

"Coating & print performance of biobased latex in European graphic papers"

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ABSTRACT

Biobased latex has been introduced to Europe for light weight coated (LWC), fine paper and board applications. This presentation summarizes the experience from lab to pilot plant scale in preparation for mill production. Learning's regarding coating preparation, runnability and paper performance in LWC papers produced under state-of-the-art pilot coater conditions are reported, as well as print performance obtained on a commercial printing press. This has demonstrated that 30 – 50% of the petroleum-based latex plus much or all of the co-binder, rheology modifier and OBA carrier can be replaced with biobased latex to provide similar performance for some properties and superior performance for others. Benefits beyond paper & print performance, improved runnability and carbon footprint were noted, including higher solids coating formulation and dryer energy savings.

1. INTRODUCTION

Biobased latex has been introduced in Europe as a substitute for petrochemical-based binders such as carboxylated- & acrylonitrile-based styrene butadiene (XSB) as well as styrene acrylate (SA) latex binders used for light weight coated (LWC), fine paper and board applications. The technology utilizes starch as the main ingredient along with other biobased and chemical components, and provides a direct replacement for petrochemical-based binders. Biobased latex binders have been demonstrated to provide coated paper performance that is comparable to XSB and SA latex systems, something one would not normally be able to expect from conventional cooked starches. Their unique behavior relates to the colloidal structure of the biopolymer nanoparticles that make up the biobased latex.¹⁻⁹

As illustrated in Figure 1, the biobased latex nanoparticles are manufactured from starch derived from corn, potato, tapioca, etc. via a proprietary twin screw extrusion process, and then shipped as a dry powder product to the coated paper and board manufacturer, which eliminates the need to ship the binder as an aqueous 50% solids latex dispersion typical of petrochemical-based XSB and SA latex emulsions.

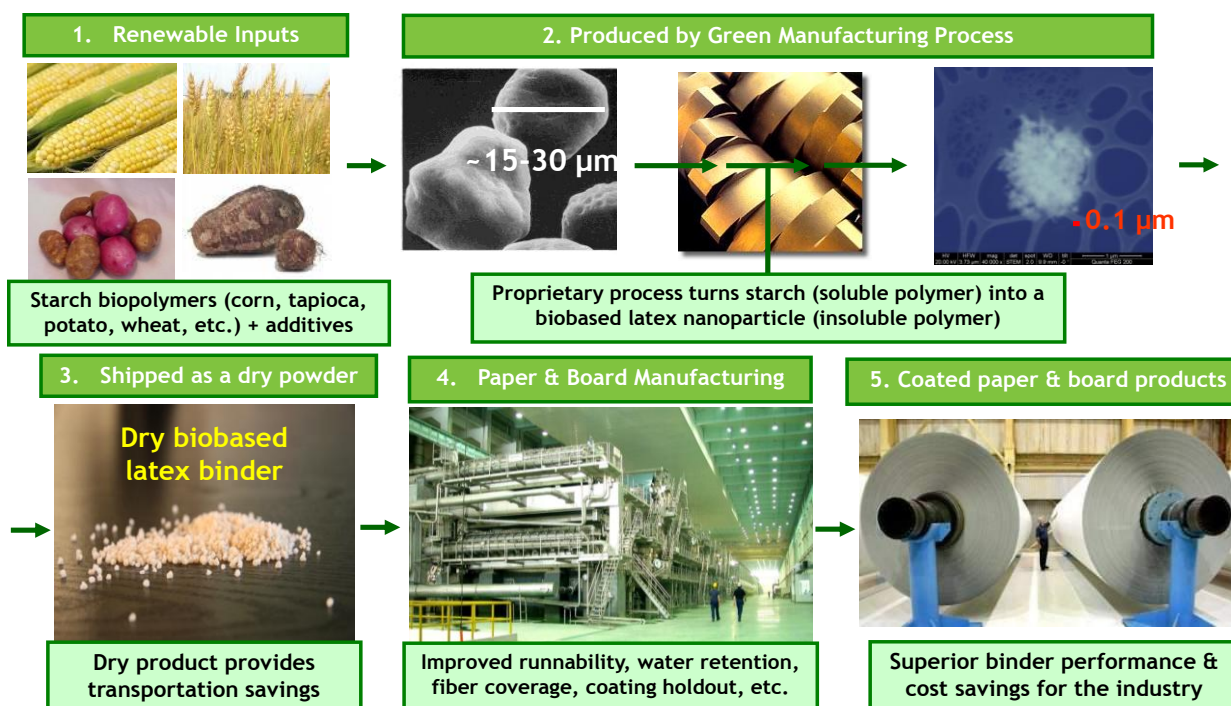


Figure 1. Schematic illustrating main raw material inputs (starch from corn, tapioca, potato, wheat, etc.), biobased latex manufacturing and coated paper manufacturing.

Crosslinked biopolymer nanoparticles have unique properties when dispersed as a latex in water. First, their swelling under conditions of extreme dilution with water achieves the maximum swelling value that is a balance between the elastic constraint due to their crosslinked network and the osmotic pressure.⁷ By measuring the relative viscosity at low concentrations for a polymer colloid, one can gather relevant information about the viscosity and swelling behavior of that colloid. Biobased latex nanoparticles de-swell with increasing solids, and by addition of water-soluble species such as electrolytes.⁷

Since biopolymer nanoparticles in dispersions exist in the form of water-swollen crosslinked nanoparticles, their effective solids are higher than their actual solids. The water-swelling of biobased latex nanoparticles significantly increases the % effective solids and volume solids over their % actual solids and volume solids as compared to typical cooked starch solutions and synthetic latexes.⁷ This increase in effective coating solids enables paper coating colors containing biobased latex binders to get close to their immobilization solids,^{7,10,11} so that they exhibit excellent coating holdout, resulting in enhanced fiber coverage and coating smoothness.

One of the characteristics of biobased latex binders for paper and paperboard coatings is that they have shear-thinning rheological properties, and therefore they exhibit superior runnability on high speed coaters. In addition, the crosslinked nanoparticles shrink much less than soluble starches upon coating consolidation during drying.^{7,12,13} Upon drying in the coated paper manufacturing process, the biobased latex nanoparticles possess a nanocellular void-like internal structure within the paper coating,^{3,4,7} and it has been proposed that the "virtual density" of the biobased latex within the dried paper coating approaches 1.0 g/cm³. This explains the ability to replace XSB latex binders (which have a density close to 1.0 g/cm³) on a one-for-one part basis.

