


# Starch-based nanoparticles as a replacement for synthetic latex: A comprehensive assessment of printability and colorimetric characteristics

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## Abstract

The papermaking, packaging, and printing industry are actively seeking sustainable material alternatives to address growing concerns about environmental consciousness and finite resources. Synthetic latex, a frequently utilized binder in paper coating formulations, present difficulties due to their dependence on fossil fuel resources and their reduced recyclability in comparison to eco-friendly sustainable products. In this study, synthetic latex was replaced with a starch-based nanoparticle (starch NP) binder at a 1:1 ratio in a coating formulation. Printing trials to assess colorimetric characteristics was made using electrophotography (EP) printing, given the current upward trajectory and expansion of EP technology into the label, packaging, and folding carton sectors. The in-depth investigations reveal that incorporating starch NP binder result in improved optical, color, and dot characteristics. Moreover, it maintains consistent and comparable coefficients of friction. Partial replacement of synthetic latex with the starch NP binder yields significant enhancements in surface roughness and text quality. Importantly, the starch NP binder not only improves the dielectric relaxation properties of the paper and enhances toner transfer but also accelerates the distribution of the electrical field compared to synthetic latex, optimizing toner transfer and thereby enhancing color gamut volume. The study demonstrates that employing the starch NP binder leads to substantial improvements in colorimetric performance without any drawbacks in EP printing, making it highly advantageous to replace 50% of the synthetic binder.

## KEYWORDS

binder, coating, color, electrophotography, latex, nanoparticle, printing, starch, styrene, toner

## 1 | INTRODUCTION

There is a growing demand for sustainable materials in papermaking, packaging, and printing industries due to heightened environmental awareness and the diminishing availability of fossil resources. In response to these requirements, there has been substantial efforts in research by manufacturers to develop eco-friendly materials. These materials encompass paper, recycled plastics, inks, coatings, and cleaning solutions all aimed at addressing the concerns.<sup>1,2</sup> To date, considerable effort has been made to adopt for cleaner manufacturing techniques to minimize the reliance on fossil resources, reduce carbon emissions, as well as reduce and eliminate harmful toxic materials.<sup>3,4</sup>

In order to replace the fossil compounds like formaldehyde and styrene that are linked to health and safety problems, green chemistry approaches have been developed to manufacture biodegradable and renewable components and chemicals. In paper coating applications, styrene-based synthetic latex chemicals are widely used as a coating binder to improve printability and surface properties and to impart functionality.<sup>4-6</sup> However, styrene-based synthetic latex like styrene butadiene (SB), polyvinyl acetate, and styrene acrylics are derived from petroleum, making them environmentally unfriendly and subject to price instability due to fluctuations in oil prices.<sup>5</sup> Despite their ability to enhance paper properties and mechanical strength in coating applications, they diminish recyclability and may lead to issues like “white pitch” deposits on calender rolls.<sup>5</sup> A renewable engineered starch NP binder, EcoSphere<sup>®</sup> Biolatex<sup>™</sup>, was developed in the early 2000's to substitute styrene-based binders at 25% to 80% in coating formulations.<sup>5,7-9</sup> In previous studies, starch NP binder was replaced the synthetic latex at 1:1 ratio in a curtain coating application of coated linerboard. The effect was examined on rheology, curtain stability, coat weight, coating surface tension (ST), brightness, gloss and IGT dry pick strength.<sup>9</sup> This study presented that the starch NP binder notably improved rheological features and curtain stability. The study also showed that ST of the formulation including starch NP was less than 40 mN/m which provided superior brightness, gloss, and IGT dry pick strength compared to the formulation that includes synthetic latex.<sup>9</sup>

In another study, a paper mill trial was conducted where synthetic latex was replaced by starch NP binder at the same 1:1 ratio.<sup>3</sup> The study presented the effect of starch NP binder on structural properties including basis weight, thickness, smoothness, wettability, porosity, compressibility and the mechanical properties of burst, tear, tensile strength and elongation. In general, coating binders assist pigment particles to bind to each other and

to the paper surface, but also affect the coating rheology, coater runnability, drying performance as well as structural, optical, mechanical, and printability properties of paper.<sup>3</sup> The study concluded that the synthetic latex binder can be replaced at 1:1 ratio by starch NP without compromising any mechanical and structural properties. The study also found that using starch NP binder resulted in paper with the same thickness, but lighter basis weight compared to synthetic latex, while maintaining equal or superior mechanical properties. Consequently, reducing the basis weight while maintaining identical mechanical properties presumably leads to cost savings in transportation for the final products and decreases carbon footprint generation. This is achieved without compromising the uniformity of paper thickness and surface quality.<sup>3</sup>

Building upon the previously mentioned research, the objective of this study is to assess the printability and color characteristics of coated papers that includes starch NP binder at 1:1 ratio in the digital electrophotography (EP) printing process, in comparison to synthetic latex. Starch replacement has been demonstrated to offer environmental benefits without compromising structural properties of the paper. However, the previous research has not addressed the question of what happens when the ink hits the paper. The choice of EP printing technology was made due to its significant presence and expansion in the market. It has even been observed to draw business away from other sectors such as offset, flexography, and gravure, owing to the industry's shift towards digital printing. Digital printing technologies provide a faster time-to-market, eliminate the need for platemaking and, consequently, the use of makeready chemicals in platemaking production. Additionally, they reduce press setup times and paper wastage by eliminating the registration requirement associated with printing technologies that utilize plates for each color and enhance sales rates through personalization and variable data printing capabilities.<sup>10,11</sup> Since the mid-1990s, there is a notable shift in label production from traditional technologies to EP printing that involves fusing dry toner onto substrates and delivers consistent, high print quality across a diverse range of materials.<sup>12</sup> Over the past two decades, EP printing has extended its reach into the packaging and folding carton industries.<sup>13,14</sup> According to market analysis, EP printing in the packaging sector is projected to undergo an 8% compound annual growth rate in the next decade, with expectations of an increase to \$45 billion by 2032.<sup>2</sup>

In EP printing technologies, toner ink is made to precise ingredients that include a pigment colorant, a charge control agent (CCA), polymer resin and additives. Depending on the manufacturer, toner particles are either charged with positive (+) or negative (−) electrical charge and attach to the discharged image areas on the

photoconductor drum.<sup>14</sup> Toner is transferred to the substrate, which possesses special properties to accept the toner from the photoconductor drum, and bonds to the paper fiber primarily through electrostatic attraction, alongside molecular interactive forces.<sup>15–17</sup> In the fusing unit, heat is applied to the toner on the paper either by contact using hot fuser rolls, transfix, or by non-contact radiation (flashlight, IR) reaching a typical surface temperature of 150–220°C, often together with applied pressure, for example, in the nip between heated rolls.<sup>17,18</sup> Because the toner is transferred to the substrate using electrostatic charges, the moisture content of substrates used in EP printing becomes critical, as the moisture level affects the dielectric properties of the substrates.<sup>14,19</sup> In general, the moisture level must be low enough to maintain the paper dielectric property while holding an adequate charge to allow the toner to transfer. In principle, the substrate must have a high conductivity to accept the charge quickly.<sup>20</sup> However, if the paper conductivity is too high or too low, it will not result in a uniform toner transfer. Additionally, if the moisture level is too low, it leads to excessive electrostatic charge that interferes with transport. In the case of too high moisture, the substrate may not be able to hold sufficient charge, resulting in poor toner transfer. An adequate amount of paper moisture is also desired for dimensional stability. As high heat is used to fuse the toner to the paper, moisture evaporation can result in curling that leads to paper jams.<sup>20</sup> The impact of heat on the substrates varies depending on the type or basis weight of paper.<sup>21</sup>

