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THE EFFECTS OF BIOLATEX BINDERS ON THE DYNAMIC WATER RETENTION PROPERTIES OF PAPER COATING FORMULATIONS

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ABSTRACT

The following paper is a continuation of findings presented by the authors at PaperCon 2012 demonstrating the interesting rheological properties of biolatex binder dispersions and their coating colors relative to conventional coating starches and SB latex binders. The previous work indicated that the rheological performance of biolatex binder is significantly different from that of conventional cooked coating starches and all-synthetic latex containing formulations. This study investigates the dynamic water retention and wall slip properties of the same materials in order improve the understanding on coater runnability performance. Ensuring the correct rheology and water retention of coating colors is important as coater speeds increase and in order to achieve good runnability, productivity and final product quality it is critical to have a comprehensive understanding. It is common that quality and runnability problems originate from the interaction between base paper and the water phase of the coating color. Failure to control this interaction can lead to excessive migration of coating color to the base paper. This results in poor machine runnability, unstable systems and a non-uniform coating layer. In these evaluations an ultra-high shear ACA Viscometer (ACAV) was used to provide further insight into the wall slip properties of coating colors at shear rates that are relevant to industrial-scale paper coating processes. Results from these studies in combination with the results from previously presented rheological studies help explain some of the fundamental differences of these binder systems.

Keywords: biolatex binders**,** dynamic water retention, rheological performances, SB latex binders, wall slip properties.

INTRODUCTION

Latin America and especially Brazil holds an important position in the history of EcoSynthetix Inc. as it was here that the first generation of biobased latex emulsion polymers, also referred to as biolatex® binders, were first commercially adopted for paper coating applications in January 2008.[1,2] It is therefore a great honor to be here 5½ years later and introducing to the audience a summary of key milestones that have subsequently occurred in the development and technical understanding of biolatex binders. In 2008 these new binders demonstrated not only their performance with excellent binding strength, but also unique rheological, coating performance, coating structure, and optical properties to both wet and dry paper coatings, respectively.[1,2] A mechanism for their unique behavior was proposed based on the understanding that these biolatex binders consist of deformable, water-swollen and internally crosslinked biopolymer nanoparticles.[3,4] In addition, a schematic was proposed, in which a biolatex nanoparticle can be considered as one crosslinked macromolecular unit, as is illustrated in **Figure 1**.[5]

The biobased nanoparticle latex is a technically competitive alternative binder system to petrochemical-based binders, such as carboxylated styrene butadiene or acrylonitrile-containing styrene butadiene latex binders, and styrene acrylate latex binders (XSB and SA latex, respectively). During the PaperCon 2012 conference, some key findings were presented regarding the fundamental rheological performance of internally crosslinked water-swollen biolatex nanoparticles relative to conventional cooked coating starches and XSB latex, both in pure dispersions and in paper coatings.[6]

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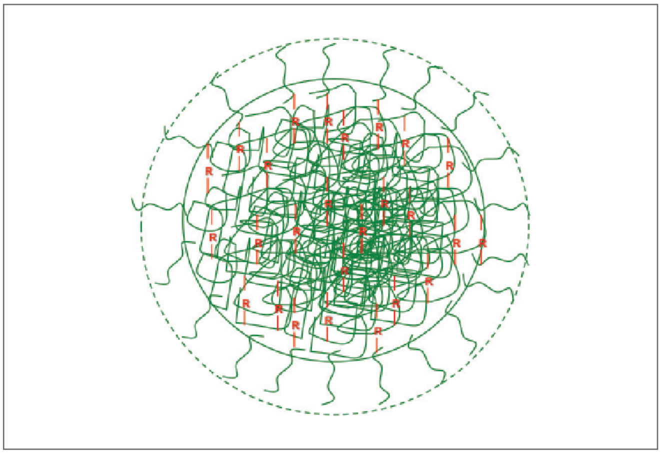

Figure 1. Illustration of internally crosslinked biolatex nanoparticle, with —R— representing an intermolecular crosslink[5]

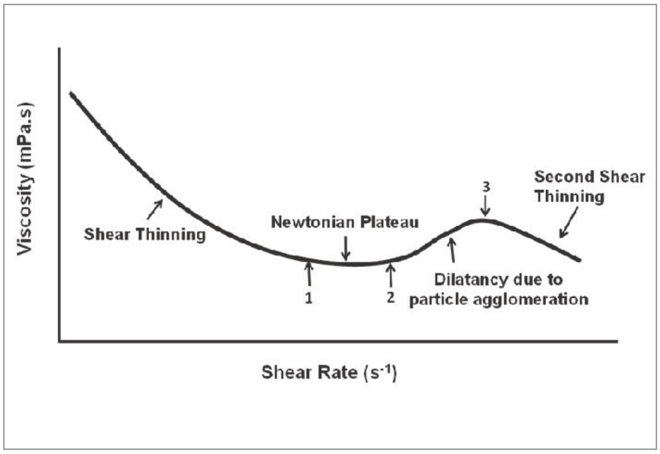

Figure 2. A generalized rheogram for high solids paper coating colors over a wide range of shear rates

The internal colloid particle swell ratio, i.e. the effective volume factor from dilute viscometry via the Einstein equation, was determined (see **Table 1**) for three different grades of internally crosslinked biobased nanoparticle latex.[3,4,6]

Coating formulations were prepared containing all-XSB latex, with and without rheology modifier, and subsequently XSB latex increasingly substituted each of either the 3 biolatex grades or soluble starch at 30% and 50% replacement levels. Their rheology was studied over a broad range of shear conditions and a generalized rheogram for high solids paper coating colors was proposed, as shown in **Figure 2**.[6] Low shear viscosities were obtained using a TA AR-2000 Stress Rheometer with double concentric cylinder geometry. Intermediate shear rate rheology was evaluated with a Hercules Rheometer. High shear rates were studied with ACAV A2 Ultra-High Shear capillary and slit rheometers. Composite rheograms compiled from experimental data using the three different viscosity measurement techniques were consistent with the generalized rheogram in **Figure 2**.[6]