The low degree of coating shrinkage and the nanocellular void-like internal structure of biobased latex containing paper coatings are responsible for a more open coating structure and higher opacity which was first observed in CLC and pilot coater studies, and has subsequently been confirmed in full scale mill operations. This low degree of shrinkage has been borne out by the preservation of gloss for biobased latex paper coating formulations cast on polyester film, thus providing substantiation of this hypothesis.^{7,9}

A model has been proposed which describes the nanoparticles (average size ~100 nm) as individual crosslinked macromolecular units, which explains why the nanoparticles do not dissolve but form latex-like colloid dispersions.⁸ The biobased latex is shipped dry for on-site dispersion and consists of much larger agglomerates (average size ~300 μm), from which nanoparticles are released only when they are dispersed in water. In dispersed form, as noted above, the water-swollen crosslinked nanoparticles possess an effective solids that is higher than their actual solids. Proper mixing and complete dispersion is critical, however, as illustrated by controlled agglomeration studies in the presence of different molecular weight dextrans.⁸

This presentation will summarize the experience from lab to pilot plant scale in preparation for mill production. The original lab test evaluations were carried out at an independent facility. An extensive test series considered the performance of the biobased latex in the mill's offset recipes. The lab results were encouraging and so led to a full scale set of pilot trials designed to provide more realistic, operational data due to the higher application speeds and enhanced drying capabilities. Learning's regarding coating preparation, runnability and paper performance in LWC papers produced under state-of-the-art pilot coater conditions are reported here, as well as print performance obtained on a commercial printing press.

2. EXPERIMENTAL

2.1 Trial targets and planning

The pilot trials were designed to evaluate a number of specific properties of the biobased latex:

- The replacement of XSB latex in combination with the evaluation of binding power. XSB and CMC were replaced on a 1:1 basis with biobased latex, PVOH on a 1:2 basis, and rheology modifier was simply removed without adding additional biobased latex;
- Study of coating color runnability with respect to water retention, immobilization solids, viscosity development and dry content. Published and lab trial results with increased water retention and viscosity suggested the removal of CMC and the reduction/elimination of rheology modifier;
- Effect of the biobased latex on wet pick strength. Formulations V4 to V7 test if an insolubilizer gives increased wet pick strength compared to the insolubilizer-free Formulations V1 to V3; and
- The potential as carrier for OBA was studied in the formulations V6 and V7, which contain high levels of biobased latex, but reduced or no PVOH which is used in V1 to V5 mainly because of excellent OBA carrier properties.

As a result, four ratios of biobased latex/XSB latex levels were evaluated, i.e. 36, 45, 52 and 60%, as illustrated in Figure 2.

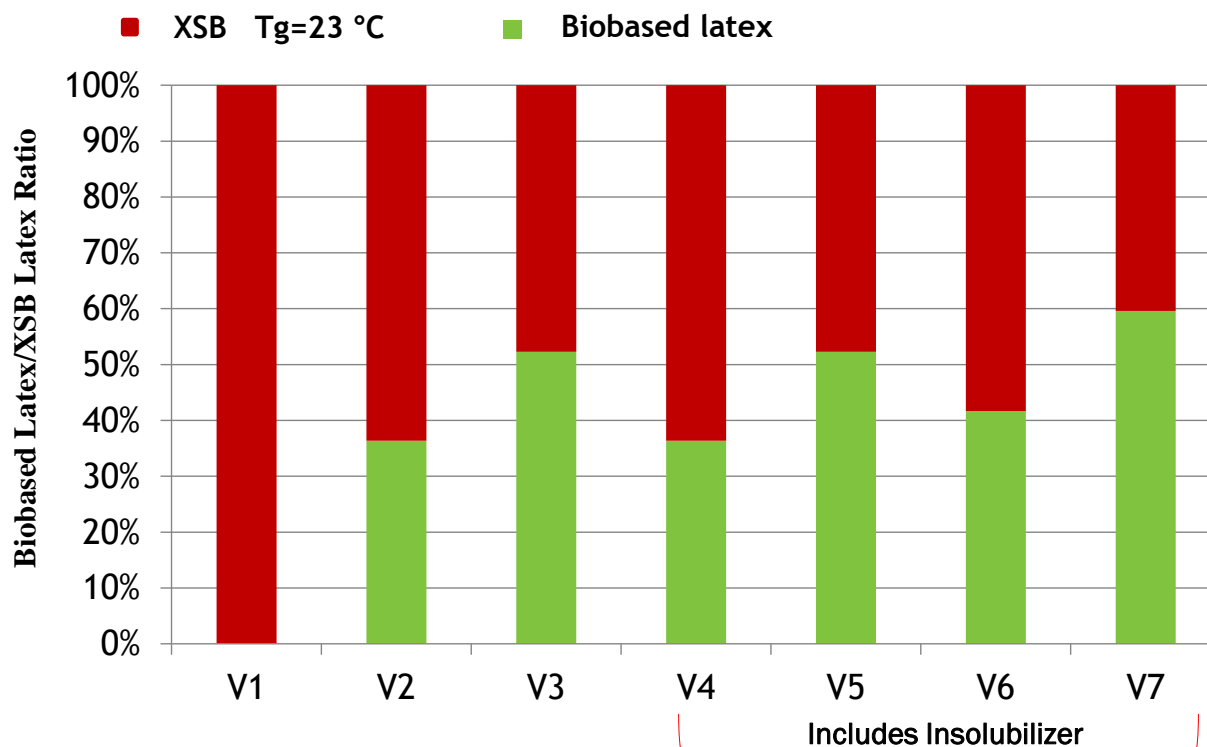


Figure 2. Ratio of the petroleum based XSB latex binder and the biobased latex binder for the 7 pilot coater runs.

2.2 Base paper and coating materials

The base paper was a 50 g/m² grade supplied by the MD Papier Albbbruck mill, a member of the Myllykoski group, based in Germany. The wire side was coated first and secondly the felt side. The biobased latex was ECOSPHERE[®] 2202 biolatex[®] binder provided by ECOSYNTHETIX INC. All materials used were commercial and part of Europe's paper coaters' widely used products. The petroleum-based XSB latex binder, designed for heat set web offset (HSWO), had a glass transition temperature, T_g of 23 °C. A polymer based on acrylic ester was used as the rheology modifier and a urea-formaldehyde resin as the insolubilizer.

2.3 Coating color preparation

The coating colors were prepared according to a plan (see Table 1) that evaluates one of the mill's offset reference formulations (V1), and subsequently substituting the synthetic latex on a 1:1 basis with increasing levels of biobased latex (V2 to V7). The biobased latex binder was added dry as early as possible directly into the calcium carbonate pigment slurry. Adequate

mixing, proper pH management (pH~10 prior to the addition of dry biobased latex), and order of addition were important in achieving complete dispersion of the dry biobased latex as efficiently and effectively as possible, without impacting batch cycle time. Given the biobased latex is supplied in dry form, it could be used to help boost the final coating solids. The pilot coater trials were carried out at the PTS facility in Munich, Germany. This state-of-the-art facility is fully equipped with variable speed high shear mixers and this enabled a straight forward and effective preparation of the coating color formulations.

