Structural Changes of the Coating Layer by Styrene/Acrylate Latex with Hydroxyethyl Methacrylate

Soojin Kwon, ‡ Kyudeok Oh, ‡,§ Sang Jin Shin, † and Hak Lae Lee*,†§

†Department of Forest Sciences, College of Agriculture and Life Sciences and ‡Research Institute of Agriculture and Life Sciences, Seoul National University, Seoul 08826, Korea
§Department of Chemical Engineering, Åbo Akademi University, Turku 20500, Finland
Basic Materials and Chemicals R&D, Research Park, LG Chem, Limited, Daejeon 34122, Korea

ABSTRACT: The coating structure is directly related to quality of coated paper, especially printability. Its structure mainly consists of pigment, binder, and additives. Binder has a significant influence on the coating structure because it is involved in the structure forming process and takes a key role in maintaining the structure. In this study, styrene acrylate (S/A) latex with hydroxyethyl methacrylate (HEMA) as a comonomer was used as a binder, and the influence of HEMA contents on latex swelling and coating structure was investigated. The S/A latex particle swelled more with an increasing HEMA content, which significantly influenced coating color and coating layer characteristics. The viscosity of coating color became thick, and the dewatering of coating color was suppressed. The HEMA monomer that swelled latex particle allowed the coating layer to consolidate rapidly, which made the coating layer more porous and more uniform.

1. INTRODUCTION

Paper coating is a widely used technique for improving the appearance and printability of paper. Paper coating enhances the gloss, opacity, brightness, and printability of paper. However, there are several quality issues for coated papers. One of the most widely occurring problems for coated paper is print mottle, an unevenness of gloss or color density of the printed surface. This print mottle is usually caused by variations in the ink-setting rate after printing, which stems from the nonuniformity of the binder distribution or the pore structure of the coating layer. 1–5 To solve the problem of print mottle, it is necessary to control the coating structure and make it more uniform.

Coating colors have pigments, binders, and additives as their main components. Pigments are the basic building blocks of the coating layer, whereas additives adjust the rheological properties of the coating colors or impart special functional properties to the coated paper. Binders that bind all components in the coating layer are used to maintain the structure of the coating. They also play an important role in the consolidation of the coating layer. 6 It is well known that the structure of coating layer changes by the binder type and its migration that occurs before the consolidation of coating layer. 7 Therefore, the physical and chemical properties of binders have a significant influence on the structure of pigment coating layers.

In this research, we investigated the role of the functional monomer hydroxyethyl methacrylate (HEMA) in styrene acrylate (S/A) latex, which is one of the most widely used latexes in paper coating. The properties of S/A latexes are affected by the glass transition temperature, cross-linking degree, particle size, and so forth. Previous research showed that it is possible to change various properties of coating colors and coated papers with the use of functional comonomers. 8,9 Among the several functional monomers tested, including acrylonitrile, acrylic acid, ethyl hexyl acrylate, allyl methacrylate, and HEMA, the most significant improvement in print mottle was obtained when HEMA was used as a comonomer. 9 The use of HEMA as a comonomer for S/A latex increased the viscosity and water retention of the coating color and the ink absorption uniformity. Previous research, however, has only investigated the effect of comonomers using a single comonomer composition. 7 In addition, the change in coating structure as a function of the comonomer ratios has not been examined.

HEMA, also called glycol methacrylate or glycol monomethacrylate, is a hydrophilic monomer first synthesized in 1936. 10 HEMA has been used in the medical field because of its stability and hydrophilic properties since hydrogel-formed polymers were introduced in 1960. 11 Through a hydroxyl group in HEMA, a polymer containing this monomer can interact with water even though hydrophobic monomers are major components of the polymer. 12–15 The effects of HEMA as a comonomer in S/A latex have been examined, 9–11 and it has been shown that HEMA can intensify the swelling of S/A latex in alkaline conditions. As most coating processes are performed under alkaline conditions, this swelling would seem to have effects on the coating structure. However, the S/A latexes used in these studies contained too much HEMA monomer to use them as paper coating binders.