In addition to moisture and electrical property of the paper, a uniformity of paper thickness and basis weight is also desired for reliable sheet feeding during EP printing due to the frictional properties of papers. Other relevant parameters to consider for EP printing include paper roughness, surface chemistry, and surface energy.<sup>19</sup> As a rule, low roughness contributes to better toner adhesion. Too rough or too smooth paper surfaces are found to cause poor toner transfer during printing or feeding problems during transportation of the substrate within the press, respectively.<sup>14</sup> To avoid these issues, a minimum value of coefficient of friction (COF) is suggested as the COF ratio gets closer to zero, the surface roughness of a material decreases.<sup>22</sup> Previous studies have shown that fused toner follows the surface roughness and conforms to the frequency of the surface.<sup>23</sup> Roughness, important to print mottle in most printing technologies, should be measured to assess substrates suitability for EP printing. Print mottle, the uniformity of optical density, can also be measured by image analysis under low angle light.<sup>24</sup> In addition to mottle, coverage and graininess are also employed to assess the quality of ink layer homogeneity.

Coverage property is a measure of the average size of pinholes excluding any smaller than the resolution of the human eyes. Graininess is the standard deviation of densities.

Paper wettability is a function of surface roughness and surface chemistry that affects ink spreading and leveling behavior during printing, therefore affecting toner adhesion. The adhesion and fusing qualities are affected by not only the toner and fusing process, but also by the porous and permeable structure of papers, in which the toner partly penetrates the paper.<sup>17,19</sup> Achieving high print quality in printing process primarily involves precise color reproduction, such as density and CIE  $L^*a^*b^*$ . Nevertheless, it is imperative to recognize that there exist other properties that are often overlooked but substantially contribute to the overall perception of quality. These parameters like text clarity and precision, micro and macro uniformity (e.g., addressing issues like mottle, coverage, and graininess), effective resolution (in terms of reproducing fine details), the presence of background artifacts (unintended toner deposits in unprinted regions), as well as the various attributes associated with dots (including attributes like area, diameter, surface area, circularity, perimeter, and dot void factors).<sup>25</sup> To attain objective results, this research utilized non-destructive image analysis to quantify color and dot quality, in conjunction with an assessment of the optical characteristics of paper. These attributes encompass the measurement of optical brightening agent (OBA) levels, whiteness, yellowness, brightness, opacity, and CIE  $L^*a^*b^*$  values.

## 2 | MATERIALS AND METHODS

### 2.1 | Coating formulation

The coating formulation includes ground calcium carbonate (GCC) and clay as coating pigments. Synthetic latex binder in the control group was replaced at a 1:1 ratio by the starch NP binder (EcoSphere 2330, EcoSynthetix: Burlington, Canada) as the experimental group, which is formed from a high amylopectin-based starch (>95% amylopectin, <5% amylose).<sup>26</sup> Detailed information regarding all the coating ingredients and their quantities can be found in our previous publication.<sup>3</sup> The coating formulation was applied onto 90 gsm (bone dry) wood-free base paper surface at average of 12 gsm coat weight using a bent blade coater operated at 3000 ft/min. The paper samples provided by EcoSynthetix were subjected to the coating process, followed by calendaring at an unspecified paper mill.

## 2.2 | Moisture content analysis

A Mettler Toledo HR83 moisture analyzer balance was used to measure the moisture content of coated paper samples. The scale was tarred before each measurement, and 1 g of each sample was placed in an aluminum tray. The apparatus weighed the sample, heated it to 105°C, and weighed the sample again after sample loss of mass had plateaued. The apparatus then calculated the moisture content. Three data points were collected for each sample.

## 2.3 | Dielectric relaxation

A QEA DRA-2000L dielectric relaxation analysis system (Quality Engineering Associates, Inc.: Acton, MA) was used to analyze samples for EP printing application. The voltage (V) response was measured for time duration of 100 s (sec).

## 2.4 | Surface analysis and COF of paper

A MultiMode 8-HR atomic force microscope (AFM) with Nanoscope Analysis software (Bruker MultiMode 8-HR: Billerica, MA) and a 3D non-contact optical profilometry (Nanovea Inc.: Irvine, CA) were used for surface analysis of coated paper samples. In AFM measurements, three data points were collected for each sample. The tip of the AFM probe scans the surface of a sample, measuring the height variations at the nanometer scale. Roughness average (Ra) is calculated by averaging the absolute values of these height deviations over a defined sampling

length, which gives a measure of the overall roughness of the surface. 3D height images were plotted to show relative roughness. In 3D optical interferometry, three data points were collected for each sample for the arithmetical mean height (Sa) measurement. Sa represents the average absolute height deviation of the surface from a reference plane within the evaluation area. Surface energy of samples was measured using an FTA200 goniometer video system (First Ten Angstrom; Portsmouth, VA) as described elsewhere.<sup>3</sup> The kinetic and dynamic COF of samples were measured using a COF tester (TMI Testing Machines Inc.: New Castle, DE) based on TAPPI T-549. Three data points were collected for each sample.

## 2.5 | Printing, color reproduction and print quality analysis

A custom test page that includes 400 color patches (Figure 1) was printed on the coated paper samples using a dry EP toner printing press (Konica Minolta, Bizhub PRESS C1070). The press specifications for media include a paper weight range of 106–135 g/m<sup>2</sup>, coated-GL paper type, CMYK color mode with black detection and composite overprint activated, Best image quality at 1200 dpi resolution, halftone simulation disabled, normal brightness set at 100%, Screen 1 for image halftone screening, toner reduction turned off, and text/graphics halftone screening as Same as image. Three data points were collected for each sample. ICC profiles were created using an i1 Profile Maker software (X-Rite: Grand Rapids, MI; version 3.6.1), i1Pro (X-Rite, Rev E, Part No: EO2-XR-ULZW) and iliO 2 automated scanning table (X-Rite). ICC profile configurations consisted of device setup using