It was reported that unlike conventional cooked and soluble starch solutions, biolatex nanoparticle dispersions with increasing intra-particle crosslink density have comparable behavior to that of petroleum based synthetic latex colloids. However, under ultra-high shear testing it was observed that their rheological properties are relatively more shear thinning compared to hard particles, including synthetic latex and pigment particles, which exhibit shear-thickening and dilatancy.[3,6]

Table 1. Effective volume factor of biobased nanoparticles *vs.* crosslink density[3,4,6]

Grade of Biolatex Nanoparticles	Relative Crosslink Density	Effective Volume Factor
Bio-A	Low	16.6
Bio-B	Medium	10.7
Bio-C	High	6.3
XSB latex		1.4 - 2.6

The proposed generalized rheogram for high solids paper coating colors indicates shear-thinning, followed by an interim Newtonian plateau (between 1 and 2 in Figure 2), subsequent shear-thickening (between 2 and 3), and shear-thinning (from 3 and on). The shear-thinning behavior of high solids particle dispersions is due to a progressive ordering of particles or a progressive disruption of aggregates by shear, and is also impacted by the shear dependence of electro-viscous effects and the compression of electric double layer repulsion. Shear-thickening behavior of high solids particle dispersions is attributed to a disruption of ordered particle arrangements or a progressive increase in shear-induced aggregation of particles.[7]

The shear rate at the onset of shear-thickening behavior (e.g., at 2 in Figure 2) coincides with the critical shear rate for shear-induced aggregation or coagulation of particles, when the hydrodynamic compressive force between the colliding particles surpasses their repulsive force. Note that the onset of dilatancy (point 2) is coating dependent and a function of % solids, coating materials and their respective levels, temperature, etc. Special emphasis has been put on the importance of solids content and its impact on coating rheology at high shear rates due to the dewatering rate of coating colors during the coating process in relationship to coater runnability.[8] Differences in high shear viscosity and apparent wall slip observed at increased concentration have been previously reported, even though the phenomenon had not been observed at the initial lower solids.[9] Depending on the coating specifics, the onset of shear-thickening can occur as low as ~10,000 s^{-1} in ACAV capillary rheograms.[9]

As shown in Figure 2, the shear-thickening and maximum viscosity of coating colors occur at lower shear rates with corresponding higher medium viscosity due to the greater hydrodynamic compressive forces.

The occurrence of geometric dilatancy (i.e. when the packing volume fraction of the aggregated particles in the dispersion under shear becomes lower than its volume fraction) increases with increasing extent of shear-thickening behavior and concentration. It can be expected that point 3 in Figure 2 is very close to the onset of geometric dilatancy, but as the volume expansion is somewhat prohibited in the confined geometry of the ACAV capillary and slit, the onset of dilatancy turns into the onset of the second shear-thinning. The latter appears to be an artifact of the ACAV equipment, and dilatancy will likely continue to build in commercial mill scale operations. These results confirm an earlier hypothesis that the shear-thickening of dispersions increases with increasing medium viscosity due to the fact that aggregation of particles under shear increases with increasing medium viscosity.[7]

The rheology and water retention characteristics of coating colors are important at increasing coater speeds, so that good coater runnability is achieved. Consequently, this work further explores the interpretation of ultra-high shear coating rheology and focuses on the dynamic water retention of the same materials to better understand effects on coater runnability. An ultra-high shear ACA Viscometer (ACAV) was used to provide insight into the wall slip properties of these coating colors at shear rates that are more relevant to commercial-scale paper coating applications.

Results from these studies are discussed in combination with key results from previously presented rheological studies, positioned here more appropriately with a statistical assessment, in order to explain some of the fundamental differences of three different coated paper binder systems, namely petroleum based XSB latex, various developments of biolatex dispersions, and a conventional soluble (cooked) coating starch.

EXPERIMENTAL SECTION

Materials and Coating Formulations

Samples used for this study include a Dow ProStar XSB latex binder and several experimental grades of EcoSphere® biolatex® nanoparticles labeled Bio-A, Bio-B and Bio-C from EcoSynthetix Inc., the coating starch 2015 was provided by Tate & Lyle. The other ingredients used in the coating formulations listed in **Table 2** are described as follows, No.1 clay: Hydragloss

Table 2. Coating formulations

Coating Color Sample #	1	2	3	4	5	6	7	8	9	10
Coating description	XSB + RM	30% Bio-A	30% Bio-B	30% Bio-C	30% Starch	50% Bio-A	50% Bio-B	50% Bio-C	50% Starch	XSB Only
Pigment										
GCC	70	70	70	70	70	70	70	70	70	70
Clay	30	30	30	30	30	30	30	30	30	30
Binder										
XSB latex	10	7	7	7	7	5	5	5	5	10
Bio-A	0	3	0	0	0	5	0	0	0	0
Bio-B	0	0	3	0	0	0	5	0	0	0
Bio-C	0	0	0	3	0	0	0	5	0	0
Starch	0	0	0	0	3	0	0	0	5	0
Additives										
Rheology modifier	0.5	0	0	0	0	0	0	0	0	0
Ca-Stearate	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Solid content, %	66.7	66.7	67.0	66.7	66.7	66.8	66.9	66.7	66.8	67.0
pH	8.0	8.0	8.1	8.1	8.1	8.0	8.1	8.1	8.2	8.0
Brookfield [mPa.s], 100 rpm	2460	1250	560	370	1380	2000	1150	520	1450	1170
Capillary viscosity (600, 000 s^{-1}) [mPa.s]	64	87	72	62	105	111	91	73	112	52
Slit viscosity (1,900,000 s^{-1}) [mPa.s]	44	45	33	35	61	63	43	36	55	35

90 (KaMin); GCC: Covercarb HP (OMYA); the rheology modifier (RM) was carboxymethyl cellulose (CMC): Finnfix 10, although others, including synthetic latex based rheology modifiers, could have been used with similar results; lubricant: calcium stearate (Ca-stearate).