The swelling of latex particles occurs when the carboxyl groups dissociate into carboxylate ions. The negatively charged carboxylate ions cause electrical repulsion between the latex particles and between the polymer chains within the particles. Electrical repulsion between the latex particles stabilizes the latex suspension, whereas the repulsion between the polymer...
chains within the particle causes swelling of the particle. A hydrophilic monomer improves the mobility of the polymer chains, which helps hydroxyl ions penetrate the latex particles, resulting in greater swelling of the particles.\(^{19}\) Thus, the properties of S/A latex may change substantially depending upon the amount of HEMA comonomer.

The immediate purpose of this study was to explore the effects of the HEMA monomer on S/A latex and its effect on the consolidation and structure of the coating layer. The structural change of the pigment coating layer associated with the use of S/A latex as a binder was investigated, and the property changes and mechanism involved in the S/A latex with different levels of HEMA as a comonomer were discussed. The final goal of this study was to elucidate the effect of the HEMA content in S/A latex on the coating structure.

2. RESULTS AND DISCUSSION

2.1. Swelling of S/A Latex Particles. The hydrophilicity of HEMA had a significant influence on the latex swelling. Figure 1a shows the hydrodynamic diameters of the S/A latex particles at pH 4 and 9 as a function of HEMA content. The particle size of the S/A latex remained almost constant at pH 4, irrespective of the HEMA content. However, the particle size increased substantially at pH 9 with increasing HEMA content. This indicates that the hydroxyethyl groups of HEMA had a synergic effect on the ionization of the carboxyl groups in alkaline conditions and made the S/A latex particles swell more. The increase in the S/A latex particle diameters in alkaline condition for the high-HEMA latex resulted in its greater swelling coefficient (Figure 1b).

The swelling was examined by measuring the relative viscosity as well as hydrodynamic diameter. The dynamic light scattering (DLS) and relative viscosity data indicated similar tendencies in the swelling properties. The relative viscosity of the S/A latex suspension increased with the increasing volume fraction of the S/A latex (Figure 2a), and the S/A latexes with more HEMA showed greater relative viscosities. Figure 2b depicts the relative viscosity data according to the Mooney equation given in eq 2. From the intercepts and slopes of the respective plots, the intrinsic viscosities and critical volume fractions were calculated (Table 1). The critical volume fractions decreased with increasing HEMA content, whereas the intrinsic viscosities increased with HEMA content. Both critical volume fraction and intrinsic viscosity were used to obtain the swelling coefficients.

The swelling coefficients obtained from all three methods increased as the HEMA content increased, corresponding with previous research\(^{16−18}\) (Figure 3). It appeared that the synergic effect of swelling occurred when carboxyl groups and hydroxyl groups coexisted in the S/A latex. This shows that the hydrophilicity of HEMA is one of the major factors responsible for S/A latex swelling. The presence of a hydroxyl group in HEMA increased the hydrophilic property of the S/A latex particles, which contributed to the particle swelling by absorbing and holding more water in the S/A latex. Consequently, the hydrophilic swelling of the S/A latex

![Figure 1](image1.png) **(a) Hydrodynamic diameters of S/A latex particles and (b) swelling coefficient of the S/A latexes.**

![Figure 2](image2.png) **(a) Relative viscosity of S/A latex suspension at pH 9 and (b) graphical display of Mooney equation from the viscosity.**

| HEMA (%) | 0   | 3   | 6   | 9   |
|----------|-----|-----|-----|-----|
| \([\eta]\) | 3.17| 3.84| 4.73| 5.31|
| \(\gamma_c\) | 0.57| 0.56| 0.53| 0.48|
particles made the particles behave like larger ones at higher solids contents.

Quadrat et al. discussed the reason why swelling coefficients from the three methods were different each other. Intrinsic viscosity is obtained when the volume fractions of suspensions are approaching zero. Thus, the swelling coefficient from the intrinsic viscosity shows the particle swelling at extremely low concentrations, which is around 0.01 wt %. On the other hands, the critical volume fraction describes the volume fraction when the viscosity of suspensions becomes infinite. The swelling of the latex particles would be restricted at such high volume fractions because not enough space is available for swelling as in low concentrations, which resulted in lower swelling coefficient from Mooney equation.

