 mL quantity of dyed oil to each sample, swirling the dyed oil in a circular pattern covering a 5 cm (2 in.) diameter circle. After the 10 s has expired, the dyed oil that did not penetrate the surface of the sample is removed with an absorbent wipe. The dyed oil chosen for this test is an oil that is typically used in the candy coloring industry.

MLCC Condition No.	1	2	3	4	5	6	7	8	9	11	12	13	14
Layer 1 (bottom)	F7	F1	F2	F3	F4	F5	F6	F2	F2	F2	F2	F2	F12
Layer 2	F2	F1	F2	F3	F4	F5	F6	F8	F9	F11	F11	F11	F11
Layer 3										F2	F2	F5	F9
Each layer is 5 g/m² unless otherwise noted										F11 @ 2 g/m²	F11 @ 4 g/m²	F11 @ 2 g/m²	F11 @ 2 g/m²

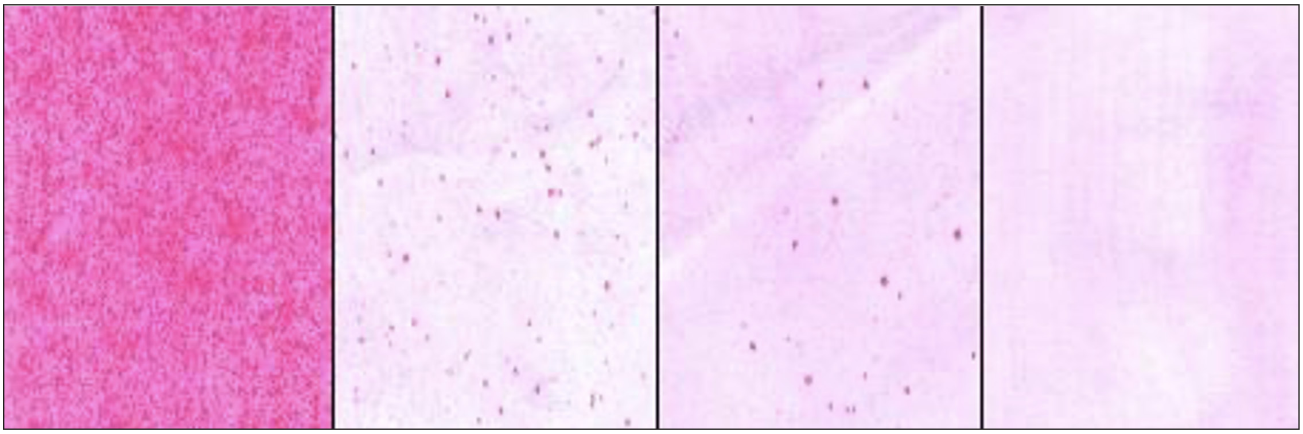
III. Multilayer curtain coater (MLCC) barrier systems.

The base ingredient is propylene glycol. The color pink was chosen because it gave the best contrast between defect and white coatings.

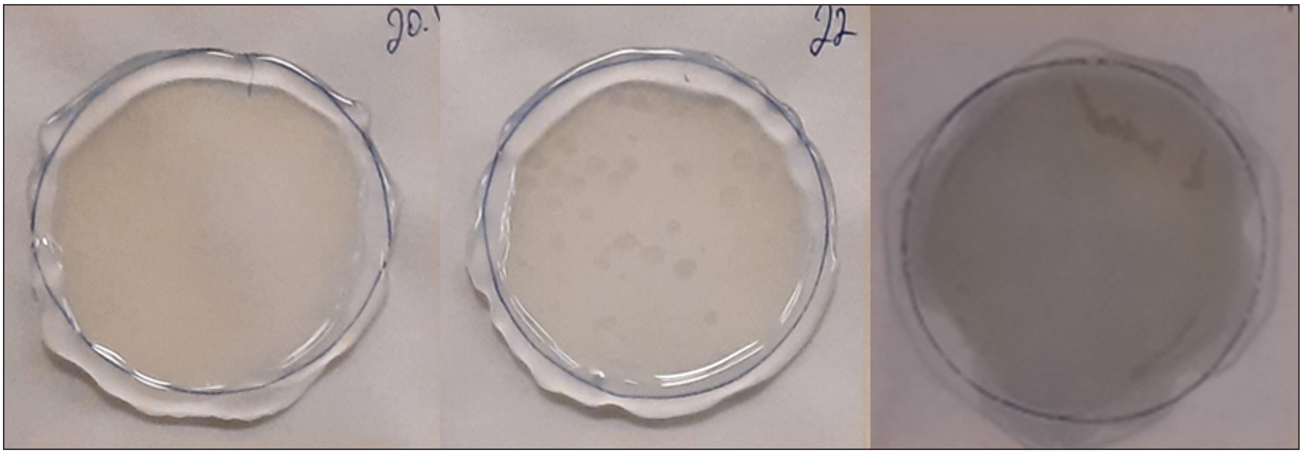
After removing the excess dyed oil from the substrate, an image analysis procedure was carried out immediately. The larger defects were readily apparent, as shown in **Fig. 6**, but to gain insightful knowledge, such as an accurate count and differences in size and shape, a combination of an Epson Perfection V750 Pro Scanner and Verity IA software (Milwaukee, WI, USA) was used.

Oil and grease resistance analysis

The "hot oil circle test" is used to analyze oil barrier properties. Preheated oil (corn oil at 60°C) is applied on the barrier surface. Two time-based treatments were evaluated, 1 h and 24 h. The front (barrier coated) and the back sides of the paper samples were evaluated for oil stain penetration. This was carried out at room temperature and in an oven set at 60°C. Visual observations were made on the back side of the paper, and Y values were taken on the front side (barrier side) before exposure to oil and after removal of the oil. Higher delta Y values equate to more penetration



6. Visual representation (after dying) showing various pinhole occurrences.



7. Example of a rating of 0 (no penetration), a rating of 3 (>26, but <50 pinholes), and a rating of 9 (complete fail).

Hot Oil Circle Test – Failure Rating System		
Rating	Characterization	Description
0	No Penetration	No pinholes, spots, or stains visible
1	< 10 Pinholes	More than 1 pinhole, less than 10 pinholes visible
2	< 25 Pinholes	More than 11 pinholes, less than 25 pinholes visible
3	< 50 Pinholes	More than 26 pinholes, less than 50 pinholes visible
4	> 50 Pinholes	More than 50 pinholes visible
5	Small Spots	Small spots visible
6	Large Spots	Large spots visible
7	Stain(s)	One or more stains; not able to tell if sample is penetrated
8	Stain/Fail	Stain is kept within barrier ring but has penetrated the sample
9	Complete barrier fail	Stain goes beyond barrier ring or caused ring to lift

IV. Hot oil rating descriptions.

of the oil. Observations were also made at various time treatments and evaluated from immediate to 24 h. The front (barrier coated) and the back sides of the paper samples can be evaluated for oil stain penetration. Visual observations were made on the functional side of the paper prior to testing, immediately after applying the tempered oil, 15 min after, 30 min after, 45 min after, 60 min after, and 24 h after oil exposure. **Figure 7** shows examples. **Table IV** shows the internally used rating system. Lower values indicate better barrier performance.