Table 1: Coating color formulations used for pilot coater runs

	Order of Add'n	V1	V2	V3	V4	V5	V6	V7
Pigments								
GCC	1	70	70	70	70	70	70	70
Clay	1	30	30	30	30	30	30	30
Binders								
XSB Binder	4	10.5	7	5.25	7	5.25	7	5.25
Biobased latex	2	0	4	5.75	4	5.75	5	7.75
Additives								
CMC	3	0.5	0	0	0	0	0	0
PVOH	5	1	1	1	1	1	0.5	0
Rheology Modifier	3	0.2	0.2	0.1	0.2	0.1	0	0
Ca-Stearate	6	0.25	0.25	0.25	0.25	0.25	0.25	0.25
OBA	7	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Insolubilizer	8	0	0	0	0.5	0.5	0.5	0.5
Coating Properties								
Solids target		65	68	68	68	68	68	68
Solids at the coater		66.1	68.0	67.5	67.1	66.8	67.8	67.9
Brookfield (100 rpm)		1670	1360	1240	1200	1140	820	1760
pH		8.8	8.7	8.8	8.7	8.8	8.8	8.8
% XSB replacement		0	33%	50%	33%	50%	33%	50%
% biobased latex/XSB		0	36.4%	52.3%	36.4%	52.3%	45.5%	60%

2.4 Pilot coater, coating operation and trial conditions

The PTS Vestra Pilot coater in Munich, Germany (see Figure 3) is a state-of-the-art facility encompassing a modern pigment make down preparation area, a fully equipped pilot coater that is unique in that it has five different coating applicators, including rod, blade, air knife, metered size press, and a 3-layer slide curtain coater that operate at speeds ranging from 50 up to 2500 m/min. The papers are normally calendered to the customer's specifications and then shipped to a printing facility of choice.

In this series of trials about 14 g/m² coating per side was applied by a rigid blade (also called "stiffblade" in Europe) coater with applicator roll, in which the blade thickness/angle = 0.381 mm/40°, at a speed of 1200 m/min.

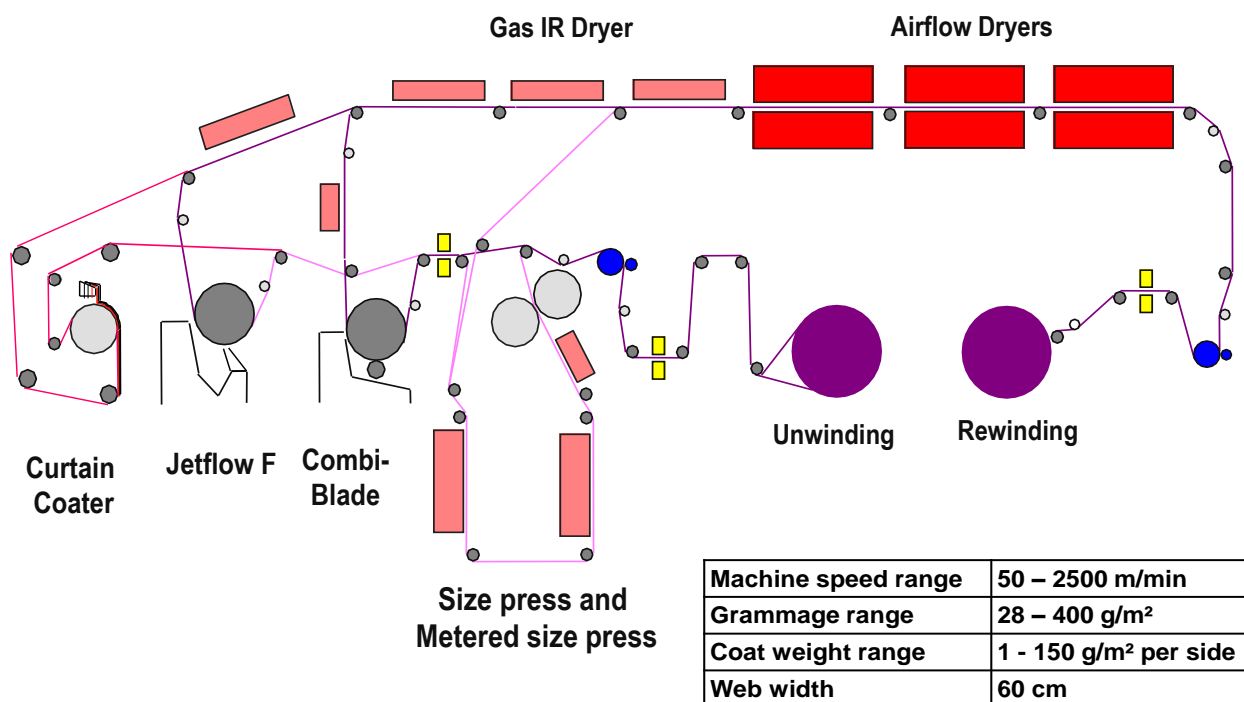


Figure 3. Schematic of the PTS Vestra pilot coater in Munich, Germany.

2.5 Calendering, paper testing, and printing

A Schematic of the supercalender at the PTS Vestra Pilot coater is shown in Figure 4. For the evaluation of the effect of calendering of coated paper with biobased latex binder, all trial rolls were tested and printed with 3 types of surfaces:

- Uncalendered: referred to as “Topcoat”;
- Matte calendered with 1 nip at 300 m/min., 40 °C and 110 N/mm line load: referred to as “Matt”; and
- Glossy calendered with 11 nips at 300 m/min., 95°C and 200 N/mm line load: referred to as “Gloss”.

These pilot supercalender conditions are known to yield about the same gloss as the mill’s calendering conditions.

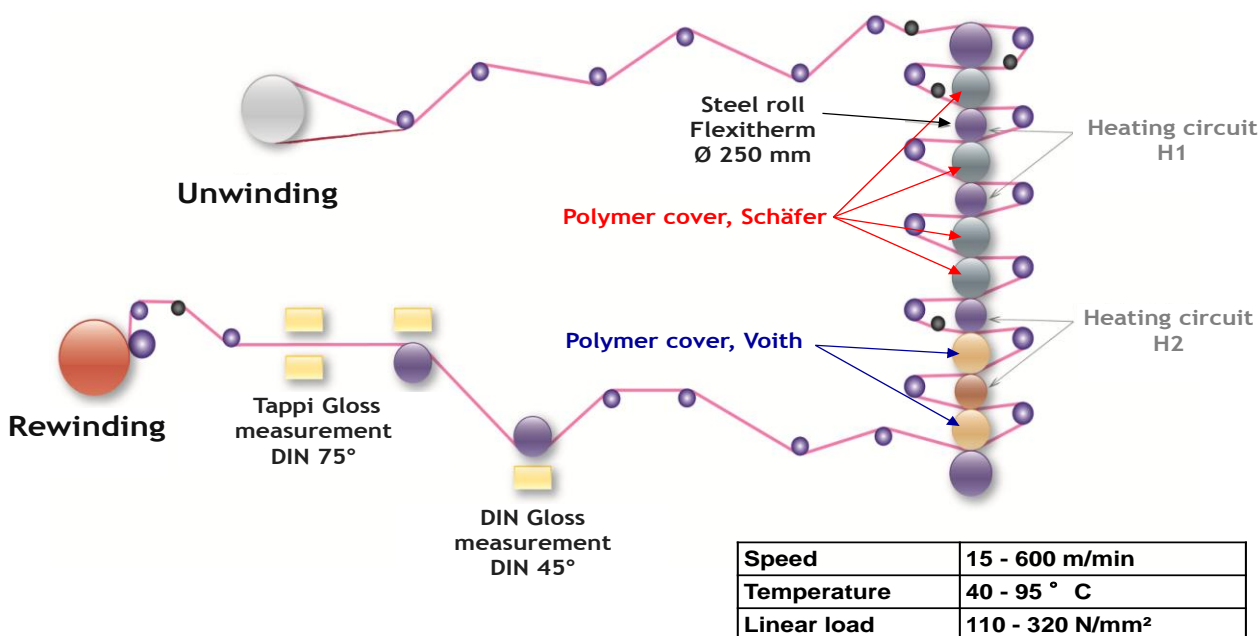


Figure 4. Schematic of the supercalender at the PTS Vestra pilot coater.