Figure 4 shows the images of S/A latex particles treated with acid and alkali. In the acidic condition, the particles had distinct surface, and the uranyl acetate, used for dyeing, was continuously attached to the surface. However, the surface was not so distinct in the alkaline condition compared with its counterpart, which appeared definitely in HEMA 9% conditions. In the alkaline condition, the S/A latex particles, containing 9% of HEMA, were larger than those in acidic conditions, indicating the swelling of the particles. The S/A latex particles had a vague boundary and the dye attached discretely, which also showed nonuniform particle swelling.

To investigate the particles in the suspension state, cryo-TEM images were acquired. Figure 5 shows the quick-frozen latex particles in acidic and alkaline conditions. The latex particles in the acidic condition had clear boundaries, and they were similar in shape, irrespective of the HEMA content. It is also clear that the color density of the outer part of the latex particle was lower than that of the core part of the latex. This suggests that the outer part had a different chemical composition from the core part. It is usual practice to use carboxylic or hydrophilic groups in latex polymerization, and these groups are mainly arranged near the outer part of the latex particle to increase the stability and binding force of the latex.

The shape of the S/A latex particles in the alkaline condition was different. Latex particles with 9% HEMA did not show a clear outline, and their shape looks stellate. This might be because the polymer chains in the outer part were highly swollen or spread in the alkaline condition. However, the degree of swelling was not the same all around the particle surface. Some parts of the latex particle swelled more than other parts, probably because the distribution of HEMA comonomer was not uniform across the whole particle surface.

2.2. Volume Fraction, Dewatering Property, and Low-Shear Viscosity of Coating Color. The solid volume fractions of coating components for four coating colors were similar when the swelling effect by HEMA comonomer was not considered. The effective volume fractions determined by applying the swelling coefficient, however, were higher than those derived without considering the particle swelling (Figure 6a). Because the swollen latex particles occupied more space in the coating color, the effective volume fraction of the coating color also increased with increasing HEMA content. However, the effective volume fraction calculated from the critical
volume fraction did not increase much. According to the previous research,\textsuperscript{5} the swelling coefficient from the intrinsic viscosity describes the low-concentration condition, but the coefficient from the critical volume fraction represents higher concentration conditions. Considering the solids content of coating color of 62 wt %, the actual volume fraction would be higher than the effective volume fraction from Mooney equation, but it would be much lower than that from DLS data. Hence, it seems that there was latex swelling in the alkaline coating colors, yet the effect was suppressed to a great extent in the high solid coating colors because of the limitation in free space and high pigment content in the coating color.

The hydrophilicity of HEMA greatly affected the low-shear viscosity of the coating color (Figure 6b). The increase in effective volume is a probable cause of the viscosity increase. Further, the water retention of the coating color was improved by HEMA, that is, the dewatering amount decreased with increasing amounts of HEMA.

### 2.3. Drying Kinetics of the Coating Layer

The consolidation of the coating layer was monitored by MS-DWS (Figure 7). The movement of the particles slowed as the coating layer dried. According to previous research,\textsuperscript{20} particles in a coating layer form a network structure and the speckle rate (SR) decreases abruptly at the specific time, that is, the immobilization point. Interestingly, the immobilization point appeared earlier in high-HEMA conditions. It was 584.4, 538.4, 490.0, and 459.8 s when the HEMA content was 0, 3, 6, and 9\%, respectively (Table 2). The solid content of the coating layer was also lower in the high-HEMA conditions compared with the low- and no-HEMA conditions. From these data, it can be deduced that the network structure formed earlier when the S/A latex binder had more HEMA monomers. Figure 4 shows that the particle size of the latex with more HEMA was larger in the alkaline condition. This suggested that the coating color was immobilized earlier because of the latex swelling. Binders in the coating layer migrate before the immobilization of the coating layer.\textsuperscript{7} Uneven binder distribution caused by nonuniform binder migration, which often associated with the late immobilization of coating, gives nonuniform printing.\textsuperscript{4} Therefore, the swelling of latex that causes early immobilization would improve the uniformity of the coating layer and printing quality of coated paper. The initial values of the SR showed differences as well, that is, the initial value decreased with increasing HEMA amount in the S/A latex, from 9.7 to 5.9 Hz. These results suggest that even in the initial stage of drying, particle movement was hindered by the swelling of the S/A latexes with HEMA.

