Development and Application of Nanosized Polymer-Stabilized Cobinders and Their Effect on the Viscoelastic Properties and Foaming Tendencies of Coating Colors

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ABSTRACT: Polymer latexes have long been used as coating binders by various branches of industry due to their capacity to adhere coating components and increase the strength of the dried final coatings. In addition, these latexes have been known to affect the rheology of coating dispersions. Currently, emulsion polymerization is the most widely used method of producing polymer latexes. While the stability of these latexes is primarily provided by electrostatic repulsion between surfactants, this property also causes foaming problems during coating processes. In this research, these problems were addressed by preparing polymer-stabilized (PS) latexes that contained different concentrations of acrylic acid. Steric protection of the latexes was provided by a protective shell consisting of starch and poly(vinyl alcohol) (PVA). The viscosity, particle size, ζ-potential, and viscoelastic behavior of the prepared latexes were investigated as a function of pH, and their surface tension and foaming tendencies were evaluated. The latexes were applied as coating cobinders in calcium carbonate and clay coating dispersions, and the viscoelastic properties, surface tensions, and foaming tendencies of these mixtures were studied. The presence of acrylic acid monomers was found to be an important factor affecting the viscosity, particle size, and ζ-potential of the PS latexes prepared in this work, which were further found to generate less foam than comparable emulsion-polymerized latexes. Finally, coating color viscoelastic properties were modified via the partial substitution of styrene–butadiene (S/B) latexes with PS latexes.

1. INTRODUCTION

Various dispersions containing mineral particles mixed with binders have been incorporated into paper coatings, paints, and dyestuffs. These mixtures have often been characterized by complicated viscoelastic behaviors that affect coating properties, such as runnability, while their rheology has been shown to be affected by solids content, pigment shape, size and distribution, and latex level and size. The rheology and water retention properties of these kinds of systems have further been shown to be affected by the co-binders and thickeners that they often incorporate, such as starch, poly(vinyl alcohol) (PVA), and carboxymethyl cellulose (CMC). These hydrophilic polymers have been shown to affect the viscoelastic and water retention properties of coating dispersions by promoting flocculation and network formation.

Paper coating dispersions are often referred to as coating colors. They commonly contain synthetic polymer latexes, which act as binders that provide strength and facilitate film formation. In the paint and paper coating industries, these latexes have been widely prepared via emulsion polymerization. The colloidal stability of the conventional emulsion-polymerized (EP) latexes has usually been provided by electrostatic protection of surfactants. While these conventional latexes have many properties that enhance their use as paper coating binders, the technology needs to be further improved. For instance, because conventional EP latexes often contain surfactants as stabilizers, they can generate large amounts of foam. Although many efforts have been made in the coating industry to produce latexes that possess good rheology and binding properties, the foaming problem caused by surfactants of these latexes is still a key challenge. To solve the foaming problems, the coating industry applies foam control additives that may cause defects like fish eyes or bird eyes. In addition, EP latexes affect the water retention properties of coating colors by lowering their viscosity. To address this, various types of thickeners and water retention agents have been added to these mixtures to adjust their viscosity.

Polymer-stabilized (PS) latex is an alternative latex that does not suffer from these drawbacks. The colloidal stability of PS...
latexes has traditionally been provided by steric protection derived from polymer stabilizers. Block-type stabilizers containing hydrophobic and hydrophilic blocks or graft copolymers containing hydrophilic chains attached to a hydrophobic backbone have shown to be efficient for stabilization. The hydrophobic portions of these polymers are insoluble in aqueous media, and thus dissolve or adsorb onto the core polymer of their associated latex, leaving their hydrophilic segments exposed and increasing latex stability. In addition to providing steric repulsion for PS latex, the hydrophilic segments of these polymeric stabilizers determine the volume fraction of the dispersed phase, which has been shown to affect the viscoelastic properties of the latex.