The Brookfield viscosity in **Table 3** is relatively low for certain coating colors, and such a low viscosity could be impractical in commercial operations, however, for demonstrating the performance in production conditions it is desirable to remove the rheology modifier and simply increase the coating solids. In this study the solids were kept the same to ensure a valid comparison of the results. The rheology modifier was only included in sample condition 1, the XSB latex control formulation, where carboxymethyl cellulose (CMC) or another rheology modified/water retention additive is normally required. The rheology modifier was removed in the following trials in order to understand the impact of the 3 biolatex grades and the conventional coating starch. It should be emphasized at this point that Brookfield viscosities can be misleading when referenced to the runnability of rod or blade coaters for which high shear viscosity is much more relevant. Similarly, Hercules viscosity, often referred to as a "high shear viscometer" is actually a low to medium shear device in this context and can therefore also be very misleading.

Rheological Experiments

Lab studies were carried out to establish a number of similarities and differences between binders, such as biobased latexes (Bio-A, Bio-B and Bio-C), XSB latex, and soluble cooked starch. The work performed included rheological measurements using a dilute capillary viscometer (Cannon-Fenske, Cannon Instrument Company), a stress rheometer (TA Instruments dynamic stress rheometer, model AR-2000), a Hercules "high" shear rheometer (relatively low to moderate shear), and ultra-high shear capillary and slit viscometers (ACAV, Model A2). This work was reported at the PaperCon presentation in 2012,[6] confirming the trends postulated in Figure 2. The most relevant ultra-high shear ACAV data from that study is included here along with improved curve fitting and also a Minitab statistical assessment to help interpret the rheological trends in this comparative study.

Water Retention and Coating Wall Slip Velocity Experiments

An AA-GWR static water retention tester was used per TAPPI standard test method for measuring coating dewatering, T-701.[10] The AA-GWR was used to determine the immobilization solids of coatings. In addition, a Paar Physica UDS 200 was used to measure dynamic water retention. Slip velocities were determined for coating samples using an ACA ultra-high shear capillary viscometer (ACAV, Model A2) at a shear stress of 25,000 N/m^2, which corresponds to shear rates of approximately 500,000 s^{-1} for the coatings used in this study.

As noted above, the Brookfield viscosity in Table 3 is somewhat low for some of the coating colors, and such a low viscosity may be impractical. For a commercial operation it is still desirable to leave out the rheology modifier and simply increase the coating solids. In this study the solids were kept the same throughout the study to ensure a valid comparison of the results.

Note that water retention performance normally tracks with viscosity, and therefore the fact that water retention is much better than the all-synthetic controls emphasizes the validity of this approach and the positive nature of the results for the biolatex binders, which are superior despite the removal of the rheology modifier that was used in the control.

RESULTS AND DISCUSSION

High Shear Rheology Experiments

Biolatex dispersions are complex, polydisperse and hydrodynamic systems. As the polymers are crosslinked within a latex particle, they are converted to form higher molecular weight insoluble polymer networks. Depending on the degree of crosslinking, the final biobased latex may consist of internally crosslinked particles only, or a mixture of insoluble particles with a minor fraction of soluble polymers.

In a related study, in which researchers studied the microstructure and swelling behavior of synthetic microgel colloids, they reported the molecular weight measured by multi-angle laser light scattering for entire particles.[11] The molecular weights reported for the colloid particles were exceedingly high, i.e. 100's of millions of daltons, and, given that each colloid particle contained multiple polymers crosslinked together; it was further reported that at low crosslinked densities (less than 1%) there was a minor fraction of soluble polymers, but at higher crosslink densities (above 1%) there was no soluble polymer fraction.[11]

Similarly, for internally crosslinked biolatex colloid particles this means that an extremely high molecular weight, in the range of 10's or 100's of millions of daltons, is likely given that each particle would contain multiple polymers crosslinked together; at low crosslink levels, as in the case of the Bio-A grade, there is likelihood that some soluble fraction is present, but at high crosslink density (Bio-C) there would not likely be much if any soluble polymers.

Accordingly, we have initiated serum replacement studies which will be reported in subsequent studies. Originally, this method was used to remove absorbed emulsifier from a particle surface, but it is also a useful method to separate the water soluble polymers in latex dispersions by size exclusion through a membrane filter.[12]

The most interesting results from the rheological evaluation were confirmed using an ACAV at ultra-high shear, using a slit rheometer.

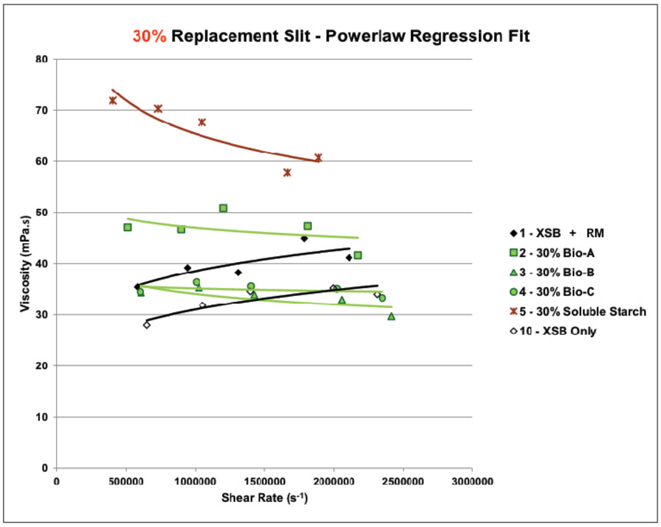

Figure 3. Ultra-high shear slit viscosity of coating colors with 30% replacement of XSB and an all-XSB latex coating color with and without rheology modifier, using the slit rheometer