### 2.4. Structure of the Coating Layer

SEM images of the coating layer were obtained to analyze the surface structure (Figure 8). A more porous structure was formed in the HEMA 9\% condition compared with the no-HEMA condition, which was more remarkable in the images at high magnification (Figure 8c,d). This result corresponds with the porosity and pore-size distribution results (Figure 9). Figure 9a shows the pore-size distribution of the coating layer. The coating layer with the HEMA 9\% S/A latex has the highest right-skewed peak, indicating that the layer has many large pores. However,
the peak of the HEMA 0% S/A latex coating is skewed left, and the peak is lower than those of the other conditions.

The porosity was investigated using mercury porosimetry and silicon saturation (Figure 9b). In both methods, the porosity of coating layer increased with increasing HEMA amount. That is, the more HEMA there was in the S/A latex, the more porous was the structure formed in the coating layer, with larger pores distributed in the structure. Two of porosity data were similar in its tendency. However, the porosity determined using silicone oil was higher than that of mercury porosimetry, probably because the silicon oil saturation method detected the surface dents as pores.

For visible verification of the structural changes in the thickness direction, a cross section of the coating layer was obtained by focused ion beam microscopy (FIB, Figure 10).

Compared with the condition without HEMA, a more porous and uniform cross section was observed for HEMA 9%. The porosities of the coating layers with HEMA 0% and HEMA 9% calculated from the FIB images were 28.61 and 37.05%, respectively. The porosity values from the image analysis were higher than those obtained from other methods. In the case of FIB images, the unstained latex binders were not clearly distinguished from the pores in the coating layer, which caused overestimation of the pores. Another possible cause lies in the difference in the measurable ranges. Very small pores, which cannot be detected as pores in mercury porosimetry or other liquid intrusion test method, can be detected in the FIB image. For instance, pores ranging from 10 to 100 nm were evaluated in the mercury porosimetry.

As shown in Figure 8, there was less latex film on the coating surface in the high-HEMA condition. It was shown that HEMA augmented the swelling of the S/A latex particles and made the coating layer immobilized earlier. Because the binders in the immobilized layer migrate less, it would be possible to obtain a coating layer with more uniform latex distribution by using S/A latex with a HEMA comonomer. In general, increased pore size and void fraction that accompanies the use of S/A latex with HEMA comonomer will influence ink absorption. Improved uniformity of the coating layer will improve the printing uniformity. Also, less migration of the S/A latex with HEMA is expected to give less print mottling and increase the mechanical properties of coating layer. Because a number of quality specifications including optical, physical, and printing properties should be met for the coated papers, optimization of the S/A latextes with HEMA comonomer should be made in the future.

### 2.5. Shrinkage Rate

The shrinkage rate of the coating layer was investigated based on the coating layer volume. The volume was derived from the MS-DWS and porosity data. Table 3 presents the volumes of the coating layer in three conditions. Before drying, all coating layers had similar volumes, regardless of the HEMA amount. However, the high-HEMA condition had a larger volume at the first critical concentration (FCC) because of the early immobilization of the high-HEMA condition. In other words, the coating layer reached the FCC earlier because of the particle swelling, and the tendency was maintained after drying.

