

Development of New Biobased Emulsion Binders

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ABSTRACT

Biobased emulsion polymers were first adopted by the industry as coating binders in 2008 with the ability to match the performance of synthetic binders with up to 35% replacement. These new binders for paper coating applications have shown to impart unique rheological, coating holdout, coating structure, and optical properties to wet and dry paper coatings, respectively. The mechanisms for these unique behaviors will be discussed based on the fact that these biobased latex binders are made up of deformable, water-swollen crosslinked biopolymer nanoparticles and tend to shrink less upon coating consolidation during drying. Furthermore, recent breakthroughs in technology have allowed us to develop new grades of biobased latex binders with improved binder properties. These new grades address the initial deficiencies of inferior optical properties and certain strength properties, specifically wet pick, that limited their use in certain coated paper and paperboard applications. A new brightness grade made by co-extruding TiO₂ particles in the production of biopolymer nanoparticles has shown that the co-extruded TiO₂ particles are many times more efficient for both brightness and opacity of paper coatings than those TiO₂ particles post-added either into biobased latex binders or coating formulations. The new wet strength grade blended with polymeric curing agents has shown that substitution levels of up to 75% are achievable in basecoat applications and up to 60% in topcoat and single coat paper and paperboard applications. Finally, Life Cycle Inventory Analysis and the reduction in carbon footprint and green house gas emissions that result through the use of biobased latex binders will be discussed.

INTRODUCTION

Biobased latex binders adopted in the paper industry in 2008 were the first use of biopolymer-based microgels and nanogels for large-scale industrial applications [1-7], although they had been explored and used for drug delivery and other bio-medical applications for a long time [8]. Both biobased latex binders and biopolymer-based microgels and nanogels can be broadly defined as a special class of latexes whose particles are made up of water-swollen crosslinked hydrophilic polymers. Since the biobased latex binders currently used in the paper industry are water-swollen crosslinked starch nanoparticles, their wet and dry properties depend mainly on their particle size and crosslink density. The crosslink density of starch molecules forming the

nanoparticles is especially important because it controls the extent of water swelling (swell ratio) [3,4], that is, as the crosslink density increases, the swell ratio of crosslinked starch nanoparticles decreases. Varying swell ratios of the water-swollen starch nanoparticles not only set them apart from conventional starches and synthetic latexes in their rheological behavior, but also differentiate themselves in paper coating performance. Their unique rheological behaviors and paper coating performance will be discussed based on theoretical considerations as well as some laboratory testing, pilot coater and mill trial results.

The current biobased latex binders are manufactured by a continuous reactive extrusion process comprising of solubilizing starch granules, i.e. converting the very high-solids starch paste into a thermoplastic melt phase, and then crosslinking and sizing the solubilized starch molecules into nanoparticles [9,10]. The resulting product from the extruder is nearly dry agglomerates of crosslinked starch nanoparticles which are subsequently pulverized as a final powder product. This process was thought to be a good way to disperse TiO₂ particles uniformly and associate them with starch nanoparticles. This is how we have developed a new brightness grade of biobased latex binders. The performance of this new biobased latex binder grade will be discussed in terms of the brightness and opacity of paper coatings.

The current biobased latex binders are cured by using glyoxal-type curing agents (starch insolubilizers) to improve their wet strength in coated paper and paperboard applications. Although such curing agents have been found to be adequate up to 35% replacement of synthetic latexes for paper coatings, it was thought that polymeric curing agents could be more effective for particulate binders such as our biobased latex binders that consist of crosslinked biopolymer nanoparticles. Preliminary results will be discussed in terms of the substitution levels of synthetic latexes in base and top coatings as well as in single coatings.

THE UNIQUE CHARACTERISTICS AND PROPERTIES OF WATER-SWOLLEN CROSSLINKED BIOBASED LATEX BINDERS: THEIR SWELLING/DE-SWELLING, HIGH-SHEAR RHEOLOGY, HIGHER EFFECTIVE SOLIDS, LESS COATING SHRINKAGE, AND PAPER COATING PERFORMANCE

The De-Swelling of Water-Swollen Crosslinked Biopolymer Nanoparticles as a Function of the Concentration of Dispersions:

Crosslinked biopolymer nanoparticles have very unique wet properties. First, their swelling under conditions of extreme dilution with water achieves the maximum swelling value that is balanced between their elastic constraint due to their crosslinked network and the osmotic pressure [4].

Secondly, they de-swell by addition of water-miscible solvents such as alcohols and many other water-soluble species such as electrolytes. Lastly, they will also de-swell with increasing solids so that their dispersions can be made at higher solids, as shown in Figure 1. This behavior can be understood by the fact that the concentration of starch networks in the particles cannot be lower than the overall dispersion concentration. Therefore, de-swelling will take place when the concentration of the dispersion exceeds that of the starch network in the nanoparticles which is

equal to the reciprocal $1/SR(W)$ of the weight swell ratio, $SR(W)$. For example, if $SR(W)$ is 5, then starch nanoparticles will start de-swelling when the concentration of such a crosslinked starch dispersion approaches or exceeds 20% solids.

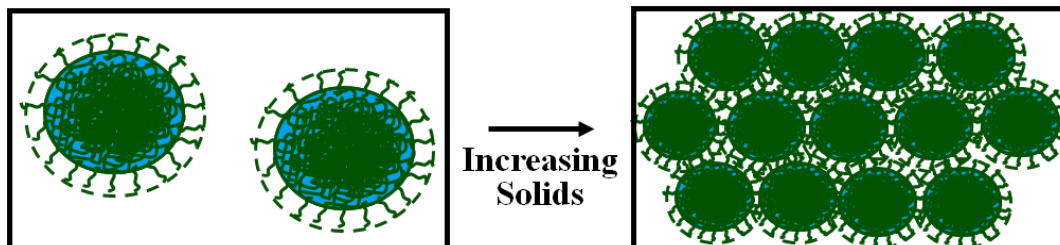


Figure 1. Schematics showing de-swelling of water-swollen crosslinked biopolymer nanoparticles with increasing solids.

Although we have not examined the de-swelling behavior of biobased latex nanoparticles with increasing solids by either transmission or scanning electron microscopy, combined with cryotechniques for quick freezing and freeze-drying to preserve their respective swollen sizes in the dry state, we have been able to elucidate such behavior from their rheological performance as a function of their volume fractions. It is known from the theories on the viscosity of dispersions that the relative viscosity (η_r) of dispersions of spherical particles depends only on their effective volume fraction (ϕ_{eff}) and close packing volume fraction (ϕ_p) and can be theoretically expressed as a function of ϕ_{eff} and ϕ_p [11-14]. Therefore, if we assume that the water-swollen biobased latex nanoparticles are spherical and monodisperse regardless of their volume fractions, then we can obtain their effective volume fractions by matching their relative viscosities with those of uniform hard-sphere dispersions which can be calculated by using theoretical equations such as the Mooney [12] and Dougherty-Krieger equations [13] with the close random packing volume fraction of uniform hard-spheres equal to 0.64 [15]. From the effective volume fractions obtained as a function of the actual volume fraction (i.e., the volume fraction of dispersed solid particles), we should be able to calculate the volume swell ratios as a function of the actual volume fraction, since the ratio of the effective volume fraction to the actual volume fraction is equal to the volume swell ratio, $SR(V)$.