Kit test

The 3M Kit test measures the repellency or anti-wicking behavior of paper and paperboard when subjected to various oils/solvent. It was conducted per the TAPPI Standard Test Method T 559 "Grease resistance test for paper and paperboard." Kit testing was conducted on flat samples and creased (scored first with a craft scoring tool). A lower Kit value represents a "less harsh" treatment (higher percentages of castor oil), while a high Kit value represents a "more harsh" treatment (higher percentages of toluene and heptane).

Cobb test

Cobb testing, which measures the amount of water absorbed into a substrate, was conducted per the TAPPI T 441 "Water absorptiveness of sized (non-bibulous) paper, paperboard, and corrugated fiberboard (Cobb test)." The testing times used were 2 min and 30 min. Lower values are better, as they indicate less water absorption.

Moisture vapor transmission rate test

The MVTR testing was conducted per TAPPI T 448 "Water vapor transmission rate of paper and paperboard at 23°C and 50% RH" for testing at 23°C (100°F) with an atmosphere of 50% relative humidity (RH). Additional testing was performed at jungle conditions per TAPPI T 464 "Water vapor transmission rate of paper and paperboard at high temperature and humidity" for testing at 37.8°C (100°F) with an atmosphere of 90% RH. Lower values are better, as they indicate less water vapor transmission.

Oxygen transmission rate test

The oxygen transmission rate (OTR) testing was conducted per ASTM F1927 "Standard test method for determination of oxygen gas transmission rate, permeability and permeance at controlled relative humidity through barrier materials using a coulometric detector" with relative humidity (RH) of 50% at 23°C using a Mocon OX-TRAN 2/21 instrument (Ametek Mocon; Brooklyn Par, MN, USA). Specimens were conditioned for 24 h and then tested over a 60-min period. Data was reported in units of $ccm/m^2/day$.

Blocking analysis

In the paper industry, blocking is defined as the tendency of the coated paper to stick to the uncoated or coated paper back side in a roll. The blocking test in the laboratory was developed to evaluate the sticking tendency that might correlate with the mill sticking performance. Blocking was measured in the laboratory using a Carver hydraulic press (Carver; Wabash, IN, USA) set at 140°F. A 15 cm x 15 cm coated sheet was placed against the reverse side of another coated sheet, and these were then placed between 2 sheets of blotter paper. This assembly was then placed in the hydraulic press under the desired pressure for 3 min. The test was done at pressures 300, 600, 900, 1200, and 1500 psi. After removing from the press and letting cool to room temperature, the sheets were separated and evaluated for blocking using the rating scale shown in **Table V**. Lower values suggest less blocking.

Value	Blocking Rating Scale – Description
0	Sheet falls apart without effort.
1	Sample sheets come apart with slight resistance.
2	Sample sheets come apart with slight stickiness.
3	Sample sheets show noticeable stickiness, but no material transfer between sheets. Coated sample sheet appears similar to untested sample.
4	Sample sheets show noticeable stickiness but with some slight picking or material transfer between sheets. Coated sample sheet appears different than untested sample.
5	Sample sheets show noticeable stickiness and cannot be completely separated without fiber tear (complete transfer of some or the entire sample sheet to the other.)

V. Blocking rating scale.

Coldset glue testing

The coldset glue strength specimens were prepared by applying a 0.205 mm thick bead of polyvinyl acetate glue, barrier coated side to uncoated side, and aged with a 0.91 kg weight resting on the glued specimen. For this study, the fiber tear was measured after a setting time of 120 min.

Surface free energy testing

Surface free energy components (dispersive surface energy and polar surface energy) were calculated using contact angle measurements made with a Fibro pocket goniometer Model-PGX (Fibro Systems AB; Hagersten, Sweden) using droplets of water and droplets of di-iodo methane.

RESULTS AND DISCUSSION

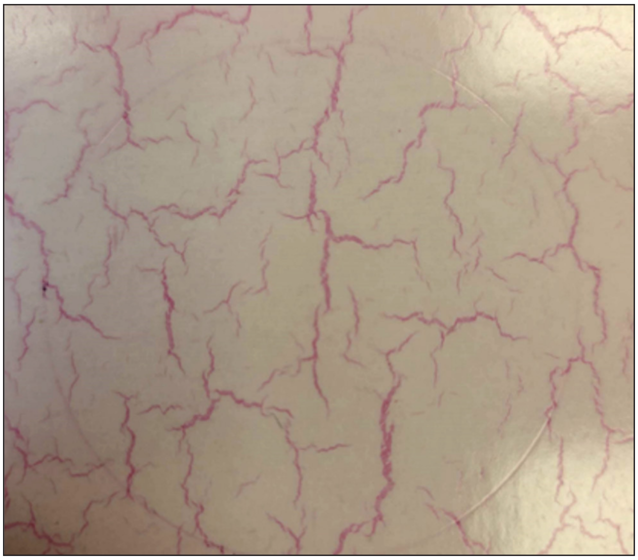
MLCC coating repeatability

Trial point number 9, with coated layers F2/F9, was repeated on the multilayer curtain coater (MLCC). This provided the opportunity to determine the repeatability of the curtain coating application, as well as the barrier testing. The data for these repeated conditions are summarized in **Table VI**. All the test data are very similar proving that the coating application is very reproducible.

Defect characterization

Defect analysis of the surface of the coated paperboard did not reveal the presence of pinholes. This verified that the coatings were degassed very well and there was no entrained air during the application, which is critical for barrier applications and the operation of the curtain coater.

The analysis found that the 3-layer systems, with the PVOH in the middle layer, had surface defects that could be best described as cracking. An example is shown in **Fig. 8** where the surface has been stained with red oil used for the defect characterization test. We noticed that as the coater flow was turned off, the wet coating that remained on top of the coater started to separate, as seen in **Fig. 9**. The pattern seen in Fig. 9 in the wet coating is very similar to what was seen in the defect testing on the dried paperboard. One possible explanation for the defect is that there was a difference in extensional viscosity between the layers. The first and top layers of pigmented coating were adjusted to have the appropriate extensional viscosity, while the PVOH dispersion was used as is. Another possibility for the defect is that the cracking was caused from a difference in surface tension between the PVOH dispersion and the pigmented coatings. It is likely that these defects in the top layer reduced the performance of these systems in the subsequent barrier testing.