![Figure 9.](image)

**Figure 9.** (a) Pore size distribution of the coating layer and (b) porosity of the coating layer.

![Figure 10.](image)

**Figure 10.** Cross section of the coating layer. (a) HEMA 0%, and (b) HEMA 9%.

![Figure 11.](image)

**Figure 11.** Shrinkage rate and gloss of the coating layer.

| HEMA (%) | before drying (cm³/100 g) | at FCC (cm³/100 g) | after drying (cm³/100 g) |
|----------|--------------------------|-------------------|------------------------|
| 0        | 64.66                    | 40.32             | 36.94                  |
| 3        | 64.56                    | 41.17             | 37.26                  |
| 6        | 64.47                    | 43.08             | 38.85                  |
| 9        | 64.50                    | 43.41             | 38.79                  |

![Table 3. Volume of the Coating Layer](image)

### Table 3. Volume of the Coating Layer
was proportional to the HEMA content. This result indicates that early immobilization increases coating shrinkage, even though it gives more porous coating after drying. Greater shrinkage of the coating after immobilization resulted in lower gloss. According to Järnström et al., the gloss of coated paper has a negative relationship with the roughness of the paper. Even though the S/A latex with a HEMA comonomer gave a more uniform coating structure, it decreased the gloss of the coating layer because of greater shrinkage of the coating. This shows that further study on the optimization of coating structure and coated paper properties should be carried out.

### 3. CONCLUSIONS

This research introduced HEMA as a comonomer for styrene-acrylate latex binder. It explored the swelling properties of S/A latex particles caused by the HEMA monomer and their effect on the properties of coating layer and coated paper. The S/A latex particles swelled increasingly with the HEMA content in S/A latex. Particularly, the swelling occurred in the outer part of the S/A latex particles because of the hydrophilic group present in the outer layer. The swelling and hydrophilicity caused by HEMA increased the solid-like volumes in the coating layer and made the coating layer immobilized earlier. Because the coating components including S/A latex particles interlocked in the earlier drying stages, high HEMA latex gave more uniform and more porous coating layer, which provides many advantages in reducing print mottle, improving picking resistance, and increasing coating uniformity. However, use of S/A latex with a HEMA comonomer reduced the gloss of coated paper, which indicated that optimization of HEMA content need to be made to obtain the target properties.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials

Four S/A latexes with different amounts of HEMA were used in this research, provided by LG Chem. Ltd. (Korea). The HEMA contents of the S/A latexes were 0, 3, 6, and 9 wt % (Table 4). All monomers including HEMA were charged to the polymerization vessel and emulsion polymerized. Properties of the S/A latex except the HEMA content, that is, the particle size, gel content, and glass transition temperature, were controlled to investigate the effect of HEMA content more systematically.

All of the coating layers and coated paper used in this research were made using the same conditions, that is, the same formulation, pH, and solid content were employed. The coating color was made with 100 parts per hundred (php) of pigment, 12 php of S/A latex, and 0.15 php of carboxymethyl cellulose (CMC, Finix 5, CP Kelco, Korea). Ground calcium carbonate (GCC, Setacarb-HG, Omya, Korea) was used as the coating pigment. GCC was dispersed in diluted CMC solution, and the S/A latex binder was added to the dispersion. A stirring time of 20 min was applied after the addition of each component. The total solids contents were 62 wt %, and the pH of the coating color was adjusted to 9 with sodium hydroxide. After mixing for 20 min, the coating color was filtered using a 100-mesh wire screen.

#### 4.2. Swelling of Latex Particles

The degree of swelling of the S/A latex particles was evaluated based on the three swelling coefficients following Horský et al. The first swelling coefficient was calculated from the hydrodynamic diameter ratio of S/A latex particles in acidic and alkaline conditions. The other two swelling coefficients were obtained from the relative viscosity of S/A latex suspensions using Mooney’s equation.

