The Recent Development of New Pigment Binders

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THE RECENT DEVELOPMENT OF NEW PIGMENT BINDERS

by

Jae Young Shin

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
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Pigment coatings are applied onto paper and paperboard to improve their appearance and printability. For pigmented coatings, pigments and binders are the most important ingredients so their selections are critical.

Pigment binders not only perform the basic required role of binding pigment particles to each other and bonding the base sheet, but also significantly influence the rheology, coater runnability, and drying behaviors of the coating formulation and the optical, viscoelastic, and printing properties of coated paper and paperboard products.

When considering the relative amount of binders to use in a coating, one may speak about main binder, co-binder and sole-binder. By sole-binder it is meant that a single binder alone can perform all the desired functions of the binder in a coating. Usually the binder systems consist of a combination of two binders, in which the main binder is responsible for the binding function.

Conventional starch is inexpensive, but it is rarely used as a sole binder. Instead, it is mostly used as a co-binder. The main reason is coating solid and viscosity. The highest dry solid for cooked starch is about 42%, but conventional latex is 50%. Eventually, conventional starch lowers the dry solid. Viscosity increase with a large portion of starch is too high for paper coatings. However, biobased latex can be used as a dry form and the viscosity is reduced by crosslinking.

As a co-binder, biobased latex was used for offset coating formulations, in which their rheological and water retention properties were investigated. This study provided an interpretation the
unknown basic nature of water-swollen starch nanoparticles and their colloidal behaviors scientifically in comparison with conventional latexes. Especially, serum replacement experiments showed that starch latexes are complex systems of particles and a minor fraction of soluble polymers.

Conventional pigments are inexpensive, but they are rarely used in inkjet coating formulations. Instead, silica is commonly used for ink-jet coatings since it provides a large surface area for quick ink absorption. However, silica grades are excluded in modern hybrid printing presses, because it is rather poorly applicable to printing processes except ink jet, so other lower-cost types of coating are being sought to replace the silica grades.

Calcium carbonate was replaced partially to silica pigment in an effort to balance coating solids, viscosity. At high solids content, a minimum viscosity was observed in mixtures of different sizes particles, so a high solid inkjet coating was feasible. The incorporation of amine functional polyvinyl alcohol with conventional silica pigments for an ink-jet coating were examined. It was determined that the silica pigment binding strength was improved with the addition of cationic copolymers, which are produced by the hydrolysis of copolymers of vinyl acetate monomer (VAM) and cationic monomers, in comparison to the conventional homopolymers, which are produced by the hydrolysis of polyvinyl acetate, due to the chemical coated paper and ink interactions. However, due to flocculation experienced during the make down and handling of these coatings, it is strongly recommended that coatings be formulated with cationically dispersed silica pigment when cationic PVOH is used.

Generally, the structure as well as chemical differences of coating layers determine the final quality of the inkjet printed image.
ACKNOWLEDGMENTS

During a doctoral program, the more I learn, the more curiosity arises as if the volume of a sphere, that is, curiosity, increased exponentially as a function of its linear diameter, that is, the learning.

I would like to thank you all for giving me the opportunity to learn a lot:

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Jae Young Shin
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Jae Y. Shin is the main author of below five papers.


Related Paper Coating Publication by the Same Author

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Particles radius</td>
</tr>
<tr>
<td>D</td>
<td>Capillary diameter</td>
</tr>
<tr>
<td>D_p</td>
<td>Primary particle diameter</td>
</tr>
<tr>
<td>d_{SiO2}</td>
<td>Density of silica</td>
</tr>
<tr>
<td>d_{CaCO3}</td>
<td>Density of calcium carbonate</td>
</tr>
<tr>
<td>f</td>
<td>Effective volume factor</td>
</tr>
<tr>
<td>F_H</td>
<td>Average hydrodynamic compressive or shearing force between two particles</td>
</tr>
<tr>
<td>H_o</td>
<td>Distance between two colliding particles</td>
</tr>
<tr>
<td>K_H</td>
<td>Hydrodynamic shape factor</td>
</tr>
<tr>
<td>MM</td>
<td>Molar mass of solute</td>
</tr>
<tr>
<td>MFFT</td>
<td>Minimum film formation temperature</td>
</tr>
<tr>
<td>M_c</td>
<td>Average molecular weight between crosslinks</td>
</tr>
<tr>
<td>N</td>
<td>Number of particles of diameter, D_p</td>
</tr>
<tr>
<td>R</td>
<td>Capillary radius</td>
</tr>
<tr>
<td>R_i</td>
<td>Bob radius</td>
</tr>
<tr>
<td>R_i</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds numbers</td>
</tr>
<tr>
<td>Re_m</td>
<td>modified Reynolds number</td>
</tr>
<tr>
<td>r_g</td>
<td>Gyration radius</td>
</tr>
<tr>
<td>S</td>
<td>Total surface area of particles</td>
</tr>
<tr>
<td>S_p</td>
<td>Particle surface area of diameter, D_p</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>V_p</td>
<td>Pore volume per unit mass</td>
</tr>
<tr>
<td>X_0</td>
<td>Annular gap</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Surface tension</td>
</tr>
<tr>
<td>( \dot{\gamma} )</td>
<td>Shear rate</td>
</tr>
</tbody>
</table>
ΔE        Color Difference
ΔSr       Difference in shear rates
ηr        Relative viscosity
η          Viscosity of the polymer solution
ηo        Medium viscosity (Viscosity of the pure solvent)
ηa        Apparent viscosity
ηd        Dynamic viscosity
θ          Contact angle
Π          Osmotic pressure
ρ          Density of fluid
Φ          Volume fraction
ΦE         Effective volume fraction
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CHAPTER 1. INTRODUCTION

1.1 Natural Binder (Biobased Latex)

Starch-based biopolymer nanoparticle dispersions, which will be sometimes called starch nanoparticle latexes or simply biobased latexes in this study, were developed in the early 2000’s for industrial applications by two patented processes: Continuous Reactive Extrusion Process [1] and Inverse Emulsion Process [2]. The current starch latexes are manufactured by a continuous reactive extrusion process comprising 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 [1]. The resulting product from the extruder is nearly dry agglomerates of crosslinked starch nanoparticles, which are subsequently pulverized into a final powder product. These pulverized agglomerates are either dispersed in water to form stable starch nanoparticle dispersions or mixed with coating pigment slurries during paper coating make-up for their uses as paper coating binders. The chemical structure of the two polysaccharide polymers contained in most starch varieties are illustrated in Figure 1.
Figure 1. Illustration of the structure of starch polysaccharide polymers: the linear polymer chain structure and the branched amylopectin chain structure [3].

An intermolecular crosslink structure of starch polysaccharide polymers in biobased latex nanoparticles is illustrated in Figure 2.

Figure 2. Illustration of one type of intermolecular crosslink structure of starch polysaccharide polymers in biobased latex nanoparticles, with —R— representing the intermolecular crosslink; note that other types of crosslinked structures exist [3].
While intramolecular crosslinks (i.e. crosslink within the same starch polymer chain) also occur, it is the intermolecular crosslinks (i.e. crosslink between two different starch polymer chains) that are critical to the morphology of the nanoparticles [3].

Although the exact submicroscopic structure is not known at this point, based upon the chemistry in Figures 1 & 2, combined with our understanding of the twin-screw extrusion manufacturing process, a biobased latex nanoparticle can be thought of as one crosslinked macromolecular unit, as is illustrated in Figure 3.

![Figure 3](image)

*Figure 3. Illustration of the hypothesis that a biobased latex nanoparticle can be thought of as one crosslinked macromolecular unit, $r_g$ is the radius of gyration which is randomly coiled linear polymer molecule; note that other types of crosslinked structures exist [4].*

Given the above hypothesis, some further discussion on the crosslink structure of starch nanoparticles may provide added insight into the unique features of these colloids.

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 [5, 6].

By measuring the relative viscosity, $\eta_r$, 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 relative viscosity ($\eta_r = \eta/\eta_o$) of a starch latex binder is obtained by simply measuring the flow times between two demarcations of a glass Ubbelohde viscometer for the starch nanoparticle dispersion ($\eta$) and for its dispersion medium ($\eta_o$), which is water. Using the Einstein equation [7] with a simple modification, $\eta_r = 1 + 2.5 f \Phi$, where $f$ is the effective volume factor and $\Phi$ is the volume fraction, one can obtain the effective volume factor ($f$) that is equal to the maximum volume swelling of starch nanoparticles with their protective shells at very low concentrations, as shown in Figure 4.

![Graph showing the modified Einstein equation](image)

**Figure 4. The relative viscosity of a starch-based nanoparticle dispersion as a function of the volume fraction of dry starch nanoparticles [5].**

It is not very difficult to visualize that the water-swollen nanoparticles would deform and de-swell under shear and pressure, as shown in Figures 5.
Figure 5. Schematics showing the deformation of water-swollen crosslinked biopolymer nanoparticles under high shear rates.

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 [8], and then may be able to lubricate jammed solid particles. As a result, it is expected that coating colors containing starch nanoparticles would be more shear-thinning than their counterpart coating colors without such nanoparticles [8]. Therefore, they may be considered as unique rheological lubricants.

Since crosslinked hydrophilic nanoparticles in dispersions exist in the form of water-swollen nanoparticles, their effective solids and solids volume will be higher than their actual solids and solids volume. The higher the swell ratio (SR) of nanoparticles, the higher their effective solids and solids volume.
Figure 6. The % effective solids volume of biobased latex nanoparticles, soluble cooked starch, and synthetic SB latex vs. % actual solids volume of starch and latex with the volume swell ratio, SR(V), as a parameter [6].

Figure 6 shows the % effective solids volume as a function of the % actual solids of a starch nanoparticle dispersion with a volume swell ratio, SR(V), of 2.5 as a parameter, along with the % solids volume of a starch solution and a synthetic latex for comparison, where the densities of starch, starch nanoparticle 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 starch nanoparticles significantly increases the % solids volume over their % actual solids volume as compared to a typical cooked starch solution and synthetic latex.

This increase in the effective coating solids enables paper coating colors containing starch latex binders to get close to their immobilization solids [9,10], so that they can 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 [11-12], high-solids coating technology [13], etc. Although high-solids coatings 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 [11] for improving coating holdout and fiber coverage in challenging situations, including applications ranging from lightweight coated to high quality fine paper grades to unbleached recycled paperboard.

### 1.2 Synthetic Binder (Polyvinyl Alcohol)

Polyvinyl alcohol (PVOH) is the binder of choice for pigmented ink-jet papers due to its excellent binding strength, affinity for water, and ability to boost optical brightener performance in high brightness ink-jet papers [14].

PVOH is made from polyvinyl acetate (PVAc). The pendant acetate groups of PVAc are simply replaced by hydroxyl groups (-OH), usually employing a process of alcoholysis, which though not strictly correct, is usually spoken of as hydrolysis. Hydrolysis is a chemical process in which a molecule of water is added to a substance. Sometimes this addition causes both substance and water molecule to split into two parts. In such reactions, one fragment of the target molecule (or parent molecule) gains a hydrogen ion. A description of its manufacture is provided by Lindeman [15]. Figure 7 provides a schematic of the chemical entities involved in the polymerization and alcoholysis [16].
It is manufactured by first producing polyvinyl acetate from vinyl acetate monomer (VAM) via a free radical polymerization. The polyvinyl acetate is in turn hydrolyzed to PVOH via a base-catalyzed saponification reaction.

The molecular weight of PVOH is controlled through the polymerization step and generally is expressed in terms of a 4% solution viscosity. The viscosities are classified as ultra-low, low, medium, and high. The molecular weight of PVOH primarily controls the binding power for pigment adhesion and determines coating rheology [15].

The degree to which the polyvinyl acetate is converted to polyvinyl alcohol is referred to as the percent hydrolysis and is controlled during the saponification reactions. The percent hydrolysis is commonly denoted as super (99.3%+ conversion of vinyl acetate to vinyl alcohol), fully (98.0–98.8%), intermediate (95.5–97.5%), and partially (87.0–89.0%) hydrolyzed [15, 17].

When PVOH solutions are combined with pigment slips, under certain conditions an interaction of the PVOH and pigment can occur. The interaction may be evidenced by a simple viscosity build-up, which then dissipates, or it may involve the actual formation of small, filterable agglomerates [17].
PVOH solutions interact with clay particles in the coating formulations via hydrogen bonding between alcohol groups (-OH) on PVOH and silanol groups (Si–OH) on clay particle faces [18]. Because of these interactions, the viscosity of coating formulations containing clays and PVOH solutions is higher than that of those coating formulations containing non-interacting latexes, such as carboxylated latexes. Such pigment-binder interacting coating formulations result in more open coatings.

The mechanism of web offset blisters was studied in the 1970s. The blister occurs when water vapor in the base paper fails to escape through channels or pores in the coating structure during the drying process [19]. This problem can be resolved by increasing the air flow permeability, which reduces the occurrence of blisters [20]. Polyvinyl acetate (PVAc) latexes, due to their higher $T_g$ in comparison to other latex binders, are more blister resistant than either styrene-butadiene (SB) or styrene-butyl acrylate (SA) latexes and have become particularly strong in web offset due to porosity advantages. The high porosity advantage is the reason that large quantities of PVAc binders are used in the United States to coat folding boxboard, in spite of disadvantages, such as low binding power and poor printability [21].

One of the most common uses of all types of coated paperboard is for folding cartons. Although excellent printability is important for this application, it is even more critical glueability. The board must be able to maintain its structure and, in many cases, give evidence of tampering. The industry defines good glueability as achieving fiber tear. Good glueability is defined as obtaining fiber tear in the area where the glue has been applied (Figure 8).
Figure 8. The schematic of glue testing, LHS (40% tearing, poor) RHS (100% tearing, good) [22]: The glue is applied to the coated surface and the backside of the sample is brought into contact with the glue layer.

Although the board may eventually reach a point where there is fiber tear in the glue applied area, a mill is interested in seeing the glueability quickly. In order to achieve the fast glue setting, the glue must be sufficiently dewatered. This dewatering occurs through the movement of the water in the glue into the paper coating. PVAc binders are known for better glueability than styrene polymers [21].
CHAPTER 2. PROBLEM STATEMENT

2.1 Biobased Latex

Much working knowledge on the basic properties of water-swollen starch nanoparticles and the rheological properties of starch latexes (i.e., water-swollen nanoparticle dispersions) and starch latex-containing paper coating formulations has been obtained. However, it is not only highly desirable and timely, but also imperative to make more fundamental studies on the basic characteristics of water-swollen starch nanoparticles. These include investigation of starch molecular structure and weights, crosslinking density, particle size, etc. as well as process variables. It is also important to investigate their responses with respect to environmental changes, such as concentration changes, various additives (e.g., electrolytes, water-miscible organic solvents, water-soluble polymeric additives, pH, etc.), and processing conditions (e.g., shear rates, shear stress, temperature, etc.), and then elucidate their unique rheological properties of starch nanoparticle dispersions and their coating formulations.

Therefore, the objectives of this proposed research project are to examine the unknown basic nature of water-swollen starch nanoparticles, their rheological behavior and water retention properties scientifically.

The following experimental methods are proposed to be able to experimentally investigate these basic properties:
2.1.1 The characterization of biobased nanoparticle dispersions

2.1.1.1 The determination of %free soluble and adsorbed soluble starch molecules contained in starch nanoparticle dispersions:

A. A serum phase replacement apparatus can be used to remove both free and adsorbed solubles from starch nanoparticle dispersions.

B. The results obtained from the serum replacement experiment may provide information on the amounts of the adsorbed starch molecules.

2.1.1.2 The measurements of the water-swelling values (Swell Ratio=SR) of starch nanoparticles as a function of %solids (volume fractions) and crosslinking density:

A. Total water swelling in the presence of free soluble starch molecules: Disperse starch nanoparticle agglomerates in the reference medium (e.g., aqueous at pH 8-9), establish the relative viscosity as a function of volume fractions, and then calculate the effective volume factors by using the Einstein Dispersion Viscosity Equation [5]. These effective volume factors are equivalent to the total water swelling of starch nanoparticles surrounded by adsorbed starch molecules in the presence of free soluble starch molecules.

B. The water-swelling in the absence of both free and adsorbed starch molecules: Determine the swell ratios of starch nanoparticles whose original serums have been previously replaced by using a serum replacement apparatus.
2.1.2 The deformability of water-swollen starch nanoparticles under shear stresses and the rheology of starch nanoparticle dispersions and their paper coating formulations to be evaluated:

A. Quantitative measurements of the deformation of water-swollen starch nanoparticles having different crosslinking densities as a function of shear stresses at different concentrations are the most critical properties of water-swollen starch nanoparticles to understand the unique rheological behavior of starch nanoparticle dispersions and their paper coating formulations. All types of rheometers such as AR 2000 rheometer and viscometers, including Brookfield, Hercules Hi-Shear, and High-Shear Capillary (ACAV) viscometers, will be used to quantitatively assess the critical shear stresses at the inception of the de-swelling of water-swollen starch nanoparticles having different crosslinking densities at different volume fractions. Also, the rheology of starch nanoparticle dispersions and their paper coating formulations will be evaluated as a function of %solids and shear rates with the synthetic latex-to-starch latex ratio as a parameter by using Brookfield, Hercules Hi-Shear, and High-Shear Capillary ACAV viscometers. Macroscopic measurements using rheometer and viscometers limited to elucidate microscopic information, but currently this method is the best way to examine the deformation in the range of the given shear rates.

B. The above-mentioned measurements are expected to verify the theoretical basis for the rheological behaviors of both starch nanoparticle dispersions and their paper coating formulations.
2.1.3 The measurements of the water-retention values of starch nanoparticle dispersions and their paper coating formulations will be measured.

A. The static and dynamic water-retention values of starch nanoparticle dispersions and their paper coating formulations can be obtained by using Abo Akademi-type Gravimetric Water Retention Analyzer and Universal Dynamic Spectrometer Paar Physica UDS 200.

2.1.4 The evaluation of the high-speed blade runnability of starch latex-containing paper coating formulations on a CLC.

2.2 Polyvinyl Alcohol

Until recently, nearly all inkjet coated paper contained amorphous silica pigments in order to provide the high capacity for ink liquids that is required. In general, silica has a high internal porosity (providing a large volume for liquid uptake) and a large surface area (in the range of 50 to 1000 m$^2$/g, available for ink adhesion) [23]. Silica gel and precipitated silica are predominantly used in coated matte finish paper; and fumed silica and colloidal silica are predominantly used in coated gloss finish paper [24].