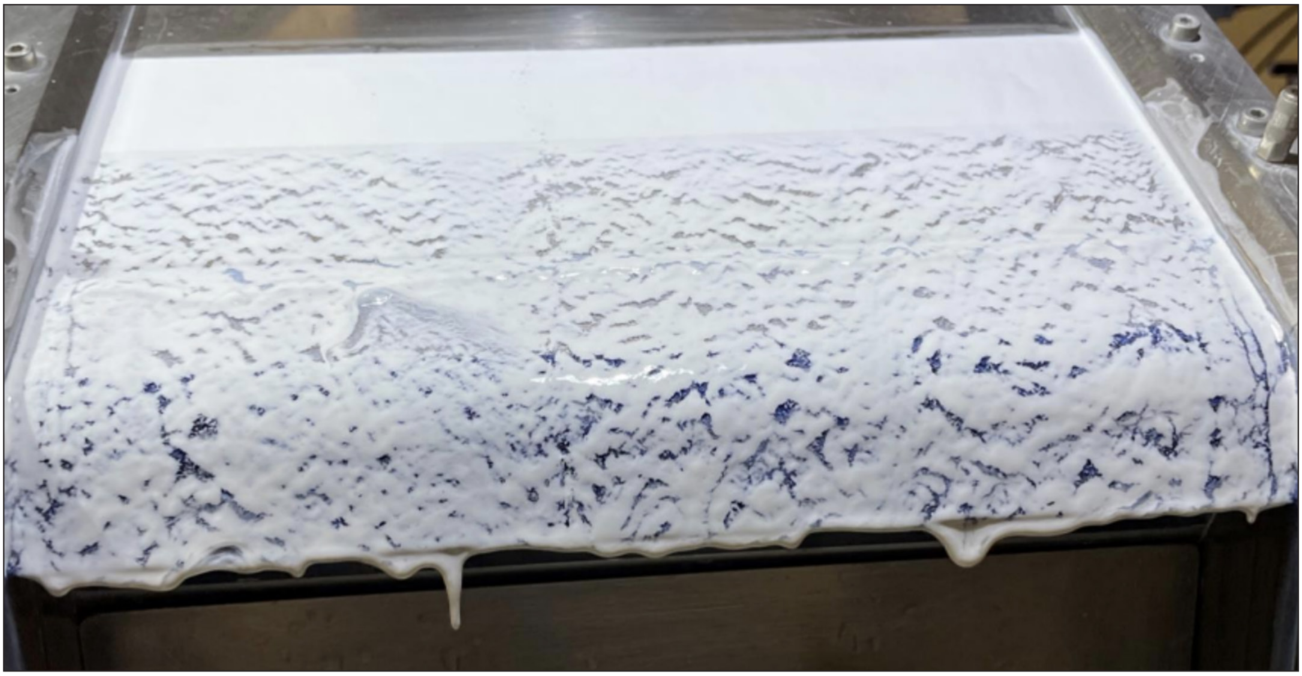
8. Surface defects on polyvinyl alcohol (PVOH)-containing systems.

Blocking

The blocking data is summarized in **Table VII** for each condition and at each pressure tested. A “0” rating indicates that the sheets fall apart cleanly after the 3 min under pres-

Trial Point/MLCC Condition	9	9
Coating Layers	**F2/F9**	**F2/F9**
Layer 1	**HC90/SB 25pts**	**HC90/SB 25pts**
Layer 2	**Clay/SA 35pts**	**Clay/SA 35pts**
Layer 3		
3M Kit test	12.0	12.0
3M Kit test – creased	0.0	0.0
Hot oil circle – room Y-value delta	0.5	0.4
Hot oil circle – oven Y-value delta	0.6	0.3
Hot oil rating (room temp): 1 h	0	0
Hot oil rating (room temp): 24 h	7	7
Hot oil rating (oven temp): 1 h	0	0
Hot oil rating (oven temp): 24 h	7	7
MVTR room, $g/m^2/24$ h	96.8	88.1
MVTR jungle, $g/m^2/24$ h	1298.4	878.2
Cobb absorptiveness (g/m^2) 2 min	65.6	66.5
Cobb absorptiveness (g/m^2) 30 min	289.3	284.5
Oxygen transmission rate, $cc/m^2/day$	n/a	n/a
Contact angle 1 s H_2O	56.7	57.1
Contact angle 1 s corn oil	38.3	38.9
Surface energy dispersive, mJ/m^2	33.0	33.9
Surface energy polar, mJ/m^2	21.5	20.9
Surface energy total, mJ/m^2	54.4	54.8
Blocking rating @ 300 psi	0	1
Blocking rating @ 600 psi	0	2
Blocking rating @ 900 psi	0	2
Blocking rating @ 1200 psi	2	2
Blocking rating @ 1500 psi	2	2
Coldset glue fiber tear @ 120 min	100	100
MLCC: multilayer curtain coater; SB: styrene butadiene; SA: styrene acrylate; MVTR: moisture vapor transmission rate.		

VI. Repeatability study.



9. Layer separation in wet coating on a curtain coater.

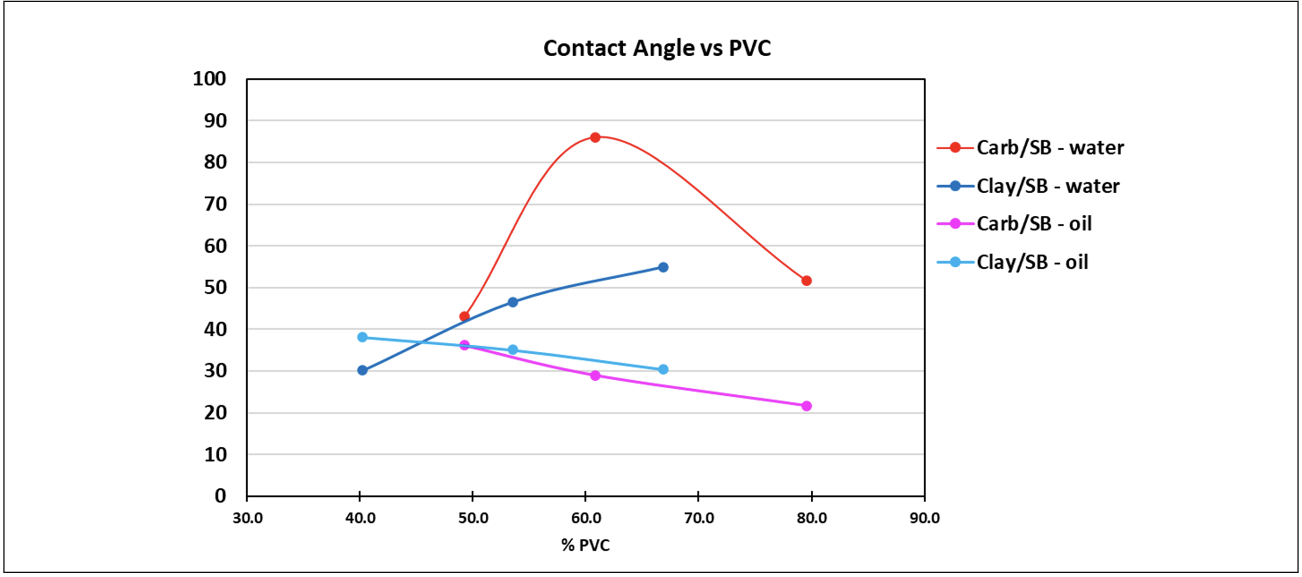
sure at 140°F. Most of the samples were rated at 0 or 1 at 300 and 600 psi. The worst performing samples were condition 7, which had 60 parts of SB with clay in the top layer, and condition 14, which had 35 parts of SA with clay in the top layer. No blocking was seen with condition 4, which had 40 parts of SB with calcium carbonate.