Brightness and L, a, b, were measured in D65/10° according ISO2470. Opacity was measured according to ISO 2471. Gloss was measured online on the supercalender according to Tappi 75°/ISO8245/1, and in the lab with Lehmann 75°/ISO8254/1. A Prüfbau multipurpose printability testing instrument and Prüfbau test methods were used with Huber test inks or Flint Novavit X800 Skinnex sheet offset inks for the dry pick, wet pick, and offset tests.

The commercial printing with 5 colors on a Heidelberg printing machine in sheet offset has been established by the mill to provide very reliable printability results.

3. RESULTS AND DISCUSSION

3.1 Runnability and Solids

Based on the mill's coating formulation, the target solids was minimum 65%. The biobased latex allowed in all cases (see Table 1) for a substantial solids increase of 1-3% at a comparable bleeding level relative to V1 and the 65% target. The coating color recipes V2 to V7 were therefore mixed with a goal of achieving 68%. Given the successful elimination of CMC, PVOH and rheology modifier, this points to the superior water retention characteristics of the biobased latex.¹ Note that the biobased latex is plasticized by water in the aqueous coating color formulation, and is therefore soft and deformable which results in excellent runnability even at elevated solids due to its deformability and highly shear-thinning rheological properties.^{7,8} In addition, these coatings even at the same % solids have a reduced immobilization point resulting from the higher effective volume of the biobased latex.^{7,8} Additional results based on runnability in the mill will be reported in the future.

3.2 Brightness

Figure 5 summarizes the brightness results for the 7 pilot coater runs for the 3 different paper grades, referred to as “Topcoat” grade (before calendering), “Matt” grade (after light calendering), and “Gloss” grade (after normal calendering). The papers were all tested (wire side and felt side) both with UV and without UV. As demonstrated in Figure 5, the biobased latex performed almost identically in brightness and the L, a, b color data were also found to be similar to the control XSB binder. It also has OBA (optical brightening agent) carrier functionality, which appears to be sufficient for standard LWC grades. In case of higher OBA content, as in the grade tested, PVOH may be reduced but still might have some advantage. The OBA carrying capacity of the biobased latex comes from its hydroxyl functionalities, shown to stabilize the stilbene trans configuration responsible for the OBA performance.^{1,6,7,9}

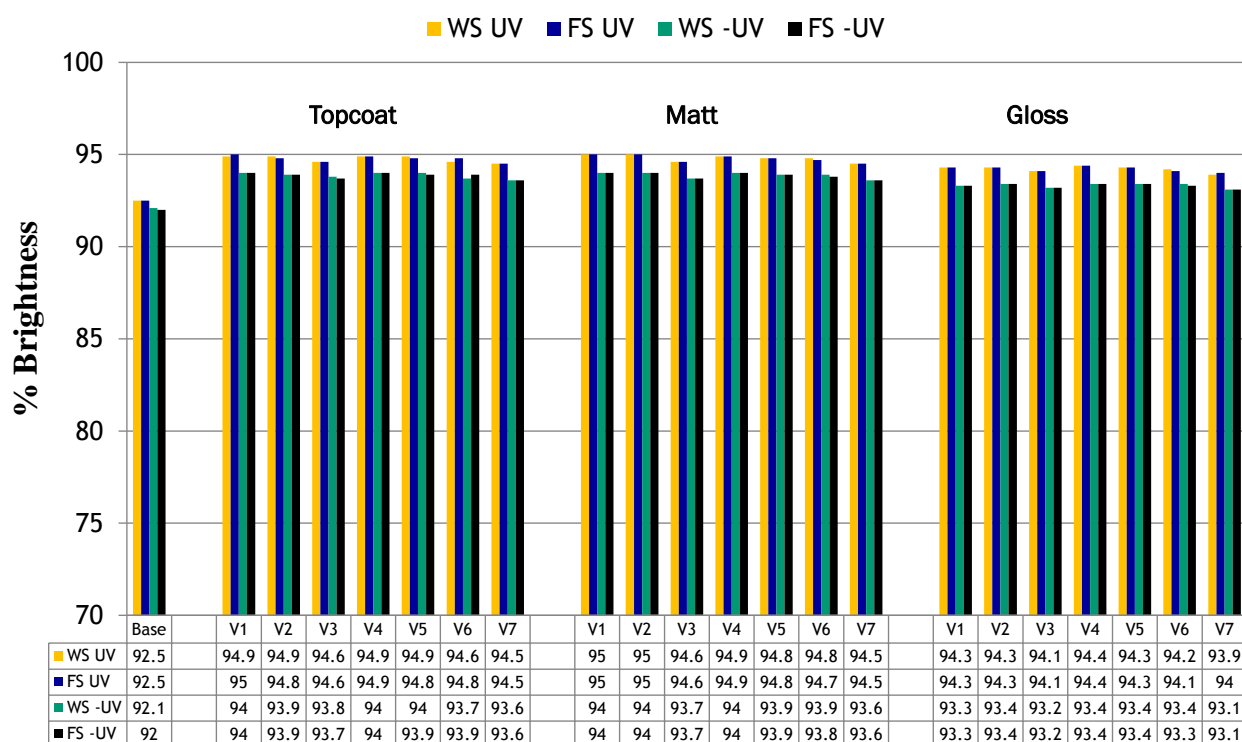


Figure 5. Brightness results for the 7 pilot coater runs for 3 different paper grades, referred to as “Topcoat” grade (before calendering), “Matt” grade (after light calendering), and “Gloss” grade (after normal calendering).

3.3 Paper Stiffness

Starch is known to be a relatively stiff polymer. The biobased latex consists predominantly of starch, plus other minor components consisting of natural and chemical ingredients. Given that the starch in the biobased latex nanoparticles has been internally crosslinked, they are as a result even more rigid. This rigidity imparts stiffness to the coated paper product, as evidenced by the results in Figure 6. Due to the nanocellular void-like internal structure of the biobased latex that forms during drying,^{3,4,6-9} it was demonstrated that higher residual stiffness is achieved when

compared to the reference binder, which in itself was a relatively hard, high-styrene HSWO (heat set web offset) polymer with a glass transition temperature, T_g , of about 23 °C.