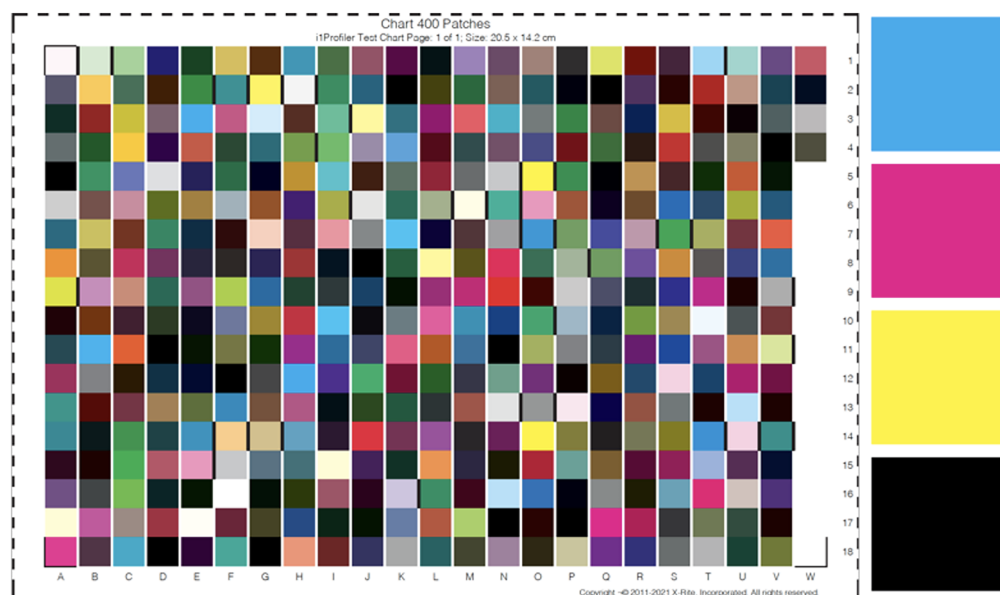


FIGURE 1 i1 Profiler test chart containing 400 different color and CMYK solid patches.

iliO 2, measurement mode set to single scan (MO), and CIE illuminant D50. The color gamut volume sizes determined using ICC profiles within ColorThink Pro 3.0.9 software (Chromix: Seattle, WA). Ink density for the cyan, magenta, yellow and key black (CMYK) solid patches were taken at five data points, while the delta E ( $\Delta E$ ) color differences were measured at two data points using a SpectroDens (Techkon: Danvers, MA) with M1, D50 illuminant and the 2° standard observer functions. The optical properties of paper including optical brightening agent (OBA) ( $\Delta b^*$  between M1 and M2 measurements), whiteness (based on E 313), yellowness (based on E 313), brightness (based on TAPPI 452), opacity and CIE  $L^*a^*b^*$  were measured with the same SpectroDens using the same M1, D50 illuminant and the 2° standard observer functions, with 27 data points. Mottle, coverage, graininess and dot attributes were measured using a BetaFlex Image Analyzer and FlexoEyePlus software (BetaIndustries: Carlstadt, NJ) from the CMYK solid patches (Figure 1), with three data points per color. Satellites and line raggedness were measured once using QEA PIAS-IIDF (Quality Engineering Associates, Inc.: Acton, MA).

## 2.6 | Cross section imaging

A modified Microm HM 355 S rotary microtome was used to cut cross sections of each sample. The modified apparatus has the blade mounted to the specimen holder and the sample mounted to the stage mount. A 3 mm × 15 mm section was cut from each sample and taped to an acrylic strip adhered to the stage mount. From this section, several cross sections measuring 4 μm were cut and placed on a glass microscope slide and mounted with a Stoddard solvent. Samples were imaged with a Canon EOS 5D Mark II Digital Single Lens Reflex camera mounted to an Olympus AX70 compound microscope with a 20× lens and 7.5× objective. Multiple images of each cross section were taken at descending planes of focus and stacked using Zerene Stacker software.

## 2.7 | Statistical analysis

The data evaluated using two-sample independent *t*-test using JMP statistical software to obtain *p*-values. The confidence level was set to  $\alpha = 0.05$  (95%). A *p*-value less than 0.05 indicates that a significant difference exists between the samples, while a value over 0.05 indicates that the difference is not significant.

## 3 | RESULTS AND DISCUSSION

The key factors among paper properties that significantly impact print quality and the transfer of toner between the photoconductor drum and paper include electrical properties of paper, moisture content, and surface roughness. The moisture content of the coated papers including synthetic latex and starch NP binder were found to be 4.4% ±0.3 and 4.2% ±0.1, respectively, indicating that both samples have an adequate amount of moisture content for the EP printability.<sup>27</sup>

In an EP system, the transfer system consists of a photoreceptor, toner layer, air gap, receiving surface (paper or a transfer tape), and a bias voltage (polarizing voltage) provided by a corona source. In order to maximize toner transfer on the coating efficiently, the electrical field (voltage, V) on the receiving substrate must be minimized (relaxed). In general, the electrical field evaluated by the ASTM D4949-89 standard for the bulk and surface resistivity of paper. However, this standard found to not giving thorough insights into paper performance in EP printing applications.<sup>24</sup> A more recent development in gaining a deeper understanding of the EP printing process is demonstrated as the introduction of the electrostatic charge depletion technique (Figure 2).<sup>28</sup> In this method, the electrical load applied in EP printing presses can be simulated and visualized using a computerized scanner.<sup>28</sup> The depletion electrostatic charges of the coated papers are found to be sufficient via the open circuit measurement technique using the scanner (Figure 3).<sup>24</sup> The plot depicts that the electrical field on the coated paper including starch NP binder is lower than the synthetic latex, indicating an improvement in toner transfer. The enhanced toner transfer can be tracked by toner film thickness, printed toner weight<sup>18,29</sup> as well as increase in color gamut.<sup>10</sup> The printing analysis suggest that starch NP binder may promote generating a larger color gamut volume and increase number of color tones printed. The polarization response of paper varies over time as a result of dielectric relaxation when it is exposed to an electric field for printing. This electric field induces a polarization response in the paper, which causes paper to become charged and affects the distribution of the electric field in the paper. The polarization has impact on how the paper's electric field is distributed, which in turn impacts how well toner is transferred. The dielectric properties of paper are influenced by a number of factors, including its composition, structure, moisture content, and temperature.