Coldset glue testing

All samples had 100% fiber tear in the coldset glue testing. Even condition 7, with the top layer containing the highest binder level of 60% SB latex, gave 100% fiber tear.

PVC study with carbonate/SB and clay/SB systems

A pigment volume concentration (PVC) study was conducted with conditions 2 to 7, in which we compared the performance of calcium carbonate/SB blends to the clay/SB blends. We attempted to determine the critical pigment volume concentration (CPVC) using tensile testing on the dried coatings, but because of the low binder levels, the tensile bars were too brittle to form into a test specimen. On the coated paperboard, there were no differences in the Kit performance, as all samples had values of 12 when tested on the flat specimen and values of 0

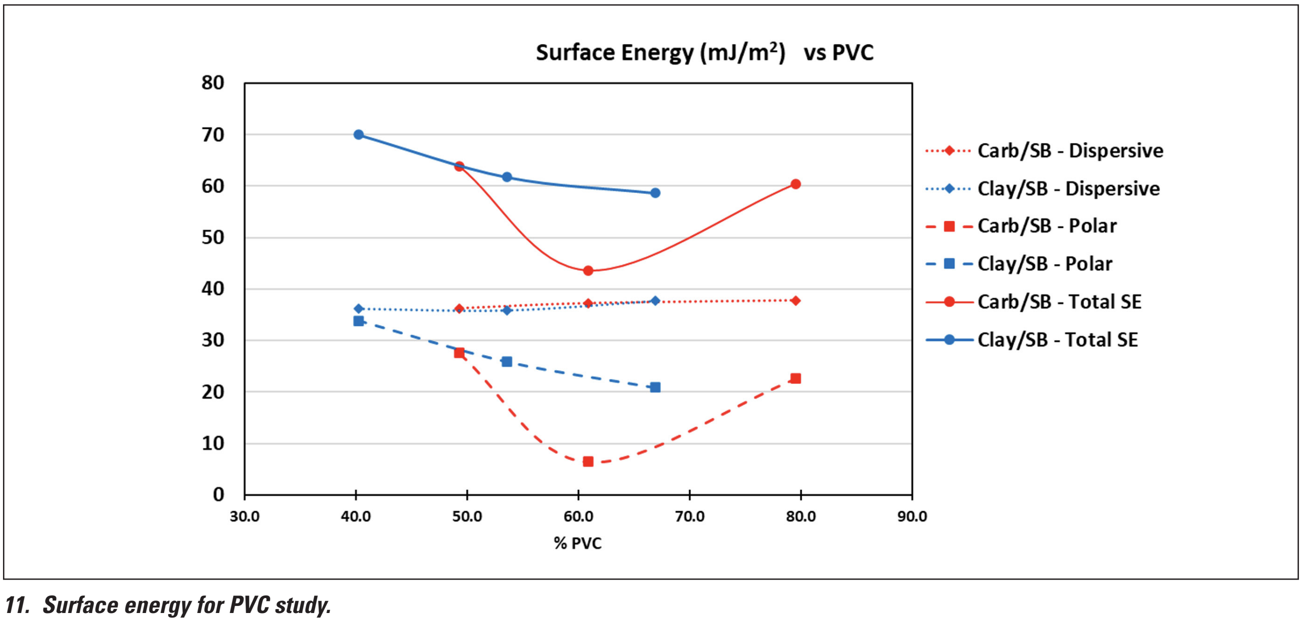


10. Contact angle for pigment volume concentration (PVC) study (SB: styrene butadiene).

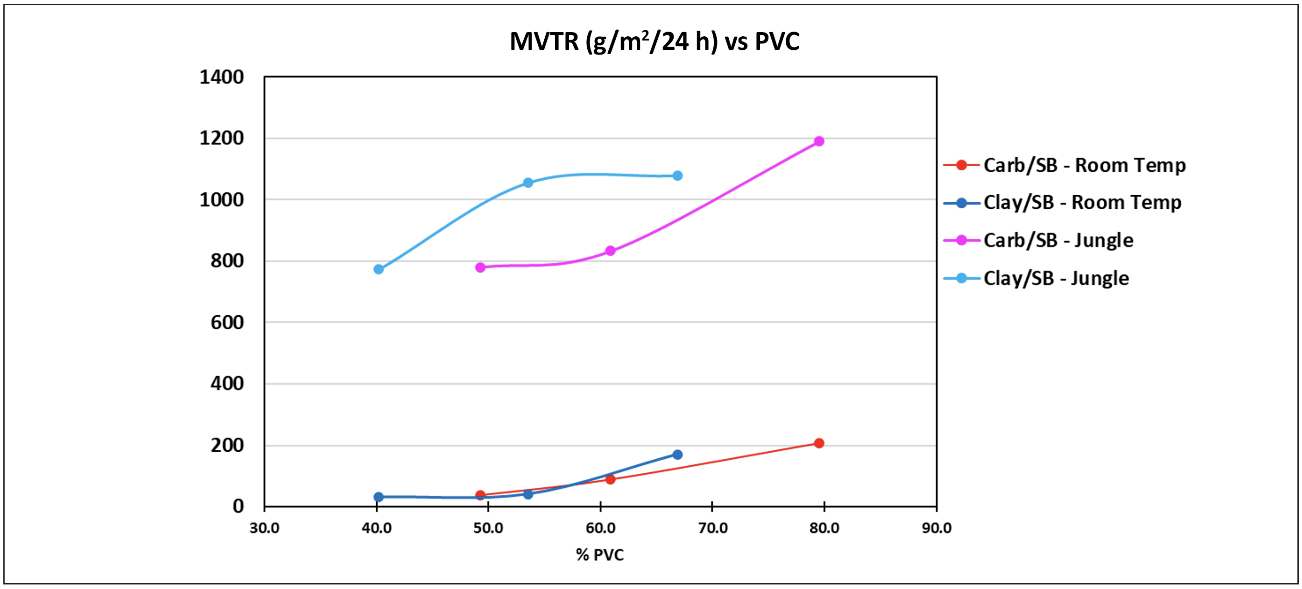
Trial Point /MLCC Condition	Coating Layers	Layer 1	Layer 2	Layer 3	Blocking Rating @ 300 psi	Blocking Rating @ 600 psi	Blocking Rating @ 900 psi	Blocking Rating @ 1200 psi	Blocking Rating @ 1500 psi
1	F7/F2	SB 100pts	HC90/SB 25pts		1	1	1	1	1
2	F1/F1	HC90/SB 10pts	HC90/SB 10pts		0	0	0	0	0
3	F2/F2	HC90/SB 25pts	HC90/SB 25pts		0	0	0	0	0
4	F3/F3	HC90/SB 40pts	HC90/SB 40pts		0	1	1	1	1
5	F4/F4	Clay/SB 20pts	Clay/SB 20pts		0	0	0	0	1
6	F5/F5	Clay/SB 35pts	Clay/SB 35pts		0	1	2	2	2
7	F6/F6	Clay/SB 60pts	Clay/SB 60pts		3	3	3	3	3
8	F2/F8	HC90/SB 25pts	HC90/SA 25 pts		0	0	0	1	1
9	F2/F9	HC90/SB 25pts	Clay/SA 35 pts		0	0	0	2	2
9	F2/F9	HC90/SB 25pts	Clay/SA 35 pts		1	2	2	2	2
11	F2/F11/F2	HC90/SB 25pts	PVOH 2 g/m²	HC90/SB 25pts	0	0	0	0	0
12	F2/F11/F2	HC90/SB 25pts	PVOH 4 g/m²	HC90/SB 25pts	0	0	1	2	2
13	F2/F11/F5	HC90/SB 25pts	PVOH 2 g/m²	Clay/SB 35pts	0	0	0	0	0
14	F12/F11/ F9	SCE	PVOH 2 g/m²	Clay/SA 35pts	3	3	3	3	4