While silica is effective once it is on the paper, silica pigments pose a production problem, because they must be coated at relatively slow speeds [25]. The coating solids level is a major limiting factor when silica pigment is used, due to the viscosity and water absorption problems involved. Silica slurries alone do not flow very well at solids levels above 15% to 20%. Another drawback of the silica pigments is their high price. As alternatives to silica, the major pigment suppliers have developed specialty engineered pigments. The specialty modified pigments designed to replace silica are; clays [26], calcium carbonates [27], and precipitated calcium carbonates [28]. The modified clays along comparison to silica were run on the CLC at a speed of 2600 ft./ min. [26].
Conventional pigments are inexpensive, yet they are rarely used for inkjet coating due to their limited surface area. However, high solid coating and viscosity drop are feasible by replacing a certain amount of silica with conventional pigments. For the better inkjet applications, inkjet coatings containing inexpensive pigments will be examined in aspect of pigment solutions.

In coating containing silica, typical binders, such as SBR latex or starch, are too weak in their binding strength, which creates dusting problems. However, PVOH has been found to be the most efficient binder [14]. Alternative binders have been introduced such as cationic starches [29] and specialty PVOH [30].

Optical brightening agents (OBA) and dye fixatives are known common additives in inkjet coatings: OBAs help to boost the brightness of the coating; dye fixatives, such as poly-DADMAC, ethyleneimine or polyvinylamine, help to attach the anionic dyes or pigments in the ink to the coating surface [29]. The cationic nature of the coating or pigmented surface of an inkjet paper provides charge neutralization between surface and anionic dyes. This gives the paper water-fastness properties and it may also enhance optical density and print quality, making it particularly suitable for color printing. In aspects of binder solutions, the incorporation of amine functional polyvinyl alcohol with conventional silica pigments will be examined for an inkjet coating.

2.2.1 Pigment Solutions: Pigments that cost less than silica

Commercial silica pigments are classified by their process of manufacture; fumed, gelled and precipitated silica. Fumed silica particles have little or no internal microporosity. Instead, porosity is obtained by sintering primary particles together to form aggregated grape-like clusters. As shown in Figure 9, the fumed silica pigment has a large surface area, so its primary particle is small.
Theoretically, if the particle is 100 nm in diameter, it has 60 m$^2$/cc (=60 $\mu$m$^{-1}$, assuming the particle has a spherical shape), so the diameter of the primary particle can be easily calculated.

For CAB-O-SPERSE$^\text{\textregistered}$PG001, 90 m$^2$/g (surface area of porous silica) [31] $\times$ 2.65 g/cc (density of non-porous silica, SiO$_2$) = 238.5 m$^2$/cc

100 nm: 60 m$^2$/cc = the diameter (D$_p$) of primary particle: 238.5 m$^2$/cc, so the (D$_p$) is 25.2 nm.

(Note: the particle size is inversely proportional related to surface area. It can be also calculated as follows: $S$ (Total Surface Area of Particles) m$^2$/cm$^3$ = $N$ (Number of Particles of Diameter, D$_p$ /cm$^3$) x $S_p$ (Particle Surface Area of Diameter, D$_p$): $S = 1/[(\pi/6) D_p^3]} \times \pi D_p^2 = 6/D_p$. Thus, $D_p = 6/S = 6/[238.5 \text{ (m}^2/\text{cm}^3)] = 0.0252 \text{ cm}^3/\text{m}^2 = 0.0252 \text{ cm}^3/(10^2 \text{ cm})^2 = 0.0252x10^{-4} \text{ cm} = 25.2 \text{ nm}$).

The effective density (bulk density) of silica (CAB-O-SPERSE$^\text{\textregistered}$PG001) is given as 1.2 g/cc [32], so pore volume per unit mass ($V_p$) can be estimated as;

$$\text{The effective density} = \frac{1}{\frac{1}{\text{d}_{\text{SiO}_2}} + V_p} \quad [1]$$

where $d_{\text{SiO}_2}$, is the density of silica (2.65 g/cc).
The pore volume per unit mass $V_p$ is 0.46 cc/g, which means about 55% of the entire volume of silica (CAB-O-SPERSE®PG001). Therefore, the large surface area of the clustered pigments absorbs ink fast, which provides its desirable printability properties for high speed inkjet.

Pigment manufacturers have developed inkjet pigments in an attempt to overcome the limitations of silica pigments. Kaolin producers have surface modified their products to enhance pore volume and surface area for inkjet coatings [26]. Carbonate producers have also offered new products designed for non-impact coated paper [27, 28].

![Figure 10. The Illustrations of a narrow (left) and a broad (right) PSD.](image)

A narrow PSD leads to a more open (porous) structure caused by the packing of the particles [33]. It has also been found that the addition of clay to a PCC slurry reduces the porosity due to a denser packing of the particles [34, 35]. On the other hand, the small particles in a pigment of broad PSD occupy spaces between the larger particles, and this results in a more closely packed structure. Therefore, if more inter-pore volume is necessary, a narrow PDS is advantageous.

![Figure 11. The Illustrations of a non-blending (left) and a blending of different size pigments (right).](image)

Mixing non-porous pigments with silica lose inter and intra pore volume, so it is negative for inkjet coating. However, at high solids content ($\Phi=0.45$, 67%), a minimum viscosity was observed in
mixtures of spheres of different particle sizes [36]. Therefore, non-porous pigment blending is feasible for high solids coating without viscosity problem for the better ink jet application.

On the other hand, for example, suppose the 30% (weight) fumed silica \((d_{SiO_2} = 2.65 \text{ g/cc})\), pore volume= 0.46 cc/g) slurry with 30 g fumed silica and 70 g water. If the silica is non-porous, the volume of the silica is 11.32 cc \(((30 \text{ g})/(2.65 \text{ g/cc}))\) and the volume of water is 70 cc, so the volume fraction \((\Phi)\) is 0.14. If the silica is porous (pore volume = 0.46 cc/g), the effective volume of the silica is 32.64 cc \((11.32 \text{ cc} + 30 \text{ g} \times 0.46 \text{ cc/g})\) and the volume of water is 56.2 cc \((70 \text{ cc} - 13.8 \text{ cc})\), so effective volume fraction \((\Phi_{E})\) is 0.37. Eventually, the medium viscosity \((\eta_0)\) rapidly increases.

As seen above simple calculations, in case of porous pigments, volume fraction \((\Phi)\) is increased a lot, so all fumed silica coating shows a strong thickening effect.

In order to obtain the absorption properties of the silica and increase productivity at the same time, the method of blending with lower cost conventional coating pigments was proposed [37]. For example, calcium carbonate, in ground and precipitated forms, has been engineered as a substitute for silica pigments. For pigment solutions, calcium carbonate can be used in an effort to balance coating solids, viscosity and print quality. The following experimental methods are proposed to be able to provide new coating formulations for inkjet.

2.2.1.1 The determination of coating quality in which calcium carbonate replaces silica pigment

A. The substitution of calcium carbonate is alternative solution for inkjet coated paper.

B. High solid coatings containing calcium carbonate in absence of runnability issues.
2.2.2 Binder Solutions: Cationic PVOHs that replace cationic additives

Many of the dyes used in inkjet inks contain sulfonic or carboxylic acid groups, which make the dyes soluble in water and may aid in binding to cellulose [38]. At ink pH, these groups are ionized and anionic and attracted to cationic sites. A common practice is to add a cationic quaternary amine to an inkjet coating formulation to provide binding sites in the non-cellulosic coating. The cationic additive further retards inkjet dye movement [39] and helps with ink water fastness and light fastness [40].

Originally, amine functional polyvinyl alcohols were set forth [41] for making recycled paper products with improvements in both the wet and dry strength. Later, the amine functionality was applied for improving coating properties suited for inkjet [40].

The following methods are proposed to be able to experimentally investigate the applicability of cationic PVOHs for high speed inkjet coating:

2.2.2.1 Cationic PVOHs provide properly a cationic charge on the paper surface

A. Evaluate that the inks become water fast on the paper surface and the lightfastness is improved in those paper products incorporating the copolymers as compared to inkjet coatings incorporating conventional homopolymers as the binder by forming an insoluble salt.

B. Determine that the pigment binding strength, and silica pigment binding strength in particular, is improved with the use of the inkjet coatings incorporating the copolymers in comparison to the inkjet coatings incorporating the conventional homopolymers due to the strong absorption
(covalent bond) of the cationic groups with the silanol group on the silica pigment.

C. Evaluate how the cationic surface helps pigmented inks immobilized on the surface.

2.2.2.2 The runnability of coating formulations containing cationic binders on CLC

A. Evaluate that the incorporation of cationic PVOHs as a binder in the inkjet coating eases the makedown procedure of the coating formulation in absence of cationic additives.

2.2.2.3 The evaluation of coated paper properties and printability
CHAPTER 3. RHEOLOGICAL PROPERTIES OF STARCH LATEX DISPERSIONS AND STARCH LATEX-CONTAINING COATING COLORS

3.1 ABSTRACT
This chapter focuses on the understanding of basic properties of water-swollen crosslinked starch nanoparticles as a function of crosslink density. The extent of their water swelling is decreased with increasing particle crosslink density and solid concentration and vice versa. This study elucidates the unique rheological properties of starch nanoparticle dispersions and paper coating formulations in comparison with water-soluble cooked starch and synthetic latex counterparts. These rheological studies extend over many decades of shear rates, using several different rheometers. Low shear viscosities were obtained using a Cannon-Fenske viscometer and 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. Unlike conventional cooked and soluble starch solutions, starch nanoparticle latex dispersions are colloids that consist of internally crosslinked particles. With increasing intra-particle crosslink density these biobased colloids have been found to behave much like petroleum based synthetic latex colloids. However, at ultra-high shear their rheological properties are relatively more shear thinning compared to hard particles, including synthetic latex and pigment particles, which exhibit shear-thickening and dilatancy. The implications of the rheological data on high-speed coater runnability are discussed.
3.2 INTRODUCTION
Starch-based nanoparticle latex provides an alternative binder system to petrochemical-based binders, such as carboxylated and acrylonitrile-containing styrene butadiene latexes, as well as styrene acrylate latexes (XSB and SA latex). When added to a coating color formulation, these binders typically replace 35% to 50% of the XSB or SA latex used in paper coating processes [3,5, 6, 42-48]. The starch nanoparticle latex binders provide a performance that is different from conventional cooked coating starches and is comparable with all-synthetic latex systems. Although considerable practical working knowledge has been reported, there exists an uncharted area in regards to fundamental characteristics of the starch latex [3,5,6, 42-48]. This study examines the fundamental rheological performance of the crosslinked water-swollen starch nanoparticles relative to conventional cooked coating starches and XSB latex both in pure dispersions and in paper coatings.

3.3 RESULTS AND DISCUSSIONS
3.3.1 Materials and Methods
Samples used for this study include Dow 620NA (XSB latex 1) and Dow ProStar (XSB latex 2) as examples of XSB latex binders (formerly The Dow Chemical Company, now Trinseo), and different experimental grades of ECOSphere® starch nanoparticles labeled Bio-A, Bio-B, and Bio-C (ECOSYNTHETIX INC.), Penford Gum PG 290 starch (Penford Corporation), and Ethylex 2015 starch (Tate & Lyle). The other ingredients used in the coating formulations, listed in Table 3, are Hydragloss 90 clay (KaMin), Covercarb HP-FL CaCO₃ (OMYA); Finnfix 10 carboxymethyl cellulose from Hercules, and Calsan 50V Ca-Stearate lubricant (BASF).
### 3.3.2 Rheological Experiments

Lab studies were carried out to establish a number of similarities and differences between binders, such as starch latexes (Bio-A, Bio-B, and Bio-C), XSB latex, and soluble 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).

#### 3.3.2.1 Characterization of Starch Latex Samples in Terms of Volume Swell Ratios by Dilute Dispersion Viscosity Measurements

The relative viscosity ($\eta_r = \eta/\eta_0$) was obtained by measuring the flow times between two demarcations on a glass Cannon-Fenske viscometer for starch latex dispersions and for the dispersion medium, which was water. Using the modified Einstein equation, $\eta_r = 1 + 2.5 f \Phi$, where $f$ is the effective volume factor and $\Phi$ is the volume fraction, one can obtain the effective volume factor, $f$, that is equal to the volume swelling of latex nanoparticles at very low concentrations. If one plots the relative viscosity, $\eta_r$, versus volume fraction, $\Phi$, the effective volume factor, $f$, can be obtained from the slope at the zero volume fraction. The volume fraction of starch nanoparticles ranged from 0.0016 to 0.0157. The temperature was maintained at 24 °C during the measurements.
By measuring the relative viscosity, $\eta_r$, at low volume fractions for latex, one can gather relevant information about the viscosity and swelling behavior of that colloid. The relative viscosity, $\eta_r = \eta/\eta_0$, is plotted in Figure 1 against the volume fraction, $\Phi$, for the different experimental starch latex binders.

The effective volume factor of the starch nanoparticle latex measured by the relative viscosity method (the initial slope of the plot at zero volume fraction in Figure 12) may be expressed as follows:
\[ f = \frac{(V_{\text{Core-swollen}} + V_{\text{Shell}})}{V_{\text{Core-unswollen}}} \]  

Since the volume of the shell, \( V_{\text{Shell}} \), of the starch nanoparticle has not been experimentally determined, \( V_{\text{Shell}} \) is included as a part of the volume swell ratio, \( \text{SR}(V) \).

\[ \text{SR}(V) \sim f = \frac{(V_{\text{Core-swollen}} + V_{\text{Shell}})}{V_{\text{Core-unswollen}}} = 16.58 \text{ (for example: Bio-A)} \]  

**Table 2. The effective volume factor of starch nanoparticles vs. crosslink density.**

<table>
<thead>
<tr>
<th>Starch Nanoparticles</th>
<th>Relative Crosslink Density</th>
<th>Effective Volume Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-A</td>
<td>Low</td>
<td>16.58</td>
</tr>
<tr>
<td>Bio-B</td>
<td>Medium</td>
<td>10.74</td>
</tr>
<tr>
<td>Bio-C</td>
<td>High</td>
<td>6.32</td>
</tr>
<tr>
<td>XSB latex</td>
<td></td>
<td>2.6 (1)</td>
</tr>
</tbody>
</table>

(1) This effective volume factor, determined by diluting the latex with a 1 mole NaCl solution, was found to be higher than its previous value of 1.4 determined by diluting the XSB latex with de-ionized water [47], since the latex particles were likely micro-flocculated. In general, the effective volume factor of synthetic latex particles is affected by both their degree of carboxylation and backbone composition as well as the environmental conditions such as pH, ionic strength, etc.

SB latex colloid particles contain virtually no water in the core, so that swelling occurs primarily as a result of electric double-layer in the shell [47, 48]. Therefore, the core swell ratio of SB latex is:

\[ f = \frac{V_{\text{core-swollen}}}{V_{\text{core-unswollen}}} = 1.0 \]  

The values in Table 2 represent the maximum volume swell ratio, \( \text{SR}(V) \), of the water-swollen starch latex nanoparticles at very low concentrations. The results in Table 2 follow an expected trend of increased swelling with lower crosslink densities. These results confirm the unique performance of crosslinked starch nanoparticles reported elsewhere [6, 47]. First, their swelling under conditions of extreme dilution with water achieves the maximum swelling value, which is a balance between their elastic constraint due to their crosslinked network and osmotic pressure.
Secondly, starch latex nanoparticles de-swell with increasing solids so that their dispersions can be made at higher solids [6,47].

The effective volume factor of SB latex at dilute concentrations has been found to be in the range of 1.1 to 1.5, depending on pH and ionic strength [47].

3.3.2.2 Low Shear Viscosity Measurements

The low shear viscosities of the pure starch-based nanoparticle and petro-latex dispersions, as well as starch solutions were measured using a TA Instruments dynamic stress rheometer at different solid contents. The results from these measurements are shown in Figure 13. Binder dispersions (internally crosslinked starch latex and XSB latex) and the conventional cooked starch binder are all shear thinning at all measured solids, while the medium crosslinked starch latex is intermediate between the XSB latex and starch solution viscosity at the same solids.
3.3.2.3 Hercules Viscosity Measurements

The response of the same samples to increased shear at different solid contents are shown in Figure 14. The starch nanoparticle dispersions and starch solutions show a shear thinning behavior. In the case of the 20% and 30% solids XSB latex, there appears to be a shear thickening behavior. However, upon further investigation, the increase in viscosity was found to be an artifact of turbulence (see Figure 14).

Figure 13. Low shear viscosity of medium crosslinked starch latex (Bio-B), soluble starch, and SB latex.
Figure 14. Hercules “high” shear viscosity of starch latex (Bio-B), soluble starch, and XSB latex, respectively.

Figure 15. Taylor-Couette flow in Hercules “high” shear viscometer.

The Hercules high shear viscometer utilizes concentric cylinders with a well-defined geometry to measure a fluid’s resistance to flow and determine its viscous behavior in this simple-shear flow field (Figure 15). Because the gap between the rotating inner (bob) and the restrained outer (cup) cylinders is small, the annular flow between the two cylinders approximates a velocity-driven Couette flow.

When the rotational speed of the bob increases beyond a critical value depending on gap dimensions and viscosity, it causes interferences in interpretation of the rheogram. Theoretically,
the onset of Taylor vortices depends on the following criterion for the modified Reynolds number (Reₘ) in Couette flows [49]. Although fluid flow with dilatancy can be recorded even when testing Newtonian fluids, confusion can be created when the fluid is non-Newtonian because the shape of the flow curve due to vortical flows resembles dilatant-type behavior. Utilizing the criterion listed in 

\[
Reₘ = \left(\frac{rpm \rho R_1 X_0}{9.55 \eta_a}\right) \sqrt{\frac{X_0}{R_1}} < 41.3
\]

where \(R_1\) is bob radius, \(X_0\) is annular gap, \(\rho\) is density of the liquid, and \(\eta_a\) is apparent viscosity of the liquid. If \(Reₘ\) is over 41.3, the fluid flow is in the turbulence regime. This is borne out by the fact that a Newtonian fluid (water, \(Reₘ=81.49\), Table 3) also shows shear thickening behavior as the shear rate increases in Figure 14.