The protective shell of PS latexes confers several advantages over the charged surfactant stabilizers associated with their EP counterparts. As the polymeric stabilizers sterically stabilize the latexes, the rheology and water retention properties of coating colors can be enhanced, meaning that the quantities of thickeners and water retention agents required are reduced. Recently, studies were published that described the polymer-stabilized latex as an additive for surface sizing. This latex remained stable during the addition of polyelectrolytes and over a wide range of pH values. In contrast, EP latex, which stabilized with anionic surfactants, was flocculated at a low pH as well as by the addition of polyelectrolytes. Because surfactants were not required for PS latexes, use of these latexes could reduce the foaming problem in surface sizing. It is expected that the use of the PS latex as a coating cobinder would provide the same advantages as surface sizing. Furthermore, it may provide a more desirable structure-forming property compared with the conventional latex binders.

In this study, PS acrylate latexes containing acrylic acid monomers were prepared and used as coating cobinders. The effect of varying the concentration of acrylic acid on the physical properties of the PS latex, such as viscosity, particle size, and ζ-potential, was examined as a function of pH. Subsequently, the water retention and viscoelastic properties of coating colors containing the PS latexes were evaluated (Table 1). Finally, the foaming tendencies and foam stabilities of the

Table 1. Formulation of Coating Colors

| pigment          | GCC          | 80 |
|------------------|--------------|----|
| clay             | 20           |
| binder           | S/B latex    | 8  |
| cobinder         | PS latex     | 3  |
| solids content   | 65%          |
| pH               | 9            |

*Component amounts are reported as parts per hundred (pph; by weight) based on 100 parts of pigment.

PS latexes and coating colors were evaluated and compared with the values derived from conventional latexes. To the best of our knowledge, the application of sterically stabilized latexes to paper coating has not been reported previously.

2. RESULTS AND DISCUSSION

2.1. Characteristics of the Latexes. Three types of PS latexes containing different acrylic acid monomers were prepared. The ratio of the core polymer to the protective shell was 60–40% w/w. The schematic and chemical structures of the sterically stabilized latexes are shown in Figure 1.

![Figure 1. Polymerization process (a). Structure of sterically stabilized latex (b). Chemical composition of the core polymer (c).](https://dx.doi.org/10.1021/acsomega.0c00154)

The properties of the synthesized PS latexes are shown in Table 2. The PS latexes were synthesized using styrene, butyl acrylate, and acrylic acid as monomers and were all stabilized by a protective shell. The weight ratios of the protective shell to the core polymer and starch to PVA in the protective shell, as well as the amount of acrylic acid monomer, were seen to affect the hydrophilicity and viscosity of the PS latexes. The carboxylic acid groups associated with acrylic acid were seen previously to expand the polymer backbone as a result of deprotonation under basic conditions, which influenced the particle size, volume fraction, and rheological properties of the PS latex dispersions.

![Table 2. Properties of PS Latexes](https://dx.doi.org/10.1021/acsomega.0c00154)

| latex | solids (%) | pH  | viscosity (cP) | acrylic acid (%) |
|-------|------------|-----|----------------|-----------------|
| PS-1  | 48.6       | 6.1 | 136            | 5               |
| PS-2  | 48.0       | 6.5 | 201            | 10              |
| PS-3  | 49.1       | 6.5 | 400            | 15              |

2.2. Viscosity and Particle Size Distribution of PS Latexes as a Function of pH. The viscosity of the PS latexes was measured as a function of pH with a Brookfield viscometer (Figure 3a). As the pH of the PS latex increased, its viscosity increased, which was attributed to the swelling and expansion of stabilizers when interacting with the base. In addition, the hydrophilic protective shell of the PS latexes may partially dissolve in an aqueous phase at alkaline pH and affect the viscosity. Moreover, the deprotonation of carboxylic acid groups within the latexes led to an expansion of their cores, which resulted in an increase in the latex volume fraction and
viscosity. When a PS latex contained more acrylic acid monomer, the increase in viscosity following exposure to base was more pronounced. The greater amount of carboxylic acid groups in PS-3 enhanced the repulsions of the charged groups within a PS latex particle, which increased the overall electrostatic repulsion of the polymers. This increase in viscosity as a function of pH may have also been partially caused by unadsorbed hydrophilic stabilizers during polymerization and also some portions of the hydrophilic protective shell of the cobinder dissolving in the aqueous phase under basic conditions.