MLCC: multilayer curtain coater; SB: styrene butadiene; SA: styrene acrylate; PVOH: polyvinyl alcohol; SCE: starch-containing emulsion.

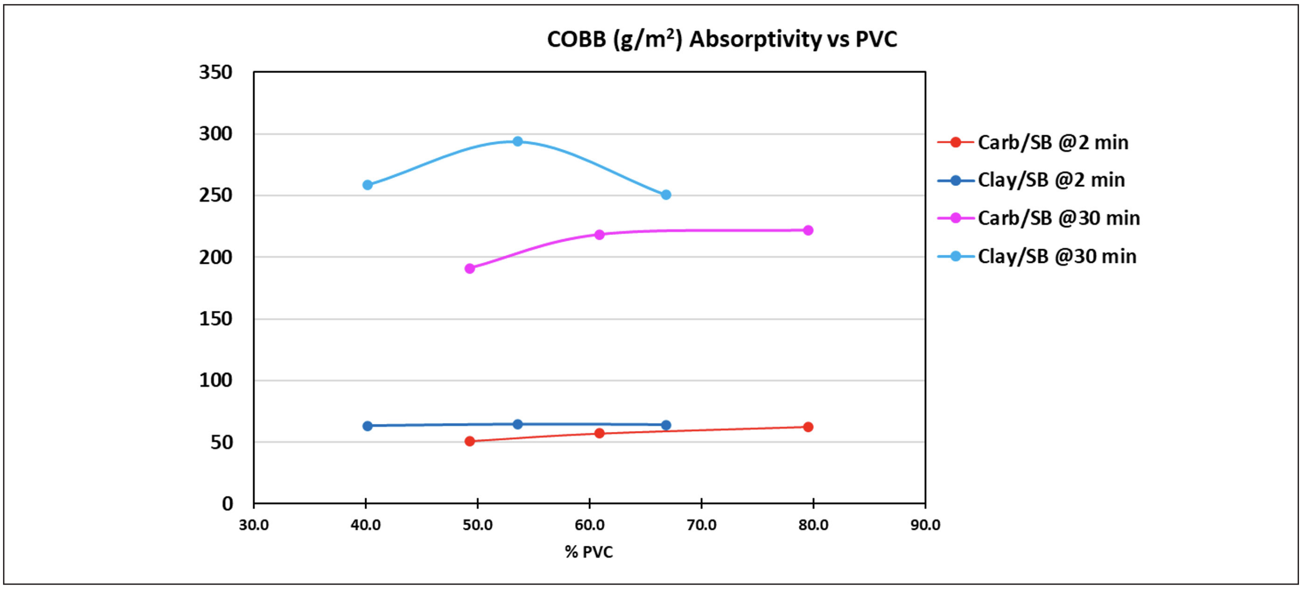
VII. Blocking data, all pressures.



11. Surface energy for PVC study.



12. Moisture vapor transmission rate (MVTR) for PVC study.



13. Cobb water absorption for PVC study.

when tested on creased specimen. The latter observation suggests all coating structures were too brittle to be creased, with the one commonality being the precoated substrate. This may suggest a more flexible first layer is required.

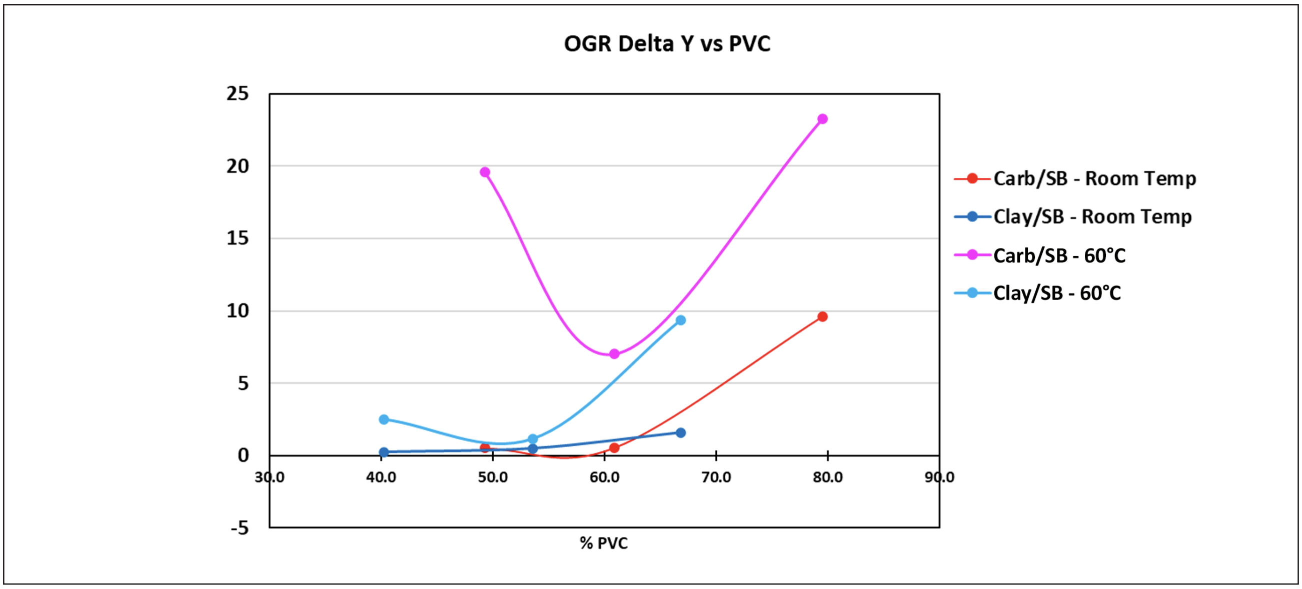
The contact angle and surface energy measurements are shown in **Fig. 10** and **Fig. 11**, respectively. The data is plotted vs. the PVC of each layer's pigment/latex blend. The MVTR and Cobb water absorption data are plotted in **Fig. 12** and **Fig. 13**, respectively. The OGR data is plotted in **Fig. 14**.