Figure 2 shows the relative viscosities of biobased nanoparticle dispersions and uniform hard-sphere dispersions plotted against the actual volume fraction of dispersed particles. In Figure 2 the relative viscosity of the nanoparticle dispersions was obtained by dividing the experimentally determined viscosity of the dispersion by the viscosity of water at 20 °C, while the relative viscosity of a uniform hard-sphere dispersion was calculated by using the Dougherty-Krieger equation, $\eta_r = (1 - \phi/\phi_p)^{-2.5/\phi_p}$, where ϕ_p is the close random packing fraction of uniform spherical particles and taken to be 0.64. As indicated in Figure 2, at a given relative viscosity the volume fraction (ϕ_H) of the hard-sphere dispersion is equal to the effective volume fraction ($\phi_{B, \text{eff}}$) of the biobased latex dispersion at ϕ_B . Thus, the volume swell ratio $SR(V)$, which is the ratio of the swollen to actual (unswollen) volumes of the biobased latex nanoparticles, can be obtained by dividing the effective volume fraction ($\phi_{B, \text{eff}} = \phi_H$) by the actual volume fraction (ϕ_B).

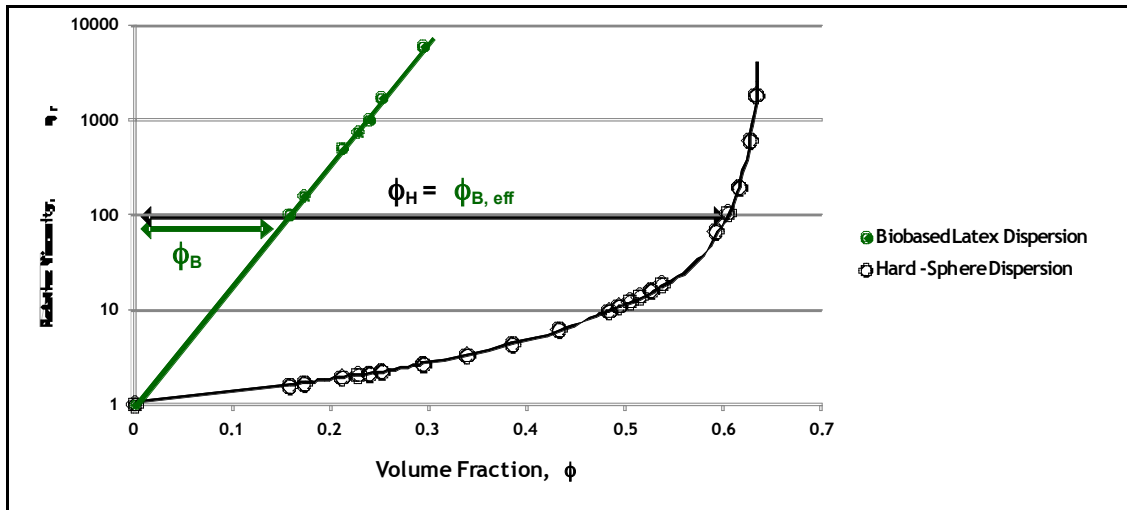


Figure 2. The experimental relative viscosity of a biobased latex compared with the calculated (Dougherty-Krieger Equation) relative viscosity for uniform hard-sphere dispersions as a function of the actual volume fraction of dispersed particles at 20 °C.

The volume swell ratio, V_s/V_o , of biobased latex nanoparticles, which is equal to the ratio of the effective to actual volume fractions, $\phi_{B, \text{eff}}/\phi_B$, at ϕ_B , was calculated by using both curves in Figure 2 as a function of their actual volume fraction, and then was plotted against the actual volume fraction of a biobased latex dispersion in Figure 3. As shown in Figure 3, it is clear that as the volume fraction of biobased latex dispersion increases, the volume swell ratio decreases, as anticipated from theoretical considerations.

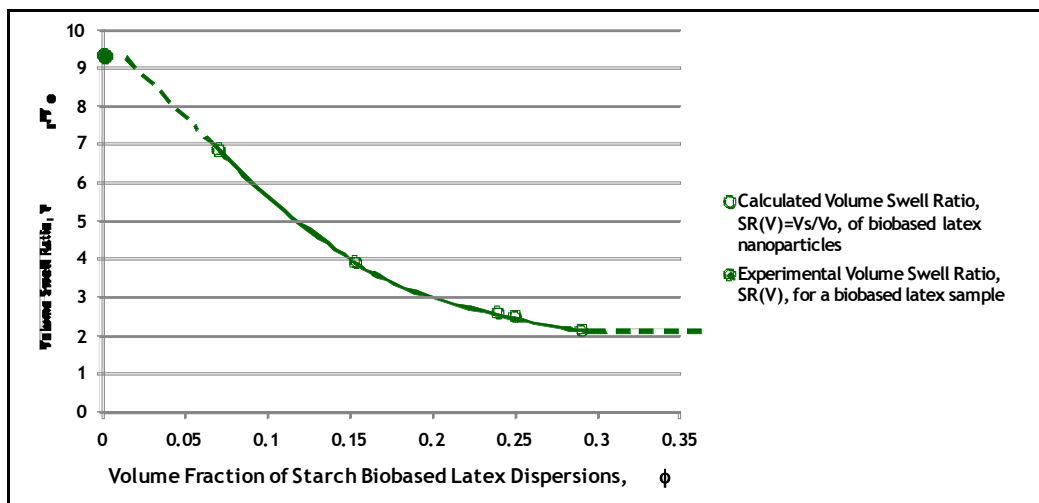


Figure 3. The volume swell ratio, $SR(V)=V_s/V_o$, of biobased latex nanoparticles as a function of volume fraction, where V_o and V_s are the actual (unswollen) and swollen volumes of biobased latex nanoparticles, respectively.

The Deformation of Water-Swollen Crosslinked Biopolymer Nanoparticles under Shear and Pressure:

It is not very difficult to visualize that the water-swollen nanoparticles would deform and deswell under shear and pressure, as shown in Figure 4.