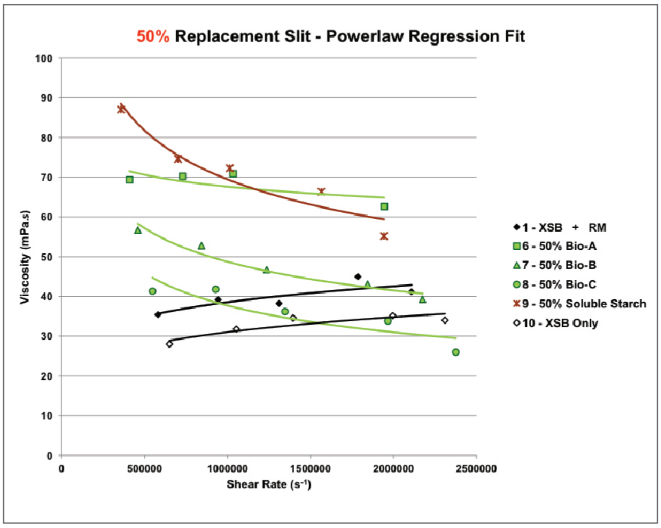

Figure 4. Ultra-high shear slit viscosity of coating colors with 50% replacement of XSB and an all-XSB latex coating color with and without rheology modifier, using the slit rheometer

These are demonstrated in **Figures 3** and **4** for coating colors with 30% and 50% replacement of XSB, respectively.[6] The slit rheometer operates at ultra-high shear conditions in the range of a commercial high speed blade coater.

A Minitab statistical analysis* was carried out for the data reported in reference 6 and shown here in Figures 3 and 4. This analysis led to the following conclusions:

1. Coating formulations containing 100% SB latex samples are dilatants with better than a 92% confidence limit, i.e. 92% confidence for coating color sample 1 ("XSB-RM"), and 96.5% confidence for sample 10 ("XSB Only").
2. All samples containing 30% or 50% biobased latex are thixotropic (i.e. shear thinning) or Newtonian in this shear rate range.
   a. Sample 2 ("30% Bio-A") is thixotropic with a 65.8% confidence limit, otherwise Newtonian.
   b. Sample 3 ("30% Bio-B") is thixotropic with a 93.6% confidence limit, otherwise Newtonian.
   c. Sample 4 ("30% Bio-C") is thixotropic with a 61.5% confidence limit, otherwise Newtonian.
   d. Sample 6 ("50% Bio-A") is thixotropic with a 84.8% confidence limit, otherwise Newtonian.
   e. Sample 7 ("50% Bio-B") is thixotropic with a 99.9% confidence limit.
   f. Sample 8 ("50% Bio-C") is thixotropic with a 98.6% confidence limit.
3. All samples with conventional starch are thixotropic in this shear rate range.
   a. Sample 5 ("30% Starch") is thixotropic with a 98.6% confidence limit.
   b. Sample 9 ("50% Starch") is thixotropic with a 99.3% confidence limit.

* All rheograms were fitted to both linear and power law models. The confidence limits are based on the fit with the best confidence limit.

As shown in Figures 3 and 4, the two coating formulations containing XSB latex as the only binder clearly demonstrate shear thickening, while coatings containing cooked starch and internally crosslinked biolatex nanoparticles continue to behave in a shear thinning mode over the profile. While the coatings containing cooked starch and the lightly crosslinked biobased latex A grade are shear thinning, their ultimate viscosities at high shear are still relatively high. This is likely to limit high speed runnability in commercial operations. Alternatively, runnability performance of the coater should theoretically be improved even with as little as 30% of the biobased latex B or C (Figure 3) and even further with 50% replacement of the petro-based binder (Figure 4).

Thus, biolatex binders consisting of internally crosslinked nanoparticles may outperform both petro-latex binders and conventional cooked coating starches in terms of fundamental rheological properties. The results help explain the improved runnability reported in ultra-high speed/high shear paper coating operations involving these deformable, internally crosslinked biolatex binders,[2,13,14] which have a higher tendency for shear thinning than hard particle synthetic latex binders. We will report further on this in future studies.

The dynamic water retention behavior and coating color wall slip properties are presented below in order to further explain the unique construction the biobased latex, and additionally to provide insight on the high speed coating runnability observed in commercial practice in Brazil and mills globally.

The rheological properties of coating colors and their runnability depend highly on their dewatering characteristics. Changes in effective solids and free water content due to dewatering under pressure (application nip and blade), or through capillary pressure of the base paper, have an impact on rheological properties and can be quite different at very high pressures such as those experienced during industrial coating processes.

Water Retention Experiments

The TAPPI standard test method for measuring coating dewatering, T-701, employs an AA-GWR static water retention tester.[10] The AA-GWR can be used to determine the immobilization solids of coatings. However, the gravimetric method has some disadvantages, such as the lack of vigorous shear during the measurement.[10] Furthermore, the contact time does not relate to practical coating processes. For these reasons, dynamic water retention test measurements are preferred.

A dynamic water retention tester operates on the principle of measuring the change in viscosity of the coating color against time, as applied to the original base paper. The method (see **Figure 5**) uses a conventional rotary viscometer fitted with two plates, and several holes are drilled into the lower plate. A sample of paper is placed on the lower plate and a standard amount of coating color is applied to the paper. The upper plate is then lowered until the coating in the gap achieves a standard thickness (usually 0.3 mm).

The increase of viscosity with time is used to characterize the kinetics of immobilization, determined by the water retention properties of the coating color, the absorbency of the base paper (Whatman® Filter paper) and the structural rearrangements during the dewatering process.