Conclusions that can be made from the data include:

- At room temperature conditions, both systems had similar MVTR properties. At jungle conditions, both systems had very poor results, and it was difficult to distinguish differences.
- The carbonate/SB system had slightly better Cobb water absorption.
- At room temperature, both systems were similar for OGR performance. At 60°C, the clay/SB system was better, especially at the lower PVC.

Base layer composition effects

One variable evaluated in this study was comparing a base layer of pure SB latex (condition 1) to a base layer of 75% carbonate and 25% SB latex (condition 3). Both conditions have the same top layer system. The data for this comparison is found in **Table VIII**.



14. Oil and grease resistance (OGR) for PVC study.

Conclusions that can be made from the data include:

- We see that both systems have flat Kit values of 12 except condition 1, with the pure SB polymer in the base giving the coating more flexibility. This resulted in a creased Kit value of approximately 5, whereas condition 3 was more brittle, with pigmented coating in both layers, and had a creased Kit of 0.
- Both conditions have similar OGR at room temperature, but condition 1 with the pure SB polymer in the base had significantly better OGR at 60°C.
- Condition 1 had better MVTR at room conditions. Both were poor at jungle conditions.
- Condition 1 has significantly lower Cobb water absorption at both 2 and 30 min.
- Condition 3 had significantly higher contact angle and lower surface energy, despite having the same top layer system as condition 1. It is possible that the surface coating structure of condition 3 is different, since the pigmented coating top layer base layer would have immobilized faster than a pure latex, resulting in a different immobilization and coating consolidation of the top layer and a different coating structure.

PVOH layer effects

Another variable studied was the effect of applying a middle layer of PVOH with the intention of improving MVTR and OTR. **Table IX** contains a summary of the testing data for the conditions containing PVOH (conditions 11, 12, 13, and 14) compared to several reference conditions without PVOH.

The defect analysis reported previously found that the 3-layer systems, with the PVOH in the middle layer, had surface defects that could be described as cracking. It is suspected that the cracking occurred during drying and could have been caused from the surface energy differences between the middle PVOH layer and the pigment/latex top layer, from a difference in surface tension between the PVOH dispersions and the pigmented coatings, or from extensional viscosity differences between the layers. It is possible that this top layer defect reduced the performance of these systems in the barrier testing. It is worth noting that we did observe a significant improvement in room condition MVTR in all the PVOH containing systems compared to the references. For example, comparing condition 11, which had the additional layer of 2 g/m^2 of PVOH, to condition 1, the MVTR was reduced by 75%. Increasing the coat weight of the PVOH layer to 4 g/m^2, as seen in condition 12, further reduced the MVTR to a half of the MVTR with 2 g/m^2 of PVOH. This would indicate that the PVOH layer remained intact and functionable as a barrier layer, at least enough for MVTR, and that the top layer compositions evaluated in conditions 11 to 14 do not significantly contribute to MVTR. Condition 14, with the SCE in the base layer, had the highest MVTR at room conditions of the PVOH systems, but was still significantly better than the reference conditions. All of the samples had very high MVTR at jungle conditions, so it is difficult to determine differences between the samples at this condition. These poor results could be due to disruptions of the PVOH layer by the defects in the top layer.

The OTR testing on the non-PVOH systems resulted in failures due to excessive oxygen transmission. One of the PVOH systems, condition 14, also experienced failure, most likely because it exhibited the most surface defects and possibly compromised PVOH layer integrity. Of the three remaining PVOH-containing conditions, all the values obtained are higher than expected, but this again could be due to the surface defects and layer-to-layer quality. How-

Trial Point/MLCC Condition	1	3
Coating Layers	**F7/F2**	**F2/F2**
Layer 1	**SB 100pts**	**HC90/SB 25pts**
Layer 2	**HC90/SB 25pts**	**HC90/SB 25pts**
Layer 3		
3M Kit test	12.0	12.0
3M Kit test – creased	4.6	0.0
Hot oil circle – room Y-value delta	0.3	0.5
Hot oil circle – oven Y-value delta	0.6	7.0
Hot oil rating (room temp): 1 h	0	0
Hot oil rating (room temp): 24 h	7	8
Hot oil rating (oven temp): 1 h	0	0
Hot oil rating (oven temp): 24 h	7	8
MVTR room, $g/m^2/24$ h	39.3	88.1
MVTR jungle, $g/m^2/24$ h	1121.4	833.0
Cobb absorptiveness (g/m^2) 2 min	65.6	66.5
Cobb absorptiveness (g/m^2) 30 min	15.0	218.4
Oxygen transmission rate, $cc/m^2/day$	Fail	Fail
Contact angle 1 s H_2O	49.3	86.1
Contact angle 1 s corn oil	28.8	29.0
Surface energy dispersive, mJ/m^2	36.4	37.2
Surface energy polar, mJ/m^2	24.3	6.4
Surface energy total, mJ/m^2	60.7	43.7
Blocking rating @ 300 psi	1	0
Blocking rating @ 600 psi	1	0
Blocking rating @ 900 psi	1	0
Blocking rating @ 1200 psi	1	0
Blocking rating @ 1500 psi	1	0
Coldset glue fiber tear @ 120 min	100	100

MLCC: multilayer curtain coater; SB: styrene butadiene; SA: styrene acrylate; MVTR: moisture vapor transmission rate.