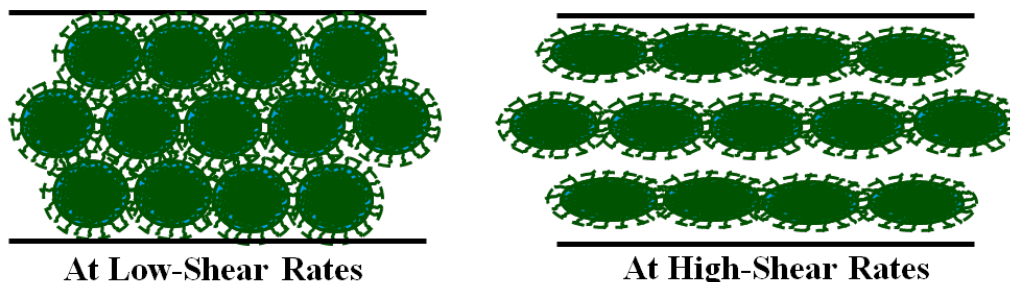


Figure 4A. Schematics showing the deformation of water-swollen crosslinked biopolymer nanoparticles under high shear rates.

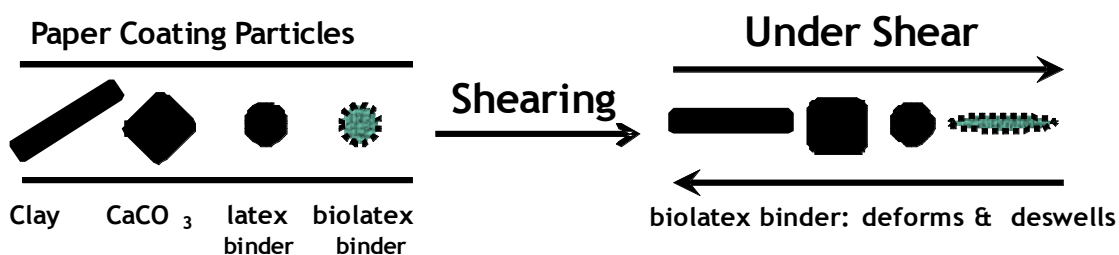


Figure 4B. Schematics showing the deformation under high shear rates of biobased latex in the presence of pigment and latex particles.

This behavior is quite unique because the water-swollen nanoparticles are not only deformable under high shear and pressure, but also de-swell and release water, and then may be able to lubricate jammed solid particles. As a result, it is expected that coating colors containing such biobased latex nanoparticles would be much less dilatant than their counterpart coating colors without such starch nanoparticles. Therefore, they may be considered as unique rheological lubricants.

Although we have not yet systematically studied the effects of starch nanoparticles on apparent slip of paper coating colors [16] and their other rheological properties resulting from the use of coating lubricants [17], numerous pilot coater and mill trials have shown excellent high-speed blade runnability. High-shear measurements with an ACAV capillary viscometer have shown that paper coating colors containing a synthetic latex as the sole binder or with a soluble starch as a co-binder exhibited dilatant behavior to a certain extent, but substituting a portion of the synthetic latex with biobased latex binder tended to moderate the dilatant behavior. This indicates that starch nanoparticles perform better than synthetic latex particles for the rheological properties of paper coating colors, as shown in Figure 5.

Figure 5 illustrates the high-shear capillary viscosities of a series of paper coating formulations as a function of shear rate. It is quite clear from Figure 5 that replacing a portion of the synthetic latex or some of the latex and all of the soluble starch of the control formulation with biobased latex binder has helped to alleviate dilatant behavior of the control formulation. Formulation 1A (Figure 5) showed unusually high interactions between soluble starch molecules and starch based latex nanoparticles and increased its viscosity so that Formulation 1B was modified with a rheology modifier which reduced such interactions.

Although the low-shear viscosity of water-swollen nanoparticle binders is higher than that of their solid particle counterparts such as styrene-butadiene and styrene-acrylic latexes at the same solids, their paper coating formulations are less dilatant at high shear rates, as shown in Figure 5. This result is believed to be attributed to their deformability under high shear. The deformability under high shear and the inherent high water retention performance significantly improve high-speed blade runnability of paper coating formulations containing biobased latex binders. We call this unique attribute “A Self-Lubricating Effect”.

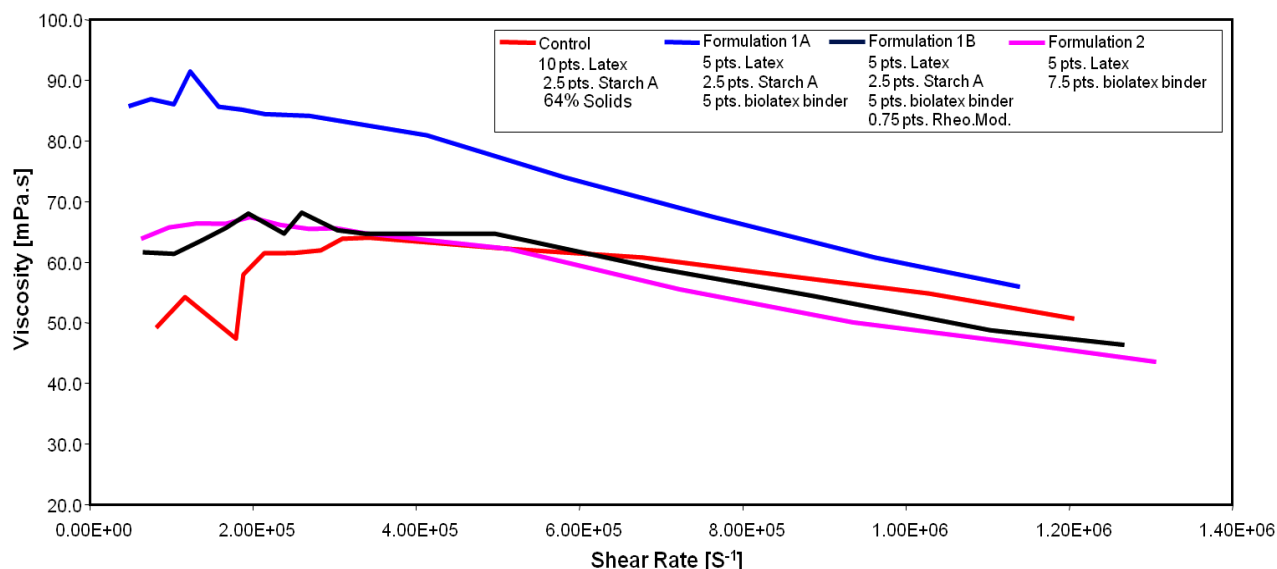


Figure 5. High-shear (ACAV) capillary rheology of a series of paper coating formulations, including a Control containing both synthetic SB latex and soluble starch, Formulations 1A and 1B containing biobased latex binder in place of a portion of the SB latex, and Formulation 2 containing biobased latex binder replacing some of the SB latex and all of the starch.