The particle sizes of the latex dispersions were evaluated at different pH levels using the dynamic light scattering (DLS) method (Figure 3b). As pH increased, the average particle size also increased as a result of acrylic acid deprotonation causing swelling of the PS latexes. PS-3 had a larger particle size than
PS-1 and PS-2, indicating that the swelling of PS-3 was more pronounced and thereby emphasizing the importance of acrylic acid for latex water absorption and swelling (Figure S2). This result agreed well with the results of the viscosity experiments shown in Figure 3a. The viscosity and particle size of the S/B latex as a function of pH were also studied, with results shown in Figure S3. It was found that the S/B latex was not stable within an acidic pH range (<6) and that the dispersion was totally aggregated (Figure S3d), suggesting that this latex was very sensitive to changes in pH. In contrast, PS latexes were found to be more stable at similar pH values as a result of the steric protection afforded by their polymeric stabilizers. As shown in Figure 3c–e, pH influenced the PSD of the PS latexes. When the pH of the PS latex dispersions changed from...
acidic to basic, a broader PSD was observed due to particle swelling.

To confirm the particle size of the PS latexes, dispersions were prepared at pH 5 and 9 and observed using TEM. DLS revealed that the differences between the average particle sizes of the PS-1 and PS-2 latexes at pH 5 and 9 were only 2 and 7 nm, respectively. Due to the polydispersity of the latexes, it was difficult to observe differences in size of the PS-1 and PS-2 latex particles using electron microscopy. However, an electron micrograph of the PS-3 samples revealed that the size of this latex increased when the pH of the dispersion was adjusted to 9 (Figure 4).

The average particle size of the PS-3 latex was measured using Image J software at pH 5 and 9 and was found to be 34 and 79 nm, respectively. The average particle size obtained from the image analysis of the TEM micrograph using Image J was smaller than the value obtained using the DLS method. While the DLS method gave the average size value after measuring many particles, TEM limited the number of particles observed. Furthermore, the swollen latex particles were found to dry and shrink under the electron beam of TEM and UHV (ultrahigh vacuum) conditions. As a countervailing tendency, a hydrodynamic diameter that was larger than the actual particle size may have been obtained from DLS as a result of the particular surface charge and electrical double layer of each individual particle.

The PS-3 latex particles were measured in acidic or basic conditions using a Cryo-EM to exclude latex particle deformation during drying and to prevent the samples being destroyed by the high energy electron beams required for analysis. Figure 4c clearly shows that in acidic conditions, PS latex particles were spherical. In contrast, the protective shell and outer portion of the latex swelled and partly dissolved in the medium at pH 9 (Figure 4d).

2.3. Rheological Properties of PS Latex and Coating Color. The viscosity of the sterically stabilized cobinders at different pH levels and as a function of the shear rate is shown in Figure 5a. The PS latexes became more viscous as the pH of the dispersion increased. The viscosity of the PS-1 and PS-2 latexes increased at higher pH, indicating some swelling or dissolving of their protective shells. Moreover, due to the deprotonation of acrylic acid groups, the polymer core of PS latexes swell, which can affect the viscosity of the PS latexes. The viscosity of PS-3 was higher than that of PS-1 and PS-2 at all pH levels, and this was associated with the higher acrylic acid content that deprotonated at alkaline pH and resulted in polymer core expansion, which would result in partial desorption of the protective shells and viscosity increase of the dispersion at higher pH. Also low-molecular weight polymers with acrylic acid may remain in the aqueous phase to increase the viscosity.