The results of surface energy analysis are given in Tables 1 and 2. Surface energy helps distinguish between the dispersive and polar components of a solid's surface

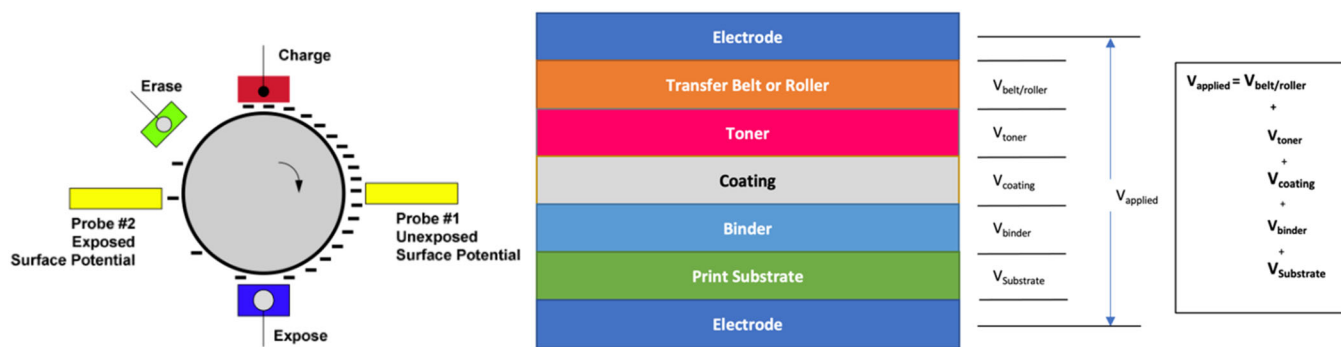


FIGURE 2 Schematic of a toner-transfer sub-system to illustrate principle of dielectric relaxation analysis. Source: QEA.

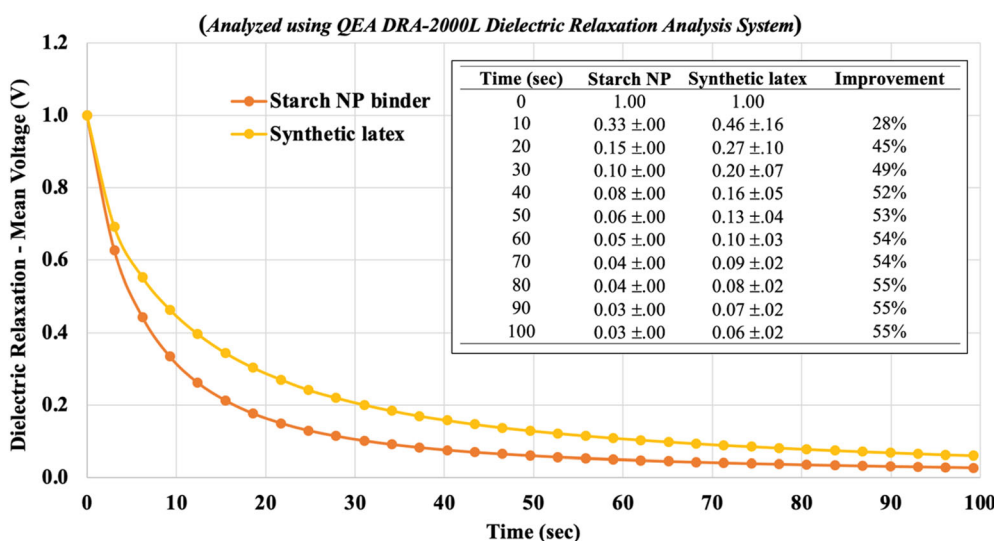


FIGURE 3 Dielectric relaxation of coated papers including starch NP binder and synthetic latex.

Test liquids	Surface tension (mN/m)	Contact angle (°)	
		Synthetic latex	Starch NP binder
DI	72.14 ± 0.59	52.76 ± 0.16	47.19 ± 0.17
MI	48.36 ± 0.38	30.24 ± 1.00	26.28 ± 1.34

TABLE 1 Surface tension and contact angle of test liquids on coated papers.

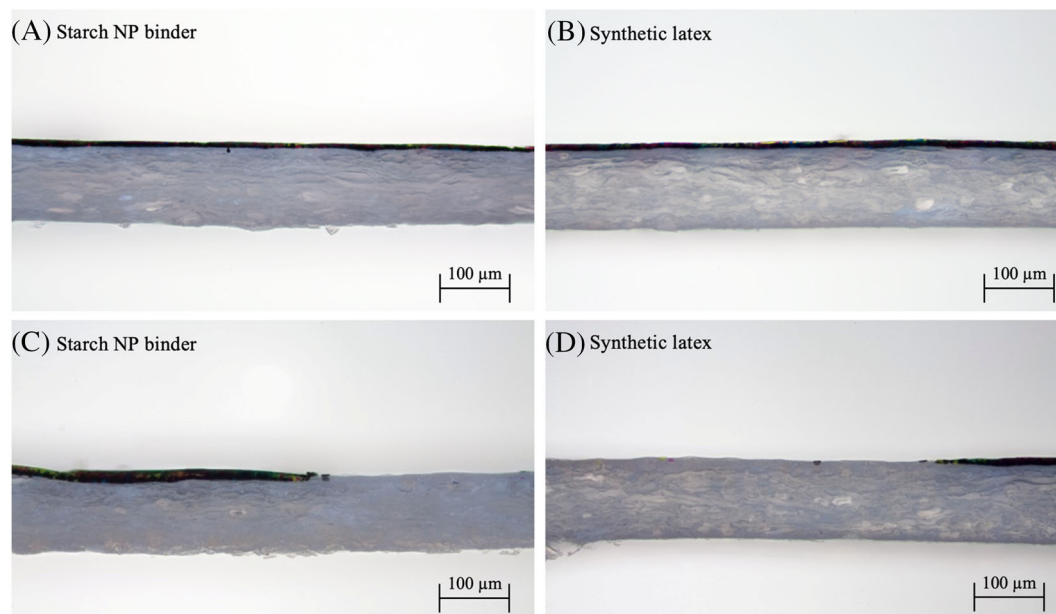
	$\gamma$ -total (mN/m)	$\gamma$ -dispersive (mN/m)	$\gamma$ -polar (mN/m)
Synthetic latex	51.51 ± 3.38	31.62 ± 2.07	19.89 ± 1.31
Starch NP binder	55.20 ± 3.71	32.01 ± 2.15	23.19 ± 1.56

TABLE 2 Surface energy of coated samples.

energy.<sup>30</sup> The dispersive component is created by London dispersion forces, while polar part of surface energy arises from polar interactions, such as dipole–dipole interactions and hydrogen bonding. Table 2 shows that the polar component is increased by 17% with the addition of starch NP binder, which indicates that it promotes hydrogen bonding.<sup>31</sup> The increase in polar level supports the polarization response of papers and leads to increased

toner transfer and color gamut volume for papers including starch NP binder.