The Influence of Higher %Effective Solids and Volume Solids of Water-Swollen Biobased Nanoparticles on Coating Immobilization and Coating Holdout:

Since crosslinked hydrophilic nanoparticles in dispersions exist in the form of water-swollen nanoparticles, their effective solids and volume solids will be higher than their actual solids and

volume solids. The higher the swell ratio (SR) of nanoparticles, the higher their effective solids and volume solids.

Figure 6 shows the % effective volume solids as a function of the % actual solids of a biobased latex nanoparticle dispersion with a volume swell ratio, SR(V), of 2.5 as a parameter, along with the % volume solids of a starch solution and a synthetic latex for comparison, where the densities of starch, biobased latex and SB latex were taken to be 1.6 g/cm³ and 1.0 g/cm³, respectively. As can be seen in Figure 6, the water-swelling of biobased latex nanoparticles significantly increases % volume solids over their % actual volume solids as compared to a typical cooked starch solution and synthetic latex.

The following example illustrates the calculations that yielded Figure 6 (for 100 g of dispersion):

%Actual Volume Solids of a soluble cooked starch at 30% solids

$$= (\text{total volume of starch} / \text{total volume of the dispersion}) \times 100\%$$

$$= [(30 \text{ g of starch} / 1.6 \text{ g/cc}) / (30 \text{ g of starch} / 1.6 \text{ g/cc} + 70 \text{ g of water} / 1 \text{ g/cc})] \times 100\%$$

$$= [(18.75 \text{ cc}) / (18.75 \text{ cc} + 70 \text{ cc})] \times 100\% = \mathbf{21.13\%}$$

%Effective Volume Solids of biobased latex binder at 30% solids

$$= (\text{total volume of water-swollen nanoparticles} / \text{total volume of the dispersion}) \times 100\%$$

$$= [(30 \text{ g} / 1.6 \text{ g/cc} \times 2.5) / (30 \text{ g} / 1.6 \text{ g/cc} + 70 \text{ g of water} / 1 \text{ g/cc})] \times 100\%$$

$$= [(18.75 \text{ cc} \times 2.5) / (18.75 \text{ cc} + 70 \text{ cc})] \times 100\%$$

$$= [46.87 / 88.75] \times 100\% = \mathbf{52.82\%}$$

Suppose that a biobased latex binder having a weight swell ratio, SR(W), of 2.0 is used at 5 parts in a paper coating color containing 100 parts pigments and 15 parts binders at 65% solids. Since the effective solids of 5 parts biobased latex binder would be 10 parts at the SR(W) of 2.0, the effective coating solids would become 65x120/115=67.83%, that is 2.83% higher. For a biobased latex binder with an SR(W) of 2.5, the effective coating solids would become 65x122.5/115=69.2%, that is 4.2% higher.

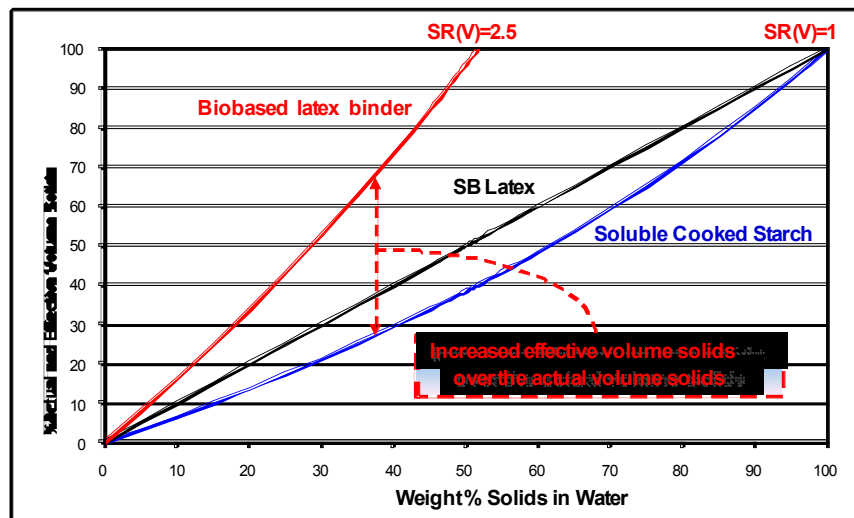


Figure 6. The % effective volume solids of biobased latex nanoparticles, soluble cooked starch, and synthetic SB latex vs. % actual volume solids of starch and latex with the volume swell ratio, SR(V), as a parameter.

This increase in the effective coating solids enables paper coating colors containing biobased latex binders to get close to their immobilization solids [18,19] so that they exhibit excellent coating holdout, resulting in excellent fiber coverage and coating smoothness. This approach to coating holdout is quite different from the previous approaches such as coating structure modifications [20-24], high-solids coating technology [25], etc. Although high-solids coating and high effective coating solids approaches are similar in concept, the latter approach is expected to result in fewer high-speed blade runnability problems due to some of the aforementioned attributes (reduced dilatancy, improved water retention, coating hold-out, fiber coverage, etc.). Moreover, beyond high-solids coating strategies, this new coating holdout technology can be beneficially combined with many existing coating structure modification approaches (20-23) for improving coating holdout and fiber coverage in challenging situations, including applications ranging from light weight coated to high quality fine paper grades to unbleached recycled paperboard.

The Influence of Less Shrinkage of Biobased Latex Binder Containing Paper Coatings on Coating Gloss, Porosity, and Opacity:

One of the most important characteristics of biobased latex binders for paper coatings is that they shrink much less than soluble starches upon coating consolidation during drying. The gloss of biobased latex containing paper coatings on polyester films is equal to or higher than that of synthetic latex containing paper coating controls [26], as shown in Table 1, thus indicating that the coating shrinkage of biobased latex containing paper coatings is equal to or less than that of synthetic latex containing paper coatings. This is unlike that of soluble cooked starch containing paper coatings [27, 28]. It has been postulated that the dry biobased latex nanoparticles within the paper coating would possess a nano-cellular void-like internal structure [4], further supporting a hypothesis that the “virtual density” of the biobased latex binder within the dried paper coating approaches 1.0 g/cm³. The low degree of coating shrinkage and the nano-cellular void-like internal structure of biobased latex binder containing paper coatings are responsible for more open coating structure and better opacity which have been observed by numerous CLC, pilot coater, and mill trials.

Table 1. The gloss of uncalendered formulated paper coatings containing all-SB latex and both SB latex and biobased latex binder on polyester films [26].