Table 3. The modified Reynolds numbers of diluted XSB latex dispersions and Newtonian fluids.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>50%</th>
<th>41%</th>
<th>30%</th>
<th>20%</th>
<th>Silicon oil</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reₘ No.</td>
<td>12.82</td>
<td>32.39</td>
<td>47.85</td>
<td>51.69</td>
<td>24.48</td>
<td>81.49</td>
</tr>
</tbody>
</table>
3.3.2.4 Ultra-High Shear Viscosity Measurements

Shear rates beyond $10^5$ s$^{-1}$ were obtained using an ACA Viscometer (ACAV) with either a slit or capillary configuration. The ACAV consists of a movable cylinder that can operate at pressures up to 400 bar. Samples contained in the cylinder are forced through a small capillary or slit, and depending on the flow rate and the slit or capillary gap, viscosities and shear rates can be achieved from $10^5$ to $2 \times 10^6$ s$^{-1}$. These shear rates are commonly known to be relevant for industrial paper coating operations using rod or blade coaters. The capillary dimensions used were 0.5 mm in diameter by 50 mm in length, while the slit dimensions were 10 mm in height by 0.095 mm in width by 0.5 mm in length. Because of the much smaller gap for the slit, these samples reached higher shear rates, and it should also be noted that the different geometries will result in different rheological behavior, where the slit is a better model for blade coating. The results from the capillary tests are shown in Figures 16 and 17, for the 25% and 35% solids biobased latex dispersions, respectively. As can be seen in Figure 16, the starch latexes exhibit a shear thinning behavior over the measured shear range. The samples are staggered in accordance with their swell ratios, with the higher swell ratio (Bio-A) corresponding to the higher viscosity, and the lower swell ratio (Bio-C) corresponding to the lower viscosity. In contrast, XSB latex is shown, which displayed a shear thickening trend over these shear rates. It should be noted that these measurements were limited at higher shear rates because of turbulence as discovered by the calculated Reynolds numbers (beyond 2000 is considered turbulent). As can be seen in Figure 17, increasing the solids of the starch latex resulted in higher dispersion viscosities. Nevertheless, the same trends can be observed, with a higher swell ratio corresponding to a higher viscosity.
To observe the rheological properties at even higher shear rates (1-3 million s⁻¹), the capillary was replaced with a slit attachment. The results obtained using the slit geometry are shown in Figure 18. Similar trends to the results for the capillary are evident, with the higher swell ratio starch nanoparticle latex resulting in a higher viscosity.
Figure 18. ACAV high-to-low slit measurements of 35% solids starch latexes and 50% XSB latex. Although the internally crosslinked starch nanoparticle latex samples are equal to or greater than their 50% XSB latex counterpart in their effective volumes, Figures 16-18 show the Bio-samples to be shear-thinning, unlike their XSB counterpart, which exhibit shear thickening behavior.

3.3.3 Coating Formulations

XSB was used as the 50% aqueous liquid and directly added to the coatings. Dry starch latex agglomerate powder (~92% solids) was dispersed under moderate shear conditions into the pigment slurry. Conventional coating starch was cooked at 95 °C for 30 minutes at 35% solids and then added to the coatings (complete gelatinization was confirmed using cross-polarizing microscopy). All coating samples were targeted to 67% solids. The formulations prepared are shown in Table 4.
Table 4. Coating formulations containing all-XSB latex with and without CMC and XSB latex with starch based latex and soluble starch as co-binders at 30% and 50% replacement levels.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Pigment</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
<td>GCC Hydrocarb 90</td>
<td>70</td>
<td>70</td>
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<td></td>
<td>Clay Fine #1 Clay</td>
<td>30</td>
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<td>30</td>
<td>30</td>
<td>30</td>
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<tr>
<td>Binder</td>
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<td>7</td>
<td>7</td>
<td>7</td>
<td>5</td>
<td>5</td>
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</tr>
<tr>
<td></td>
<td>Bio-A</td>
<td>0</td>
<td>3</td>
<td>0</td>
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<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Bio-B</td>
<td>0</td>
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<td>5</td>
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</tr>
<tr>
<td></td>
<td>Bio-C</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td></td>
<td>T&amp;L 2015</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
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<tr>
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<td>Ca-Stearate</td>
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<td>0.25</td>
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<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Solid Content, %</td>
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<td>67.1</td>
<td>67.3</td>
<td>67.0</td>
<td>67.1</td>
<td>66.3</td>
<td>67.1</td>
<td>67.3</td>
</tr>
<tr>
<td></td>
<td>pH</td>
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<td>8.6</td>
<td>8.4</td>
<td>8.2</td>
<td>8.2</td>
<td>8.3</td>
<td>8.3</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>Brookfield (mPa-s), 100 rpm</td>
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<td>1330</td>
<td>536</td>
<td>378</td>
<td>1440</td>
<td>2008</td>
<td>1156</td>
<td>536</td>
</tr>
</tbody>
</table>

3.3.3.1 Low Shear Rate Viscosity of Coating Colors

The low shear and high shear rheological properties were systematically studied to determine the effect of crosslinked starch nanoparticles on the rheological properties of the coating samples. The results from the low shear measurements are shown in Figures 19, 20 and 21.
Figure 19. Low shear rate of coating colors.

As shown in Figure 19, all coating samples are shear thinning from 0.01 to 4000 s\(^{-1}\).

Figure 20. Low shear viscosity of coating colors at initial shear rate up to 1 s\(^{-1}\).
Table 5. The grouping of the coating samples based on their Brookfield viscosity.

<table>
<thead>
<tr>
<th>Group</th>
<th>Viscosity (Pa-s)</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>First group</td>
<td>High</td>
<td>1,9</td>
</tr>
<tr>
<td>Second group</td>
<td>Middle</td>
<td>2,5,6,7,10</td>
</tr>
<tr>
<td>Third group</td>
<td>Low</td>
<td>3,4,8</td>
</tr>
</tbody>
</table>

As shown in Figure 20, the coating samples can be divided into three groups (see Table 5) in the very low shear regime (< 1 s\(^{-1}\)). The first group consists of sample No. 1 containing carboxymethyl cellulose (CMC) at 0.5 parts-per-hundred and sample No. 9, the coating where 50% of the XSB latex was substituted with soluble starch. The viscosities of the first group are the highest up to the 1 s\(^{-1}\) shear rate.

The second group consists of coating No. 2 replacing 30% of the XSB latex with starch nanoparticles Bio-A, coating No. 5 replacing 30% of the XSB latex with soluble starch, coating No. 6 replacing 50% of the XSB latex with starch nanoparticles Bio-A, the coating No. 7 replacing 50% of the XSB latex with starch nanoparticles Bio-B, and coating No. 10 which is without XSB replacement in the absence of CMC, which is generally not a feasible coating composition in mill operations, due to the relatively poor water retention properties of pure XSB. The viscosities of the second group are between the first group and the third group.

The third group consists of coating No. 3 replacing 30% of the XSB latex with starch nanoparticles Bio-B, coating No. 4 replacing 30% of the XSB latex with starch nanoparticles Bio-C, and coating No. 8 replacing 50% of the XSB with starch nanoparticles Bio-C. The viscosities for this group are the lowest up to 1 s\(^{-1}\) shear rate.
As shown in Figure 21, near 4000 s\(^{-1}\), there are changes in flow characteristics of coating No. 1, (containing 0.5 parts of CMC), belonging to the first group. The coating shows a decrease in viscosity as the shear rate increased. Coating No. 10 with no XSB replacement, belonging to the second group, shows a drastic decrease in viscosity. Coating No. 8, with half the XSB latex replaced with starch nanoparticles Bio-C, shows a viscosity plateau, as shear rate increases. The viscosities of the other coatings are shear-thinning.
### 3.3.3.2 Hercules “High” Shear Rate Viscosity of Coating Colors

Results from the Hercules measurements are shown in Figures 22. As shown in Figure 22, coating samples No. 5 and especially No. 9, show a minimal decrease in viscosity with increasing shear rate. This is most likely because the soluble cooked starch polymer forms a “particle-like” random coil at low shear, but then becomes extended and linearized as shear increases. This is why soluble polymers typically cannot shear thin and perform as effectively as colloidal latex binders at the high shear rate conditions of rod and blade coaters. Latex binders that contain colloidal particles, on the other hand, contribute to shear thinning at the high shear rates encountered in commercial high speed paper and paperboard coating operations.

![Figure 22. Hercules “high” shear viscosity of coating colors.](image)

The most noticeable behavior in Figure 22 is that coating No. 9, which contains the conventional cooked coating starch, as well as coating sample No. 6, which contains the starch latex with the
highest swell-ratio, have extremely high viscosities at moderate shear. Coating samples No. 3 and 7, which contains the starch latex with the middle swell-ratio, and coating No. 4 and 8, which contains the starch latex with the low swell-ratio, demonstrate lower viscosities and performance similar to the all-synthetic coatings No. 1 and 10. It is logical that a crosslinked starch latex having a low crosslink density and relatively high swell ratio would exhibit soluble starch-like behavior, while those starch latexes having higher crosslink densities and relatively lower swell ratios would behave more like XSB latexes. It may be worthwhile to point out that the rapid drop in viscosity of some of the coating formulations at high shear rates might be due to the concomitant temperature rise in the rheology experiment.

3.3.3.3 Ultra-High Shear ACAV Viscosity of Coating Colors (Capillary Rheometer)

The results for the rheological evaluation using an ACAV ultra-high shear capillary rheometer are given in Figure 24 for coating colors containing XSB latex as the only binder. Note that ‘a’ denotes going from high to low pressure, while ‘b’ denotes from low to high pressure conditions. Using the capillary module, the shear rate conditions are up to about 1 million s⁻¹, spanning the conditions valid for metered size press and rod coaters, but largely below the conditions applied during blade coating (see the ACAV slit results in the next section).
Figure 23. Ultra-high shear capillary viscosity of coating colors containing all-XSB latex with and without CMC. Note that ‘a’ denotes going from high to low pressure, while ‘b’ denotes from low to high pressure conditions.

As shown in Figure 23, the coating colors containing XSB latex as the only binder, at ultra-high shear display shear thickening behavior.
Comparing the results in Figures 23 and 24, at 30% and 50% replacement of the XSB latex with a conventional cooked coating starch, the coatings behave substantially more shear thickening and have much higher viscosities than the pure XSB coating colors.

---

**Sample No. 5 & 9 (Soluble Starch)**

![Graph showing viscosity vs. shear rate for samples 5 and 9 with different marks for high and low pressure conditions.]

*Figure 24. Ultra-high shear capillary viscosity of coating colors containing soluble starch at 30% and 50% replacement levels. Note that 'a' denotes going from high to low pressure, while 'b' denotes from low to high pressure conditions.*

---

**Sample No. 2 & 6 (Bio-A)**

![Graph showing viscosity vs. shear rate for samples 2 and 6 with different marks for high and low pressure conditions.]

*Figure 25. Ultra-high shear capillary viscosity of coating colors containing crosslinked starch latex (Bio-A) at 30% and 50% replacement levels. Note that 'a' denotes going from high to low pressure, while 'b' denotes from low to high pressure conditions.*
Comparing the results in Figures 23, 24 and 25, the coatings containing starch nanoparticles with the high swell ratio (Figure 25) perform only slightly better than the conventional cooked coating starch.

Comparing the results in Figures 23 to 26, the coatings containing starch nanoparticles with the medium swell ratio (Figure 26) perform better than the conventional cooked coating starch and shifted to lower viscosities overall in the range of the pure XSB coatings.

Figure 26. Ultra-high shear capillary viscosity of coating colors containing crosslinked starch latex (Bio-B) at 30% and 50% replacement levels. Note ‘a’ denotes high to low pressure, ‘b’ denotes low to high pressure conditions.

Comparing the results in Figures 23 to 26, the coatings containing starch nanoparticles with the medium swell ratio (Figure 26) perform better than the conventional cooked coating starch and shifted to lower viscosities overall in the range of the pure XSB coatings.
Comparing the results in Figures 23 to 27, the coatings containing starch nanoparticles with the low swell ratio (Figure 27) perform much better than the conventional cooked coating starch and shifted to even lower viscosities overall in the range of the pure XSB coatings.
Figure 28. Ultra-high shear capillary viscosity of coating colors with 30% replacement of XSB latex, along with all-XSB latex coating colors with and without CMC. Note that ‘a’ denotes going from high to low pressure conditions.

As shown in Figure 28, at a 30% replacement level of XSB latex, consistent staggering is observed for the coatings containing soluble starch (coating No. 5), to low crosslinked starch nanoparticles (coating No. 2), decreasing to middle (coating No. 3) and high crosslinked starch nanoparticles (coating No. 4). For simplicity, only the high-to-low pressure (“a”) conditions are compared here, which is in accordance with the recommendations of ACA for optimum experimental conditions.
As shown in Figure 29, at the 50% replacement level of XSB latex, again consistent staggering is observed for the coatings containing soluble starch (coating No. 9), to low crosslinked starch nanoparticles (coating No. 6), decreasing to middle (coating No. 7) and high crosslinked starch nanoparticles (coating No. 8). For simplicity, only the high-to-low pressure ("a") conditions are compared.

3.3.3.4 Ultra-High Shear ACAV Viscosity of Coating Colors (Slit Rheometer)

The results for a rheological evaluation using an ACAV ultra-high shear are given in Figure 30 for coating colors with 30% replacement of XSB, using the slit rheometer.
Figure 30. Ultra-high shear slit viscosity of coating colors with 30% replacement of XSB and an all-XSB latex coating color with CMC, using the slit rheometer.

As shown in Figure 30, coating No.1 containing XSB latex as the only binder behaves mildly shear thickening, while coatings containing medium and high level internally crosslinked starch nanoparticles (coatings No. 3 & 4) fall below at all shear rates, with additional shear thinning over the profile. The coating with the highest viscosity is coating No. 5 containing the conventional cooked coating starch, which is higher than the low-level crosslinked starch nanoparticles (coating No.2).
Figure 31. Ultra-high shear slit viscosity of coating colors with 50% replacement of XSB, along with all-XSB latex coating colors with and without CMC, using the slit rheometer.

The results for coating colors with 50% replacement of XSB, using the slit rheometer, are given in Figure 31. The overall trend at the higher substitution level is similar to the results in Figure 30. Figure 31 shows that coatings containing starch nanoparticles with low crosslinking are high in viscosity (coating No.6), which is not conducive to good runnability on high speed blade coaters. The same is true for the conventional cooked coating starch at 50% replacement level (coating No. 9). With increasingly more internal crosslinking (coatings No.7 & 8) of the starch nanoparticles a significant decrease in viscosity at these ultra-high shear rates occurred, with coating No. 8 having the lowest high shear viscosity of all coatings evaluated, including the all-XSB coating colors. Thus starch latex binders consisting of internally crosslinked nanoparticles may outperform conventional cooked coating starches as well as petro-latex binders in terms of fundamental rheological properties and experimental high speed coating runnability [6].
3.3.3.5 Composite Rheograms

Composite rheograms are constructed by combining the viscosity data obtained using a low shear stress rheometer, a Hercules “high” shear rheometer (relatively low to moderate shear), and ultra-high shear capillary and slit viscometers (ACAV) in Figures 32-35.

Figure 32. The composite rheograms of coating colors with 30% XSB replacement, along with all-XSB latex coating colors with and without CMC, using the capillary viscometer.

It is interesting to note that all coating colors appear to be shear-thickening between ~30,000 and ~80,000 s⁻¹, while their viscosities peaked between ~300,000 and ~600,000 s⁻¹.
Figure 33. The composite rheograms of coating colors with 50% XSB replacement, along with all-XSB latex coating colors with and without CMC, using the capillary viscometer.

It appears that all coating colors at 50% replacement appear to be shear-thickening at lower shear rate ranges than those at 30% replacement, while their viscosities also peaked at the lower shear rate ranges. These changes can be explained by the higher viscosities of their medium phase excluding the hard particles such as XSB latex and pigment particles. It has been indeed found that the shear-thickening of dispersions increases with increasing medium viscosity ($\eta_0$) due to the fact that aggregation of particles under shear increases with increasing medium viscosity ($\eta_0$) [49]. This will be discussed later in a generalized rheogram for high solids paper coatings over a wide range of shear rates.
The results from the ACAV are repeatable experimental values found from having repeated each experiment 3 times. The results reported are the average values. The shear thickening trend was observed in all of these measurements, regardless of whether the sample was run from low-high or high-low shear. As this is at a lower shear rate, turbulence effects are minimal with Reynolds numbers (Re) well below the 2000 cut-off. Additionally, it should be noted that the ACAV is calibrated using water in between each run, and so the shear thickening (or dilatancy) is an observable trend relative to water.

From a theoretical standpoint, the key difference between hard particle latexes and soft bio-based latex is the deformability of the particles. At moderately high shear, hard latex particles, such as XSB, first align, which lowers the viscosity, explaining the shear thinning. As shear increases, the forces on the hard particles overcome the electrostatic repulsion of the double-layer, and agglomeration occurs. We correspondingly see a Newtonian plateau as the alignment of particles is in balance with aggregation-type effects. As shear rates increase, the interactions between particles continues to increase, and with aggregation the particles, the particles become more randomly arranged and dilatancy or shear-thickening occurs. Conversely, the bio-based “soft” latex particles are believed to exhibit shear-induced de-watering. Under high shear, the swollen particles deform by releasing water, thus lubricating the system and allowing better particle alignment and a smaller effective volume fraction. Consequently, these bio-based latex particles show shear thinning properties over the entire measured range of shear rates.
Figure 34. The composite rheograms of coating colors with 30% XSB replacement, along with all-XSB latex coating colors with and without CMC, using the slit viscometer.
3.3.3.6 A Generalized Rheogram for High Solids Paper Coating Colors over a Wide Range of Shear Rates

Based on composite rheograms shown in Figures 32-35, as well as the fact that high solids dispersions of hard particles exhibit shear-thinning, and a Newtonian plateau, followed by shear-thickening over a wide range of shear rates, the following rheogram is proposed as a generalized rheogram for high solids paper coating colors.

Figure 35. The composite rheograms of coating colors with 50% XSB replacement, along with all-XSB latex coating colors with and without CMC, using the slit viscometer.
Figure 36. A generalized rheogram for high solids paper coating colors over a wide range of shear rates.