Other than moisture content and electrical property of paper, thickness and basis weight are reported to be desired for reliable sheet feeding during EP printing.<sup>14,17</sup> The fused toner layer on the substrate, including the edge, of starch NP binder and synthetic latex were shown in Figure 4. The thickness (z-direction) is reported to be

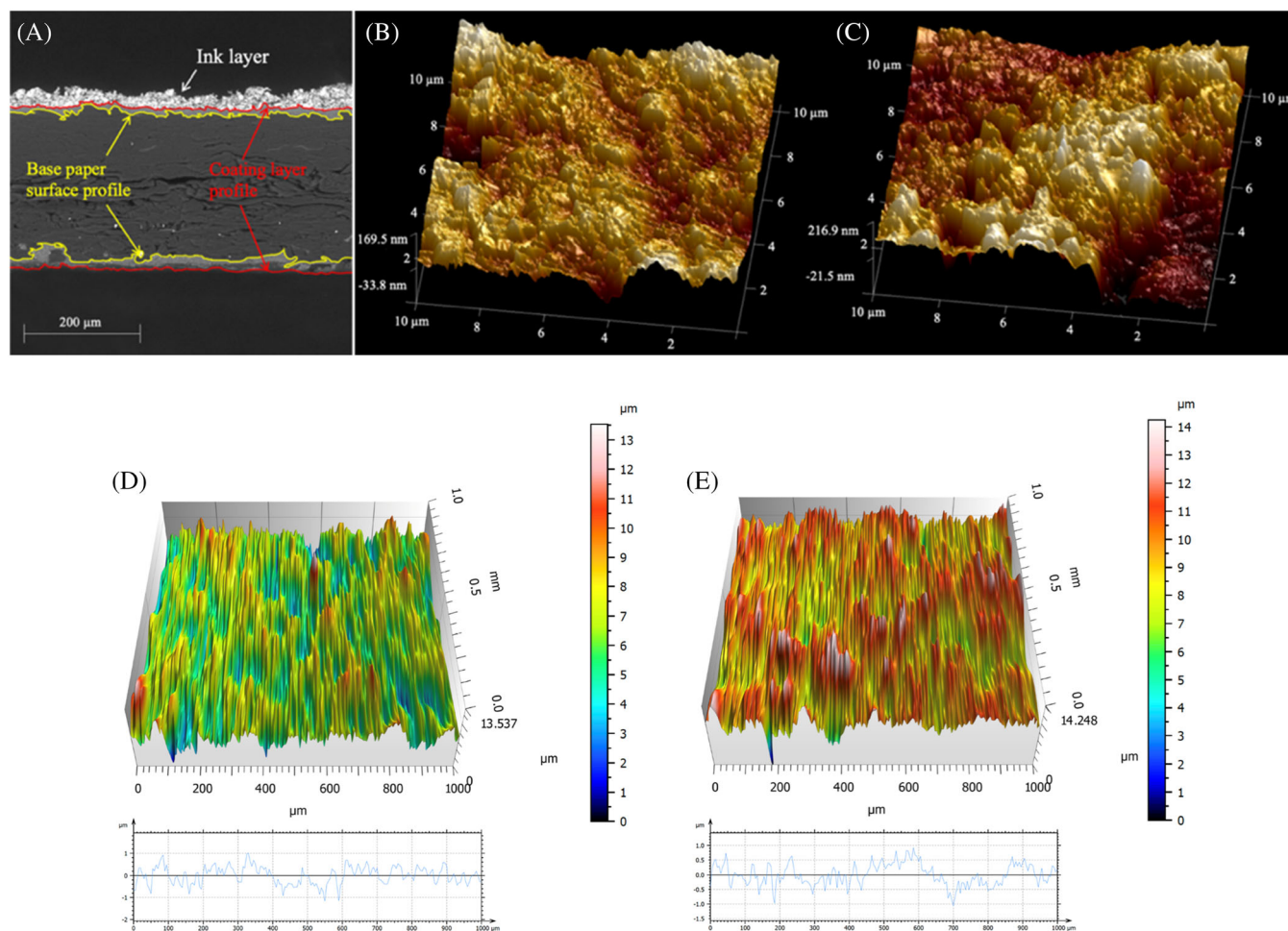


**FIGURE 4** Z-direction (cross section): Fused toner layer on the surface of coated paper including (A) starch NP and (B) synthetic latex. The edge of fused toner layer on coated paper including (C) starch NP and (D) synthetic latex.

$110 \pm 2 \mu\text{m}$  and  $109 \pm 3 \mu\text{m}$  for the coated papers including synthetic latex and starch NP binder, respectively. The thickness of the samples were nearly identical within statistical confidence limits ( $p$ : 0.2232). The slight difference in the z-direction (thickness) can be observed visually in Figure 4. For the basis weight, the results are in line with the previous study where the basis weight of the coated paper including synthetic latex and starch NP binder found to be  $121 \pm 1 \text{ g/m}^2$  and  $118 \pm 1 \text{ g/m}^2$  ( $p$ : 0.0002\*), indicating the papers including starch NP are lighter than papers including synthetic latex.<sup>3</sup>

The surface roughness of paper represents a critical parameter that significantly influence toner transfer. In EP printing, the utilization of coated papers typically leads to a significant enhancement in details, including raster dots and edge sharpness.<sup>32</sup> The applied coating effectively fills the void areas or hollows on the surface of the base paper, thereby reducing not only surface roughness (as depicted in Figure 5A) but also improving color rendition, tone, and printing quality.<sup>27</sup> Employing the AFM microscope, the roughness of a surface is determined by moving a fine-pointed probe over the sample and detecting the forces between the probe and the surface. AFM offers exceptional lateral resolution, generally within a few nanometers, which enables the characterization of surface features at the atomic and molecular scale. The roughness of coated samples including starch NP binder and synthetic latex was measured to be  $54 \pm 13 \text{ nm}$  (Figure 5B) and  $58 \pm 13 \text{ nm}$  (Figure 5C), respectively, using the AFM. The measurements indicate

that the samples are statistically identical ( $p$ : 0.6471). In contrast, when 3D interferometry was employed, the roughness of samples coated with starch-based NP binder and synthetic latex measured  $1.6 \pm 0.4 \mu\text{m}$  (Figure 5D) and  $3.1 \pm 0.7 \mu\text{m}$  (Figure 5E), respectively, which there is a statistically significant difference ( $p$ : 0.0271\*). It is worth noting that the disparity in roughness values between the two measurement systems (AFM vs. 3D interferometry) can be attributed to the fact that 3D interferometry provides a larger measuring range but lower lateral resolution, while AFM excels in lateral resolution but has a more limited measuring range.<sup>33,34</sup> The AFM roughness measurement operates at a lateral scale much smaller than the wavelength range of visible light, making the surface non-scattering to incident light. As a result, it does not directly reflect surface gloss or predict light scattering, thus unable to anticipate the “smooth means higher density” effect. In contrast, 3D interferometry’s lateral resolution, employing visible light, aligns with surface-reflected light scatter. Seymour explains that when considering how a smoother surface leads to enhanced color, it is important to note that the total amount of light reflected from the surface is not significantly affected by its smoothness.<sup>35</sup> Instead, what changes is the angle at which the reflection occurs. Under directional lighting, a glossy surface will produce a shiny effect, called a specular highlight, which our brains typically overlook when assessing color. This shine is not captured by a 0:45 spectrophotometer, so it does not contribute to color measurement in either case.<sup>35</sup> On



**FIGURE 5** (A) Roughness profile comparison of a base paper and coating layer.<sup>33</sup> AFM topography profile of coated papers including (B) starch NP and (C) synthetic latex. 3D interferometer surface roughness profile of coated papers including (D) starch NP and (E) synthetic latex.