The ζ-potential of the PS latex dispersions is depicted as a function of pH in Figure 5b. The ζ-potential of the PS-3 latexes was more negative than that of the PS-1 and PS-2 samples. When the pH of a PS latex increased from 5 to 9, a lower ζ-potential was obtained due to the greater extent of ionization of the carboxylic acid groups. This change in magnitude was more pronounced for PS-3, indicating that the latex contained a higher concentration of carboxylic acid groups. Analyses revealed that the PS-1 and PS-2 latexes had Newtonian fluid characteristics and were not shear-dependent at all pH levels. The PS-3, however, showed a shear-thinning behavior and was more shear-dependent indicating a shear destructible network formation. The shear-thinning behavior of the PS-3 latex was thought to be related to particle swelling, as swollen particles would deform more easily when exposed to shear stress to ellipsoidal-shaped ones. An amplitude sweep test was carried out to study the microstructure of the PS-3 latex. Storage ($G'$) and loss ($G''$) moduli...
were evaluated at a constant angular frequency (1 Hz) and a changing shear stress (Figure 5c). \( G' \) was larger than \( G'' \) at all pH levels across the entire shear stress range, indicating that the PS-3 latex dispersion was viscoelastic liquid. There was no crossover point observed between \( G' \) and \( G'' \), which revealed that the yield point also increased as pH increased. A frequency sweep test was carried out to elucidate the microstructure of the latex dispersions. Figure 5d shows that there was no crossover point between \( G' \) and \( G'' \) and that the loss modulus was larger than the storage modulus at all pH levels. These results indicated that liquidlike behavior predominated in the PS-3 latex dispersion.

To study the effect of the PS latex on the viscoelastic properties of coating colors, three PS latexes were used as cobinders. Three parts of the main S/B latex binder were substituted with a PS latex, and amplitude and frequency sweep tests were performed. The tests revealed that \( G' \) was greater than \( G'' \) in the linear viscoelastic region, indicating that the coating color was a viscoelastic solid material. Substitution of the S/B latex with an PS cobinder resulted in a greater elastic modulus relative to the coating color that contained the S/B latex only. This indicated that the coating color became more solidlike with the addition of a PS latex (Figure 6a), with the use of PS-3 as a cobinder leading to a most pronounced effect. This increase in coating color solidity was attributed to swelling of the cobinder, which was analogous to increasing the coating solids content. In addition, when S/B latex was substituted with PS latex, a greater number of the PS latex would be present, which contributed to the closer interaction among coating components.10 The amplitude sweep results further showed that when a PS latex was added to a coating color, a higher shear was needed for the latter to flow. This property revealed the existence of a stronger interaction between the components of the coating color. Finally, when PS-3 latex was added to the system, its flow point increased, further confirming the formation of a stronger network.

The frequency sweep tests showed that \( G' \) was higher than \( G'' \) for all coating systems. Both \( G' \) and \( G'' \) increased as the frequency increased, indicating that weakly flocculated structures were formed. Substituting S/B with PS latexes resulted in stronger interactions between coating components, and this effect was more pronounced with greater concentrations of acrylic acid. The complex modulus (\( G^* \)) of the coating colors was described similar to the storage modulus (Figure 6c): using a PS latex cobinder resulted in more solidlike coating color behavior and coating colors containing a PS-3 cobinder displayed a higher complex moduli value than other coating colors due to the stronger interaction between coating components.

The \( \zeta \)-potentials of the coating colors are shown in Figure 6d. The \( \zeta \)-potential of the coating color containing only S/B latex as a binder was \(-31.8 \text{ mV} \). When three parts of the S/B latex were substituted with an PS latex cobinder, the \( \zeta \)-potential did not change significantly. As the pigments were negatively charged, PS cobinders with a like charge would not adsorb onto the pigment surfaces. Portions of the hydrophilic polymers that stabilized the PS latexes remained in the aqueous phase of the dispersion. Previous studies have shown that these kinds of polymer portions, which are smaller to pigment particles within a dispersion, remain unadsorbed in the dispersed system by electrostatic repulsions between polymers and particles. In a colloidal dispersion of particles and unadsorbed polymers, when two particles approach, the polymer is expelled from the gap between the approaching particles. According to this mechanism, which is called depletion flocculation, the concentration of polymers around pigment particles is changed and this leads to an osmotic pressure difference that attracts the particles to each other.36–38 A previous study by Xing and coauthors examined the depletion interaction of colloidal particles caused by the presence of soft particles. The authors found that the larger hydrodynamic diameter of these particles, which consisted of a solid core surrounded by a soft shell, had a critical effect on depletion attraction.39 The larger particle size of the PS-3 latex was thus expected to induce a greater depletion interaction between components within a coating color.