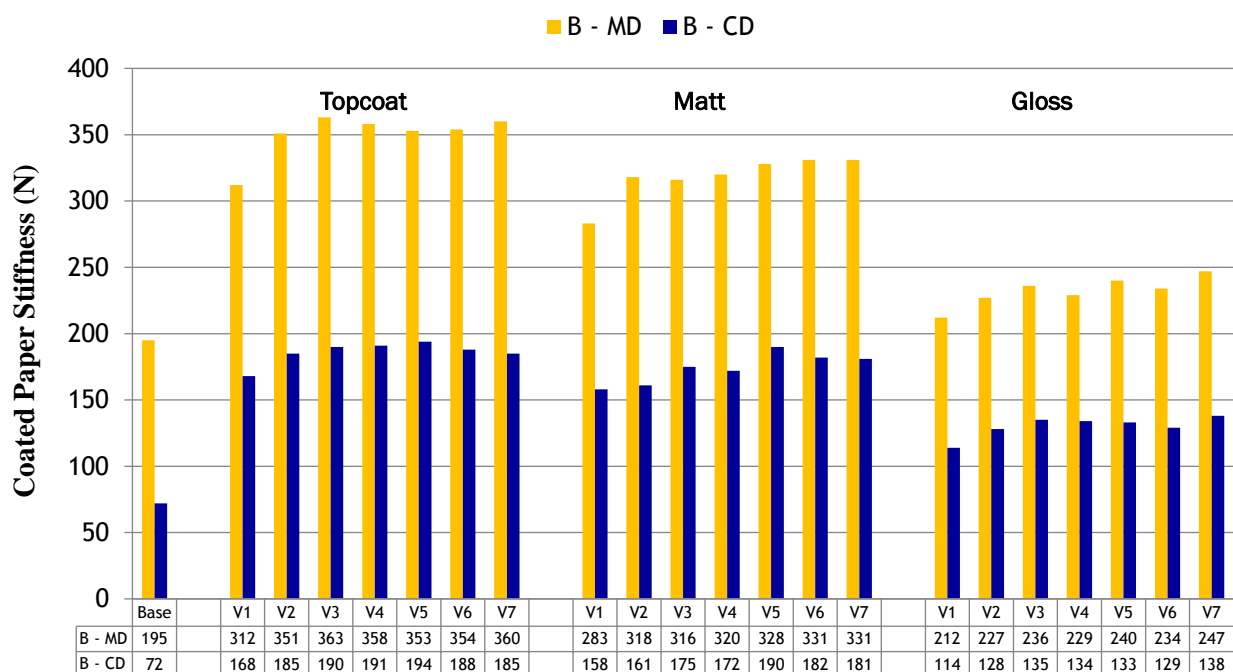


Figure 6. Coated paper stiffness results for the 7 pilot coater runs for 3 different paper grades, referred to as “Topcoat” grade (before calendering), “Matt” grade (after light calendering), and “Gloss” grade (after normal calendering).

3.4 Paper Gloss

The results in Figure 7 and 8 represent what is typically observed in lab and pilot coater results. Note that the non-calendered and lightly calendered papers containing the biobased latex are all equal or higher in gloss than the XSB binder control, which is believed to result from the low film shrinkage of the biobased latex.¹⁻⁹ Paper gloss has been shown to match when up to 70% of XSB and SA latex binders were replaced on a one-for-one basis with biobased latex in a variety of LWC, fine paper and board applications.³⁻⁸ It is well known that all polymers in the recipe have an effect on gloss as well as the solids content during coating. All water soluble co-binders like cooked starch, CMC, and PVOH, but also to some extent rheology modifiers usually reduce paper gloss. It appears that recipes with the biobased latex can reach similar or even higher gloss potential as the standard, as soon as the whole recipe is optimized by using less co-binders. More needs to be done to optimize calendering, but there is the potential for increased gloss as a result of the more open coating structure by increasing paper moisture by about 0.5 – 1%.

Experience from various mills operations emphasizes that the biobased binder benefits from a slightly different total approach to achieve optimal results. Note also that the comparison in Figure 7 & 8 is to that of a relatively stiff, high-styrene (gloss-enhancing) XSB latex. Additional results based on runnability in the mill will be reported in the future in order to confirm this.

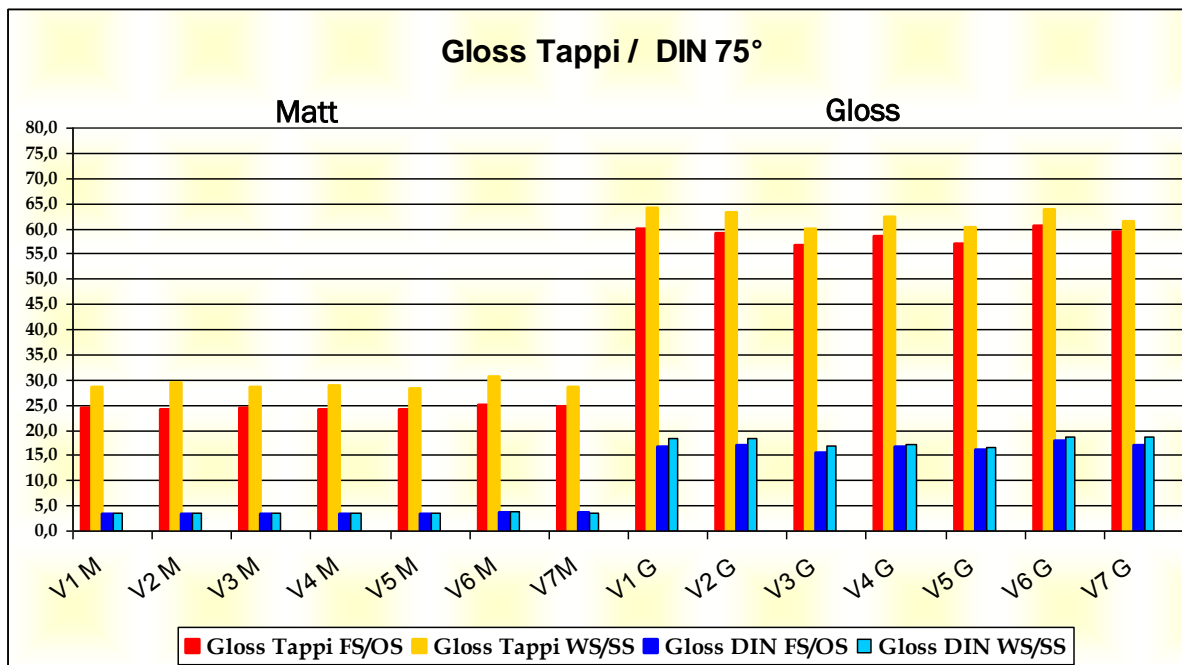


Figure 7. Online gloss measured in supercalender for the 7 pilot coater runs for “Matt” (light calendering) and “Gloss” grades (normal calendering).