the contrary, a rougher surface scatters reflected light in multiple directions, creating a mix of surface and internal reflections perceived throughout the image. Unlike with a glossy surface, there is no mechanism for human brains to ignore the shine on a rougher surface, making it an essential aspect of color perception. This principle holds true for a 0:45 spectrophotometer as well. As a result, a rough surface appears brighter and lighter in color compared to a glossy or smooth surface.<sup>35</sup>

Previous studies showed that surface roughness influences COF, the property that effects papers' runnability within the press. A minimum value close to zero is preferred for COF to avoid problems such as paper feeding at the beginning of the press or paper transport within the press.<sup>22</sup> Using the COF tester, the force required to initiate movement between two surfaces, called static COF, was measured  $0.42 \pm 0.01$  and  $0.42 \pm 0.04$  ( $p$ : 0.3242) for the coated papers including starch NP binder and synthetic latex, respectively. The kinetic COF, the

**TABLE 3** Coefficient of friction test results.

	Static	Kinetic
Synthetic latex – 121 gsm	$0.448 \pm 0.045$	$0.352 \pm 0.014$
Starch NP binder – 118 gsm	$0.418 \pm 0.010$	$0.372 \pm 0.001$
Commercial B – 120 gsm	$0.336 \pm 0.026$	$0.289 \pm 0.013$
Commercial A – 118 gsm	$0.405 \pm 0.054$	$0.296 \pm 0.021$

force required to cause the continuation of the movement at uniform speed, was measured at  $0.37 \pm 0.01$  and  $0.35 \pm 0.01$  ( $p$ : 0.0740), respectively. The samples were also compared to two commercial papers for EP printing where the data suggest that the runnability of samples including starch NP binder and synthetic latex in EP presses would be problem free since there is not a significant difference between the samples (Table 3).

Optical properties of coated samples presented in Table 4 show a statistically significant difference between

**TABLE 4** Optical properties of coated samples.

	Synthetic latex	Starch NP binder	<i>p</i> -values
OBA	4.46 ± 0.66	5.29 ± 0.25	0.0001
Whiteness	92.35 ± 3.03	94.46 ± 1.10	0.0013
Yellowness	−0.60 ± 1.19	−1.28 ± 0.40	0.0073
Brightness (%)	90.89 ± 1.09	91.68 ± 0.63	0.0020
Opacity (%)	93.87 ± 0.89	93.80 ± 1.30	0.8365
<i>L</i>	95.75 ± 0.11	95.84 ± 0.26	0.1012
<i>a</i>	1.18 ± 0.14	1.33 ± 0.07	0.0001
<i>b</i>	−0.76 ± 0.67	−1.23 ± 0.24	0.0011

**TABLE 5** Density of CMYK patches.

	Synthetic latex	Starch NP	$\Delta E_{00}$	<i>p</i> -values
Cyan	1.57 ± 0.01	1.58 ± 0.01	0.2 ± 0.0	0.5528
Magenta	1.46 ± 0.01	1.46 ± 0.03	0.3 ± 0.2	1.000
Yellow	0.93 ± 0.00	0.95 ± 0.01	0.2 ± 0.1	0.0955
Black	1.76 ± 0.01	1.79 ± 0.01	0.4 ± 0.3	0.1548

**TABLE 6** Toner film thickness.

	Synthetic latex (μm)	Starch NP (μm)
Cyan	2 ± 2	5 ± 3
Magenta	4 ± 2	5 ± 1
Yellow	3 ± 4	5 ± 3
Black	4 ± 1	4 ± 2

the OBA, whiteness, yellowness, brightness, *a*\* and *b*\* values; however, the difference in optical properties cannot be detected by the human eye as the  $\Delta E_{00}$  is  $0.34 \pm 0.03$ , which is less than 1 and therefore imperceptible.<sup>27</sup> One could argue that the enhancements in brightness, whiteness, and roughness, along with the improvements in *L*\* facilitated by employing the starch NP binder, imply the potential for a wider color gamut during the printing process. Generally, the perception of paper whiteness is influenced by its lightness value.<sup>36,37</sup> Thus, suggesting the properties of paper including starch NP binder might be more ideal to obtain larger color gamut in printing. However, prior research has indicated no direct association between the optical performance of the substrate and the ability to achieve colorful prints.<sup>38</sup> The authors indicated that there seems to be a correlation between color gamut and substrate permeability; substrates with less permeability tend to offer a higher color gamut volume.<sup>38</sup> Previous studies revealed that the permeability coefficient of paper samples including starch NP was determined to be  $1.34 \pm 0.06 \times 10^{-5} \mu\text{m}^2$ , while papers including synthetic latex showed a permeability

coefficient of  $1.16 \pm 0.06 \times 10^{-5} \mu\text{m}^2$ .<sup>3</sup> The permeability coefficient represents the rate at which a particular substance can pass through a unit area. The literature presents that the former would allow easier ink penetration into the substrate.<sup>39</sup>

The density of the CMYK printed patches were measured using a spectrophotometer. The data presented in Table 5 show that there is no difference between how the colors appear, which is evidenced by  $\Delta E_{00}$  values being less than 1 and *p*-values greater than 0.05. Table 6 presents the thickness of the toner film on the coated papers, indicating a thicker film on papers containing starch NP. Earlier, the dielectric relaxation test demonstrated that the electrical field on the coated paper including starch NP binder improves toner transfer, which is confirmed by the thickness of the toner film. Moreover, it was revealed that substrates with higher permeability allow easier ink penetration into the substrate.<sup>39</sup> The paper containing starch NP binder exhibited a higher permeability coefficient, promoting increased ink transfer onto the paper, as further supported by the toner film thickness.

The magnified CMYK patches and 10% cell area images in Figure 6 shows print mottle, coverage, graininess, and dot structure of the samples. In general, the values close to zero for mottle, coverage and graininess represent high-quality ink layers whereas numbers close to 100 represent bad quality. The data indicates that both papers reproduced high-quality ink layers, as supported by the *p*-values in Table 7, which show no statistical difference between the paper samples. In terms of dot attributes, the dot area % values, which is the percentage