To confirm the sterically stabilized latex-induced interaction between coating color components, a sedimentation experiment was carried out. This experiment involved centrifugation of the coating color followed by measurement of the residual sediment volume that remained after the supernatant fluid was decanted (Figure 6e). Substituting three parts of the S/B latex with a PS latex was seen to result in a higher sedimentation volume, indicating that a weakly flocculated structure had formed.

The effect of addition of the PS cobinder on the viscosity of the coating color is depicted in Figure 6f as a function of the shear rate. All coating colors showed a shear-thinning behavior. Furthermore, the viscosity of all coating colors was seen to increase when three parts of the S/B latexes were substituted with PS latexes. The interaction between coating components caused by the addition of PS latexes resulted in a higher viscosity of the parent coating color. Moreover, the smaller PS latexes compared with S/B latex would increase the low shear viscosity because their surface areas are larger than that of S/B latex.10

Table 3 illustrates the low shear viscosity and water retention properties of a coating color with a solid content of 65% at pH 9. The addition of PS latexes increased the viscosity of the coating color. Dewatering of a coating color is known to be influenced by its hydrophilicity and the interactions between the coating components it contains. Adding the sterically stabilized PS latexes was found to increase the water retention value of the coating colors due to the hydrophilic polymer stabilizers. In addition, higher acrylic acid content enhanced the hydrophilicity of the cobinder and consequently increased the water retention of the coating color.

### Table 3. Effect of PS Co-binders on Viscosity and Dewatering of Coating Colors

|                | S/B latex only | PS-1 3 (pph) | PS-2 3 (pph) | PS-3 3 (pph) |
|----------------|---------------|--------------|--------------|--------------|
| dewatering (g/m²) | 114.9         | 103.5        | 97.0         | 74.6         |
| viscosity (cPs)    | 213.9         | 284.3        | 414.0        | 488.4        |

2.4. Foaming Tendencies of Coating Colors. The surface tension of latexes with a concentration of 1% w/w was measured at pH 9. The S/B and PS latexes were found to have similar surface tensions, which ranged from 44.4 to 49.5 mN/m. Previous studies have established that polymer stabilizers can adsorb at the air–liquid interface and reduce surface tension.25 The PVA polymer contains both hydrophilic and hydrophobic portions and therefore acts like a surfactant.25 The surface tension of PS-1 as a function of solids content was
measured and compared with that of the S/B latex. The comparison revealed that the PVA contained in the PS latexes behaved as surface active agents (Figure S5a).