Paper Coating Sample	Coat Weight, g/m2	%Gloss at 75°
13.6 Pts. SB Latex Control	37.6	37.6 +/- 0.20
38% Replacement of SB Latex with Biobased latex Binder	38.4	46.1 +/- 2.06

EXPERIMENTAL RESULTS AND DISCUSSION

The Low-Shear Viscosity of Biobased Latex Binder Dispersions:

Dry biobased latex powder produced by a reactive extrusion process can be added directly into pigment slurries and dispersed during coating color preparations. The pigment particles act effectively as grinding vehicles to help break up the dry agglomerate powder (ave. particle size of $\sim 300 \mu\text{m}$) into the individual biopolymer nanoparticles (ave. particle size of $\sim 100 \text{nm}$) in order to form the biobased latex dispersion. If direct addition to the coating formulation is not possible, in the event of low shear or inadequate mixing facilities, the biobased latex powders can also be dispersed into GCC or clay to make a masterbatch concentrate. If neither of these is possible at the mill, the dry agglomerate product can be dispersed directly in water. In all cases, the factors affecting the dispersion of biobased latex powders are common in that any additives and conditions reducing the hydrogen-bonding, such as electrolytes, high pH, high temperature, etc. and increased shear are beneficial.

To illustrate this, dry biobased latex agglomerate powder was dispersed under moderate shear conditions at concentrations up to 60% solids into a GCC slurry (Figure 7) and at high shear conditions in pure form in water up to 40% solids (Figure 8). The low-shear viscosity was measured as a function of % solids and temperature using a Brookfield-type viscometer.

For example, Figure 7 illustrates that if a typical mill runs its coating formulations after make-down at temperatures at or above $30 \text{ }^\circ\text{C}$ ($>85 \text{ }^\circ\text{F}$), it can handle the GCC-biobased latex masterbatch up to 60% solids, provided it can manage pumping viscosities up to about 2200 cps.

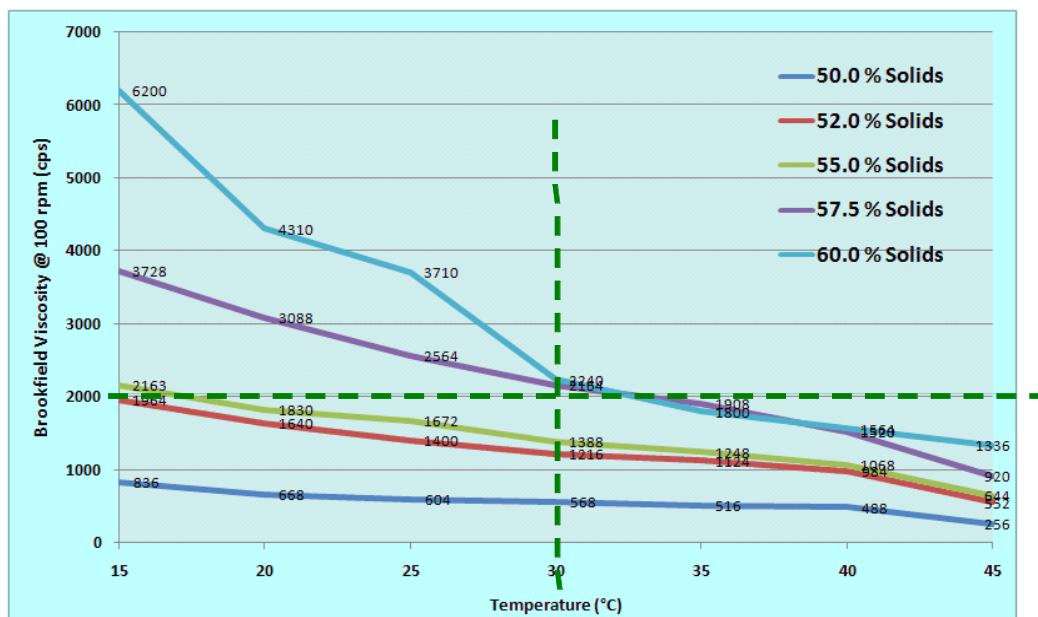


Figure 7. Brookfield viscosity of a GCC-biobased latex masterbatch dispersion (2:1 GCC:biobased latex binder on a dry basis) as a function of % solids at temperatures ranging from 15 to $45 \text{ }^\circ\text{C}$ (59 to $113 \text{ }^\circ\text{F}$).

The biobased latex powder was also dispersed at concentrations up to 35% solids under high shear, and the Brookfield viscosity was measured as a function of % solids at 20 °C and plotted in Figure 8.

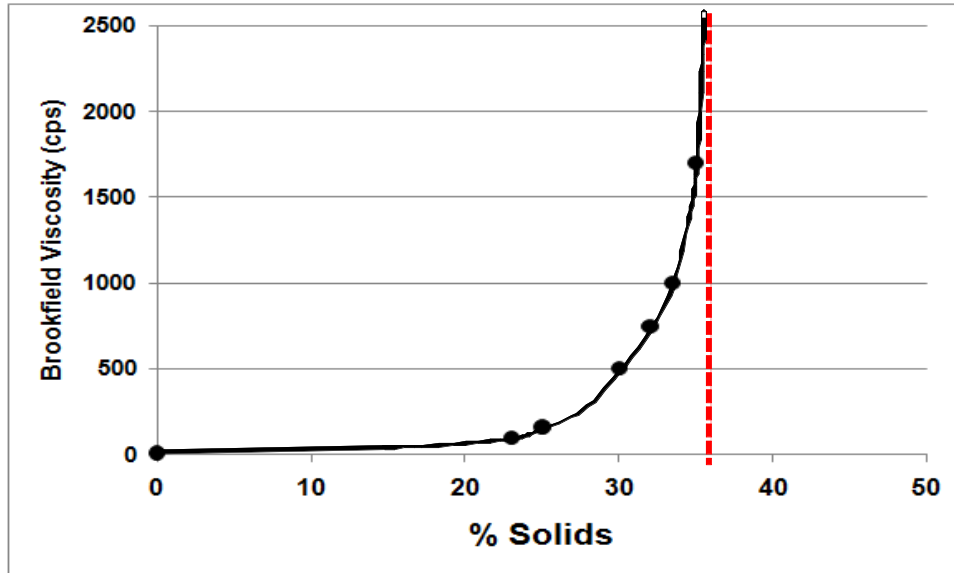


Figure 8. Brookfield viscosity of a biobased latex sample dispersed in water, as a function of % solids at 20 °C.