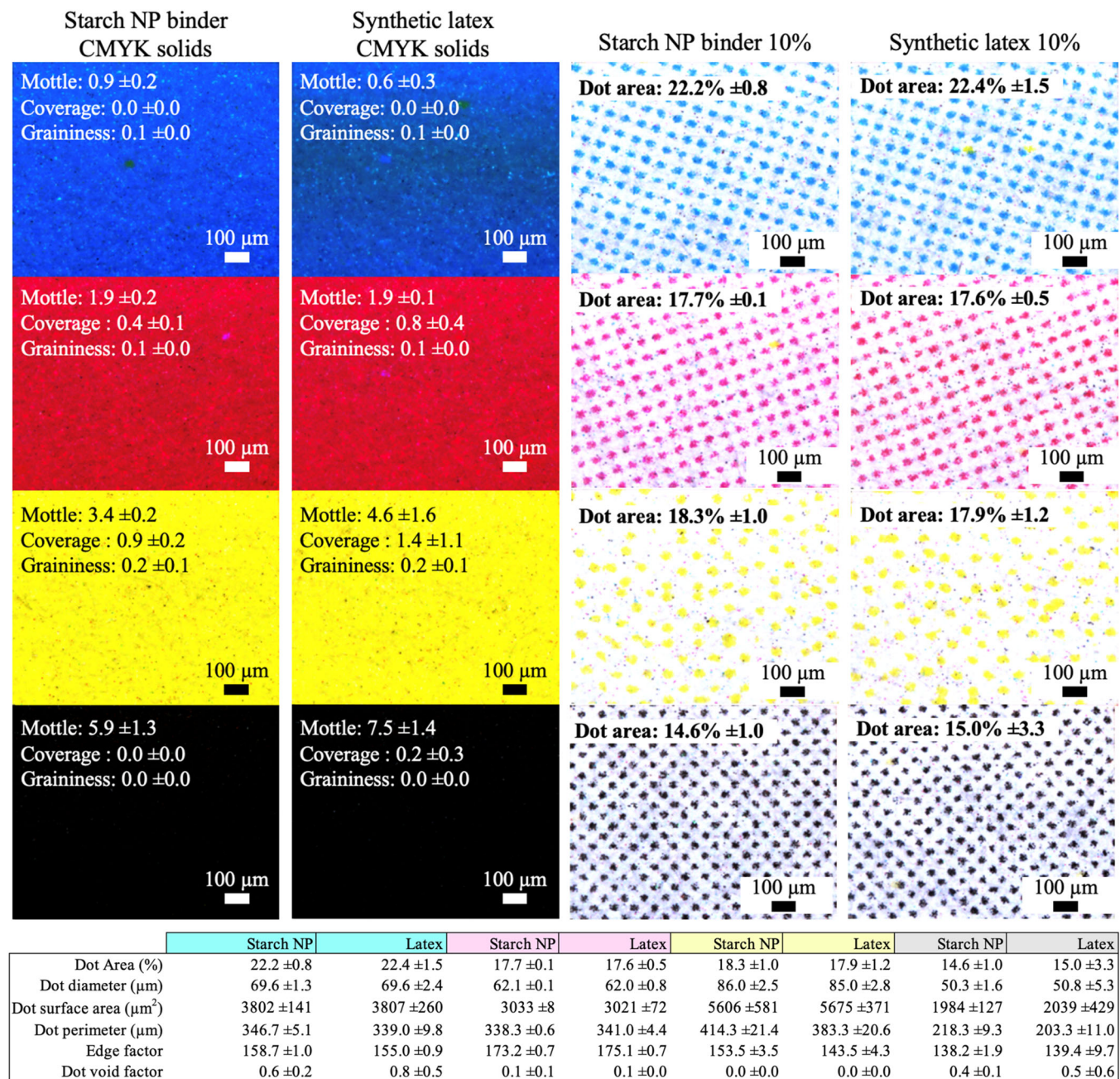


FIGURE 6 Print mottle and graininess of CMYK solid patches and 10% CMYK dot attributes.

ratio of the dot area to the cell area, were similar between the coated papers. The digital 10% dot area was printed as 22% for C, 17% for M, 18% for Y and 15% for B. This increase, called dot gain, is a phenomenon in almost every printing technology caused by the nip pressure being used while transferring inks/toners onto the substrate.<sup>10,16</sup> The difference in dot gain per color may be caused by the difference in toner pigment particle size used in the CMYK toner formulations. Based on the dot diameter data, the Y toner appears to generate a larger dot size relative to other colors supported by the dot surface area and perimeter. In terms of dot void factor, the

low-density areas inside the dots in relation to the entire dot area, all colors performed well, especially M and Y toners.

Background is toner deposits on unprinted parts of papers (Figure 7). The data quantified for background using the image analysis microscope presents that the dot counts on coated papers including starch NP binder (1133) is slightly less than of the papers including synthetic latex (1166). Dry toner formulations include colorant (CMYK pigments) dispersed in the CCA, typically styrene-acrylate copolymer thermoplastic resins.<sup>40</sup> The CCA conveys and govern the electrostatic charge

necessary to direct the toner particles to the image area on the photoconductor drum. They either carry a negative or positive charge, but are not completely uniform, which causes some toner particles to hold less charge than others during printing.<sup>40</sup> The less charged particles transfer more slowly and settle near the edge of a text, dot, line, or image and cause edge raggedness.<sup>40</sup> An alternative hypothesis suggests that as all the toner particles have the same charge, Coulombic repulsion between the particles should be significant, causing individual particles to become separated from the mass of toner particles and form a background.<sup>41</sup> Background is sometimes referred to as satellite; however, the two terms and their impact on image quality are different.<sup>25</sup> Satellites (Figure 8) fall near the printed element (text, image), while background (Figure 7) is considered as extraneous marks further away from the element typically produced in EP printing.<sup>17,24</sup> Figure 8 also shows the text quality on the coated samples being identical.

**TABLE 7** Comparison of *p*-values for dot attributes between the papers including starch NP and synthetic latex binders.

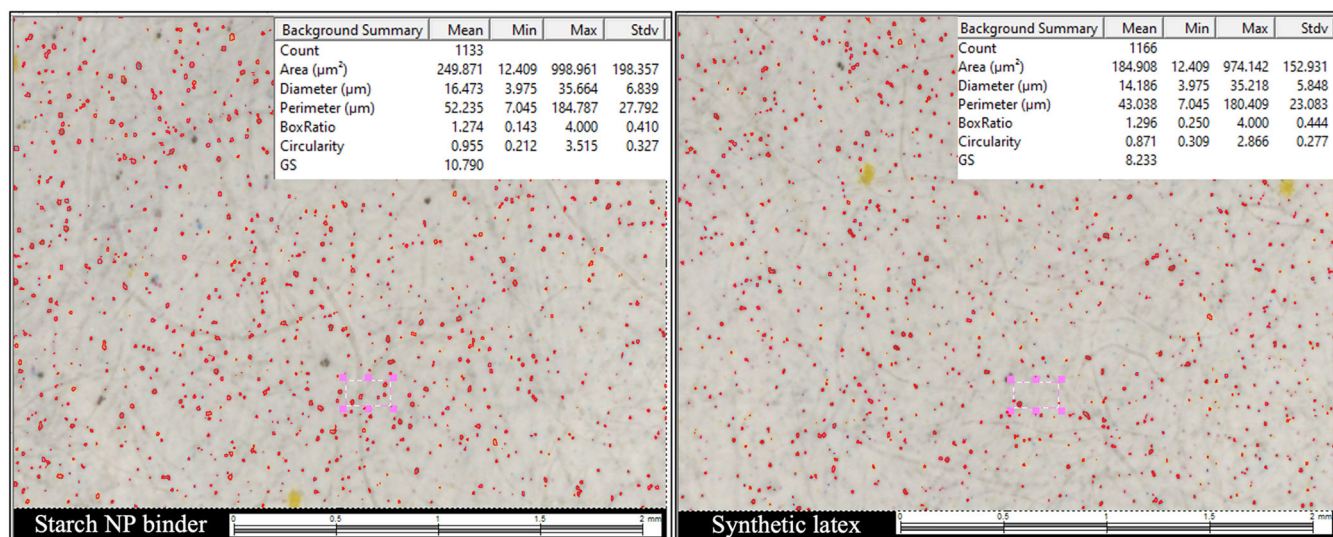
Dot attributes	<i>p</i> -values
Mottle	0.5433
Coverage	0.3078
Graininess	0.8406
Dot area	0.9791
Dot diameter	0.9784
Dot surface area	0.9601
Dot perimeter	0.6731
Edge factor	0.6505
Dot void factor	0.6644