The foaming tendency and foam stability of the latexes were compared at a concentration of 1% w/w and a pH of 9. For this comparison, the latex dispersions were transferred to plastic tubes and foam was generated by shaking for 30 min. The stabilities of the foams were studied by monitoring their natural break-up. This simple method, which has also been described as free drainage, is based on the self-destabilization of a foam by gravity. The S/B latexes generated more foam after 30 min of shaking than their PS counterparts, and this was partly attributed to a more stable foam being generated in the presence of surfactants, which reduced surface tension and increased foam elasticity and stability.41 In contrast, PS latexes generated less foam and a faster rate of bubble breakage. Previous studies have suggested that foaming tendency is dependent on the diffusion rate of surface-active agents to the interface.42 In the present study, dynamic surface tension of PS-3 and S/B latexes were compared and the measurements revealed a comparable final surface tension of these latexes. However, a higher transfer rate for the S/B latex relative to its PS counterpart was observed (Figure S5b). This result agreed with the finding reported above, which suggested that the PS latexes had a tendency to form less foams because their steric stabilization was provided by protective shells rather than surfactants.27 As the acrylic acid content increased in the PS latexes, their foaming tendency also increased. The stability of foam would be increased by electrostatic repulsions, which slow foam drainage and breakup.42 PS-3 latex displayed the greatest foam volume and stability. Despite these characteristics, the PS latexes were assumed to have a reduced potential to generate foam during coating processes relative to their S/B counterparts. To examine this hypothesis, the foaming tendencies of coating colors with and without the addition of three parts of PS latex were measured (Figure 7b). When only S/B latex was used as the binder, the largest volume of foam was generated. When three parts of the S/B latex were substituted by PS latex, the foaming tendency of the coating colors was reduced. The addition of PS-3 latex resulted in the smallest amount of foam. It was shown that the higher acrylic acid content of the PS cobinder resulted in a greater viscosity of the coating color (Table 3). These differences in viscosity may have affected the foam volume at a constant mixing time and force. Coating industry, however, controls the viscosity of coating colors using additives at a certain range. Hence, the effect of acrylic acid content of the PS latexes on foaming tendencies of coating colors needs to be investigated further.

As the coating color medium is responsible for surface tension and foaming tendency, the prepared coating colors were centrifuged and the ensuing supernatant fluid, which mostly contained latex or low-density components, was used for the measurement of these properties. Figure S5 shows the turbid supernatants corresponding to the coating colors, while Table 4 shows their static surface tensions. The supernatant derived from the coating color containing three parts of PS-1 showed the highest surface tension, while the values recorded for all other latexes were comparable.

The dynamic surface tensions of the coating color supernatants were studied, revealing that the surface-active agents in supernatant fluids derived from PS latexes showed slower adsorption than their S/B counterparts (Figure 7c). This result suggested that coating colors containing PS latexes
would show a reduced foaming tendency. The effect of the PS latexes on foaming tendency and foam stability was evaluated by shaking the supernatant fluids derived from the coating colors for 30 min and then measuring their foam volumes as a function of time (Figure 7d). Substituting S/B latex with three parts of PS latex reduced the foam stability of the coating color. When 3 pph of PS-1 was added to a coating color, the foaming ability was significantly reduced. Although greater volumes of foam were generated by supernatant fluids derived from coating colors containing PS-2 and PS-3 latexes, the foams were not stable and broke up rapidly such that they finally established foaming characteristics that were comparable to those of the PS-1 containing supernatant. This result suggested that the use of an PS latex as a cobinder would reduce foaming problems during the coating processes.

3. CONCLUSIONS

Three PS latexes containing different concentrations of acrylic acid monomers were prepared. The prepared latexes were sterically stabilized by a 3:1 ratio of starch/PVA, which formed a protective shell. The ratio of the core polymer to this shell was 60–40%. The protective shells and polymer cores of the PS latexes swelled in basic conditions, which increased the volume fraction of the dispersed phase and resulted in increased viscosity. The PS-3 latex, which contained 15% acrylic acid monomer, had a higher viscosity than the other PS latexes. This viscosity was greater at higher pH, as a greater proportion of carboxylic acid groups was deprotonated. At high pH, latex particle size increased and $\zeta$-potential became more negative. The PS cobinder containing coating color showed more elastic behavior than the control sample. Hydrophilic parts on the polymer stabilizers absorbed water from the liquid phases of the dispersed systems and thus rendered coating colors more solidlike. Moreover, very weak, shear-dependent interactions between coating components were formed upon addition of PS latexes, which resulted in higher viscosities of the coating colors. The PS-3 cobinder increased viscosity to a greater extent than the other two PS cobinders, and this was attributed to greater amounts of acrylic acid in the core polymer, increasing the interactions between pigment molecules as well as the rate of water absorption. The surface tensions and foaming tendencies of the PS latexes were studied. The PS latexes produced less foam than their S/B counterparts. When three parts of PS latex was added to the coating color, the foaming tendency was reduced. This study has demonstrated that PS latexes have a great potential to be used as cobinders for paper coating.