As shown in Figure 8, the % solids at the point of close packing of a pure dispersion of biobased latex nanoparticles was estimated to be 36%. This is the point at which the water-swollen starch nanoparticles touch each other and show a very high viscosity. Depending on the crosslink density of the biobased latex, the temperature and certain additives, the maximum solids of the pure dispersion ranges from about 35 to 45%. The close random packing of spherical particles is known to be about 64% solids by volume [15]. Using these values, we can calculate the volume swell ratio, SR(V), of nanoparticles of this particular biobased latex dispersion at the close packing, as follows:

The %Volume Solids at Close Packing

$$\begin{aligned}
 &= \left\{ \frac{36\% \text{ solids}}{\rho(\text{starch})} \right\} / \left\{ \frac{36\% \text{ solids}}{\rho(\text{starch})} + V(\text{total H}_2\text{O}) \right\} \times 100\% \\
 &= \left\{ \frac{36\% / 1.6}{(36\% / 1.6) + (100\% - 36\%)} \right\} \times 100\% \\
 &= [22.5 / (22.5 + 64)] \times 100\% = 26.01\% \text{ volume solids}
 \end{aligned}$$

Thus, $SR(V) = 64\% / 26.01\% = 2.46$

$$\begin{aligned}
 SR(W) &= [36\% \text{ solids} + W(\text{H}_2\text{O contained in nanoparticles})] / 36\% \text{ solids} \\
 &= [36 + (22.5 \times 2.46 - 22.5)] / 36 = 1.91
 \end{aligned}$$

Although we have not determined the swell ratios of biobased latex binders in actual paper coating formulations, it is expected that they would be more or less similar to the above-

calculated values. It is important to note that the swell ratios of biobased latex binders can be controlled as needed, since the reactive extrusion process is capable of controlling the crosslink density of the nanoparticles.

By measuring the relative viscosity, η_r , at low concentrations (i.e. low volume fraction) for a latex (a polymer colloid), one can gather relevant information about the viscosity and swelling behavior of that colloid. The viscosity is a simple measurement that is obtained by measuring the flow time for a given distance (between two demarcations of a glass Ubbelohde viscometer) for the polymer colloid (η) and for the dispersion medium (η_0), which is water. Using the Einstein equation, $\eta_r = 1 + 2.5 f \phi$, where f is the effective volume factor, which is equivalent to the volume swell ratio, and ϕ is the volume fraction, one can gain valuable insight on the fundamental difference in colloidal behavior for different polymer latex dispersions.

Table 2. The Effective Volume Factor determined for samples of biobased latex binder with different crosslink densities.

Biobased Latex Sample	Relative Crosslink Density	Effective Volume Factor
1	Low	16.0
2	Medium	9.33
3	High	6.67

Since different methods to determine the swell ratios of water-swollen crosslinked starch nanoparticles yield either volume or weight swell ratios, it will be convenient to use the following relationship between the volume and weight swell ratios:

$$SR(W) = 0.625 \times [SR(V) + 0.6]$$

The Brookfield viscosity of a biobased latex dispersion at 30% solids was measured as a function of temperature and plotted in Figure 9.

From Figure 9, we can find that a viscosity-temperature transition occurs near 30 °C. This viscosity transition temperature agrees well with that of GCC-biobased latex masterbatch dispersions (2:1 GCC:biobased latex binder on a dry basis) shown in Figure 7. Based on these results, it is desirable to disperse biobased latex nanoparticle agglomerates at temperatures above 30 °C.

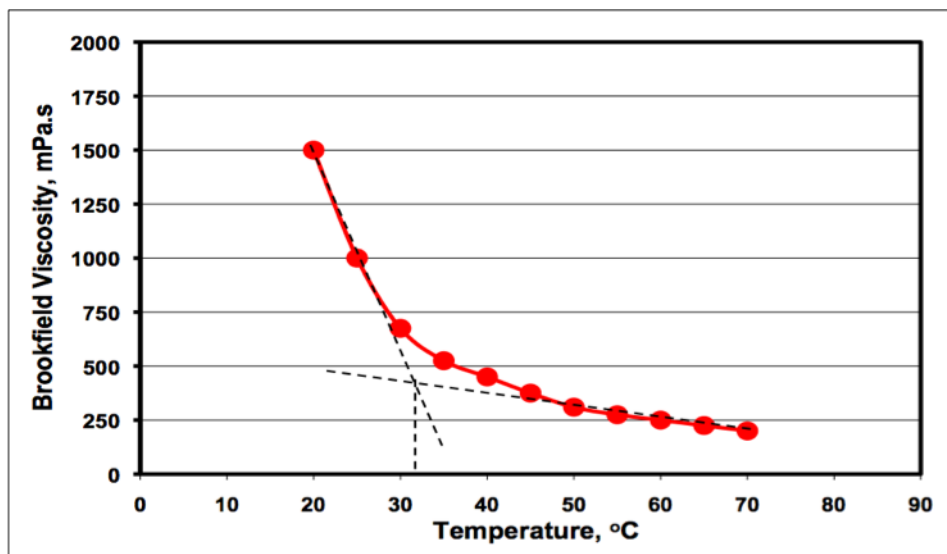


Figure 9. The Brookfield viscosity of a biobased latex dispersion at 30% solids vs. temperature in °C.

The Development of High Brightness Biobased latex Binders Made by Co-Extruding TiO₂ Particles:

Although a preliminary result on paper coatings containing the high brightness biobased latex binders was reported elsewhere [26], we would like to report some of the exciting findings and provide some insight into the efficiency issue of TiO₂ particles in paper and architectural coatings. A CLC coating study was carried out to test whether or not co-extruded TiO₂ particles would be any different from post-added TiO₂ particles.

A series of biobased latex binders co-extruded with 1 part TiO₂ each from two different types (hydrophilic and hydrophobic) as well as 3 parts hydrophilic TiO₂ was evaluated by using the Western Michigan University CLC coater with a coating formulation of 98 parts clay/GCC pigments and 2 parts TiO₂, 8.5 parts SB latex, 5.1 parts biobased latex binder, and 0.25 part PVOH, 0.9 part OBA, and 0.4 part glyoxal curing agent at pH 8.5-9.5 and 63% solids. The average coat weight was 13.5 ± 0.7 lb/ream. The substitution level of SB latex with biobased latex binders was 37.5%. Their % brightness of the coated paper samples was measured with and without UV (see Figure 10). Note that all of the coated paper samples in Figure 10 had similar % gloss (75°, MD: 72% ± 2%; CD: 68% ± 2%).

The most striking finding is that a miniscule amount of additional 0.051 part of TiO₂ co-extruded with biobased latex binders made so much impact on the brightness of paper coatings, whereas the post-added 0.051 part TiO₂ did not do anything, as expected. In addition, the % whiteness showed a similar trend. This finding has clearly demonstrated that the efficiency of TiO₂ particles is highly dependent on their uniform distribution in the final dry coatings, as predicted by the theory [29]. This motivated us to find better ways to distribute the TiO₂ particles uniformly in dry coatings.