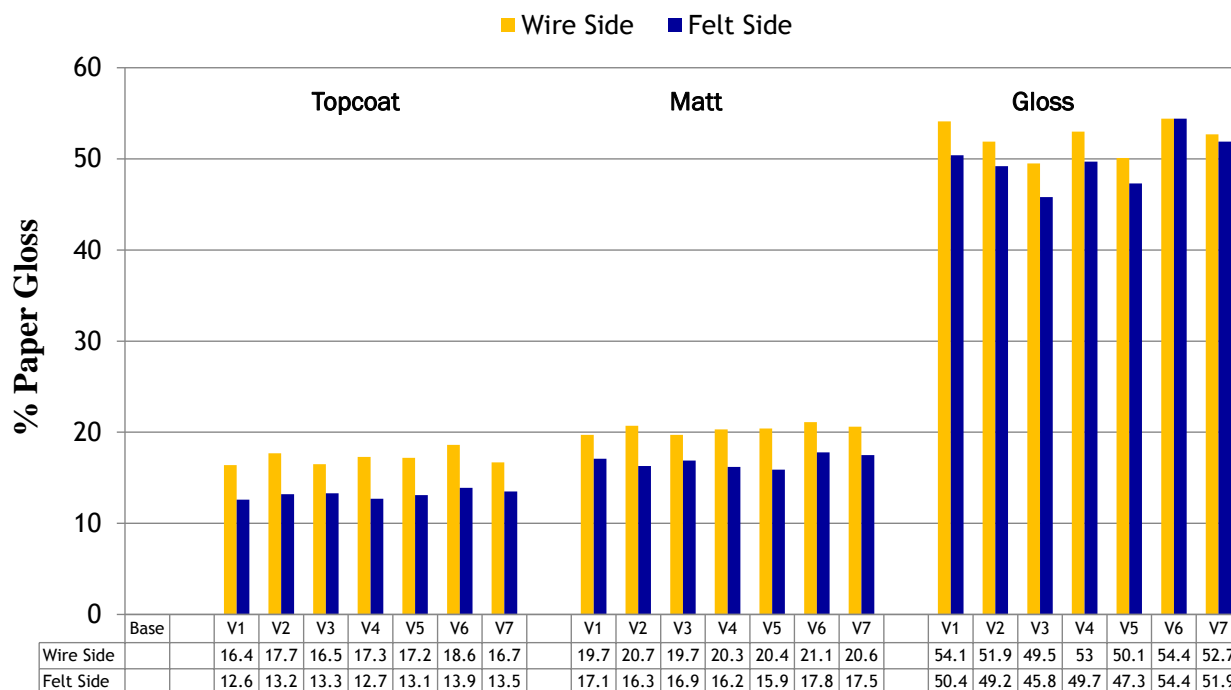


Figure 8. Paper gloss lab testing results for the 7 pilot coater runs for 3 different paper grades, referred to as “Topcoat” grade (before calendering), “Matt” grade (after light calendering), and “Gloss” grade (after normal calendering).

3.5 Opacity

In Figure 9 a general improvement of opacity is observed as the level of biobased latex is increased. This matches what has been reported,^{3,6,8} and widely observed in pilot scale and mill operations, i.e. that biobased latex can contribute to improving opacity from 0 to about 3%, the extent of which depends on the overall coating color composition.

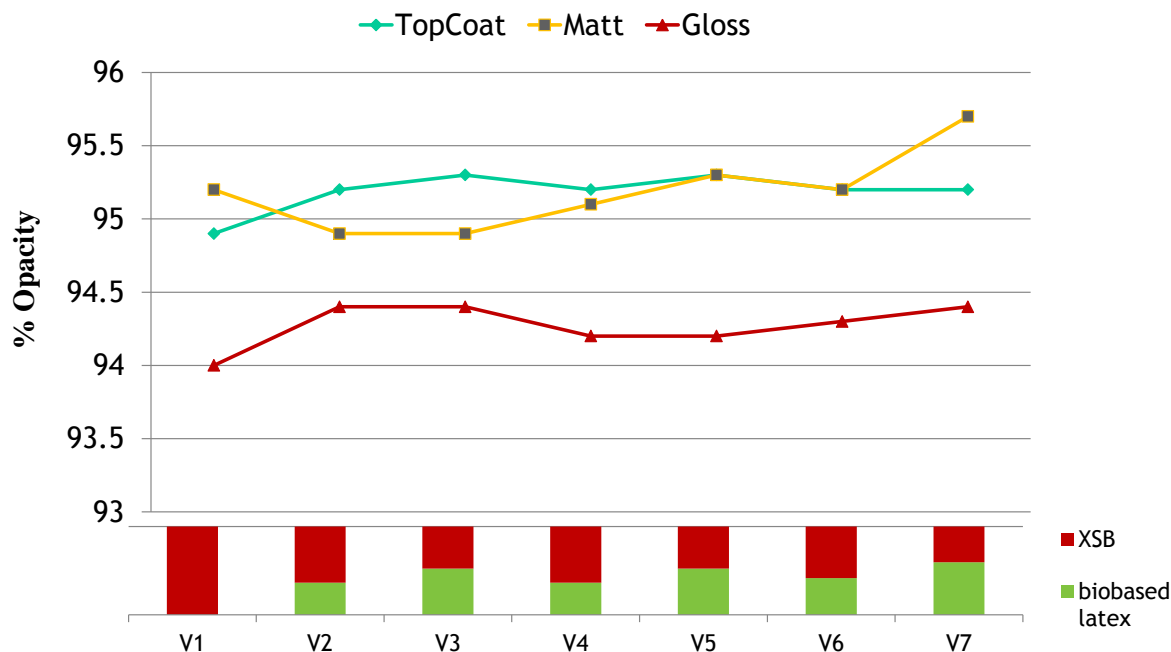


Figure 9. Paper opacity results for the 7 pilot coater runs for 3 different paper grades, referred to as “Topcoat” grade (before calendering), “Matt” grade (after light calendering), and “Gloss” grade (after normal calendering).

3.6 Offset Print Performance

3.6.1 Dry Pick Performance

The first impression of the dry pick results in Figure 10 is a little better surface strength of the uncalendered samples with biobased latex, but a little weaker for the glossy calendered. There is no simple explanation for the different effect in uncalendered and calendered samples. This difference can readily come about from normal variation within the test method and sample inhomogeneity. The good dry pick strength indicates that the mixing of the coating colors was sufficient, which is very critical for optimum quality. A drop in IGT dry pick was sometimes observed during other lab, pilot or even mill trials, when the dry biobased latex agglomerate product had not been fully dispersed into its substituent nanoparticles to form the well-dispersed latex colloid which has high surface area required for high binding strength.^{7,8}