As indicated in Table 2, fresh coating colors were used for measuring water retention. Biobased latex was used as a synthetic binder replacement, with varying crosslink densities (Table 1). The coating colors containing biolatex binder were compared with all-synthetic latex systems with and without rheology modifier (RM), and also with samples containing a cooked starch. It is well understood in the industry that, for high speed coating operations, an all-synthetic paper coating formulation generally requires the addition of a rheology modifier/water retention aid to provide adequate coater runnability performance. In practice, it has been found that the incorporation of biolatex binder in a coating formulation facilitates the elimination of rheology modifier with superior runnability.[2,13,14]

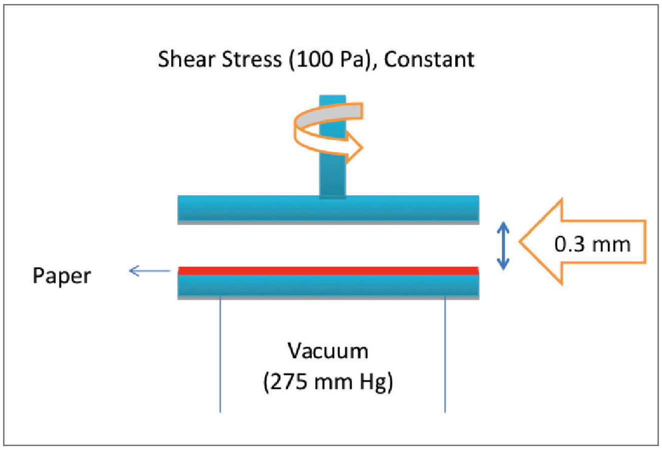

Figure 5. Schematic of the Universal Dynamic Spectrometer Paar Physica UDS 200

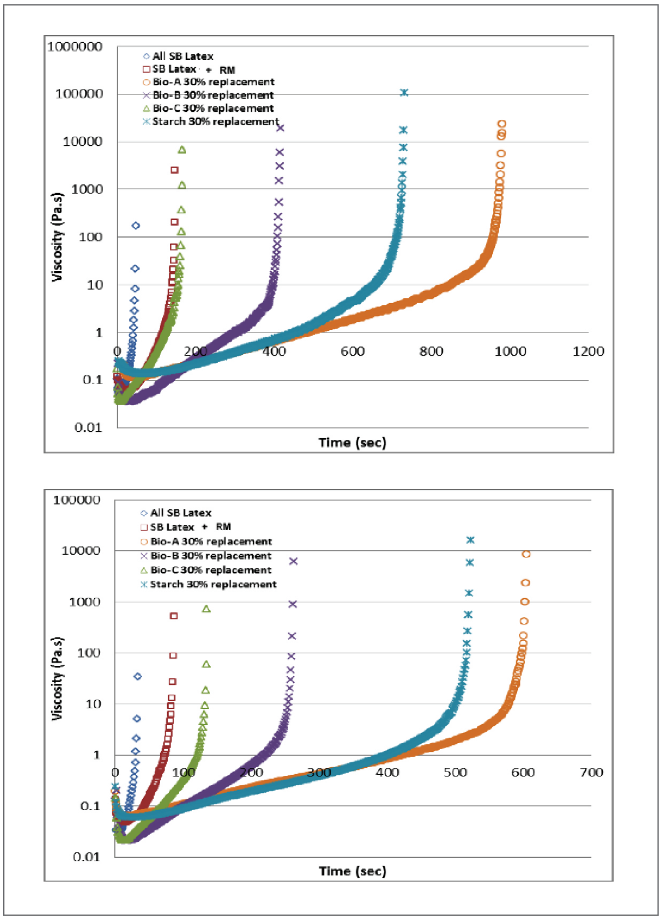

Figure 6. Coating immobilization time characterization at room temperature (top) and 37°C (bottom)

As shown in **Figure 6**, all coatings show clear immobilization times. Bio-A (low crosslinked biobased latex) shows the highest dynamic water retention, while all-synthetic latex systems gave poor water retention. The temperature was increased to replicate conditions in a commercial scale by raising the sample chamber from room temperature to 37°**C**. The results demonstrate that even the more highly crosslinked Bio-C grade of biobased latex has superior water retention performance as compared to the all-synthetic binder coating formulations with or without rheology modifier.

As further indicated in Figure 6, immobilization times were shortened at the higher temperature. At the elevated temperature the medium viscosity was reduced and the resulting penetration was greater. However, the immobilization time of Bio-C (high crosslinked) was relatively unchanged. This can be explained to be due to the higher crosslinking level, such that the average molecular weight between crosslinks (referred to as M_c) is relatively lower, and thus, even as the temperature is increased, the particles are able to retain and release less water.

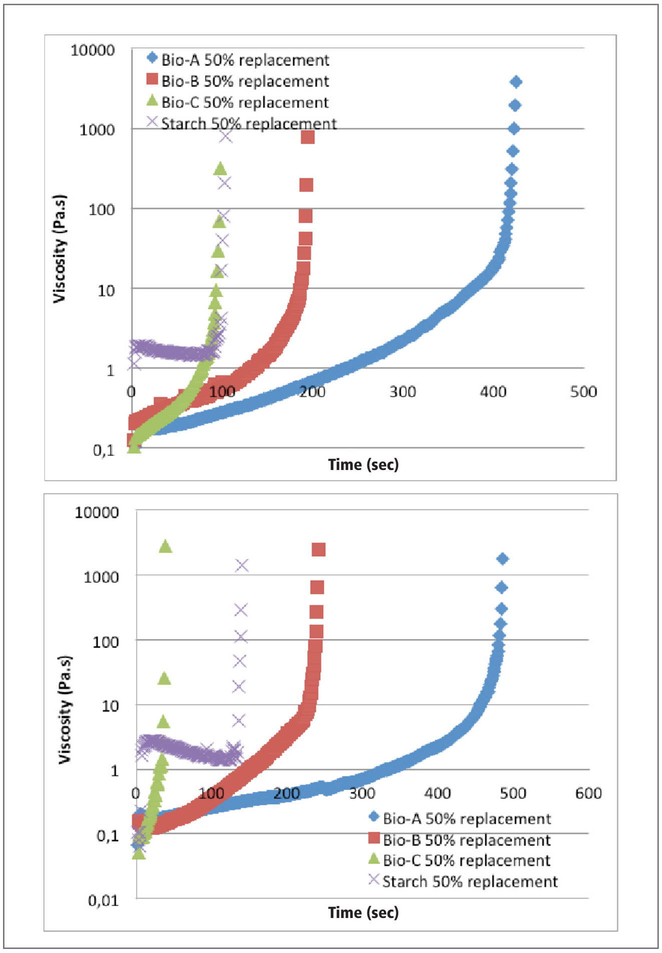

Figure 7. Coating immobilization time characterization at room temperature (top) and 37°C (bottom)