4. EXPERIMENTAL SECTION

4.1. Polymerization. Styrene (S), butyl acrylate (BA), and acrylic acid (AA) (Sigma-Aldrich) were used as monomers. 2,2′-Azobis(2-amidinopropane)dihydrochloride (AAPH, Wako, Japan) was used as the initiator for the polymerization process. Oxidized starch (Kurary, Japan) and poly(vinyl alcohol) (PVA, Poval, Korea) with a hydrolysis degree of 98–99.5% and a molecular weight of 75 000–80 000 g/mol were used as latex stabilizers. Ammonium hydroxide was used as a buffer for pH regulation.

Polymerization was carried out in a 3 L reactor that consisted of a reflux condenser, thermometer, and mechanical stirrer. The temperature was set by a water bath at 80 °C, and the stirring speed was maintained at 500 rpm or lower. Metering pumps were used to supply monomers, stabilizers, and initiator to the reactor with a controlled rate of addition. The ratio of stabilizers for starch/PVA was 3:1. The ingredients supply and polymerization processes were completed after 5 h, at which point the mixtures were cooled and their pH was adjusted.

4.2. Coating Color Ingredients. A commercial emulsion-polymerized S/B latex (Trinseo, Korea) with a solid content of 50% and average particle size of 147 nm and pH value of 7.3 was used as the main binder. Ground calcium carbonate (GCC, Setacarb HG, Omya Korea) in a slurry form and dry kaolin clay (Hydrogloss 90, KaMin, Korea) were used as pigments. Sodium polyacrylate with a molecular weight of 5100 g/mol (Sigma-Aldrich) was used as a dispersing agent. HCl and NaOH (1 N) were purchased from Samchun (Korea) and used to adjust the pH of the coating color. Deionized water was used in all of the experiments. All of the chemicals and raw materials were used as received, without any further modification or purification.

4.3. Electron Microscopy and Fourier-Transform Infrared Spectroscopy (FTIR). Images of the latexes were obtained using a LIBRA 120 (Carl Zeiss) transmission electron microscope (TEM) with an operating voltage of 120 kV. To evaluate the effect of pH on latex particle size, the latexes were diluted to a concentration of 0.01% w/v and the solution pH was adjusted to 5 or 9 using HCl or NaOH, respectively, before being allowed to stand for 1 h. Once this time had elapsed, the latex particles were deposited onto Formvar film-coated grids that were subsequently stained via exposure to a drop of uranyl acetate (UA) solution for 10 s. The stained grids were then washed for 1 s with two drops of deionized water, and the samples were dried at room temperature after residual water had been removed with filter paper.

Cryogenic electron microscopy (Cryo-EM) involving a Talos L120C transmission electron microscope (Thermo-Fisher Scientific) operating at 4 °C and with a humidity of 100% was used to observe the latex particles. The samples were prepared at least 48 h before microscopic imaging.

FTIR spectra of the latexes were obtained using a Nicolet 6700 Spectrometer (Thermo Electron Corporation) in attenuated total reflectance mode and across the 600–4000 cm$^{-1}$ frequency range. A film obtained after drying latex samples in aluminum dishes at 70 °C was used for FTIR spectroscopy.

4.4. Preparation of Latex Dispersions and Coating Colors. Latex dispersions were diluted with deionized water to 38% w/w. HCl and NaOH solutions were used to adjust the pH of the latex dispersions to 5, 7, and 9, respectively. The rheological properties of the pH-adjusted dispersions, with a solid content of 38%, were then determined. To examine the foaming tendencies, $\zeta$-potentials, and particle sizes of the latex dispersions, each PS latex was diluted to 1, 0.1, and 0.01% w/w, respectively, and the pH values were adjusted to 5, 7, and 9 using HCl and NaOH for each type of PS latex.