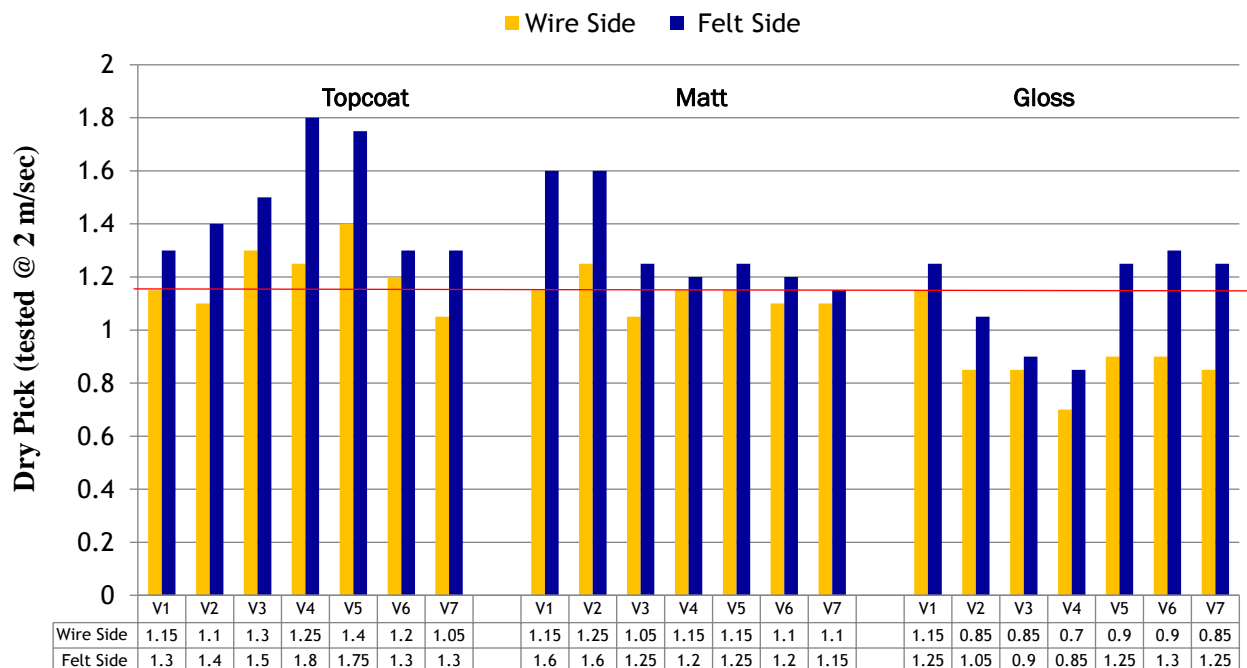


Figure 10. IGT Dry Pick test results for “Topcoat” (before calendering), “Matt” (light calendering) and “Gloss” paper grades (normal calendering).

3.6.2 Wet Pick Performance

Figure 11 demonstrates that the wet pick performance of all trials is sufficient, and that the biobased latex has no significant effect. The addition of the insolubilizer in formulas V4 – V7 didn’t result in a higher wet pick resistance, and there seems to be no need to use or increase an insolubilizer for biobased latex in this application. Note that this is not always the case.

It must be noted that the use of, and value attributed to insolubilizers tends to differ amongst different mills and geographies. Although the print properties for these coated paper grades are generally superior, one common concern with the use of biobased latex binders for paper coating applications especially in North America relates to wet pick performance in lithographic offset printing. Whether this concern is valid has yet to be established, but the excellent print performance that is generally observed would suggest that current wet pick tests may not be totally applicable to this new biobased binder system. Nevertheless, to address any possible concerns, insolubilizers are more commonly used in North America to protect against the potential of wet pick deficiencies in offset printing. As a result, the biobased latex binders typically replace 35% to 50% of XSB or SA latex in North American fine paper applications today.^{3,4,6,7} Glyoxal-type curing agents (i.e. insolubilizers) have been able to overcome wet strength limitations to replace synthetic latexes up to about 40%, matching the Nancy Plowman wet pick performance of the all-synthetic controls.^{3,4,6,7} In certain applications, the use of polymeric insolubilizers has facilitated higher substitution levels.⁷

In Asia, where little value is associated with wet pick performance, levels well above 50% of XSB latex are being substituted with biobased latex binder on a one-for-one basis for fine paper, board and high quality magazine cover applications, without the use of any insolubilizers.⁶

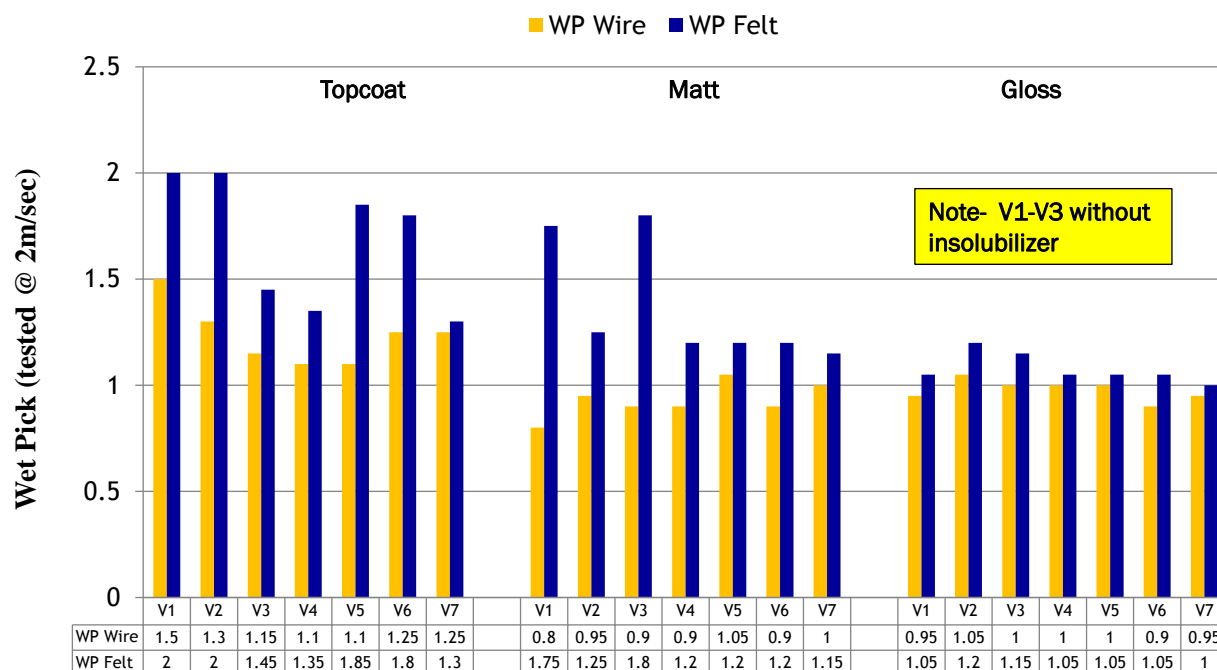


Figure 11. Wet Pick test results for “Topcoat” (before calendering), “Matt” (light calendering) and “Gloss” paper grades (normal calendering).

Nevertheless, simply based on chemical composition, a carbohydrate based binder system is likely to be more water sensitive than a petroleum-based XSB or SA latex system. The use of insolubilizers therefore provides a level of confidence to a coated paper manufacturer that one should not expect offset print performance issues. However, as also shown in Figure 11, a number of examples exist where biobased latex binder is being used at the 35-60% replacement level even without the use of any insolubilizer, and no commercial print problems have been observed. This further suggests that the current wet pick tests may not be directly applicable to the commercial print performance of biobased latex binders in paper coatings, which may be related to an ability of the biobased binder to recover in the relatively short exposure cycles to fountain solutions at high commercial printing speeds.^{7,14} Currently Prüfbau and Nancy Plowman test methods are commonly used in R&D to predict print performance, but their time scales of water exposure are longer than in commercial printing operations. Test procedures such as Taber or Adams wet rub have no predictability for wet pick performance. Therefore, there is a need to develop new test standards that more accurately predict printability for biobased latex binders.