VIII. Base layer composition effects.

Trial Point /MLCC Condition	1	3	6	9	11	12	13	14
Coating Layers	**F7/F2**	**F2/F2**	**F5/F5**	**F2/F9**	**F2/F11/F2**	**F2/F11/F2**	**F2/F11/F5**	**F12/F11/F9**
Layer 1	**SB 100pts**	**HC90/SB 25pts**	**Clay/SB 35pts**	**HC90/SB 25pts**	**HC90/SB 25pts**	**HC90/SB 25pts**	**HC90/SB 25pts**	**SCE**
Layer 2	**HC90/SB 25pts**	**HC90/SB 25pts**	**Clay/SB 35pts**	**Clay/SA 35pts**	**PVOH 2 gsm**	**PVOH 4gsm**	**PVOH 2 gsm**	**PVOH 2 gsm**
Layer 3				**HC90/SB 25pts**	**HC90/SB 25pts**	**Clay/SB 35pts**	**Clay/SA 35pts**	
3M Kit test	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
3M Kit test – creased	4.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hot oil circle – room Y-value delta	0.3	0.5	0.5	0.4	0.5	0.0	0.2	0.1
Hot oil circle – oven Y-value delta	0.6	7.0	1.1	0.3	-0.1	0.0	0.0	2.8
Hot oil rating (room temp): 1 h	0	0	0	0	0	0	0	0
Hot oil rating (room temp): 24 h	7	8	7	7	4	4	4	7
Hot oil rating (oven temp): 1 h	0	0	0	0	0	0	0	2
Hot oil rating (oven temp): 24 h	7	8	7	7	4	4	4	8
MVTR room, g/m²/24 h	39.3	88.1	41.2	88.1	8.8	4.6	8.6	13.2
MVTR jungle, g/m²/24 h	1121.4	833.0	1055.4	878.2	1492.4	954.2	864.8	878.1
Cobb absorptiveness (g/m²) 2 min	2.2	57.1	64.6	66.5	55.9	54.5	58.4	65.7
Cobb absorptiveness (g/m²) 30 min	15.0	218.4	293.8	284.5	179.6	164.5	193.3	n/a
Oxygen transmission rate, cc/m²/day	Fail	Fail	Fail	n/a	1915	1518	2461	Fail
Contact angle 1 s H_2O	49.3	86.1	46.6	57.1	26.3	25.3	21.3	33.5
Contact angle 1 s corn oil	28.8	29.0	35.0	38.9	37.6	39.2	39.6	40.9
Surface energy dispersive, mJ/m²	36.4	37.2	35.9	33.9	35.0	33.7	34.3	35.0
Surface energy polar, mJ/m²	24.3	6.4	25.9	20.9	36.0	36.9	37.9	32.7
Surface energy total, mJ/m²	60.7	43.7	61.7	54.8	71.0	70.6	72.2	67.8
Blocking rating @ 300 psi	1	0	0	1	0	0	0	3
Blocking rating @ 600 psi	1	0	1	2	0	0	0	3
Blocking rating @ 900 psi	1	0	2	2	0	1	0	3
Blocking rating @ 1200 psi	1	0	2	2	0	2	0	3
Blocking rating @ 1500 psi	1	0	2	2	0	2	0	4
Coldset glue fiber tear @ 120 min	100	100	100	100	100	100	100	100

MLCC: multilayer curtain coater; SB: styrene butadiene; SA: styrene acrylate; MVTR: moisture vapor transmission rate.

IX. Polyvinyl alcohol (PVOH) layer effects.

ever, the data showed that a 21% reduction in OTR was obtained by increasing the coat weight from 2 to 4 g/m² (comparing condition 12 vs. condition 11).

We also saw a slight improvement in the OGR performance with the PVOH containing systems at room temperature and 60°C.

For all the other properties, we did not see significant differences or trends. The surface defect "cracking" could have contributed to this observation for the PVOH containing layers.

Condition 13, with clay in the top layer, had the same MVTR, Cobb, and OGR performance as the similar condition 11 with carbonate in the top layer. Condition 13 was significantly worse for OTR performance.

One interesting observation is that the cold-set glue testing showed 100% fiber tear for all the 3-layer systems. With the cracking experienced in the top layer, we expected coating layer delamination during the glue testing. The 100% fiber tear indicates that the coating layers had excellent adhesion and that the cracking most likely was caused from a difference in surface tension between the PVOH dispersion and the pigmented coating dispersion or extensional viscosity differences.

SB vs. SA top layer

A comparison of top layers containing SB and SA binders were made on the conditions with a similar base layer to determine if the polymer type can affect barrier properties. The results are summarized in **Table X**.

Overall, Kit values were all similar, but conditions 6 and 9, with the clay top layer, had the best OGR performance. One reason is most likely due to the more tortuous path with a clay coating composition and the higher polarity of the SA polymer, as seen in the polar surface energy measurement. At similar PVC, the SB-based top layer gave a higher contact angle with water, but the SA system had a higher contact angle when the test was done with corn oil.

The SB-based top layer had better MVTR performance, but Cobb performance was similar. The SB polymers will tend to provide higher moisture or water resistance due to lower water sensitivity.

CONCLUSIONS

Some key findings from this study include:

- The repeatability study demonstrated that the MLCC coating technology is reproducible from run to run.
- Defect characterization of the multilayered systems did not reveal any pinholes, proving that the coatings were degassed properly, which is critical for barrier applications. The analysis did find that the 3-layer systems, with the PVOH in the middle layer, had surface cracking. It is suspected that the cracking was likely caused from the surface tension differences between the PVOH dispersion and the pigmented coating dispersions or from a difference in extensional viscosity of the wet coatings.
- Most conditions had minimal blocking, except for two conditions containing high levels of SA latex with clay in the top layer.
- All conditions had 100% fiber tear, most likely due to the higher PVC levels.
- This paper shows that, in a multilayer system applied with a curtain coating, having a base layer of pure polymer will significantly improve the creased Kit performance and have better oil, water, and moisture resistance compared to a base layer containing a polymer/pigment blend.
- Applying a middle layer of PVOH in a 3 layer system resulted in a significant improvement in MVTR performance. For example the addition of a 2 g/m² layer of PVOH produced an MVTR value a quarter of the control system. Increasing the coat weight of the PVOH to 4 g/m² resulted in an additional 50% improvement.
- Only systems with the PVOH layer were found to have OTR performance. Increasing the coat weight of the PVOH layer from 2 to 4 g/m² resulted in an OTR reduction of 21%.
- In blends of similar pigment type and similar PVC, SB polymers give better MVTR performance and SA polymers give better OGR performance. **TJ**

ACKNOWLEDGEMENTS

We would like to acknowledge Trinseo LLC for sponsoring this paper. Additionally, the efforts of the staff members at the Application Testing Laboratories in Rheinmuenster, Germany, and Midland, MI, USA, are greatly appreciated. We would also like to thank the technical experts at Kuraray for providing input and products for the PVOH experimentation.

LITERATURE CITED

1. Urscheler, R., Roper, J., Dobler, F., et al., "Multilayer curtain coating – an enabling technology for increased efficiency and new paper grades," *PTS Coating Symp.*, *22nd*, Papiertechnische Stiftung, Heidenau, Germany, 2005.
2. Miyamoto, K. and Katagiri, Y., "Curtain coating," in *Liquid Film Coating* (S.F. Kistler and P.M. Schweizer, Eds.), Springer, Dordrecht, 1997. https://doi.org/10.1007/978-94-011-5342-3_13.
3. Doll, H. "Curtain coating for paper industry – Single and multilayer," *PaperCon*, TAPPI Press, Peachtree Corners, GA, USA, 2017.
4. Larsson, T., Emilsson, P., "Optimization of coating with water based barrier," *PaperCon*, TAPPI Press, Peachtree Corners, GA, USA, 2018.
5. Tietz, M., "Curtain coating of pigment coats," *PTS Coating Symp.*, *22nd*, Papiertechnische Stiftung, Heidenau, Germany, 2005.