The formulation of the coating colors is reported in Table 1. The coating colors were prepared by combining all of the ingredients with vigorous stirring. The coating color with a solid content of 65% w/w was used to evaluate rheological properties and foaming tendencies. A 70% w/w dispersion of kaolin clay was prepared by dispersing the clay in water containing 0.3 pph of sodium polyacrylate. The clay dispersion was then sequentially mixed with GCC, S/B latex, and PS latex.
cobinder. The pH of the final coating color was adjusted to 9 using NaOH.

4.5. Evaluation of the Properties of Latexes and Coating Colors. The low shear viscosity of the latexes and coating colors was measured at 100 rpm using a Brookfield viscometer (DV-2), while their viscoelasticity was determined using a stress-controlled rotational rheometer (CVO, Bohlin Instruments) with a cone-plate geometry ($R = 40 \text{ mm}, \text{ angle} = 4^\circ$). Prior to the measurements, the samples were presheared at a rate of $10 \text{ s}^{-1}$ for 5 min. The samples were allowed to rest for 10 min before measurements were taken.

Particle size distributions (PSD) and $\zeta$-potentials were measured using a Zetasizer (nano-ZS, Malvern, U.K.). For the particle size measurements, normal disposable plastic sample cells (Kartell, Italy) were used. For the $\zeta$-potential measurements, specially designed disposable folded capillary cells (DTS1060, Malvern, U.K.) were used. An equilibrating time of 2 min was allowed before the measurements, and at least three measurements were made for each sample.

The sediment volume of coating colors was measured to evaluate the porosity of the sediments. Ten grams of the sample was injected into a 20 mL cylindrical plastic tube, which was then subjected to centrifugation at 3000g for 3 h using a large capacity refrigerated centrifuge (Hanil Scientific Industrial, Korea). After centrifugation, the supernatant of the samples was removed and their sediment volume was recorded and compared.

The dewatering profile of the coating colors was investigated using an Åbo Akademi gravimetric water retention meter (ÅA-GWR, Kaltec Scientific). Ten milliliters of coating color was injected into a cylindrical vessel that was placed on a mixed cellulose ester membrane filter with a pore size of 0.2 µm (Advantec, Taiwan) and blotter papers. Dewatering of the samples was performed under 1.5 bar of pressure for 60 s.

The static surface tension of the latex and coating color supernatant fluids was measured at a concentration of 1% w/w using a Krüss tensiometer (K-12, Germany). To study the diffusion and adsorption rate of active agents on the sample surfaces, a bubble pressure tensiometer (Krüss, BP2, Germany) was used.

To evaluate the foaming tendencies of the latexes, 25 mL of latex dispersion with a concentration of 1% w/w was transferred to plastic tubes. The filled tubes were shaken at a constant intensity for 30 min using a laboratory shaker to generate foams. The heights of the foams were then measured as a function of time.

To study the foaming tendencies of the coating colors, 100 g samples of coating color were filtered with a 100 stainless steel mesh and transferred to 1000 mL beakers. A laboratory stirrer was used to mix the coating color samples at 1500 rpm. The same beaker, stirrer, and impeller were used for all samples, and the mixer position was controlled. To generate a foam, the beaker containing the coating color sample was evacuated using a laboratory vacuum pump. The pressure was then adjusted to 75 mbar and maintained at this value for 5 min. Then, the height of foam generated via this process was measured and the foam volume, calculated.

In another set of experiments, to eliminate the effect of coating pigments on foaming, the sediment of the coating color was removed after centrifugation at 3000g for 3 h using a large capacity refrigerated centrifuge (Hanil Scientific Industrial, Korea). The concentration and pH of the sample supernatant fluid were adjusted to 1% w/w and 9, respectively, and 25 g from each sample was transferred to plastic tubes. Foam was then generated by shaking the tubes for 30 min at a constant intensity using a laboratory shaker. The sample foam height was measured as a function of time, and the foam volume was calculated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c00154.

TEM of S/B latex and properties of S/B latex; TEM of PS-3 latex with particle size diameter; comparison between the acid level of S/B latex and PS latexes; effect of latex concentration on surface tension and foaming volume (PDF)

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Notes

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