The proposed generalized rheogram for high solids paper coating colors shows shear thinning, followed by an interim Newtonian plateau (between 1 and 2), subsequent shear-thickening (between 2 and 3), and shear thinning (from 3 and on), as shown in Figure 36. The shear-thinning behavior of particle dispersions is due to either an ordered arrangement of particles and a progressive disruption of aggregates by shear or the shear dependence of electro-viscous effects and electric double layer repulsion, while their shear-thickening behavior is attributed to either a disruption of ordered particle arrangement or a progressive increase in shear-induced aggregation of particles. The shear rate at the onset of shear-thickening behavior (e.g., at 2 in Figure 36) 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:

\[ F_H = 6 \eta_o a (a + H_o/2) \dot{\gamma} \]  

[6]
where $F_H$ is the average hydrodynamic compressive or shearing force between two particles of radius $a$, $\eta_o$ the medium viscosity, $H_o$ the distance between two colliding particles, and $\dot{\gamma}$ the shear rate [50].

For small separations ($H_o \ll a$), the hydrodynamic force equation becomes $F_H = 6 \eta_o a^2 \dot{\gamma}$. As shown in Figures 32-35, 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, when the packing volume fraction of the aggregated dispersion under shear becomes lower than its volume fraction, increases with increasing extent of shear-thickening behavior and concentration. It is speculated that the point 3 in Figure 36 is very close to the onset of geometric dilatancy, but since the volume expansion is somewhat prohibited in the confined geometry of the ACAV capillary, the onset of dilatancy turns into the onset of the second shear-thinning.
3.4 CONCLUSIONS
The unique characteristics and properties of starch latex binders for paper coating were presented. While low shear Brookfield and Hercules rheograms are commonly used in the industry to assess the runnability of coatings, these results demonstrate that such low shear techniques can be extremely misleading when it comes to the prediction of coating performance on high speed metered size press, rod and blade coaters. The use of more specialized “ultra-high” shear equipment such as the ACAV might be needed to better understand the rheological properties under true coating conditions. The unique characteristics of starch based latex binders were found to be attributed to the fact that they are made up of water-swollen internally crosslinked nanoparticles, which depending on their crosslink densities have varying degree of water swelling. The swell ratio determined for various experimental grades of internally crosslinked starch nanoparticle based latexes correlated systematically with the degree of crosslinking and rheological performance. Although the internally crosslinked starch nanoparticle latex samples are equal to or greater than their 50% XSB latex counterpart in their effective volumes, they are shear-thinning, unlike their XSB counterpart, which exhibits shear thickening behavior. These findings enable starch latexes to meet low and high shear rheological requirements for better paper coating runnability by controlling their crosslink densities. The results presented here demonstrate that these nanoparticles can in principle outperform conventional cooked coating starches as well as petro-latex binders in terms of fundamental rheological properties and practical high speed coating runnability performance.
CHAPTER 4. DYNAMIC WATER RETENTION PROPERTIES OF BIOBASED LATEX CONTAINING COATING COLORS

4.1 ABSTRACT
This work focuses on the dynamic water retention and wall slip properties of biobased latex containing coatings to better understand their coater runnability performance. The correct rheology and water retention of coating colors are important at increasing coater speeds in order to achieve good runnability, productivity and product quality. Many quality and runnability problems originate from the interaction between the base paper and the continuous water phase of the coating color. If this interaction is not controlled, an excessive material shift from the coating color to the base paper can occur. This can result in poor machine runnability, unstable systems and an uneven coating layer.

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. A dynamic water retention test was used to characterize the kinetics of immobilization, determined by the water retention properties of the coating color, during the dewatering process.

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.
4.2 Introduction

The rheology and water retention characteristics of coating colors are important at increased coater speeds in order to achieve good runnability, productivity and product quality. 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 coater runnability performance. 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 industrial-scale paper coating processes and also a dynamic water retention test was used to characterize the kinetics of immobilization that has a good correlation to actual coating processes.

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

4.3.1 Materials and Coating Formulations

Binders used for this study include Dow ProStar 5405 XSB latex binder and different experimental grades of ECOSPHERE® biobased nanoparticles labeled Bio-A, Bio-B, and Bio-C from EcoSynthetix Inc., and coating starch 2015 from Tate & Lyle. The other ingredients used in the coating formulations listed in Table 6 are described as follows, No.1 clay: Hydragloss 90 (KaMin); GCC: Covercarb HP (OMYA); CMC: Finnfix 10; lubricant: Ca-Stearate.

Table 6. Coating formulations.

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<th>Coating Color Sample #</th>
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<th>2</th>
<th>3</th>
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<th>5</th>
<th>6</th>
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<td>XSB + CMC</td>
<td>30% Bio-A</td>
<td>30% Bio-B</td>
<td>30% Bio-C</td>
<td>30% Starch</td>
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<td>50% Bio-B</td>
<td>50% Bio-C</td>
<td>50% Starch</td>
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<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Additives</td>
<td>CMC</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ca-Stearate</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Solid Content, %</td>
<td>66.7</td>
<td>66.7</td>
<td>67.0</td>
<td>66.7</td>
<td>66.7</td>
<td>66.8</td>
<td>66.9</td>
<td>66.7</td>
<td>66.8</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>8.0</td>
<td>8.0</td>
<td>8.1</td>
<td>8.1</td>
<td>8.1</td>
<td>8.0</td>
<td>8.1</td>
<td>8.2</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Brookfield [mPa-s], 100 rpm</td>
<td>2460</td>
<td>1250</td>
<td>560</td>
<td>370</td>
<td>1380</td>
<td>2000</td>
<td>1150</td>
<td>520</td>
<td>1450</td>
</tr>
<tr>
<td></td>
<td>Capillary Viscosity (600,000 s⁻¹) [mPa-s]</td>
<td>64</td>
<td>87</td>
<td>72</td>
<td>62</td>
<td>105</td>
<td>111</td>
<td>91</td>
<td>73</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Slit Viscosity (1,900,000 s⁻¹) [mPa-s]</td>
<td>44</td>
<td>45</td>
<td>33</td>
<td>35</td>
<td>61</td>
<td>63</td>
<td>43</td>
<td>36</td>
<td>55</td>
</tr>
</tbody>
</table>

The Brookfield viscosities in Table 6 are quite low for some of the coating colors, and such a low viscosity may not be practical. In this study the solids were kept the same to ensure a valid
comparison of the results. Therefore, CMC was added in sample condition 1, the XSB latex control formulation, where CMC or another rheology modified/water retention additive is normally required. CMC was left out in the other trials in order to see the impact of the 3 biobased latex grades and the conventional coating starch by themselves.

**4.3.2 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 [51]. 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 kPa, which corresponds to shear rates of approximately 500,000 s^{-1} for the coatings used in this study.
4.4 RESULTS AND DISCUSSIONS

4.4.1 High Shear Rheology Experiments

The most interesting results from the rheological evaluation were obtained using an ACAV at ultra-high shear using a slit rheometer, which are shown in Figures 37 and 38 for coating colors with 30% and 50% replacement of XSB, respectively [8]. The slit rheometer operates at ultra-high shear conditions in the range of a commercial high speed blade coater.

![30% Replacement Slit - Powerlaw Regression Fit](image)

Figure 37. Ultra-high shear slit viscosity of coating colors with 30% replacement of XSB and an all-XSB latex coating color with CMC, using the slit rheometer.

A Minitab statistical analysis* was carried out for the data reported in reference 1, to shed further light on the rheological trends in this study. This analysis led to the following conclusions:
1. Coating formulations containing 100% SB latex samples are dilatant with better than a 92% confidence limit, i.e. 92% confidence for coating color sample 1 (“XSB-CMC”), and 96.5% confidence for sample 10 (“XSB Only”).

2. All samples containing either 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. Generally, 65.8% confidence limit is regarded as insignificant. Actually, it is the confidence limit for the value of the coefficient. The coefficient is $-2.68 \times 10^{-6}$ with a standard error of the estimate of $2.39 \times 10^{-6}$. Thus, the probability of the coefficient being negative (i.e. between 0 and $-\infty$) is the cumulative distribution corresponding to 1.21 sigma ($2.68/2.39$) is 88%. Thus, we can say that the coefficient is negative (thixotropic) with an 88% confidence limit.

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. The coefficient is $-0.81 \times 10^{-7}$ with a standard error of the estimate of $0.80 \times 10^{-7}$. Thus, the probability of the coefficient being negative is the cumulative distribution corresponding to 1.01 sigma ($0.81/0.80$) is 84%. Thus, the coefficient is negative (thixotropic) with an 84% confidence limit.

d. Sample 6 (“50% Bio-A”) is thixotropic with an 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.

![Graph of Rheology](image)

*Figure 38. Ultra-high shear slit viscosity of coating colors with 50% replacement of XSB and an all-XSB latex coating color with CMC, using the slit rheometer.*

As shown in Figures 37 and 38, the 2 coatings containing XSB latex as the only binder clearly behave shear thickening, while coatings containing medium and high level internally crosslinked
biobased nanoparticles continue to behave in a shear thinning mode over the profile. Therefore, runnability performance on the coater should theoretically be improved even with as little as 30% of the biobased latex (Figure 37) and even further with 50% replacement of the petro-based binder (Figure 38).

Below the dynamic water retention and coating color wall slip properties are presented in order to help explain the unique make-up of the biobased latex, as well as, to provide insight on the high speed coating runnability observed in commercial practice.

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.

4.4.2 Water Retention Experiments
The TAPPI standard test method for measuring coating dewatering, T-701, employs an AA-GWR static water retention tester [51]. 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 [51]. Furthermore, the contact time does not relate to real coating processes. For these reasons, dynamic water retention test measurements are preferred.

A dynamic water retention test operates on the principle of measuring the change in viscosity of the coating under shear over time. The method (see Figure 39) uses a conventional rotary viscometer fitted with two plates, and several holes are drilled into the lower plate. A standard blotter paper (Whatman® Filter 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).

Figure 39. Schematic of the Universal Dynamic Spectrometer Paar Physica UDS 200.

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 and the structural rearrangements during the dewatering process.

As shown in Figure 40, 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 better reflect conditions in a paper mill 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 better water retention performance as compared to the all-synthetic binder coating formulations with or without CMC.
Figure 40. Coating immobilization time characterization at room temperature (top) and 37 °C (bottom).
As further shown in Figure 40, the immobilization times were shortened at the higher temperature. At higher temperature, the fluid-medium viscosity within the coating is lowered and dewatering is greater. However, the immobilization time of Bio-C (high crosslinked) was relatively unchanged. This might be explained by 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 hold onto the water.
Figure 41. Coating immobilization time characterization at room temperature (top) and 37 °C (bottom).
Since the Paar Physica dynamic water retention tester instrument measures the increase in viscosity with time under constant stress (100 Pa), the more viscous coatings of 50% replacement reach the immobilization point sooner than of 30% replacement (see Figure 41). In the Figure 41, quickly increased viscosity indicates more close packed coating structure or interaction. The 50% replacement shows totally different behavior compared with the 30% replacement. High viscosity dominated water retention in replacement of 50% SB latex, so the impact of temperature was unlike the 30% replacement.

In the case of the conventional cooked starch co-binder, an ethylated starch, the viscosity of the coating suddenly jumped up to just above 1 Pa-s at the initial point, and then remained at a relatively constant viscosity for a while before immobilization. This behavior was somewhat unexpected and is likely 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.

It is not clear whether the water holding ability of biobased latex is due to the viscosity effect of the coatings or the biobased latex particles themselves. It would be possible to deduce this if the viscosity of all of the coatings were equal or at least reasonably close in value. Commonly, an increase in aqueous phase viscosity slows down dewatering. 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 6, except for the levels of each biobased latex and ethylated starch, which were optimized in order to better match the Brookfield viscosity as shown in Table 7.
Under these nearly same viscosity conditions (see Figure 42), Bio-B shows the highest water retention behavior. As shown, the water retention appears to be lower for Bio-A, followed by Bio-C and finally ethylated starch. It can be suggested that there is a trade-off for biobased latexes between a) water retention, where a lower crosslinking gives higher water retention, and b) medium viscosity, where higher crosslinking gives better overall performance. Thus, an intermediate level of crosslinking should give better results when compared on this basis. At higher temperature (Figure 42, 37 °C), the fluid-medium viscosity within the coating is also lowered and dewatering is greater. In comparison to gravimetric water retention in Table 8, coatings (trial # 5 and 9) containing conventional starch indicate the better static water retention, which is speculated that hydrogen bonds more easily occur between linear starch molecules and water molecules than crosslinked starch nanoparticles under the static state. However, crosslinked starch nanoparticle be able to hold water longer than linear starch molecule under the dynamic state, so the better dynamic water retention properties observed in crosslinked starch nanoparticle than conventional starch as shown in Figure 42.

Table 7. Coating formulations designed to match viscosity (same recipe as in Table 6, except for the levels of biobased latex and ethylated starch, which were optimized to better match the Brookfield viscosity).

<table>
<thead>
<tr>
<th></th>
<th>Bio-A</th>
<th>Bio-B</th>
<th>Bio-C</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookfield (mPa-s), 100 rpm</td>
<td>540</td>
<td>600</td>
<td>580</td>
<td>590</td>
</tr>
<tr>
<td>Solid, %</td>
<td>66.8</td>
<td>66.7</td>
<td>66.7</td>
<td>66.8</td>
</tr>
<tr>
<td>Replacement, parts</td>
<td>0.58</td>
<td>3</td>
<td>4</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Figure 42. Coating immobilization time characterization at room temperature (solid) and 37 °C (blank).

The low to medium shear rheology of the coating colors in Table 7 were measured using a Hercules rheometer. The results in Figure 43 show a reasonably similar performance for the coatings with similar Brookfield viscosities.
Figure 43. Low to medium shear viscosity of coating colors in Table 7 measured using a Hercules rheometer.

4.4.3 Coating Color Wall Slip Properties

A further property that impacts coater runnability is the rheological interaction 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 [51-54].

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 8.
Table 8. Coating formulations used for ACAV wall slip studies.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>1 XSB + CMC</th>
<th>3 30% Bio-B</th>
<th>4 30% Bio-C</th>
<th>5 30% Starch</th>
<th>7 50% Bio-B</th>
<th>8 50% Bio-C</th>
<th>9 50% Starch</th>
<th>10 XSB Only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Content, %</td>
<td>67.11</td>
<td>67.3</td>
<td>66.7</td>
<td>66.8</td>
<td>67.7</td>
<td>67.3</td>
<td>66.8</td>
<td>67.1</td>
</tr>
<tr>
<td>pH</td>
<td>8.3</td>
<td>8.6</td>
<td>8.5</td>
<td>8.3</td>
<td>8.6</td>
<td>8.6</td>
<td>8.5</td>
<td>8.4</td>
</tr>
<tr>
<td>Brookfield (mPa-s), 100 rpm</td>
<td>2250</td>
<td>491</td>
<td>235</td>
<td>1384</td>
<td>800</td>
<td>276</td>
<td>2070</td>
<td>832</td>
</tr>
<tr>
<td>Gravimetric Water Retention</td>
<td>122.3</td>
<td>88.9</td>
<td>146.6</td>
<td>52.9</td>
<td>63.0</td>
<td>134.8</td>
<td>19.4</td>
<td>223.5</td>
</tr>
</tbody>
</table>

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.

Figure 44. Schematic representation of apparent slip flow in capillary (radius, R) [51].

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. When a thin layer, typically on the order of microns, forms near the capillary wall, it 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 or polymers will on average migrate towards the capillary wall to form an “Apparent slip layer [53], Zone I” in Figure 44. The apparent slip will continue to increase with higher shear at
higher flow rates, which results 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. [53] discussed 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, $\Delta S = S_{\text{small}} - S_{\text{large}}$ is then used via the following *Eqn. 7* to determine a “slip velocity” [m/s], where $D$ is the capillary diameter:

$$V_{\text{slip}} = \frac{1}{8} \frac{\Delta S}{\Delta D}$$

Slip velocities were determined for coating samples at a shear stress of 25 kPa, 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 reach local equilibrium and due to turbulent effects, while lower shear stresses result in minimal slip. These slip velocities are tabulated in Table 9 for each of the coating samples.

*Table 9. Tabulated Slip Velocities measured using the ACAV rheometer.*

<table>
<thead>
<tr>
<th>Coating Sample</th>
<th>Slip Velocity [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.64</td>
</tr>
<tr>
<td>3</td>
<td>0.78</td>
</tr>
<tr>
<td>4</td>
<td>0.69</td>
</tr>
<tr>
<td>5</td>
<td>2.50</td>
</tr>
<tr>
<td>7</td>
<td>4.93</td>
</tr>
<tr>
<td>8</td>
<td>4.55</td>
</tr>
<tr>
<td>9</td>
<td>3.10</td>
</tr>
<tr>
<td>10</td>
<td>0.43</td>
</tr>
</tbody>
</table>
It has been reported that the standard error in these measurements is proportional to the Reynolds number [53]. Based on this, we estimated for these data that the error is ±5%. Comparing these results to previous 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 CMC) 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 [54].

It has already been reported elsewhere 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 [54].
How then can it be explained that biobased latexes tend to show higher apparent slip velocities? Let us first remember that biobased latexes are water-swollen due to their osmotic pressures [6]. If hydrodynamic compressive forces in capillary flows exceed the osmotic pressures of biobased latex 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 closely packed 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 [6].

Increasing the crosslink density of the biobased latex 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 biobased latex 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%).

4.5 CONCLUSIONS

This work furthers the understanding of biobased latexes and the impact of these binders on high shear rheology and coating dewatering. The results indicate that biobased latex 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 tradeoff between water retention and coating color viscosity as a function of the biobased latex 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 biobased latex particles resulted in more slippage than for the CMC or cooked starch polymer containing coatings.

Considering the results from previous rheological studies of biobased latex containing coatings [6], these additional findings provide a clear indication of the benefits of biobased latexes as a binder replacement for XSB binder or cooked starch. The biobased latex systems show unusual rheological, water retention, and wall slip properties that suggest better coater runnability.
CHAPTER 5. THE CHARACTERIZATION OF BIOBASED LATEX DISPERSIONS BY SERUM REPLACEMENT

5.1 ABSTRACT
An interpretation is given to the unknown basic nature of water-swollen starch nanoparticles and their colloidal behaviors scientifically. Serum replacement experiments showed that starch latexes are complex systems of particles with a minor fraction of soluble polymers. Increasing the degree of crosslinking decreased the soluble fraction and lowered the dispersion viscosity. Coatings applied using a cylindrical laboratory coater showed the plasticity of SB latex to play a role as a lubricant during calendering and an aid to improve gloss. Crosslinked and graft starch polymers improved water retention, but were lower in gloss.