Trial Point/MLCC Condition	3	6	8	9	9
Coating Layers	**F2/F2**	**F5/F5**	**F2/F8**	**F2/F9**	**F2/F9**
Layer 1	**HC90/SB 25pts**	**Clay/SB 35pts**	**HC90/SB 25pts**	**HC90/SB 25pts**	**HC90/SB 25pts**
Layer 2	**HC90/SB 25pts**	**Clay/SB 35pts**	**HC90/SA 25pts**	**Clay/SA 35pts**	**Clay/SA 35pts**
Layer 3					
3M Kit test	12.0	12.0	12.0	12.0	12.0
3M Kit test – creased	0.0	0.0	0.0	0.0	0.0
Hot oil circle – room Y-value delta	0.5	0.5	3.2	0.5	0.4
Hot oil circle – oven Y-value delta	7.0	1.1	10.0	0.6	0.3
Hot oil rating (room temp): 1 h	0	0	0	0	0
Hot oil rating (room temp): 24 h	8	7	8	7	7
Hot oil rating (oven temp): 1 h	0	0	0	0	0
Hot oil rating (oven temp): 24 h	8	7	8	7	7
MVTR room, g/m²/24 h	88.1	41.2	124.2	96.8	88.1
MVTR jungle, g/m²/24 h	833.0	1055.4	1079.5	1298.4	878.2
Cobb absorptiveness (g/m²) 2 min	57.1	64.6	58.6	65.6	66.5
Cobb absorptiveness (g/m²) 30 min	218.4	293.8	222.2	289.3	284.5
Oxygen transmission rate, cc/m²/day	Fail	Fail	n/a	n/a	n/a
Contact angle 1 s H_2O	86.1	46.6	64.2	56.7	57.1
Contact angle 1 s corn oil	29.0	35.0	33.8	38.3	38.9
Surface energy dispersive, mJ/m²	37.2	35.9	35.0	33.0	33.9
Surface energy polar, mJ/m²	6.4	25.9	17.0	21.5	20.9
Surface energy total, mJ/m²	43.7	61.7	52.0	54.4	54.8
Blocking rating @ 300 psi	0	0	0	0	1
Blocking rating @ 600 psi	0	1	0	0	2
Blocking rating @ 900 psi	0	2	0	0	2
Blocking rating @ 1200 psi	0	2	1	2	2
Blocking rating @ 1500 psi	0	2	1	2	2
Coldset glue fiber tear @ 120 min	100	100	100	100	100

MLCC: multilayer curtain coater; SB: styrene butadiene; SA: styrene acrylate; MVTR: moisture vapor transmission rate.

X. Styrene butadiene (SB) vs. styrene acrylate (SA) top layer.

6. Erdem, B., "Waterfall of polymer colloids (multilayer curtain coatings)," *Polymer Colloids Gordon Res. Conf.*, Gordon Research Conferences, West Kingston, RI, USA, 2007.
7. Kilcher, G. and Dahlvik, P., "Multilayer curtain coating – back to the future!", *PTS Coating Symp., 29th*, Papiertechnische Stiftung, Heidenau, Germany, 2019.
8. Ventresca, D. and Welsch, G.W., "Multi-functional barrier coating systems created by multi-layer curtain coater," *PaperCon*, TAPPI Press, Peachtree Corners, GA, USA, 2021.
9. Burton, D., Ventresca, D., Welsch, G.W., *TAPPI J.* 21(11): 625(2022). https://doi.org/10.32964/TJ21.11.625.

ABOUT THIS PAPER

Cite this article as:
Ventresca, D., Benz, B., Eisenhauer, D., et al., *TAPPI J.* 22(11): 706(2023). https://doi.org/10.32964/TJ22.11.706

DOI: https://doi.org/10.32964/TJ22.11.706

ISSN: 0734-1415

Publisher: TAPPI Press

About this journal

ABOUT THE AUTHORS

There is a high demand and urgency by paper and paperboard producers to find water based barrier coatings to replace fluorochemicals and extruded plastic laminates due to regulatory issues. The purpose of this research was to develop coated substrates with multipurpose barrier properties that use water based coatings, as well as the most cost efficient coating application method. The goal was to find barrier solutions to the current regulatory issues using water based coatings.

Most research presented so far concentrates on the single layer application of a water based barrier coating. Our research is different from previous research and current practice in that we are applying multiple barrier layers with a single pass, using multilayer curtain coater technology and thus achieving multiple barrier properties. This is also impossible to accomplish with sequential conventional coaters.

The most difficult aspect of the research was to optimize the rheology and extensional viscosity of the coating formulations to process on a curtain coater at speeds typically run in mills. This was accomplished with a series of preliminary studies. Without the optimized rheology and extensional viscosity, we would have experienced unstable curtain and also defects such as holes and skips, producing a very poor barrier.

The research confirmed the enormous advantage of curtain coaters over conventional coaters. Curtain coaters give very uniform coating thickness, thus allowing for possible reduction in coat weights. Also, application of wet coatings, each with different barrier properties, applied in one pass results in no loss of performance for any of the layers.

The most interesting discovery was that, despite the perfect contour coating that the multilayer curtain coater produces, it is still advantageous to apply these coatings onto a pre-coated substrate. The pre-coated substrate improves barrier performance not because the pre-coat is a barrier, but because it allows for the laydown of a smoother and more consistent coating thickness.

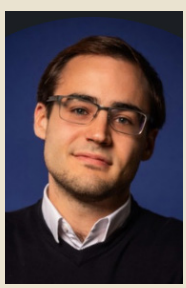
With the information from this research, mills contemplating a new coater should strongly consider the installation of a multilayer curtain coater due to the flexibility it gives in developing barrier structures. For mills who currently have multilayer curtain coaters, we hope this research will help them develop new barrier coating solutions fairly quickly.

The next step for us is to explore different barrier options with the multilayer curtain coater. This includes developing structures with 4 or 5 layers of water based coatings, including coatings for excellent oxygen barrier, water barrier, and OGR barrier. This would result in the optimum food packaging barrier grade.

Ventresca is senior application development specialist, Binders, at Trinseo LLC in Calabogie, ON, Canada. Benz is TS&D specialist, Binders, at Trinseo Deutschland Anlagengesellschaft mbH in Rheinmunster, Germany. Eisenhauer is technical sales representative, Binders, at Trinseo Europe GmbH in Pfaeffikon, Switzerland. Welsch is global innovation and TS&D leader, Binders, and Burton is senior research technologist, Binders R&D, for Trinseo LLC in Midland, MI, USA. Email Ventresca at dventresca@Trinseo.com.

Ventresca

Benz



Eisenhauer

Welsch

Burton