3.6.3 Offset test

The results in Figure 12 demonstrate a slight reduction in the possible offset passes, but the mill’s acceptable pass level of 3 passes-to-fail was achieved in all cases. There may be a link between this results and the more open and therefore more opaque coating layer.

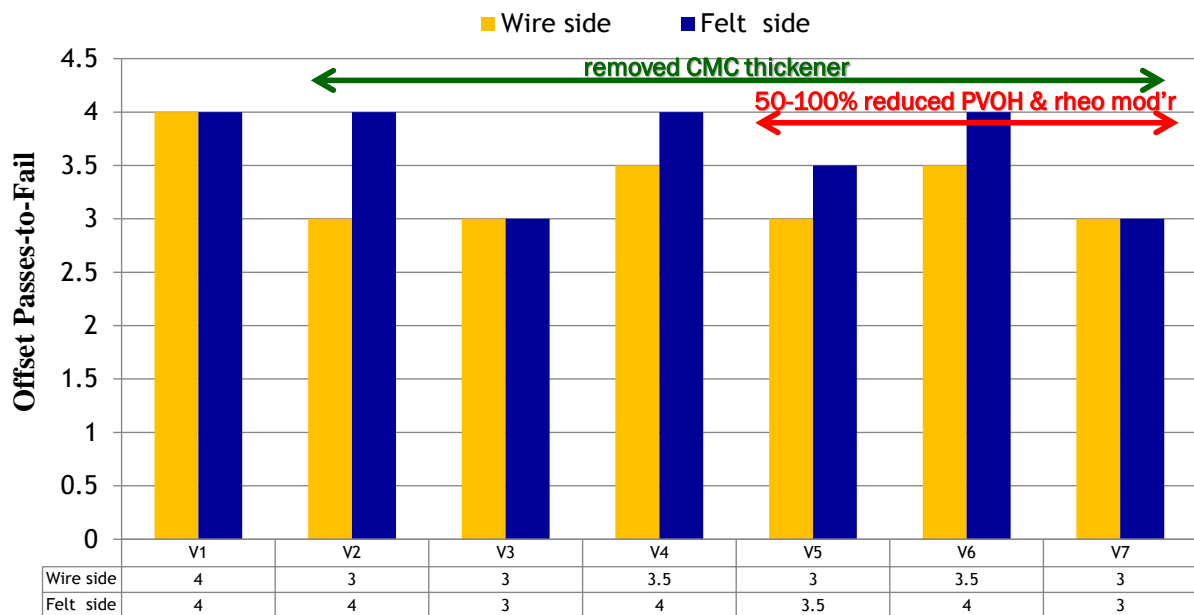


Figure 12. Offset test results for the “Gloss” calendered trial runs.

3.6.4 Print quality

Figure 13 indicates that the print gloss of reference and trial papers is very similar. The coating structure with the biobased latex does not negatively affect how the ink is retained.

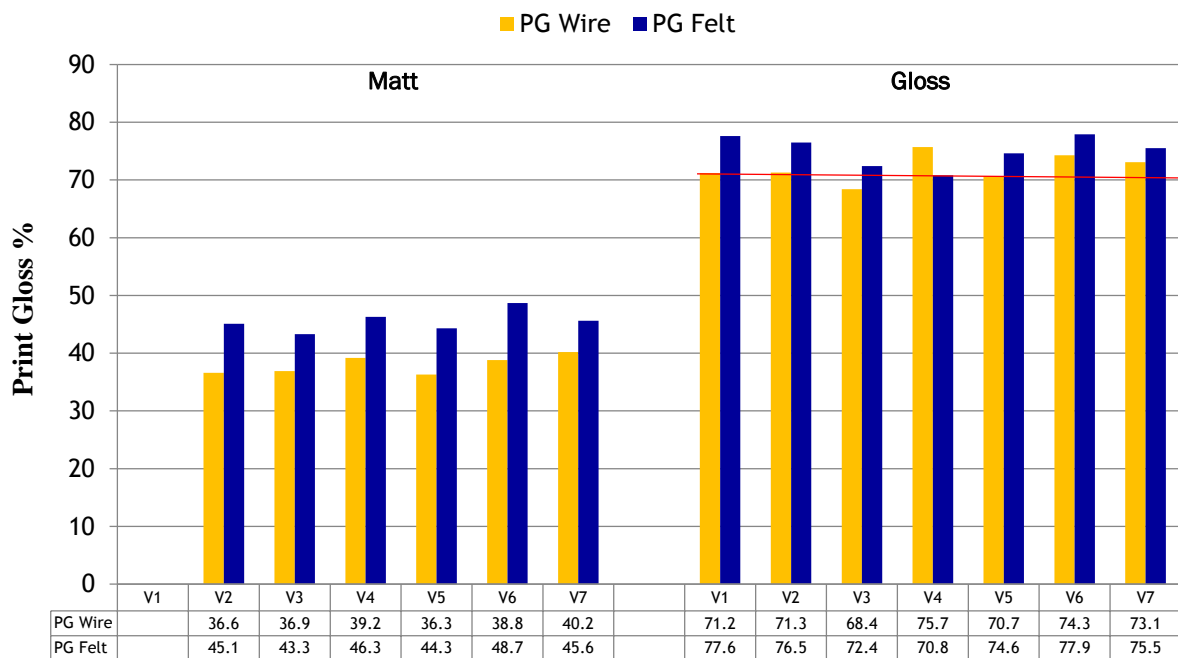


Figure 13. % Lab print gloss test results “Matt” grade (light calendering) and “Gloss” grades (after normal calendering).

The printing trials in sheet offset were run without problems. No significant differences from the different coating formulation recipes were found. Print mottle results were comparable for all the 7 conditions for all three paper grades.

4. CONCLUSIONS

Biobased latex binders consist of a re-engineered starch biopolymer that is unique because its discrete particles are not water soluble, but instead they form a colloid dispersion in water. Learning's regarding coating preparation, runnability and paper performance in LWC coatings produced under state-of-the-art pilot coater conditions are reported here, as well as print performance obtained on a commercial printing press. The excellent runnability, paper and print performance have demonstrated that 30 - 50% of XSB latex plus much or all of the cobinder, rheology modifier and OBA carrier can be replaced with biobased latex to provide similar performance for some properties and superior performance for others. The pilot coater results further point to the need to optimize the whole formulation, and quite likely also the paper moisture. Therefore, this experience emphasizes the need to handle the biobased binder in a slightly different way to achieve optimal results.

Since biobased latex nanoparticles in dispersion exist in the form of water-swollen crosslinked nanoparticles, their effective solids are higher than their actual solids. This increase in effective coating solids enables paper coating colors containing biobased latex binders to get closer to their immobilization solids, and because it is supplied in dry form, it can be used by the mill to further boost solids and as a result to provide for dryer energy savings.

5. ACKNOWLEDGEMENTS

We very much appreciate the contributions made by Mr. Michael Zettel, Development Engineer, Myllykoski Group, MD Papier Albbbruck Mill, Albbbruck, Germany, as well as Mr. Alfred Kramm, Pilot Plant Leader, and Mr. Thomas Koch, Pilot Plant Supervisor, PTS Vestra, Munich, Germany.

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