5.2 INTRODUCTION
The following works build upon the findings mentioned in previous chapters on the rheological properties and dynamic water retention properties of starch latex-containing coating colors. The previous works have shown that the rheological performance of starch latex and dynamic water retention of starch latex are different from conventional cooked coating starches. In this chapter, the basic nature of water-swollen starch nanoparticles and their colloidal behaviors provided by serum replacement.

5.2.1 Starch Nano Particle Dispersion
Starch latex dispersions are complex, polydisperse and hydrodynamic systems. As starch polymers are crosslinked, they are converted to form higher molecular weight insoluble polymer networks, or starch particles.
Depending on the degree of crosslinking, the final starch latex will consist of a mixture of insoluble starch particles, with some soluble starch polymers as shown Figure 46. After crosslinking, a certain amount of starch molecules is converted to starch particles and some color bodies also form during the extrusion manufacturing processes.
Figure 47. The new concept of Bio-C (heavy brown), Bio-B (brown), and Bio-A (light brown) dispersions. As shown in Figure 47, a highly crosslinked starch latex has less swellable particles and less solubles, so its viscosity is low, but a less crosslinked starch latex has more swellable particles and more soluble starch molecules, so its viscosity is high.

Figure 48. The color intensities of biobased latexes (solid 1%) Left: Bio C (heavy brown), Middle: Bio B (brown) Right: Bio A (light brown).

Starch latexes under the current study have different color intensities (Figure 48) and it is speculated that some color bodies form as a consequence of crosslinking conditions during the processes. When examining the manufacturing of biobased latex, starch is plasticized by shear
forces, and a crosslinking agent is added during the reactive extrusion process. After the processing, the starch can be dissolved or dispersed in an aqueous medium to a concentration between 4 and 40 wt. %. This results in biobased latexes that are characterized by an average particle size of less than 400 nm [1]. During the extrusion processes, more crosslinked starch nanoparticles undergo the higher shearing and temperatures by friction [1]. Therefore, the higher cross-linked starch particles are shown as darker brown (Figure 48).

In this work, a serum phase replacement apparatus was used to remove both free and adsorbed solubles from starch nanoparticle dispersions. The results provide information on the amounts of the free and adsorbed starch molecules. Finally, total water swelling in the presence of free soluble starch molecules was compared with the water-swelling in the absence of both free and adsorbed starch molecules.

5.3 EXPERIMENTAL

5.3.1 Materials and Methods

5.3.1.1 The Unique Properties of Biobased Latex

Osmosis is the movement of water molecules from regions of higher water potential (high osmotic pressure) to regions of lower water potential (low osmotic pressure) across a semipermeable membrane. To count osmosis flow, osmotic pressure \([\pi]\) functions as a pressure needed to nullify the effects of osmosis and is directly influenced by the amount of solute in the system as shown in Eqn. 8.

\[
\pi = \text{MMR} \cdot R \cdot T
\]  

[8]

where \(\pi\) is osmotic pressure, MM is the molar mass of solute, \(R\) is the ideal gas constant, and \(T\) is absolute temperature. For example, a red blood cell in a hypotonic solution (Figure 49) has a lower
concentration of solutes outside the cell than inside the cell. In an attempt to balance the concentrations of solutes inside and outside the cell, water will rush into the cell. When there is no concentration gradient for water across the cell membrane, the cell neither swells nor shrinks. At this state (no osmotic flow), the osmotic pressure is applied to inside the blood cell to prevent the inward flow of water across a semi-permeable membrane of blood cell.

Figure 49. The depiction of a red blood cell in a hypotonic and isotonic solution [56].

Analogously, crosslinked biopolymer nanoparticles have their wet properties. The medium surrounding the dry starch particle in water has a higher water concentration than the inside of the starch particle. Therefore, the starch particle gains water along with crosslinked network for swelling [Initial State]. However, since starch particles do not have semipermeable membranes surrounding them, water-soluble solutes and much smaller nanoparticles would be uniformly distributed in serum phase and inside particles, as long as they can pass through the particle networks in Figure 50.
When the concentration gradient reaches equilibrium state, the particles neither swell nor shrink \([\text{Equilibrium}]\). At the moment, starch particles achieve the maximum swelling value that is balanced between their elastic constraint due to their crosslinked network and osmotic flow induced by concentration-driven forces \([5]\). However, when an external pressure is larger than the osmotic pressure of starch particles, the particles de-swell \([\text{External pressure applied}]\).

Generally, osmosis can be demonstrated using a U-tube as shown Figure 51, which is analogous to that of biobased latex. At initial state, a dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. At equilibrium, the pressure differential, equal to the osmotic pressure of the solution, equalizes the flow rate of solvent in both directions. Applying an external
pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

The biggest difference between crosslinked and non-crosslinked starch is whether or not an elastic constraint exists, so crosslinked starch latex is dispersed as particles in water. However, when non-crosslinked starch granules are added into water, the water penetrates into the granules due to osmotic pressure and then eventually the starch granules become uniformly dissolved as an individual molecule in water.

The viscosity of the suspensions is greater than the viscosity of the liquid. The relation of both to each other is called relative viscosity $\eta_r$. For a suspension with particles without any interaction in a Newtonian liquid, Einstein [7] calculated the viscosity of a laminar flow as follows:

$$\eta_r = 1 + K_H \Phi$$  \hspace{1cm} [9]

where $K_H$ is the hydrodynamic shape factor and $\Phi$ is the volume fraction. In suspensions of particles with an aspect ratio (length to diameter) greater than 1 (sphere), particle rotation during flow results in a large effective hydrodynamic volume, and hydrodynamic shape factor is larger than 2.5 in Figure 52 [56].

Figure 52. Effect of hydrodynamic shape factor on effective particle size in a flow field [58].
By measuring the relative viscosity, $\eta_r$, at low concentrations for a spherical latex particle, one can gather relevant information about the viscosity and swelling behavior of that colloid using a modified Einstein Eqn. 10, where $f$ is the effective volume factor

$$\eta_r = 1 + 2.5 f \Phi$$

[10]

The effective volume factor ($f$) that is equal to the maximum volume swelling of biobased latex nanoparticles at very low concentrations.

**5.3.2 Serum Replacement Experiment**

Originally, a serum replacement method [59] was used for the removal of absorbed emulsifier from a particle surface, but it is also a useful method to separate the water soluble starch in a starch latex dispersion by size exclusion through a membrane.

Using starch latexes of different crosslink densities (Bio-A, Bio-B, Bio-C), the relative proportions of soluble starch and starch particles can be characterized through serum replacement studies. As shown in Figure 53, the starch latex was added to the container, where it was replaced with buffered deionized water located in the reservoir, which was adjusted to pH 8.0 using a sodium carbonate buffer.

The container is comprised of a cylindrical polycarbonate reservoir held between two polyacetal plates. A Nuclepore polycarbonate (hydrophilic) 30 nm membrane is supported by a porous polyethylene disk at the bottom of the cell. A Teflon-coated magnetic stirring bar rotates close to the membrane to prevent fouling of the membrane by starch latex particles over the lengthy experimental duration. The buffered water was fed from the reservoir into the top of the container cell to replace the starch latex dispersion by flushing it through the Nuclepore filtration membrane.
The pressure head applied by the water reservoir was calculated using Bernoulli’s equation. The filtration rate for a membrane of given pore size varied according to the concentration of the starch latex dispersions, the pressure head, and the porosity of the membrane. When high pressure is applied to the container, starch particles clog the membrane and also squeeze out through pores due to their deformability. Therefore, the pressure head applied by water head was 0.44 psi. Replacing 1% solid with the pressure head gave satisfactory results, with no deposition of starch particles on the membrane. 5% solid dispersion could not pass through membrane due to its high viscosity under the pressure. The filtrates were collected and the concentration of filtrate measured every day until the solids reached nearly 0%. Generally, approximately 1-2 weeks were required for the serum replacement process.

![Diagram](image)

*Figure 53. Schematic representation of serum replacement apparatus.*
5.4 RESULTS AND DISCUSSIONS

5.4.1 Serum Replacement of Biobased Latex Dispersions

As shown in Table 10, biobased latexes show different filtrate flow rates, because each starch latex has its own viscosity, which is related to its crosslinked density. The flow rate of each starch latex was almost constant, indicating that there was little or no clogging of the surface of the membrane.

Table 10. The flow rates of biobased latex dispersions by serum replacement (Bio-A, Bio-B, and Bio-C at 1% solids).

<table>
<thead>
<tr>
<th>Bio-A</th>
<th>gram/day</th>
<th>Bio-B</th>
<th>gram/day</th>
<th>Bio-C</th>
<th>gram/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>36.6</td>
<td>1 day</td>
<td>74.2</td>
<td>1 day</td>
<td>111.6</td>
</tr>
<tr>
<td>2</td>
<td>28.1</td>
<td>2</td>
<td>74.3</td>
<td>2</td>
<td>101.6</td>
</tr>
<tr>
<td>3</td>
<td>26.9</td>
<td>3</td>
<td>74.2</td>
<td>3</td>
<td>97.0</td>
</tr>
<tr>
<td>4</td>
<td>26.5</td>
<td>4</td>
<td>75.4</td>
<td>4</td>
<td>98.0</td>
</tr>
<tr>
<td>5</td>
<td>28.8</td>
<td>5</td>
<td>75.1</td>
<td>5</td>
<td>96.9</td>
</tr>
<tr>
<td>6</td>
<td>28.3</td>
<td>6</td>
<td>75.9</td>
<td>6</td>
<td>90.0</td>
</tr>
<tr>
<td>7</td>
<td>28.5</td>
<td>7</td>
<td>73.3</td>
<td>7</td>
<td>95.9</td>
</tr>
<tr>
<td>8</td>
<td>28.9</td>
<td>8</td>
<td>76.2</td>
<td>8</td>
<td>96.3</td>
</tr>
<tr>
<td>9</td>
<td>28.8</td>
<td>9</td>
<td>72.7</td>
<td>9</td>
<td>100.3</td>
</tr>
<tr>
<td>10</td>
<td>33.4</td>
<td>10</td>
<td>77.2</td>
<td>10</td>
<td>109.8</td>
</tr>
<tr>
<td>11</td>
<td>32.9</td>
<td>11</td>
<td>75.3</td>
<td>11</td>
<td>109.8</td>
</tr>
<tr>
<td>12</td>
<td>32.8</td>
<td>12</td>
<td>78.4</td>
<td>12</td>
<td>109.8</td>
</tr>
<tr>
<td>13</td>
<td>32.8</td>
<td>13</td>
<td></td>
<td>13</td>
<td>109.8</td>
</tr>
<tr>
<td>14</td>
<td>32.4</td>
<td>14</td>
<td></td>
<td>14</td>
<td>109.8</td>
</tr>
</tbody>
</table>

As shown in Figure 54, the entire container volume (400 cc) was replaced within a two-week period of time for the low crosslinked starch, Bio-A sample. The flow rate is inversely related to the viscosity of the solution, so a lower solution viscosity (higher crosslink density) resulted in a faster replacement of the serum. This replacement of the Bio-A solution was longer than the other samples due to its higher viscosity. The total amount of serum replaced after the two weeks was 7.89%.
The medium crosslinked starch, Bio-B, had the full container volume replaced twice within twelve days. At the end of 12 days, 33.17% of the original serum was replaced.

The high crosslinked starch Bio-C had the full container volume replaced twice within just nine days, and 52% of the original serum was replaced within this time period.
Figure 54. The daily amount of starch passed through the 30 nm membrane.

In Table 11, the amounts of replaced starch provided results that were verified by performing a mass balance around the system.

Table 11. The mass balance of serum replacement experiments.

<table>
<thead>
<tr>
<th>Starch latex</th>
<th>Bio-A</th>
<th>Bio-B</th>
<th>Bio-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (g)</td>
<td>5.17</td>
<td>4.12</td>
<td>4.81</td>
</tr>
<tr>
<td>Container (g)</td>
<td>4.32</td>
<td>2.94</td>
<td>1.96</td>
</tr>
<tr>
<td>Total Amounts in Ftrants (g)</td>
<td>0.48</td>
<td>1.37</td>
<td>2.52</td>
</tr>
<tr>
<td>Unaccounted Amount (g)</td>
<td>0.37</td>
<td>0.19</td>
<td>0.33</td>
</tr>
<tr>
<td>The amount of replaced starch (%)</td>
<td>9.28</td>
<td>33.17</td>
<td>52.39</td>
</tr>
<tr>
<td>Unaccounted Amount (%)</td>
<td>7.88</td>
<td>6.9</td>
<td>14.4</td>
</tr>
<tr>
<td>Biocide (ppm)</td>
<td>5.1</td>
<td>12.1</td>
<td>12.2</td>
</tr>
</tbody>
</table>

For example, the total original weight of Bio-A was 5.17 g before replacement. The total weight, consisting of starch particles and soluble starch was 4.90 g, sodium carbonate (buffer): 0.26 g, and biocide: 0.00211 g, 5.1 ppm. The amount of starch latex in the container after replacement was 4.32 g. The total amount of starch latex in filtrates was 0.48 g.

\[
\text{Loss or Gain} \% = \frac{V_1 - V_2}{V_1} \times 100
\]  

[11]
According to loss or gain equation Eqn. 11,

\[ V_1: \text{initial value} \quad V_2: \text{ending value} \]

\[ \begin{align*}
V_1 & = 5.17 - 0.48 = 4.69 \text{ g} \\
V_2 & = 5.17 - 0.85 = 4.32 \text{ g}
\end{align*} \]

Therefore, the unaccounted for amount was 7.88\% \((\frac{(4.69-4.32)}{4.69} \times 100)\). It is likely that this loss is due to the adsorption of starch latex particles onto the container wall or pipes of the apparatus.

As starch in solution can spoil at room temperature, biocide was added to the starch latex dispersions and water reservoir. Similarly, to control the pH of the solution a Na\(_2\)CO\(_3\) buffer was added to the reservoir. However, the amount of these components added was minimal relative to the total water volume, thus their masses were neglected within the weight calculations.

To assess the molecular structure of materials in each filtrate, its swell ratio was determined as shown in Table 5. The composite swell ratio of all the effluents and the material remaining in the container was then calculated according to Eqn. 12

\[
\begin{align*}
\text{Composite Swell Ratio} &= \frac{\sum_{i=1}^{n} (A \times C)_i + (B \times C)}{\sum_{i=1}^{n} A_i + B} \\
\end{align*} \quad [12]
\]

where A is the starch volume of each filtrate, B is the starch volume remaining in the container, and C is the swell ratio. If the mass balance is correct, the original sample swell ratio should be equal to the composite swell ratio. Also, the swell ratio of each filtrate helps to provide a clearer picture of the molecular structure of materials that passed through the membrane filter (Table 12).

The calculation of swell ratio was determined by the same method used in Chapter 3.
Table 12. Swell ratios of filtrates, original samples, and composites: Bio-A (low crosslinked) and Bio-C (high crosslinked).

<table>
<thead>
<tr>
<th>Bio-A</th>
<th>SR</th>
<th>Bio-C</th>
<th>SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>7.82</td>
<td>1 day</td>
<td>5.42</td>
</tr>
<tr>
<td>2</td>
<td>2.69</td>
<td>2</td>
<td>6.12</td>
</tr>
<tr>
<td>3</td>
<td>2.41</td>
<td>3</td>
<td>6.07</td>
</tr>
<tr>
<td>4</td>
<td>2.32</td>
<td>4</td>
<td>7.29</td>
</tr>
<tr>
<td>5</td>
<td>2.85</td>
<td>5</td>
<td>7.68</td>
</tr>
<tr>
<td>6</td>
<td>2.95</td>
<td>6</td>
<td>6.65</td>
</tr>
<tr>
<td>7</td>
<td>3.08</td>
<td>7</td>
<td>7.71</td>
</tr>
<tr>
<td>8</td>
<td>1.79</td>
<td>8</td>
<td>10.48</td>
</tr>
<tr>
<td>9</td>
<td>1.78</td>
<td>9</td>
<td>17.79</td>
</tr>
<tr>
<td>10</td>
<td>1.35</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.72</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.55</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.58</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.47</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Original SR</td>
<td>14.28</td>
<td>Original SR</td>
<td>6.88</td>
</tr>
<tr>
<td>Container</td>
<td>15.85</td>
<td>Container</td>
<td>8.34</td>
</tr>
<tr>
<td>Composite SR</td>
<td>14.55</td>
<td>Composite SR</td>
<td>7.50</td>
</tr>
</tbody>
</table>

As shown in Table 12, the original swell ratios, SR, before replacement are quite similar to the composite swell ratios, which help to validate the mass balance calculations. Each of the filtrates showed different swell-ratio with time in Table 13. Unfortunately, all filtrates of Bio-B were lost, but high and low crosslinked biobased latexes clearly show their characteristics in swell ratios.

Starch latex is mixed with low and high linear and branched polymer molecules and particles, so the original swell ratio is an average swell ratio of the low and high linear polymer and particles. Each of filtrates shows a different swell-ratio with time in Table 12.

In Bio-A, from 2\textsuperscript{nd} to 14\textsuperscript{th}, the swell ratios were much lower than the average which means those are very low molecular weight soluble starch molecules. Bio-A appears to mostly have water-
swollen particles larger than 30 nm and large soluble starch molecules which cannot pass through the 30 nm pore filter, based on the serum replacement measurements.

In Bio-C, from 1st to 3rd, the swell ratios were lower than the average for which those are believed to be high crosslinked small particles or very low molecular weight soluble starch molecules. From 8th to 9th, the swell ratios were higher than average swell ratio in which those are also believed to be high molecular weight soluble starch. Bio-C appears to have more nanoparticles smaller than 30 nm, compared to Bio-A. Although the serum-replaced materials in the filtrates have not been quantitatively analyzed, their swell ratios suggest that they have both nanoparticles that are smaller than 30 nm and low molecular weight soluble starch molecules.

5.4.2 Particle Size of Biobased Latex

A particle size analyzer, using dynamic light scattering, was used for analyzing the size distribution of starch particles suspended in water. Light from a laser is focused into a glass tube containing a dilute suspension of particles. The intensity of light scattered by a single isolated particle depends on its molecular weight and overall size and shape, and also on the difference in refractive indices of the particle and surrounding solvent [60].

The particle size or particle size distribution (PSD) fundamentally affects the biolatex performance. For example, a large particle size provides better flow properties because the larger particles play role of lubricants under high shear rate [5].