Toner formulations traditionally incorporate plastic resin to ensure strong adhesion of toner particles to the substrate. This resin undergoes a melting process, achieved by heating it beyond its glass transition temperature. This elevated temperature is essential for toner particles to effectively bond with one another and adhere to the paper surface. Notably, prior research has indicated that the bonding of toner to paper (as illustrated in Figure 4) remains unaffected by the paper's wettability. Nevertheless, within an EP printing system, the quality of adhesion and fusion is not solely contingent on the characteristics of the toner and the fusing process. The porous and permeable nature of the paper itself plays a pivotal role in influencing these aspects of print quality. The toner partially penetrates the paper through the porous structure of paper and follows the surface roughness profile.<sup>17,19,23</sup> The use of new materials in coating formulation can change the optical, structural, mechanical, and ink-substrate interaction properties of the paper as presented in previous studies,<sup>3</sup> which suggests a change in print and color characteristics due to different interaction with light<sup>36</sup> and lead to difference in color gamut volume. Incorporating the starch NP binder into the coating formulation in this research yielded a color gamut volume of 362 585 ( $\pm 9510$ ), while papers containing synthetic latex produced a volume of

361 554 ( $\pm 9816$ ) (Figure 9) (*p*: 0.9023), indicating no statistically significant difference.

## 4 | CONCLUSION AND FUTURE PERSPECTIVES

In this study, an environmentally friendly starch-based nanoparticle binder was used in a paper mill trial to



**FIGURE 7** The background on the coated samples.

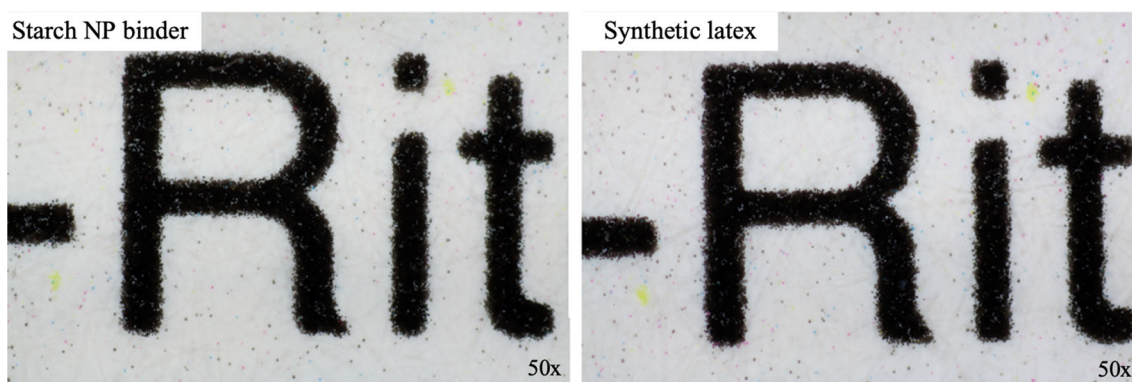


FIGURE 8 Text quality on the coated samples.

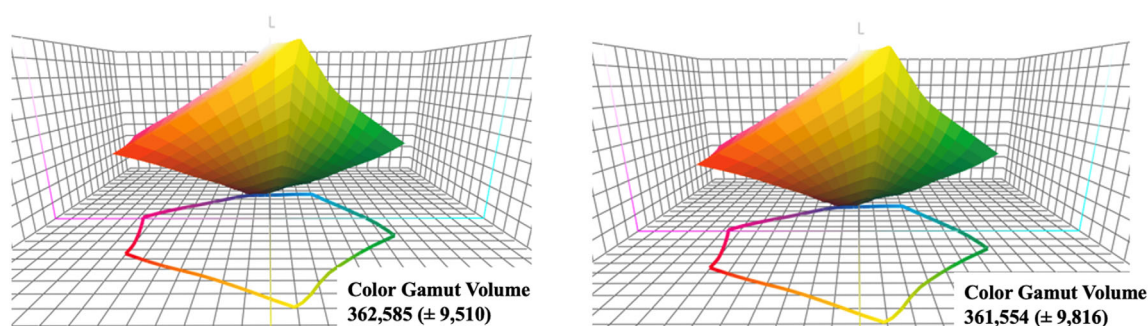


FIGURE 9 Color gamut volume comparison on ColorThink Pro between the coated samples including starch NP binder and synthetic latex.

replace synthetic latex in a paper coating formulation at a 1:1 ratio. The introduction of the starch nanoparticle binder triggered a significant increase in hydrogen bonding, consequently elevating both the surface energy and the polar component of the paper substrate. The increase in polar component improved various aspects of paper behavior, including the distribution of electrical fields, polarization response, and dielectric relaxation. These enhancements were evident through the improved toner transfer efficiency facilitated by the starch nanoparticle binder, supported by thicker toner film thickness. At the 1:1 replacement level, the findings revealed an increase in OBA and yellowness, higher whiteness and brightness, alongside alterations in the  $a^*$  and  $b^*$  values due to the utilization of starch nanoparticles. However, despite these changes, the capacity for color reproduction remained unchanged. Hence, substituting synthetic binder with starch nanoparticles is deemed acceptable without compromising color quality. Certain findings could potentially apply to other printing methods, though some effects are exclusive to EP. Future investigations should consider examining different substitution ratios for synthetic latex, including the prospect of complete

replacement. Additionally, it is advisable to investigate the printability of alternative printing technologies such as liquid EP, inkjet, flexography, and such.

#### AUTHOR CONTRIBUTIONS

**B.N.A.:** Methodology; resources; data curation; formal analysis; visualization; writing—original draft; project administration. **A.C.:** Methodology; writing—review and editing. **S.W.:** Resources; writing—review and editing. **M.S.:** Data curation. **A.H.:** Data curation. **Y.D.:** Data curation. **A.Z.:** Data curation. **C.A.:** Writing—review and editing. **A.K.:** Writing—review and editing.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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