Another important finding is that although the biobased latex binder co-extruded with 3 parts TiO_2 showed much higher brightness measured without UV, as expected, it showed lower brightness measured with UV, thus indicating that TiO_2 particles interfered with the OBA activity by absorbing UV light (referred to as “OBA quenching”) in the region where the OBA molecules are most active. This finding indicates that for OBA containing paper coatings the use of anatase TiO_2 particles would be preferred because they are less interfering with OBA than rutile TiO_2 particles.

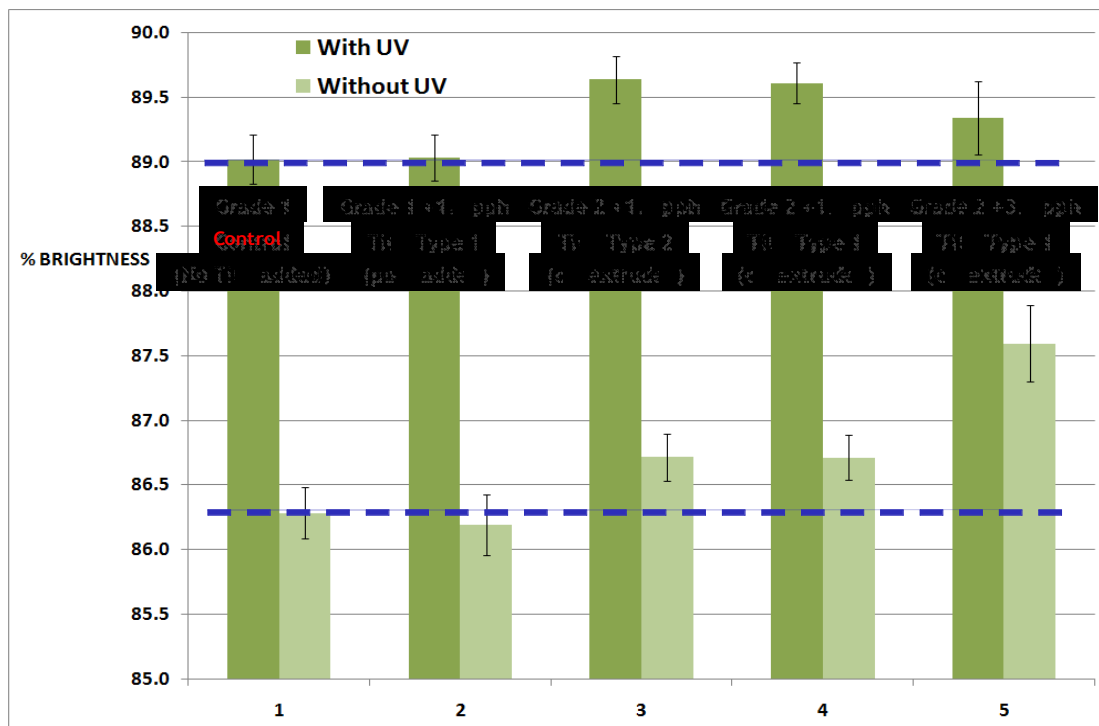


Figure 10. % Brightness of paper coatings containing a series of biobased latex binders co-extruded with 1 part TiO_2 each of two types (Type 1: Hydrophilic and Type 2: Hydrophobic) and 3 parts TiO_2 of Type 1 and two biobased latex binder controls. Measurements were made with and without UV light.

The Development of High Wet-Strength Biobased Latex Binders Cured by Polymeric Curing Agents:

As stated in the abstract and introduction, one shortcoming of biobased latex binders for paper coating applications in terms of lithographic offset printing has been wet pick performance, although glyoxal-type curing agents have been able to improve the wet strength enough to replace synthetic latexes up to about 35%. For this reason, we have attempted to find better curing agents. Since the biobased latex binders are particulate, it was thought that polymeric curing agents would likely form stronger networks even in the wet state.

A series of polymeric carbohydrate-based curing agents (referred to as “Polymeric Insolubilizer” in Table 3) was formulated with two typical grades of biobased latex binder (referred to as

“Biobased Latex, Grade 1 and Grade 2” in Table 3). The preliminary results obtained for CLC coated paper are very promising.

The control coating in Table 3 is an “all synthetic” fine paper coating formulation that does not contain either starch or an insolubilizer. Trial 1 in Table 3 shows that at a 37.5% replacement of the SB latex (replaced on a one-for-one basis), the Nancy Plowman wet pick result is similar to the control and well below 10, which is generally considered an excellent result that would predict good performance for offset printing. Without the addition of the glyoxal-based insolubilizer, the wet pick would be in the range of 15-20. At the 50% replacement level, even with the glyoxal-based insolubilizer, the wet pick test result of 19 indicates there is a probability that one might experience performance issues in commercial offset printing.

By using a polymeric carbohydrate-based insolubilizer, the performance at 50% replacement of the petro-latex is reduced to an acceptable level well below a wet pick of 10.

The use of insolubilizers is a conservative approach that provides a level of confidence to a coated paper manufacturer that one should not expect offset print performance issues. However, it is noteworthy that a number of examples exist where biobased latex binder is being used at the 35-50% replacement level even without the use of any insolubilizer, and no commercial print problems have been observed. This suggests that the current wet pick tests may not be directly applicable to the commercial performance of biobased latex binder in paper coatings, and this may be related to the ability for the biobased latex binder to recover in the relatively short exposure cycles to fountain solutions at the high commercial printing speeds [30].

Table 3. Study of the impact of conventional and polymeric carbohydrate-based insolubilizers on Nancy Plowman wet pick performance.

Formulas are in parts-per-hundred											
SB Latex replacement level with biobased latex :			0.0%	37.5%	50.0%	50.0%	50.0%	50.0%	50.0%	50.0%	62.5%
Material	Comments	Material Solids	Control	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8
Pigment											
Clay		70%	34	34	34	34	34	34	34	34	34
GCC		72%	64	64	64	64	64	64	64	64	64
TiO ₂		72%	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Binder											
SB Latex		50%	13.6	8.5	6.8	6.8	6.8	6.8	6.8	6.8	5.1
PVOH		23%	0.50	0.50	0	0	0	0	0	0	0
Biobased Latex, Grade 1		92%	0	5.1	6.8	6.8	6.8	6.8	6.8	0	8.5
Biobased Latex, Grade 2		92%	0	0	0	0	0	0	0	6.8	0
Additive											
Dispersant		30%	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
OBA		100%	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Thickener		33%	0.13	0	0	0	0	0	0	0	0
Glyoxal insolubilizer	7% b.o. ECOSPHERE	45%	0	0.36	0.48	0	0.48	0	0	0	0.51
Polymeric Insolubilizer 1	5% b.o. ECOSPHERE	10%	0	0	0	0.34	0.34	0	0	0.34	0.43
Polymeric Insolubilizer 2	5% b.o. ECOSPHERE	10%	0	0	0	0	0	0.34	0	0	0
Polymeric Insolubilizer 3	2.3% b.o. ECOSPHERE	10%	0	0	0	0	0	0	0.16	0	0
Defoamer		100%	0.05	0	0	0	0	0	0	0	0
	INK TRANSFER %		90	98	81	96	96	96	97	92	71
	INK REFUSAL %		6	0	0	0	0	0	0	4	0
	WET PICK %		4	2	19	4	4	4	3	3	29