In order to determine the particle size distribution of the biolatex suspensions, the solution was diluted to get the appropriate intensity i.e. in between 200 to 400 counts, and then the particle size was measured with a NICOM 370 DLS particle sizing systems submicron analyzer.
In data analysis, there are two methods; Gaussian Distribution Analysis (unimodal distribution) and NICOMP Distribution Analysis (Multimodal distribution).

Finding the best fit means to minimize the deviation between the measured autocorrelation function and the model function [60]. This deviation is measured by the quantity called the chi-square ($\chi^2$). If the value of Chi Squared ($\chi^2$) is larger than 3, which suggests that the Gaussian Analysis result is inappropriate, the Gaussian analysis is changed to NICOMP Analysis for accuracy.

In reality, biobased latex dispersions are polydisperse, so all the analysis follows NICOMP Analysis. First, we measured the size of standard sample (nanobead) for reference. The mean number diameter is $505.0 \pm 6.4$ nm for the polystyrene latex (solid 1%) 100 times diluted for appropriate intensity.

**Figure 55. Intensity-weighted Gaussian analysis of nanobead.**
As shown in Fig 5, Chi Square ($\chi^2$) is smaller than 3, so we used Gaussian Analysis. As expected, monodisperse polystyrene latex shows a unimodal distribution and also the mean particle size (526 nm) is very close to original known the mean diameter (505 nm). Next, we prepared 1% solid biobased latex dispersions for measuring their particle sizes. Before measuring the particle size, all samples were sonicated, because starch molecules can be associated due to hydrogen bonding in water.

In Table 1, all Chi squared values were very extremely high, so the multimodal distribution is appropriate.

NICOMP 370 DLS has three different types of weighting systems; (a) intensity-weighted, (b) volume-weighted, (c) number-weighted for data analysis, but in Table 1, intensity-weighted data were used.

The dispersions of starch nanoparticles contain linear or branched starch molecules as well as starch particles, so these associate with each other by hydrogen bonding during measurement. Conclusively, uniform particle size could not be obtained through a number of experiments. Because the probability of such hydrogen bonding is proportional to the dispersion concentration, reliable particle size of biobased latex also could not be gained at different concentrations.

Table 13. Intensity-weighted NICOMP analysis of biobased latexes, M.D. (Mean Diameter, nm).

<table>
<thead>
<tr>
<th>chi-square ($\chi^2$)</th>
<th>Bio- A</th>
<th>Bio-B</th>
<th>Bio-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.D.</td>
<td>21.1</td>
<td>35.9</td>
<td>16.6</td>
</tr>
<tr>
<td>%</td>
<td>7.9</td>
<td>21.8</td>
<td>5.8</td>
</tr>
<tr>
<td>2 peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.D.</td>
<td>60.8</td>
<td></td>
<td>127.9</td>
</tr>
<tr>
<td>%</td>
<td>19.3</td>
<td></td>
<td>48.2</td>
</tr>
<tr>
<td>3 peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.D.</td>
<td>542.2</td>
<td>282.4</td>
<td>396.1</td>
</tr>
<tr>
<td>%</td>
<td>72.8</td>
<td>78.2</td>
<td>46.1</td>
</tr>
<tr>
<td>Average M.D.</td>
<td>398.8</td>
<td>226.4</td>
<td>483.7</td>
</tr>
</tbody>
</table>
5.4.3 CLC (Cylindrical Lab Coater) Trial

The 6 coating formulations with 30 % replaced (Table 14) were used on a CLC trial at Western Michigan University on 42 lbs/3300 ft\(^2\) (63 gsm) paper, using a rigid blade at 2000 ft./min, with a drying time of 15 to 25 seconds at 100 % power. They were calendared using 2 passes over a chrome-finished heated metal roll (mated up to the coated paper surface) and a cotton roll (uncoated side) at 750 PLI pressure at 60 °C. The target gloss of control was 72.

Table 14. Coating formulations with 30% XSB replacement.

<table>
<thead>
<tr>
<th>Coating Color Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Description</td>
<td>XSB + CMC</td>
<td>30% Bio-A</td>
<td>30% Bio-B</td>
<td>30% Bio-C</td>
<td>30% Starch</td>
<td>XSB Only</td>
</tr>
<tr>
<td>Pigment</td>
<td>GCC 70</td>
<td>GCC 70</td>
<td>GCC 70</td>
<td>GCC 70</td>
<td>GCC 70</td>
<td>GCC 70</td>
</tr>
<tr>
<td>Binder</td>
<td>XSB Latex 10</td>
<td>XSB Latex 7</td>
<td>XSB Latex 7</td>
<td>XSB Latex 7</td>
<td>XSB Latex 7</td>
<td>XSB Latex 10</td>
</tr>
<tr>
<td>Bio-A</td>
<td>Bio-A 0</td>
<td>Bio-A 0</td>
<td>Bio-A 0</td>
<td>Bio-A 0</td>
<td>Bio-A 0</td>
<td>Bio-A 0</td>
</tr>
<tr>
<td>Bio-B</td>
<td>Bio-B 0</td>
<td>Bio-B 0</td>
<td>Bio-B 0</td>
<td>Bio-B 0</td>
<td>Bio-B 0</td>
<td>Bio-B 0</td>
</tr>
<tr>
<td>Bio-C</td>
<td>Bio-C 0</td>
<td>Bio-C 0</td>
<td>Bio-C 0</td>
<td>Bio-C 0</td>
<td>Bio-C 0</td>
<td>Bio-C 0</td>
</tr>
<tr>
<td>Starch (Hydroethylated)</td>
<td>Starch 0</td>
<td>Starch 0</td>
<td>Starch 0</td>
<td>Starch 0</td>
<td>Starch 0</td>
<td>Starch 0</td>
</tr>
<tr>
<td>Additives</td>
<td>CMC 0.5</td>
<td>CMC 0</td>
<td>CMC 0</td>
<td>CMC 0</td>
<td>CMC 0</td>
<td>CMC 0</td>
</tr>
<tr>
<td>Ca-Stearate</td>
<td>Ca-Stearate 0.25</td>
<td>Ca-Stearate 0.25</td>
<td>Ca-Stearate 0.25</td>
<td>Ca-Stearate 0.25</td>
<td>Ca-Stearate 0.25</td>
<td>Ca-Stearate 0.25</td>
</tr>
<tr>
<td>Solid Content, %</td>
<td>Solid Content, % 66.7</td>
<td>Solid Content, % 66.7</td>
<td>Solid Content, % 67.0</td>
<td>Solid Content, % 66.7</td>
<td>Solid Content, % 66.7</td>
<td>Solid Content, % 67.0</td>
</tr>
<tr>
<td>pH</td>
<td>pH 8.0</td>
<td>pH 8.0</td>
<td>pH 8.1</td>
<td>pH 8.1</td>
<td>pH 8.1</td>
<td>pH 8.0</td>
</tr>
<tr>
<td>Brookfield [mPa-s], 100 rpm</td>
<td>Brookfield [mPa-s], 100 rpm 2460</td>
<td>Brookfield [mPa-s], 100 rpm 1250</td>
<td>Brookfield [mPa-s], 100 rpm 560</td>
<td>Brookfield [mPa-s], 100 rpm 370</td>
<td>Brookfield [mPa-s], 100 rpm 1380</td>
<td>Brookfield [mPa-s], 100 rpm 1170</td>
</tr>
</tbody>
</table>

A CLC coating study was conducted for the overall performances of biolatex and Table 15 & 16 to illustrate the coated paper properties for the 6 trials. Except for gloss, all the coated paper properties, which are dependent on coat weight, were all similar. In Table 15, the gloss of Bio-A was the worst compared with other coated papers, which implicates the amount of soluble starch.
in Bio-A and cross-linking density affects film formation. Shrinkage leads to rougher paper coating surfaces, which can reduce critical optical properties, such as gloss and conventional cooked (water-soluble) starches have been reported to shrink upon drying and lead to a reduction in paper optical properties (especially gloss) relative to petroleum-based SB latex binders [61]. Therefore, the larger amount of soluble starch molecules compared with Bio-B and C helps the shrinkage a lot. However, highly crosslinked particles behave like hard spheres. Thus, Bio-C is durable for the shrinkage during drying.

In Table 16, the gloss of coated papers containing XSB dominates the others, which is caused by plasticizing of petroleum based polymers during calendaring. Starch graft polymers (Hydro-Ethylated) with 1,3-butadiene and styrene appear to have good film forming properties in Tables 15&16.

### Table 15. The properties of uncalendered coated papers.

<table>
<thead>
<tr>
<th>Base Paper</th>
<th>Brightness</th>
<th>Opacity</th>
<th>Gloss</th>
<th>PPS (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CW, g/m²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XSB Only</td>
<td>10.0</td>
<td>83.36</td>
<td>91.22</td>
<td>34.4</td>
</tr>
<tr>
<td>XSB Only</td>
<td>11.7</td>
<td>83.52</td>
<td>91.52</td>
<td>36.2</td>
</tr>
<tr>
<td>XSB + CMC</td>
<td>11.0</td>
<td>84.54</td>
<td>91.48</td>
<td>32.8</td>
</tr>
<tr>
<td>XSB + CMC</td>
<td>12.2</td>
<td>84.50</td>
<td>91.76</td>
<td>33.4</td>
</tr>
<tr>
<td>30% Bio-A</td>
<td>13.3</td>
<td>84.48</td>
<td>92.02</td>
<td>34.7</td>
</tr>
<tr>
<td>30% Bio-A</td>
<td>10.0</td>
<td>84.20</td>
<td>91.20</td>
<td>32.9</td>
</tr>
<tr>
<td>30% Bio-B</td>
<td>12.9</td>
<td>84.82</td>
<td>91.64</td>
<td>35.6</td>
</tr>
<tr>
<td>30% Bio-B</td>
<td>13.7</td>
<td>84.90</td>
<td>92.10</td>
<td>35.1</td>
</tr>
<tr>
<td>30% Bio-C</td>
<td>11.8</td>
<td>84.26</td>
<td>91.44</td>
<td>34.9</td>
</tr>
<tr>
<td>30% Bio-C</td>
<td>12.8</td>
<td>84.20</td>
<td>91.54</td>
<td>36.8</td>
</tr>
<tr>
<td>30% Bio-C</td>
<td>10.3</td>
<td>84.14</td>
<td>90.24</td>
<td>33.3</td>
</tr>
<tr>
<td>30% Bio-C</td>
<td>11.8</td>
<td>84.36</td>
<td>91.20</td>
<td>36.0</td>
</tr>
<tr>
<td>30% Starch</td>
<td>10.0</td>
<td>83.44</td>
<td>91.60</td>
<td>34.3</td>
</tr>
<tr>
<td>30% Starch</td>
<td>12.0</td>
<td>84.08</td>
<td>91.74</td>
<td>35.3</td>
</tr>
</tbody>
</table>
Table 16. The properties of calendered coated papers, condition: 750 PLI (2 passes), 60 °C.

<table>
<thead>
<tr>
<th></th>
<th>CW, g/m²</th>
<th>Brightness</th>
<th>Opacity</th>
<th>Gloss</th>
<th>FFS (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSB Only</td>
<td>10.0</td>
<td>80.36</td>
<td>86.48</td>
<td>71.38</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>11.7</td>
<td>80.70</td>
<td>88.38</td>
<td>71.58</td>
<td>0.94</td>
</tr>
<tr>
<td>XSB + CMC</td>
<td>11.0</td>
<td>81.34</td>
<td>88.72</td>
<td>68.38</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td>81.14</td>
<td>89.18</td>
<td>71.40</td>
<td>0.89</td>
</tr>
<tr>
<td>30% Bio-A</td>
<td>10.0</td>
<td>81.90</td>
<td>88.82</td>
<td>65.46</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>12.9</td>
<td>82.22</td>
<td>89.34</td>
<td>69.70</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>82.02</td>
<td>89.90</td>
<td>71.62</td>
<td>0.98</td>
</tr>
<tr>
<td>30% Bio-B</td>
<td>11.8</td>
<td>81.96</td>
<td>88.82</td>
<td>66.16</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td>82.34</td>
<td>89.40</td>
<td>70.06</td>
<td>0.96</td>
</tr>
<tr>
<td>30% Bio-C</td>
<td>10.3</td>
<td>81.16</td>
<td>86.64</td>
<td>67.24</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>11.8</td>
<td>81.74</td>
<td>89.48</td>
<td>68.32</td>
<td>0.98</td>
</tr>
<tr>
<td>30% Starch</td>
<td>12.5</td>
<td>82.04</td>
<td>89.62</td>
<td>68.78</td>
<td>0.99</td>
</tr>
</tbody>
</table>

As shown in Figure 56, the formation of a latex film arises from the coalescence (i.e. compaction, deformation, cohesion and polymer chain interdiffusion) of the individual latex particles [62].

![Figure 56](image)

*Figure 56. The illustration of idealized latex film formation as it transitions from a wet latex dispersion (upper) to a dried film (lower).*

The formation of a continuous film (i.e. transparent and crack-free) is then dependent on the minimum film formation temperature (MFFT) of the polymer. If the film is cast above its MFFT, then deformation and cohesion of the latex particles can occur [62]. In film formation, SB latex is
not subject to significant shrinkage upon drying and is known to deliver good optical properties such as gloss [61]. However, the lowest crosslinked Bio-A undergo very severe shrinkage during drying (Table 15 & 16).

5.5 CONCLUSIONS

A serum phase replacement apparatus separated both free and adsorbed low molecular weight solubles and crosslinked small starch particles from starch nanoparticle dispersions. The results obtained from the serum replacement experiment provided information on the amounts of replaced starch molecules and particles. The amounts of replaced starch were dependent on crosslinked density (Table 11). The swell ratios of filtrates elucidated the components of starch latex mixed with low and high linear and branched polymer molecules and particles (Table 12). Bio-A appeared to have mostly large water-swollen particles and large molecular weight soluble starch, based on the serum replacement measurements. Bio-C appeared to have more nanoparticles smaller than 30 nm, compared to Bio-A.

In regard to particle size of biolatex, hydrogen bond associated starch molecules are formed during measurement, so consistent results could not be obtained.

In the CLC trial, the deformation of solid SB latex occurred due to plasticity during calendering, which improved the gloss of all SB latex coated paper, but the roughness caused by shrinkage occurred regardless of the better rheological performance and water retention in coatings containing starch. The graft starch polymer (hydroethylated starch) functioned well as a rheology modifier, such as improving water retention and shows good film-forming rather than Bio-A. The large amount of soluble starch molecules (mostly linear and branched) in Bio-A affect the most shrinkage, but grafted and crosslinked polymers (Bio-B and Bio-C) were durable against shrinkage.
CHAPTER 6. THE EVALUATION OF EXPERIMENTAL CATIONIC POLYVINYL ALCOHOLS FOR INKJET APPLICATIONS

6.1 ABSTRACT
There is an increased trend for the use of inkjet coatings in high-speed commercial printing and this challenges the absorptive properties of the surface. To keep pace with the change in market, two approaches have been proposed for investigation:

The examination of coatings replaced partially by calcium carbonate in comparison with conventional inkjet coatings and the estimation of amine functional polyvinyl alcohol as a sole-binder in the formation of the coating structure is needed.

At high solids content, a minimum viscosity was observed in mixtures of different sizes particles, so high solid inkjet coating is feasible. However, the print quality of coatings replaced by calcium carbonate did not reach that of all silica coatings, because the replacement induced a decrease of intra pore volume.

The incorporation of amine functional polyvinyl alcohol with conventional silica pigment increased viscosity as a result of flocculation of positive and negative components. The cationic binder was compatible with cationic pigment without flocculation, so cationically dispersed silica pigment is recommended with the cationic PVOHs.

6.2 INTRODUCTION
Non-porous pigments, such as clay or calcium carbonate are not fractal pigments. As a result, they lack the needed interstitial pore volume required for inkjet printing. For this reason, fractal porous silica pigments [63] are used in the inkjet coatings when high print quality is desired. However,
the disadvantage of using fractal pigments is their high viscosity at low solids and high binder demand. In preliminary experiments, fractions of calcium carbonate were used to replace silica in an effort to balance coating solids, viscosity and print quality. Based on the preliminary results, CLC runs executed to estimate the replacement of conventional pigment and cationic polyvinyl alcohols for inkjet application.

6.3 PRELIMINARY EXPERIMENTAL

6.3.1 Materials and Methods
Commercial silica pigments are classified by their process of manufacture; fumed, gelled and precipitated silica. Fumed silica particles have little or no internal microporosity. Instead, porosity is obtained by sintering primary particles together to form aggregated grape-like clusters [31].

As shown in Table 17, CAB-O-SPERSE®PG001 (Fumed Silica Pigment) has a large surface area (90 m²/g), so its primary particle should be relatively small. The large surface area of the clustered pigments absorbs ink fast, which provides its desirable printability properties by high speed inkjet.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade Name</th>
<th>Solids, %</th>
<th>Density, g/cc</th>
<th>Surface Area, m²/g</th>
<th>Particle size, nm</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>CAB-O-SPERSE®PG001</td>
<td>Anionic dispersed slurry, 30%</td>
<td>1.2 (Bulk)</td>
<td>90</td>
<td>225</td>
<td>11.1</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>HydroCarb®90</td>
<td>Powder</td>
<td>2.7</td>
<td>8 ~11</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>PVOH</td>
<td>Selvol 205</td>
<td>Powder</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3.1.1 Coating Formulations
The maximum packing volumes of large and small particles occur between 70:30 and 80:20 by volume. Based on this reference [36], a carbonate (Ps: 700 nm) to silica (Ps: 225nm) ratio of 70:30 or 80:20 by volume should provide the maximum packing volume. Even though a minimum
viscosity is obtainable in the mixtures of different sized particles at the maximum packing volumes [64], any greater replacement of carbonate for silica can cause an unacceptable loss in intra-pore volume, which would be highly detrimental to the inkjet printing properties. Therefore, in this work, the ratio of silica to carbonate was fixed to 70: 30. Maximizing the solids level of coatings has been an important issue, as the high solids coating gives potential advantages not only in production cost but as enhancement in product quality as well [65].

The binder demands for various pigments depend on the total surface area of pigment particles, that is, the larger surface area of the pigment (silica), the greater the binder demand. In North America, a binder level for silica pigment of 30 parts PVOH per 100 parts pigment has been shown to be sufficient [66], so if we assume that the binder level for carbonate is 5 to 10 parts, then the binder demand can be estimated for the mixture. This led to the experimental design shown in Table 18.