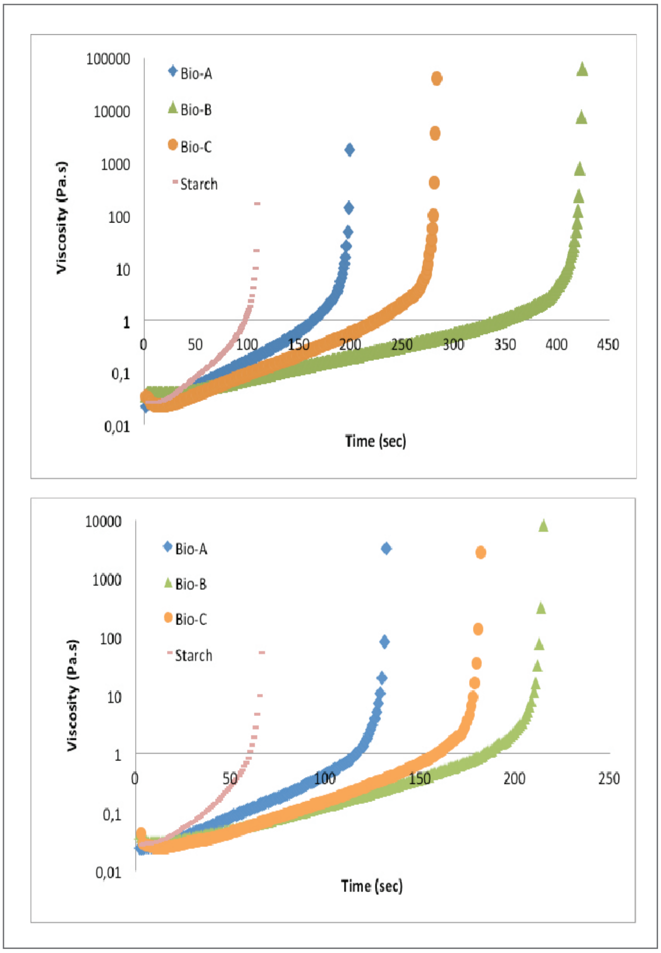

Figure 8. Coating immobilization time characterization at room temperature (top) and 37°C (bottom)

At 50% replacement levels, all immobilization times were reduced (see **Figure 7**), because the viscosity of 50% replacement is higher than at 30% replacement levels. The Paar Physica dynamic water retention tester instrument measures the increase in viscosity with time under constant stress (100Pa), and therefore higher viscosity coatings reach the stop point earlier under a given stress. However, at 37°C (lower viscosity condition), all immobilization times were increased, though the coating containing the high-crosslinked Bio-C had a lower viscosity and immobilized relatively faster.

In the example of the conventional cooked starch co-binder, an ethylated coating starch, the viscosity of the coating suddenly increased to just above 1 Pa.s at the initial point, and it subsequently remained at a relatively constant viscosity before stopping. This behavior was unexpected and is possibly the result of the relatively low shear conditions of this measurement in which soluble starch could act somewhat like a particle because polymers in solution form random coils under low shear conditions. Another possibility is that such a high concentration of starch might have caused depletion flocculation of pigment and latex particles.

The 50% replacement shows totally different behavior compared with the 30% replacement. However, it challenging to determine whether the water holding ability of biobased latex is due to the viscosity effect of the coatings or the biolatex particle itself. Commonly, an increase in aqueous phase viscosity slows down penetration. It is possible to deduce this if the viscosities of all of the coatings are equal or at least reasonably close in value. To separate these effects, additional experiments were performed where the solids of the coating colors and the ratio of pigment, the XSB latex binder, and all additives were kept the same as in Table 2. The exceptions were the levels of the biolatex binder and conventional coating starch, which were optimized in order to match the Brookfield viscosity as shown in Table 3.

Under the same viscosity condition (see **Figure 8**), Bio-B shows the highest water retention behavior. Under these conditions, the water retention performance appears to be lower for Bio-A, followed by Bio-C and finally conventional coating starch. It can be postulated that there is a trade-off with biobased latexes in terms of a) water retention, where a lower crosslinking gives higher water retention, and b) medium viscosity, where higher crosslinking gives better overall performance. Therefore, an intermediate level of crosslinking gives better results when compared on this basis.

Table 3. Coating formulations designed to match viscosity. (Same recipe as in Table 2, except for the levels of biobased latex and conventional coating starch, which were optimized to match the Brookfield viscosity)

	Bio-A	Bio-B	Bio-C	Starch
Brookfield (cps), 100 rpm	540	600	580	590
Solid, %	66.8	66.7	66.7	66.8
Replacement, parts	0.58	3	4	0.42

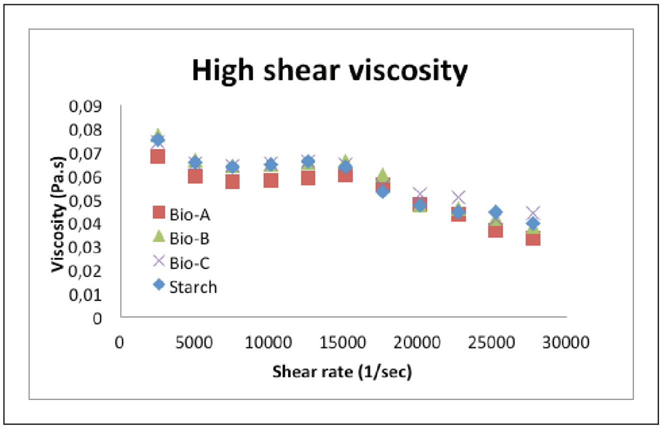

Figure 9. Low to medium shear viscosity of coating colors in Table 3 measured using a Hercules rheometer

The low to medium shear rheology of the coating colors in Table 3 were measured using a Hercules rheometer showing reasonably similar performance for these coatings with similar Brookfield viscosities.