LIFE CYCLE INVENTORY ANALYSIS (LCIA) AND REDUCTION IN CARBON FOOTPRINT THROUGH THE USE OF BIOBASED LATEX BINDERS

The type of carbon used in paper coating binders can be determined using an established methodology using ASTM D-6866 [31]. This test measures the amount of radiometric carbon and therefore the amount of fossil based carbon versus biogenic (crop based) carbon. This test has shown that synthetic binders, such as SB latex, contain 99% fossil carbon since they are produced from monomers that are derived from fossil based resources such as oil and gas [7].

At the end of its useful life cycle, coated paper will be burned, land-filled, composted or recycled. During recycling the coated paper will be separated during the various paper recycling, screening, and flotation deinking steps into reusable fiber and ink, pigment and synthetic binder residues that are disposed of. Eventually this disposed residue will decompose and release CO₂ into the environment [31]. Synthetic binders therefore have a positive carbon footprint which in the case of SB latex is equivalent to 7.4 Kg CO₂ per 1 Kg of SB latex binder. This amount is composed of 3.4 Kg CO₂ per 1 Kg of SB latex from the raw materials or monomers: styrene and butadiene, and 4.0 Kg CO₂ per 1 Kg of SB latex from the production processes involved in taking oil and gas out of the ground and all the way to delivering the finished SB latex polymer to the paper mill. These calculations were carried out by an independent organization called Delphi Institute.

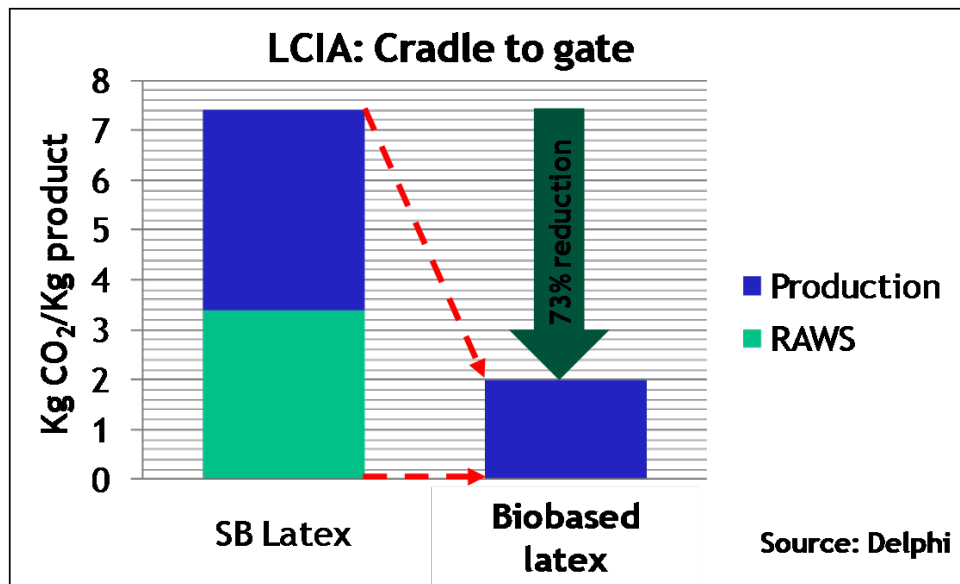


Figure 11. Life Cycle Inventory Analysis (LCIA) and reduction of carbon foot print through the use of biobased latex binders

Biobased latex binders on the other hand are made from renewable raw materials or crops that were grown in a single season by capturing and sequestering CO₂ in the plant via its photosynthesis reaction. At the end of its lifecycle, biobased latex binder will be removed the same way synthetic binders are removed, namely the various paper recycling steps including flotation deinking during the paper recycling process. The difference is that the decomposition of biobased latex binder will only release as much CO₂ as was initially captured by the plant to

grow the biopolymer. The biobased latex binders are therefore carbon footprint neutral from a raw material perspective and have a significantly lower carbon footprint when the production process is considered: 2.0 Kg CO₂ per 1 Kg of biobased latex binder. A cradle-to-gate life cycle inventory analysis comparison between SB latex and biobased latex binder is shown in Figure 11.

The LCIA comparison of SB latex binder to biobased latex binders shows a 73% reduction in carbon footprint on the “Cradle to Gate” basis, as shown in Figure 11. The calculation carried out by Delphi Institute took into account a Life Cycle Inventory Analysis (LCIA) by looking at it on a “Cradle to Gate” approach. In other words, the carbon footprint of synthetic and biobased binders up to the gate of the paper mill. It does not take into account the LCIA involved with making the coated paper, its use by the consumer and its eventual end of life, in other words the “Gate to Cradle” portion. Since biobased binders are delivered substantially dry to the paper mill, they can be used to improve coating solids and therefore reduce drying energy required to make the coated paper.

As can be seen from Figure 11, the use of biobased latex binders has the immediate ability to reduce carbon dioxide emissions by 73%, as compared to the use of a petroleum-based latex, such as SB latex binders.

SUMMARY

The unique characteristics and properties of biobased latex binders for paper coatings were presented: Their swelling and de-swelling, deformability under shear and pressure and self-lubricating effect for high-speed blade runnability, higher effective solids for improved coating holdout, fiber coverage, and coating smoothness, and less shrinkage for high coating gloss (uncalendered), porosity, and opacity. These unique characteristics were found to be attributed to the fact that biobased latex binders are made up of water-swollen crosslinked nanoparticles having varying degrees of water swelling (SR) and tend to shrink less upon coating consolidation during drying.

New high brightness biobased latex binders developed by co-extruding TiO₂ particles showed higher brightness, whiteness, and opacity than those of their counterpart biobased latex binders with the post-added TiO₂ particles. A series of new polymeric curing agents was evaluated for the wet strength of biobased latex binder-containing paper coatings. Preliminary results are very promising.

Finally, a cradle-to-gate life cycle inventory analysis was carried out which demonstrated that the use of biobased latex binders has the immediate ability to reduce carbon dioxide emission by 73% as compared to the use of a petroleum-based latex.

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