Table 18. The ratios of pigment to binder.

<table>
<thead>
<tr>
<th>Dry parts per 100 parts pigments</th>
<th>Group</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Silica</td>
<td>100</td>
<td>70</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Carbonate</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>PVOH</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>24</td>
</tr>
<tr>
<td>Coat Weight (g/m²)</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>Solid, %</td>
<td>30</td>
<td>36</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>Nip Pressure (¹), PLI</td>
<td>550</td>
<td></td>
<td>1500</td>
<td>1500</td>
</tr>
</tbody>
</table>

(¹) Supercalendering: 1 pass, no heat
30 parts × 0.7 = 21 parts binder for silica pigment, 5 to 10 part × 0.3 = 1.5 to 3 parts binder for carbonate, so the binder demand of the mixture is 22.5 to 24 parts. (In case of pigment blending ratio, Silica: Carbonate=7:3).

When using a certain amount of binders and additives, these components reduce the free volume in the coating according to the loss of pore space by the presence of the polymer [67]. Eventually, the loss of free volume limits the absorption rate by reducing inter-pore volume. In preliminary experiments, the different levels of PVOH (Table 18) were used for inkjet coatings to investigate the loss of pores and the surface strength of inkjet printed papers.

### 6.3.1.2 Coating Colors Properties

*Table 19. The physical properties of coatings.*

<table>
<thead>
<tr>
<th>Group</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Volume Fraction, Φ</td>
<td>0.31</td>
<td>0.26</td>
<td>0.30</td>
</tr>
<tr>
<td>Viscosity(1), mPa-s</td>
<td>60</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>pH</td>
<td>10 ± 0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Brookfield Viscometer (23 °C, 20 rpm)

Since the volume concentration of dispersed particles is a key variable for rheology dispersions, pigment solids concentrations were converted into volume concentrations. For example, when make down 30% (solids concentrations) fumed silica slurry with 30g (dry weight) silica and 70g water, if the silica pigment is non-porous, the volume of the silica is 11.3 cc (30 g / 2.65g/cc) and the volume of water is 70cc, so the volume fraction (Φ) of silica is 0.14.

If the silica pigment is porous (Porosity = 0.46 cc/g), the effective volume of the silica is 25.1 cc (11.3cc + 30 g× 0.46 cc/g) and the volume of water is 56.2 cc (70cc-13.8cc), so the effective volume fraction (ΦE) of silica is 0.30. As shown in Table 19, all silica coatings show a higher
volume concentration due to the filled water in the pores, but as the amount of carbonate was increased, the volume concentration decreased.

### 6.3.1.3 Drawdown of Coating Colors

The pH of all coatings (Table 19) were adjusted with sodium carbonate and the coatings were drawn down on a base-paper (Table 20) using Meyer rods. After drawdowns were performed, the coated papers were dried immediately with a heat-gun for 3 minutes. All dried coating weights were calculated gravimetrically. Before calendering, the dried coated papers were put into a TAPPI standard conditioning room for 24 hours (23°C and 50% RH). The coated papers were then passed through a polished roll and filled roll calender nip one time with no heat (PLI, see Table 18). Before inkjet printing, all coated papers were again put in the conditioning room for 24 hours, because humidity affects ink-absorption.

**Table 20. The physical properties of base paper.**

<table>
<thead>
<tr>
<th>Base Paper</th>
<th>Gloss, 75°</th>
<th>PPS Roughness (µm)</th>
<th>PPS Porosity (ml)</th>
<th>R∞</th>
<th>R_0</th>
<th>S (m²/g)</th>
<th>K (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW: 92 g/m²</td>
<td>5.8</td>
<td>4.3</td>
<td>515.1</td>
<td>96.3</td>
<td>90.98</td>
<td>0.1071</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

S: scattering coefficient, K: absorption coefficient, R∞: reflectance of the layer so thick that further increase in thickness does not change the reflectance, R_0: reflectance of the layer with ideal black background.

### 6.4 RESULTS AND DISCUSSIONS

#### 6.4.1 The Effects of Low Binder Level (The First Group)

#### 6.4.1.1 Coating Properties

Pore volume is a key variable in inkjet printing. There are two different types of pore volume in paper coating; inter-pore volume. Inter-pore volume is the space among particles, which is changed by mixing different pigments, but this change is relatively small compared with intra-pore volume. The intra-pore volume results from the pores within the pigment itself. In reality, using a porous pigment is more effective for gaining the desired porosity for high quality inkjet printing [68].

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The use of 30 parts binder level per 100 parts silica is common in North America [66], because of the large surface area of the silica. However, a large amount of binder clogs inter-pores more than a small amount of binder [67]. Therefore, by tuning the amount of binders, the loss of pores can be examined by inkjet printability. While 4.5 parts binder was a fairly small amount of binder to change, it was expected to provide more inter-pores available in the coating to receive ink in comparison to the use of 24 parts binder.

Mixing particles of different shapes resulted in a more closed coating structure, but the viscosity decreased in comparison to all silica coating. As shown in Figure 55, the replacement of 30 parts grounded calcium carbonate increased the packing volume, which improved the rheological performance at both the low and high shear rates in No.2 coating. The high solid coating (No.3 coating) performed as a thick dispersion in comparison to the others at high shear (Figure 57).

![Figure 57. The low and high shear viscosity of low binder level (4.5 parts).](image)
The actual target coat weight of inkjet coated paper was 10 g/m², but this was difficult to coat by drawdown in the lab. To achieve uniformity, a higher coat weight was required. The range of coat weight was 22 to 26 g/m². Since the binder level was low (4.5 parts), a low pressure (550 PLI) was applied to coated paper during calendering to avoid cracking of the coating layer.

As shown in Figure 58, the No.2 coating had the lowest gloss, while the high solid No.3 coating had the highest gloss before calendering. The large particle size (700 nm, Table 17) of carbonate affected the gloss of the No.2 coating, since gloss increases with decreasing particle size [69]. However, high solid No. 3 coating improved the hold out of coating by faster immobilization [65]. After calendering, the differences of the gloss were decreased and the range of roughness was within 0.3 microns.

The high solid coating (No.3) showed the highest PPS porosity both before and after calendering, but the coating (No.2) showed the lowest PPS porosity in both. PPS porosity was decreased with increasing packing structure, which indicates the high solid coating (No.3) caused a decrease in
packing due to faster immobilization. The low solid coating (No.2) caused an increase in packing, while the high solids coating increased smoothness and permeability at low amount of binder (4.5 parts).

6.4.1.2 Color Reproduction

In color management, an ICC (International Color Consortium) profile is a set of data that characterizes a color input or output device, that is, profiles describe the color attributes of a particular device [70]. A profile is only valid for conditions it was made for. This means that if we use particular coated paper to print the test chart, our profile is only valid for the printer when it is using this paper type [71]. Figure 60, 64, and 68 are the views of ICC profiles.

The printer used to generate ICC profiles was an Epson Stylus Photo R3000 Inkjet Printer with 9-color Epson UltraChrome K3 with Vivid Magenta pigment ink. Pigment based inks behave differently than dye-based inks. The spreading behavior of dye-based inks is determined by the hydrodynamic properties such as the Weber or Reynolds’s number [72]. On the other hand, in pigment-based inks, after initial spreading, the pigment particles coagulate on the surface of the microporous layer, creating a filter cake that limits the penetration of the carrier liquid. This results in longer absorption times and recessed dots that stay on the top of the substrate layer, and affect all the other printability properties [72].

To obtain color gamut data, a patches chart with a small number of patches used for inkjet printability, as shown in Figure 59 was used, because the width of coated paper on the CLC coater is narrow.
The chart was sent to the printer without color management settings applied through RIP (Raster Image Processor). No linearization of the printer was conducted because the process did not improve the final print quality and might even decrease the amount of ink deposited on the media and thus alter the total color gamut that could be obtained [73]. Ink level were set to 300% and resolution to 720 dots per inch (dpi), color precision to best, media type to archival matte paper, print quality to high, and color mode to CMYK. The conditions were kept the same for all the substrates in the experiments. The printed sample were analyzed in terms of L*, a*, b* values. The original L*a*b* values of target were compared with the test values. The results of the profile accuracy measurements were expressed as Root Mean Square Delta E employing the formula for color difference Eqn. 13 [74].

\[ \Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \]

The chart consisting of 406 patches were measured using an automated spectrophotometer (i1iO, X-Rite), and the data collected were used to calculate the ICC profile. The color gamut was calculated with CHROMiX ColorThink Pro 3.0.3. This software also was used as a tool for 3-D color gamut comparison at different L* values shown as Figure 60, 64, and 68. An ICC profile plotted in color space (XYZ) and volume in the space can be interpreted as the number of colors.
that are discernable within a tolerance of $\Delta E = \sqrt{3}$ [75], as shown in Table 21. Based on the profiles, the substrate or ink properties that can provide for better results can be predicted.

Table 21. The color gamut volumes of coated papers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Ink Coverage 400</th>
<th>Total Ink Coverage 300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.1</td>
<td>No.2</td>
</tr>
<tr>
<td>CW (g/m²)</td>
<td>26.8</td>
<td>25.3</td>
</tr>
<tr>
<td>Number (²)</td>
<td>578,000</td>
<td>530,000</td>
</tr>
</tbody>
</table>

(²) Color gamut volume number

Figure 60. The 2-dimensional color volumes of different ink coverage, left (400) and right (300).

The results of PPS porosity (Figure 58) correlated with the color gamut volumes (color reproduction, Table 22 and Figure 60), but a consistent relationship between PPS porosity and color gamut number could not be obtained experimentally. In case of porous pigment coating, the intra-pore volume of silica pigment functioned as a variable that gives us complexity in correlation between porosity and color gamut volume.

Originally, ink absorption into a substrate is driven by capillary action, which is affected by pore size in the coating layer. Small pores separate the solvent from ink rather than pulling the whole ink down into the pores so that the rate of ink setting increases with the number of smaller pores [76]. However, PPS porosity did not give us enough detailed information such as pore size, size...
distribution, although an estimated capillary diameter could be obtained by converting PPS porosity to Darcy [77] permeability [78]. Mercury porosimetry is a useful tool to show the correlation between porosity and color reproduction [79].

As shown in Figure 61, a picking problem occurred due to low binder level (4.5 parts), so the amount of binder should be increased to avoid these problem.

6.4.2 The Effects of High Binder Level (The Second Group)

6.4.2.1 Coating Properties

The amount of binder was increased up to 24 parts, so the mixing of different particle shapes did not make as much difference at low shear viscosity, but the differences were clear at high shear viscosity as shown in Figure 62.
Figure 62. The low and high shear viscosity of higher binder level (24 parts).

Figure 63. The physical properties of uncalendered (left) calendered (right) coated paper.

The range of coat weights obtained was from 13 to 18 g/m². No.3 coating showed good gloss and smoothness while No.2 coating showed poor gloss and smoothness in Figure 63.

The all silica coating (No.1) showed the lowest PPS porosity, while the high solid coating (No.3) showed the highest PPS porosity after calendering. However, the PPS porosity did not provide a
correlation between porosity and color gamut volume number (Table 22). PPS porosity (ml/min) is a measure of air flow (permeability) [78], but not a measure of porosity (percent pore volume). Therefore, a large number of small connected pores can hold a large volume, but PPS porosity (permeability) will be low.

6.4.2.2 Color Reproduction

When the binder level was increased, the inter-pore volume was decreased. Therefore, the all-silica coating having more intra-pore volume provided more favorable conditions for printing. The color gamut volume of the all-silica coating was much different from the other two coatings, Table 22.

Table 22. The color gamut volumes of coated papers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Ink Coverage 400</th>
<th>Total Ink Coverage 300</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>No.2</td>
<td>No.3</td>
</tr>
<tr>
<td>CW (g/m²)</td>
<td>16</td>
<td>15.3</td>
</tr>
<tr>
<td>Number</td>
<td>629,000</td>
<td>569,000</td>
</tr>
<tr>
<td>No.1</td>
<td>No.2</td>
<td>No.3</td>
</tr>
<tr>
<td>CW (g/m²)</td>
<td>13.2</td>
<td>13.9</td>
</tr>
<tr>
<td>Number</td>
<td>607,000</td>
<td>580,000</td>
</tr>
</tbody>
</table>

Figure 64. The 2-dimensional color volumes of different ink coverage, left (400) and right (300).
Figure 65. Printed patches, No.1 (left), No.2 (middle), No.3 (right) respectively.

As shown Figure 65, picking did not occur at the 24 parts binder level, but ink bleeding occurred, which was caused by the clogging of pores. To avoid this problem, the amount of binder should be decreased. For better inkjet printability, enough pore spaces should exist in the coating layer, while maintaining binder strength.

6.4.3 The Effects of Porous Pigment on Ink-Jet Printing (The Third Group)

6.4.3.1 Coating Properties
Figure 66. The low and high shear viscosity of coatings compared with low and high binder demand coatings.

In Figure 66, the low and high shear viscosities obtained from the coatings formulated with 4.5, 10, and 24 parts binders are shown. Coating (No.1, 10 parts) replaced by 80 parts carbonate demonstrated the maximum packing volume at low and high shear rates as mentioned previously [36]. At high shear rates, the behavior of all of silica coating (No.2, 10 parts) was similar to high solid coating (No.3, 24 parts) which was replaced by 30 parts carbonate.

Figure 67. The physical properties of uncalendered (left) calendered (right) coated paper.
Small particle size of silica (d50 = 225nm) affected gloss and roughness as shown in Figure 67. The brightness of all silica coating (No.2, 10 parts) was clearly higher than the maximum packing coating, due to its light scattering in the bulky coating layer. A structured pigment coating led to better coverage and more porosity, a bulkier coating, but rheological problems occurred as shown in Figures 66 and 67.

**6.4.3.2 Color Reproduction**

In view of the results so far achieved, structured pigment coating proved good color reproduction while the maximum packing coating showed poor color reproduction, Table 23.

**Table 23. The color gamut volumes of coated papers.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Ink Coverage 400</th>
<th>Total Ink Coverage 300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.1</td>
<td>No.2</td>
</tr>
<tr>
<td>CW (g/m²)</td>
<td>16.5</td>
<td>15.7</td>
</tr>
<tr>
<td>Number</td>
<td>382,000</td>
<td>644,000</td>
</tr>
</tbody>
</table>

*Figure 68. 3-dimensional color gamut volumes of different ink coverage, left (400) and right (300) wire frame volume (No.2) vs. solid volume (No.1).*
The 4.5 parts binder level led to picking problems and ink bleeding occurred at 24 parts level. However, the structured pigment coating did not have picking and bleeding problems at the 10 parts binder level, as shown in Figure 69.

The all silica coating (No. 8) demonstrated the best performance (Table 24), but there are limitations such as solids level, rheology, and cost. The faster immobilization solids resulted in good fiber coverage and coating smoothness, so the high solid coating using carbonate performed similarly to the all silica coating for ink holdout.

Table 24. The results of preliminary experiments.

<table>
<thead>
<tr>
<th>Group</th>
<th>Dry part per 100 parts pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
</tr>
<tr>
<td>#</td>
<td>1</td>
</tr>
<tr>
<td>Silica</td>
<td>100</td>
</tr>
<tr>
<td>Carbonate</td>
<td>30</td>
</tr>
<tr>
<td>PVOH</td>
<td>4.5</td>
</tr>
<tr>
<td>Cost</td>
<td>Low binder level</td>
</tr>
<tr>
<td>Color Reproduction</td>
<td>Picking Problem</td>
</tr>
<tr>
<td>Solid, %</td>
<td>30</td>
</tr>
</tbody>
</table>
6.5 CLC (Cylindrical Lab Coater) TRIAL

Table 25. The coating formulations for CLC trial.

<table>
<thead>
<tr>
<th></th>
<th>Dry parts per 100 Parts Pigment</th>
<th>Optional</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base</td>
<td>Optional</td>
</tr>
<tr>
<td>No.1</td>
<td>No.2</td>
<td>No.3</td>
</tr>
<tr>
<td>Silica</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCC</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Selvol 205 PVOH</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Poly-DADMAC</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>CW-C PVOH (+)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>CW-A PVOH (+++)</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>CW-B PVOH (++)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Selvol 523 PVOH</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Solid, %</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>pH</td>
<td>10.0</td>
<td>9.5</td>
</tr>
<tr>
<td>Brookfield (mPa-s), 20 rpm</td>
<td>320</td>
<td>400</td>
</tr>
</tbody>
</table>

The best color reproduction was found for the No. 8 coating (Table 24), so the coating formulations experimental design (Table 25) was based on the No. 8 coating. Poly-DADMAC helps to attach the anionic pigments in the ink to the coating surface, so the poly-DADMAC was used in both commercial 205 and 523 PVOH for that purpose. The performance of the fixative was compared with new-copolymers at the same amount of binder level.

Generally, silica grades are excluded in modern hybrid printing presses, because it is rather poorly applicable to printing processes except ink jet, so other lower-cost types of coating are being sought to replace the silica grades. Based on preliminary experiments, high solids coating (solid 35%, ratio 7:3) performed an alternative for better holdout, so the high solids coating was selected for
testing on the CLC. Finally, Selvol 523 PVOH was to be excluded in the optional coating formulations due to its poor rheology (high viscosity).

In the CLC trial, coating formulations as shown Table 25 were conducted. Actually, all 30% solid coatings (except No. 7) were targeted, but No. 2 and No. 3 coatings were very thick due to flocculation, so the coatings had to be diluted down to 27% to run on the CLC.

Originally, CW-A PVOH, which was the highest charge density among the three new co-polymers, was designed to mix with silica (CAB-O-SPERSE® PG001), but the coating was like cement after makedown. Therefore, the anionic silica pigment had to be replaced with a cationic pigment (Omyajet® 5010). The cationic pigment was an aqueous slurry of high surface area modified calcium carbonate for premium inkjet printability. No flocculation occurred during makedown the coating.

Silica pigments (PG 001) were dispersed with anionic surfactant, so the order of addition was important to prevent the flocculation of the pigments with cationic polymers. All pigment slurries were slowly added into cationic PVOH solutions and especially Poly-DADMAC (20 wt. % in H₂O, 40903-Aldrich), which were diluted to 10%, by carefully dropping into coatings to avoid the flocculation for long times.
6.5.1 Materials

6.5.1.1 Pigments

Table 26. The physical properties of pigments and binders (All data given by manufactures).