Coating Color Wall Slip Properties

A further property that impacts coater runnability is the rheological interactions at boundary conditions, such as at the blade or nip. Several studies have linked this to the "apparent wall slip", which can be measured using a high-shear capillary viscometer with multiple different capillary diameters.[15-17]

Previous literature in this field examined for a variety of coating formulations, for example, the impact of coating color solids and lubricants,[15] the effect of the level of rheology modifier,[16] and the impact of different types of thickeners.[17] In this work, we intend to contribute to this field by considering alternative coating binders in the formulation.

Coatings were prepared with the same formulations as used in the immobilization study above. Note that the low-crosslinked Bio-A grade of biobased latex, which behaved somewhat similar to conventional starch (i.e. coating formulations #2 and #6) was not included in this study. Basic coating data (Brookfield viscosity, pH, solids, and gravimetric water retention) are included in **Table 4**.

These coatings were prepared in ~3 kg batches, to provide for sufficient coating material for multiple ACAV runs using various diameter capillaries. It was noted that temperature increased over each ACAV measurement from about 25°C to about 30°C as a result of frictional forces, however, this was neglected in subsequent calculations and the system was assumed to be isothermal.

It is understood that the mechanism for creation of slip is the relatively lower concentration of suspended particles adjacent to the wall rather than in the bulk, as the wall boundary physically restricts the orientation and packing of particles near it. Thus, for our experiment, a thin layer typically on the order of microns forms near the capillary wall and has a lower viscosity than the bulk coating. Particles and polymers in the coating will have a tendency to facilitate flow and smaller or "lubricating" particles

Table 4. Coating formulations used for ACAV wall slip studies

Trial #	1 XSB + RM	3 30% Bio-B	4 30% Bio-C	5 30% Starch	7 50% Bio-B	8 50% Bio-C	9 50% Starch	10 XSB Only
Solid content, %	67.11	67.3	66.7	66.8	67.7	67.3	66.8	67.1
pH	8.3	8.6	8.5	8.3	8.6	8.6	8.5	8.4
Brookfield (cps), 100 rpm, 21 °C	2250	491	235	1384	800	276	2070	832
Gravimetric water retention	122.3	88.9	146.6	52.9	63.0	134.8	19.4	223.5

or polymers will on average migrate towards the capillary wall to form a "slip layer".[14] The apparent slip will continue to increase with higher shear as the higher flow rates will result in more particle migration to the lower shear stress regions in the middle of the capillary flow field.

Apparent slip is thus a function of shear stress, and can be facilitated by the presence of particles or polymers that can "lubricate" the wall and facilitate flow.

Triantafillopoulos *et al.*[15] discuss a procedure for determining the apparent wall slip that involves comparing data for shear rate *vs.* shear stress for two different capillary sizes. A linear fit can be approximated for the data and shear rates can then be determined at a specific shear stress for each capillary. The difference in shear rates, $\Delta S_R = S_{r\ small} - S_{r\ large}$ is then used via the following equation to determine a "slip velocity" [m/s], where D is the capillary diameter:

$$V_{slip} = \frac{1}{8}\frac{\Delta S_R}{\Delta \frac{1}{D}} \qquad \text{Eq. 3}$$

Slip velocities were determined for coating samples at a shear stress of 25,000 N/m^2, which corresponds to shear rates of approximately 500,000 s^{-1} for the coatings used in this study. It was suggested in the literature that a higher shear stress results in noisier data as the flow fields take a longer time to equilibrate and due to turbulent effects, while lower shear stresses result in minimal slip. These slip velocities are tabulated below in **Table 5** for each of the coating samples.

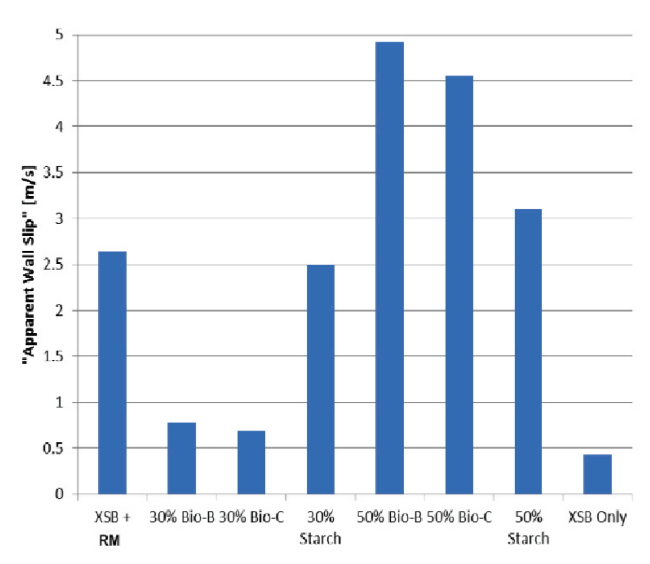

Figure 10. Apparent slip velocity of coating colors measured using the ACAV rheometer

Table5. Tabulated Slip Velocities measured using the ACAV rheometer

Coating Sample	Slip Velocity [m/s]
1	2.64
3	0.78
4	0.69
5	2.50
7	4.93
8	4.55
9	3.10
10	0.43

It has been reported that the standard error in these measurements is proportionate to the Reynold's number.[15] Based on this we estimated for this data that the error is ±5%. Comparing these results to previous published literature, it was observed that the slip velocities are an order of magnitude lower because of the much higher coatings solids. It is important to note that a comparison of coating sample 1 (XSB with RM) to coating sample 10 (XSB only) shows the presence of thickener to increase the wall slip velocity and water retention, as has been previously shown.[16]

It has previously been reported that water retention does not readily correlate with apparent slip velocity and the presence of some lubricants can act to increase slip and improve water retention simultaneously.[16]