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade Name</th>
<th>Solids, %</th>
<th>Density, g/cc</th>
<th>Surface Area, m²/g</th>
<th>Particle size, nm</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>CAB-O-SPERSE® PG001</td>
<td>Anionic dispersed slurry, 30%</td>
<td>1.2 (Bulk)</td>
<td>90</td>
<td>225</td>
<td>11.1</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>HydroCarb®90</td>
<td>Powder</td>
<td>2.7</td>
<td>8 ~11</td>
<td>700</td>
<td>10.4</td>
</tr>
<tr>
<td>Modified Calcium Carbonate (MCC)</td>
<td>Omyajet® 5010</td>
<td>Cationic dispersed slurry, 50 %</td>
<td>1.4 (Bulk)</td>
<td>40</td>
<td>2000</td>
<td>8.0</td>
</tr>
</tbody>
</table>

As mentioned previously, the pore volume of MCC was calculated as shown below. According to data sheet of manufacture [80], MCC consists of 70% structured calcium minerals, 20% calcium silicate, and 10% amorphous silica, so the density of MMC is assumed to be the same as calcium carbonate (2.7 g/cc).

For Omyajet® 5010, 40 m²/g (surface area of porous MCC) × 2.7 g/cc (density of non-porous CaCO₃) = 108 m²/cc.

If the particle is 100 nm in diameter and has 60 m²/cc, the diameter of primary particle with 108 m²/cc is 55.6 nm.

In Table 26, the effective density (bulk density) of MCC (1.4 g/cc) is given, so pore volume per unit mass (Vₚ) can be estimated as:

\[
\text{The effective density} = \frac{1}{\frac{1}{\text{density}_{\text{CaCO}_3}} + V_p}
\] [14]
where \( d_{\text{CaCO}_3} \), is the density of calcium carbonate (2.7 g/cc), the pore volume per unit mass \( V_p \) is 0.34 cc/g, which means about 48% of the entire volume of MCC.

When compared with CAB-O-SPERSE®PG001 (pore volume 55%), MCC has a slightly smaller pore volume (pore volume 48%), high solid (50%), and large particle size (2 microns).

### 6.5.1.2 Binders and Fixatives

Table 27. The physical and chemical properties of PVOHs.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Hydrolysis %</th>
<th>Viscosity (1) mPa-s</th>
<th>( M_W )</th>
<th>pH</th>
<th>Functional Group</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selvol 205</td>
<td>87 ~ 89</td>
<td>0 ~ 10</td>
<td>26,000 ~ 31,000</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selvol 523</td>
<td>87 ~ 89</td>
<td>30</td>
<td>87,500 ~ 92,500</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CW-C</td>
<td>98 ~ 98.8</td>
<td>10 ~ 20</td>
<td>15,000 ~ 24,000</td>
<td>7.5</td>
<td>Pyrrolidone</td>
<td>Neutral</td>
</tr>
<tr>
<td>CW-A</td>
<td>98 ~ 98.8</td>
<td>10 ~ 20</td>
<td>21,000 ~ 24,000</td>
<td>7.4</td>
<td>Amide</td>
<td>Slightly Cationic</td>
</tr>
<tr>
<td>CW-B</td>
<td>98 ~ 98.8</td>
<td>10 ~ 20</td>
<td>21,000 ~ 24,000</td>
<td>11.4</td>
<td>Amine</td>
<td>Cationic</td>
</tr>
<tr>
<td>Poly DADMAC</td>
<td></td>
<td>600 ~ 900 (2)</td>
<td>400,000 ~ 500,000</td>
<td>5.5</td>
<td>DADMAC</td>
<td>Cationic</td>
</tr>
</tbody>
</table>

All the above data were provided by manufactures, except for viscosity and pH.

(1) 4% ± 0.2 aqueous solution, 22 °C, 20 rpm

(2) 25 °C, 20 wt. % in H₂O

Co-monomers (Amine, Amide, Pyrrolidone) were copolymerized with vinyl acetate in which copolymers have different charge strengths as shown Table 27.

### 6.6 RESULTS AND DISCUSSIONS

#### 6.6.1 The Rheological Behaviors of Coatings Containing Cationic Polymers

Couette flow is driven by virtue of viscous drag forces acting on the fluid and the applied pressure gradient parallel to the plates [81], so the gap between the plates should be constant whenever measuring viscosity. A Brookfield viscometer is commonly used in industry, but if the gap is not constant, it is not an accurate measurement and just estimates the viscosity. For more information of fluid flows, all coating flows examined by using stress rheometer (AR-2000) and their behaviors are shown in Figure 70.
Figure 70. The low shear viscosities of No.2 and No.3 coating w or w/o P-DADMAC.

Table 28. The Brookfield viscosities (mPa·s) of No.2 and No.3 coating w or w/o P-DADMAC.

<table>
<thead>
<tr>
<th></th>
<th>No.2 30% P</th>
<th>No.3 30% P</th>
<th>No.2 27% P</th>
<th>No.3 27% P</th>
<th>No.2 30%</th>
<th>No.3 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 rpm</td>
<td>2600</td>
<td>11240</td>
<td>400</td>
<td>6100</td>
<td>320</td>
<td>5700</td>
</tr>
<tr>
<td>100 rpm</td>
<td>1140</td>
<td>3940</td>
<td>296</td>
<td>2500</td>
<td>200</td>
<td>1870</td>
</tr>
</tbody>
</table>

All coatings measured by No.4 spindle except No.3 30% D (No.5 spindle)

As mentioned above, P-DADMAC caused severe pigment flocculation, so the coatings were diluted down to 27% to run on the CLC. As shown Figure 70, 27% solid coatings containing P-DADMAC performed as rheological behaviors of 30% solid coatings without P-DADMAC, which could run on the CLC. Among all given coatings (Table 25), the coating containing Selvol 523
and P-DADMAC showed the highest Brookfield viscosity. Both Brookfield (Table 28) and Stress-rheometer (Figure 68) provided complementary information to analyze their performances.

![Low Shear Viscosity](image)

Figure 71. The low shear viscosities of all coatings.

As mentioned previously, carbonate (Ps: 700 nm) to silica (Ps: 225 nm) a ratio of 70:30 or 80:20 by weight makes for maximum packing volume, but this formulation loses significant color gamut volume as shown in Table 29. Instead of the formulation, silica to carbonate a ratio of 70:30 (No.8) does not lose much pore volume and shows the lowest viscous behaviors in Figure 71 and 74.

Cationic pigment (Omyajet 5010) coating containing CW-A PVOH indicated excellent rheological performance even though its solid is the highest (42%) in all coatings as shown Figure 71 and 74.
As illustrated in Figure 72, the increase in viscosity is a result of flocculation of negative and positive charged components. After a certain dose level of cationic polymer, the system is cationically stabilized and the viscosity drops back near to its original level. In reality, very viscous coatings containing P-DADMAC indicated the severe reduction of viscosity as shear rate increases in Figure 73.
Figure 73. The high shear viscosities of No.2 and No.3 coating w or w/o P-DADMAC.

Except for CW-A PVOH, co-polymers did not show any problems during preparing coating colors and running the CLC. On the other hand, the coating structure with Poly-DADMAC broke and flocculated repeatedly, which means the rheological performance is not good.
Figure 74. The high shear viscosities of all coatings.

While the shear viscosity of No. 8 coating was the lowest, that of No. 2 No.3 and No. 7 were the highest all the way through the shear range in Figure 74.
6.6.2 The Physical Properties of Coated Papers

Low Coat Weight g/m²

Porosity, sec/100 ml (304, 450)

Sheffield Roughness (12, 32)

Brightness (93, 98)

Max . . . . . . . No.1
No.2 . No.3
No.4 . No.5
No.6 . No.7
No.8

Mid Coat Weight g/m²

Porosity, sec/100 ml (378, 463)

Sheffield Roughness (13, 31)

Brightness (93, 98)
As shown in Figure 75, the results of 1 nip calendering, the Omyajet coating (No.5) was an outlier in all properties most likely because of its larger particle size (2 microns) [80]. In brightness, No.5 and No.8 showed lower values, so the better brightness seemed to be imparted by silicon dioxide rather than calcium carbonate at 457 nm. High solid coating No.7 (35%) showed good gloss, but another high solid coating No.5 (42%) did not, so the gloss and roughness properties of coated paper seemed likely to be dominated by particle size rather than rheological performance.
After 2 nips calendering, the differences between coated papers decreased as shown in Figure 76. While the gloss of Omyajet (No.5) was still the worst, all spots of other properties fall within a narrow range. Especially, in brightness, all spots fell between 94.5 and 95.5.

### 6.6.3 Color Reproduction

**Table 29. The color gamut volumes of all coated papers at different nip number.**

<table>
<thead>
<tr>
<th>Nip</th>
<th>No.1</th>
<th>No.2</th>
<th>No.3</th>
<th>No.4</th>
<th>No.5</th>
<th>No.6</th>
<th>No.7</th>
<th>No.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PASS</td>
<td>705000</td>
<td>690000</td>
<td>697000</td>
<td>680000</td>
<td>358000</td>
<td>673000</td>
<td>591000</td>
<td>568000</td>
</tr>
<tr>
<td>2 PASSES</td>
<td>713000</td>
<td>693000</td>
<td>728000</td>
<td>693000</td>
<td>393000</td>
<td>688000</td>
<td>597000</td>
<td>581000</td>
</tr>
</tbody>
</table>

Coat weight: 10 g/m²

Generally, the color gamut volumes slightly increased as nip number increased in Table 29. Coatings mixed with calcium carbonate (No.7 and No.8) clearly showed lower color gamut volumes. Carbonate did not help to increase color gamut volume because the replacement of silica
loses the pore volume in the coating. High surface area (41 m²/g) of Omyajet pigment did not work in color reproduction because of its large pore structure.

As porosity clearly decreased, the highly packed coating structure (2 passes) induced good printability in Table 29, which is caused by smaller capillary pores with lower permeability. It has been found experimentally that the rate of ink setting increases with decreasing pore size [76]. These facts suggest that small pores separate the solvent from ink rather than pulling the whole ink down, so that the rate of ink setting increases with smaller pores. However, large particles make large pore structure, so bulk inks more deeply penetrate into coated paper as shown in Figure 77. As the case stands, Omyajet coating (2 microns) showed the poorest printability in Table 29.

![Figure 77. The depiction of how pores may trap ink particles. Four main ingredients of a printing ink: pigment (colorant), binder (resin), solvent (oil or water), and additives [82].](image)

As shown in the Lucas-Washburn equation Eqn. 15, it can be stated that capillary penetration through a pore increases with increasing surface tension, pore size, and time, while it decreases with increasing contact angle and increasing ink viscosity [83]. However, this equation is derived by considering fully developed laminar flow in cylindrical capillary pores without applied external
force (no inertia term). It has shown many disagreements with experiments [84, 85]. Most printing inks are pigmented, high viscosity, and non-Newtonian fluids.

\[ l = \left( \frac{2 \gamma R \cos \theta}{4 \eta_d} \right)^{\frac{1}{2}} (t)^{\frac{1}{2}} \]  

[15]

where \( l \): Penetration length, \( \gamma \): Surface tension, \( R \): Capillary radius, \( \theta \): Contact angle, \( \eta_d \): Dynamic viscosity of the liquid, \( t \): Time, and \( \left( \frac{\gamma}{\eta} \right)^{\frac{1}{2}} \): the surface tension-to-viscosity ratio represents the speed of ink penetration into the substrate in inkjet printing.

### 6.6.4 Light Fastness

A spectrophotometer (i1iO, X-Rite) was used to determine the color gamut volume before samples were put into an Atlas fadometer. The fading chamber is equipped with an 1100-watt air cooled xenon arc lamp light source. They were submitted to 129,600 kJ/m\(^2\) of energy over 48 hours. This represents about 4.5 months (June) of daylight exposure in Florida [86].

**Table 30. The differences (%) of color gamut volumes of all coated papers after light fading, No.4: 2 passes.**

<table>
<thead>
<tr>
<th></th>
<th>No.1</th>
<th>No.2</th>
<th>No.3</th>
<th>No.4</th>
<th>No.5</th>
<th>No.6</th>
<th>No.7</th>
<th>No.8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before</strong></td>
<td>705000</td>
<td>690000</td>
<td>697000</td>
<td>693000</td>
<td>358000</td>
<td>673000</td>
<td>591000</td>
<td>568000</td>
</tr>
<tr>
<td><strong>After</strong></td>
<td>671000</td>
<td>666000</td>
<td>673000</td>
<td>666000</td>
<td>358000</td>
<td>652000</td>
<td>562000</td>
<td>547000</td>
</tr>
<tr>
<td><strong>Diff. %</strong></td>
<td>4.82</td>
<td>3.48</td>
<td>3.44</td>
<td>3.90</td>
<td>0.00</td>
<td>3.12</td>
<td>4.91</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Note - No.1, No.7 & 8 do not contain cationic polymers

As shown in Table 30, Poly-DADMAC and cationic copolymers worked effectively for fade resistance. Coated papers containing cationic functionality showed less than 4% difference in color gamut volume after light exposure. Based on fade test results, all cationic coating (No.5) containing large particles size was very stable for light fading. With regard to the chemical coated paper–ink interactions, ionic bonding between ink and coating was beneficial for light fastness.
6.6.5 Water Fastness

Coated papers faded by light were wetted in water by which a wet tissue distributed evenly with a roll. After being wet for 30 seconds, the coated papers were covered with another dry matte papers to absorb water left on the coated papers. Finally, all wet papers were dried for one minute and then placed in the conditioning room (23°C, 50% RH) for one day.

Table 31. The differences (%) of color gamut volumes of all coated papers after wetting. No.4: 2 passes

<table>
<thead>
<tr>
<th>No.</th>
<th>No.1</th>
<th>No.2</th>
<th>No.3</th>
<th>No.4</th>
<th>No.5</th>
<th>No.6</th>
<th>No.7</th>
<th>No.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>671000</td>
<td>666000</td>
<td>673000</td>
<td>666000</td>
<td>358000</td>
<td>652000</td>
<td>562000</td>
<td>547000</td>
</tr>
<tr>
<td>After</td>
<td>661000</td>
<td>621000</td>
<td>644000</td>
<td>645000</td>
<td>338000</td>
<td>607000</td>
<td>521000</td>
<td>477000</td>
</tr>
<tr>
<td>Diff. %</td>
<td>1.5</td>
<td>6.8</td>
<td>4.3</td>
<td>3.2</td>
<td>5.6</td>
<td>6.9</td>
<td>7.3</td>
<td>12.8</td>
</tr>
</tbody>
</table>

In Table 31, the coatings a high portion of carbonate proved to be poor for water fastness, which suggests coating composition has a major effect on water fastness. Overall, using cationic polymer helps the interaction between inks and coating for fastness, provided that the interacting coating component is insoluble in water.
6.7 CONCLUSIONS

The inkjet ink penetration speed depends on the binder level and pore volume in the coating layer. At high binder level (24 parts), this acted to close the nano-size pores and therefore slows down the ink penetration speed in the coating structure. The PVOH binder can allow diffusion of the inkjet liquid phase, and swells under the influence of the ink [87]. In the absence of picking problems, a low binder level is recommended to acquire pore volume. In replacement of pigment, a minimum viscosity was observed in mixtures of different sizes particles, but the print quality of coatings was not as good as all silica coatings, because the replacement loses intra pore volume. The structure of Omyajet coatings allowed the ink penetration into coated paper, since the coatings encourage whole inks to penetrate deeply into the coated paper.

The incorporation of amine functional polyvinyl alcohol with conventional silica pigment increased viscosity as a result of flocculation of positive and negative components. Cationic PVOHs are six times more expensive than conventional PVOHs, but their performances were not much superior to the conventional PVOHs.

Generally, the structure as well as chemical differences of coating layers determined the final inkjet print quality formation.
7. CONCLUSIONS

Conventional starch is rarely used as a sole binder. Instead, it is mostly used as a co-binder because of coating solids and viscosity. However, biobased latex can be used as a dry form and the viscosity is reduced by crosslinking. The biobased latex was used to affect the rheology and water retention properties of coating colors.

The unique characteristics of starch based latex binders were found to be attributed to the fact that they are made up of water-swollen internally crosslinked nanoparticles, which depending on their crosslink densities have varying degree of water swelling. Because the dispersions of biobased latex exist in the form of water-swollen nanoparticles, their effective solids be higher than their actual solids. The increase of the effective coating solids enables high solid coating resulting in excellent fiber coverage and coating smoothness.

Biobased latexes showed better dynamic water retention, while all synthetic latex systems gave poor water retention. In comparison to gravimetric water retention, coatings containing conventional starch indicated better static water retention, where it is speculated that hydrogen bonds easily occur between linear starch molecules and water molecules than for biobased latex under the static state. However, the biolatex be able to hold water longer than linear starch molecule under the dynamic state, so better dynamic water retention properties are observed in biobased latexes than relative to conventional starch.

A serum phase replacement apparatus separated both free and adsorbed low molecular weight solubles and crosslinked small starch particles from starch nanoparticle dispersions. The results obtained from the serum replacement experiment provided information on the amounts of replaced starch molecules and particles. The swell ratios of filtrates elucidated the components of starch.
latex mixed with low and high linear and branched polymer molecules and particles. The
dispersions of starch nanoparticles contain linear or branched starch molecules as well as starch
particles, so these associate with each other by hydrogen bonding during measurement.
Conclusively, uniform particle size could not be obtained through a number of experiments. In the
CLC trial, the deformation of solid SB latex occurred due to plasticity during calendering, which
improved the gloss of all SB latex coated paper, but the roughness caused by shrinkage occurred
regardless of the better rheological performance and water retention in coatings containing starch.

Silica grades are commonly used for ink-jet coatings since they provide a large surface area for
quick ink absorption. However, the silica grades are quite expensive as well as having difficulty
in runnability. Alternatively, calcium carbonate was used to partially replaced silica pigment in an
effort to balance coating solids and viscosity.

Since the effective volume of the porous silica is larger than that of non-porous pigment, a mixtures
of calcium carbonate increased coating solid and decreased the viscosity. However, the print
quality of coatings was not as good as all silica coatings, because the replacement loses intra pore
volume. The incorporation of amine functional polyvinyl alcohol with conventional silica pigment
increased viscosity as a result of flocculation of positive and negative components. Cationic
PVOHs are six times more expensive than conventional PVOH, but their performances were not
far superior to the conventional PVOH.
8. REFERENCES


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