This poses the question: how to explain why biobased latexes tend to show higher apparent slip velocities? Let us first remember that biobased latexes are water-swollen due to their osmotic pressures.[3] If hydrodynamic compressive forces in capillary flows exceed the osmotic pressures of biolatex particles, then these particles will de-swell and release water at the capillary wall, where the shear rates are highest in the capillary flow. The act of deforming and releasing water may be able to lubricate jammed solid particles and facilitate flow. Therefore, this provides further indication that internally crosslinked biobased latexes may be considered as unique rheological lubricants, as was originally reported.[3]

Increasing the crosslink density of the biolatex particles reduces the relative wall slip, i.e. coating sample 3 (30% Bio-B) shows slightly higher slip than sample 4 (30% Bio-C), and sample 7 (50% Bio-B) notably higher than sample 8 (50% Bio-C), and though the water retention data for the more tightly crosslinked biolatex particles show that they release less water than the lighter crosslinked Bio-B and Bio-A grades, the Bio-C latex particles still have better water retention and wall slip characteristics as compared to all-synthetic coatings containing hard XSB particles. It can be further suggested that the particles facilitate better slip than soluble polymers, particularly at high levels of replacement (50%).

O PAPEL vol. 75, num. 3, pp. xx - xx MAR 2014

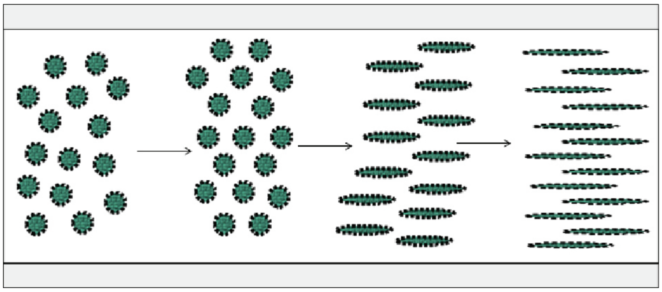

Figure 11. Proposed model for rheological performance of internally crosslinked biolatex colloid particles under increasing shear conditions

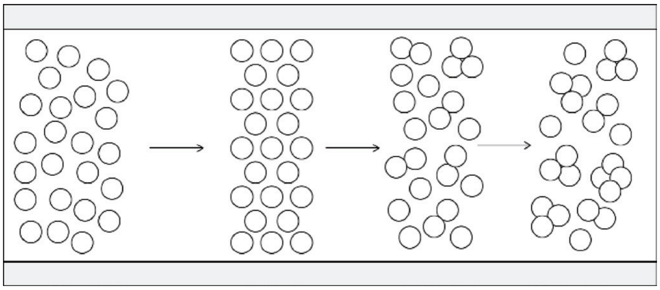

Figure 12. Proposed model for rheological performance of petro-based XSB colloidal latex particles under increasing shear conditions

Thus, it has been found, from a pure shear thinning and water holding perspective, that the internally crosslinked biopolymer latex binders have excellent water retention performance, in addition to being more shear thinning than the petroleum XSB latex binders. This can explain the superior runnability consistently observed for these biopolymer latex binders in high speed coated paper and board trials observed in mills worldwide. Other findings conclude that the biolatex colloid particles achieve the maximum swelling value under conditions of extreme dilution with water, and that they de-swell with increasing solids so that their dispersions can be made at higher solids.[3,4]

While traditional soluble cooked starch polymers can form a "particle-like" random coil in solution at very low shear, they become chain extended and linearized as shear increases, resulting in the loss of water retention and shear thinning characteristics. This is why soluble polymers cannot perform as effectively as colloid particles such as petro-based latex and internally crosslinked biolatex colloid particles. The water-swollen colloid particles deform and de-swell under shear and pressure, which is a unique property of the biolatex technology. When stress is applied to the fluid, the biolatex colloid particles start deforming in the coating color. It is proposed that the swollen biolatex colloid particles, when exposed to high shear, are compressed and release water, thereby decreasing the effective solid volume fraction at which time they begin to act as a lubricant and allow better particle alignment. This is depicted schematically for a biopolymer latex in **Figure 11** and for an "all synthetic" petroleum-based latex in **Figure 12**.

With ever more internal crosslinking of the biolatex particles, a significant decrease in viscosity at ultra-high shear rates occurred. Thus, biolatex binders – in principle – may outperform conventional cooked coating starches as well as "all-synthetic" petro-latex binders in terms of fundamental rheological properties and commercial high speed coater runnability.

Further testing continues to be conducted at Western Michigan University and various other universities to help us enhance our fundamental understanding of these novel biobased latex binder systems.

CONCLUSIONS

This work furthers the understanding of biobased latexes and the impact of these binders on high shear rheology and dynamic water retention. Today's industry expects SB latex coatings to be problem-free, but it is known that all-synthetic SB latex coating colors cannot readily be run at increased solids. Our study clearly shows that it is because of their tendency towards dilatancy at the blade coating shear rate range of 500,000 to 2,000,000 sec^{-1} and their lack of dynamic water retention. Biolatex binder systems help to limit coating color dewatering both at low (gravimetric) and higher (dynamic) shear stresses. This was observed independently of the coating viscosity, and for a controlled viscosity the intermediate level of crosslinking had the best water retention properties. Thus, there appears to be a compromise between water retention and coating color viscosity as a function of the biolatex crosslink density. The capillary wall-slip measurements of the coatings showed that the presence of higher levels of hydrophilic polymers or particles increases wall slip. Decreasing the crosslink density of biobased latex and replacement of latex with biolatex particles demonstrated better slippage than the rheology modifier or cooked starch polymers. These results provide a strong indication of superior coater runnability, a feature that has been observed in commercial coating operations in Brazil and mills globally.

Considering the results from previous rheological studies of biolatex containing coatings,[6] these additional findings provide a clear indication of the benefits of biobased latexes as a binder replacement for XSB binder. The biolatex systems show unusual rheological, water retention, and wall slip properties that suggest better coater runnability.

The results help explain the improved runnability reported in ultra-high speed/high shear paper coating operations involving these deformable, internally crosslinked biolatex binders,[2,13,14] which have a higher tendency for shear thinning than hard particle synthetic latex binders.

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O PAPEL vol. 75, num. 3, pp. xx - xx MAR 2014

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