The hydrodynamic diameters of the S/A latex particles were measured using Zetasizer Nano ZS (Malvern Instrument, UK). This instrument measures the particle size by DLS. To evaluate the swelling degree, the S/A latex suspensions were diluted to 0.01% in pH 4 and pH 9 conditions. The suspensions were stabilized for 2 days after adjusting the pH and concentration before the measurement. The swelling coefficient was obtained from the ratio of the diameters in alkaline and acid conditions according to eq 1.

\[
q = \left( \frac{d_{\text{alkali}}}{d_{\text{acid}}} \right)^3
\]  

The relative viscosity was measured using a glass capillary viscometer (Cannon-Fenske Routine Viscometer, USA) at 25 °C in several concentrations. The intrinsic viscosity \([\eta]\) and critical volume fraction \(\phi_c\) were obtained from the intercept and slope of the Mooney equation in eq 2. The swelling coefficients were defined as the ratio of the intrinsic viscosity and critical volume fraction in alkaline conditions to the values in acid conditions (eqs 3 and 4). Theoretical values rather than experimental values were used for the acidic conditions because S/A latex aggregates in acidic conditions.

\[
\frac{1}{\ln(\eta)} = \frac{1}{[\eta]} + \frac{1}{[\eta]d_2^2\phi_c^2}
\]  

\[
q_0 = \frac{[\eta]}{2.5}
\]  

\[
q_\infty = \frac{0.64}{\phi_c}
\]  

The equations described above provide the hydrodynamic changes of the latex particle, but they do not provide any information on the physical changes of the latex. The physical changes of the latex particles were investigated by TEM (LIBRA 120, Carl Zeiss, Germany). Latex particles, however, show physical changes at room temperature by forming films. Therefore, it is necessary to measure the sizes of the particles.

#### Table 4. Monomer Compositions and Properties of S/A Latexes

| S/A latex   | BA (wt %) | SM (wt %) | AA (wt %) | HEMA (wt %) | IA (wt %) | pH | \(T_g\) (°C) | 130 °C gel (%) | S/T (mN/m) | TSC (%) | \(\eta\) (cPs) |
|------------|-----------|-----------|-----------|-------------|-----------|----|-------------|---------------|-------------|---------|--------------|
| SA-HEMA 0% | 56.4      | 39.1      | 3.7       | 0.0         | 0.8       | 6.31| 13.37       | 96.0          | 47.0        | 50.4    | 686          |
| SA-HEMA 3% | 55.3      | 37.2      | 3.7       | 3.0         | 0.8       | 6.31| 16.23       | 96.3          | 45.7        | 49.2    | 704          |
| SA-HEMA 6% | 54.4      | 35.1      | 3.7       | 6.0         | 0.8       | 6.31| 13.27       | 96.1          | 43.9        | 49.3    | 1048         |
| SA-HEMA 9% | 53.5      | 33.0      | 3.7       | 9.0         | 0.8       | 6.31| 15.97       | 95.6          | 43.4        | 48.8    | 1192         |

BA: butyl acrylate, SM: styrene monomer, AA: acrylic acid, HEMA: hydroxyethyl methacrylate, IA: itaconic acid, pH: glass transition temperature, 130 °C gel: gel content of latex film dried at 130 °C, S/T: surface tension, TSC: total solid content, \(\eta\): viscosity.
while they are in suspension. The S/A latex particles in alkaline suspension were analyzed by using cryo-TEM (Talos L120C, FEI, USA) after quick-freezing. The solid content of the S/A latex suspensions was 0.5 wt % at pH 9. The samples were stabilized for 2 days at room temperature before quick-freezing by Vitrobot (FEI, USA).

4.3. Dewatering Property and Low-Shear Viscosity of Coating Color. The dewatering of the coating color was evaluated with an Åbo Akademi Gravimetric water retention meter (ÄA-GWR). Ten milliliters of coating color was loaded onto a membrane filter (mixed cellulose ester membrane filter, pore size 0.2 μm, Advantec), and 1.8 bar of pressure was applied for 60 s. The coating color was dewatered to the blotter paper under the membrane filter. The dewatering amount was calculated by the weight difference of blotter papers before and after dewatering, and it was divided by the dewatering area to obtain the water retention value.

The low-shear viscosity of the coating color was measured by a Brookfield viscometer (Brookfield DV2Y, USA). All of the measurements were made using the same containers at room temperature.

4.4. Drying Kinetics of the Coating Layer. The drying kinetics of the coating layer was investigated by multispeckle-diffusing wave spectroscopy (MS-DWS; Horus, Formulaction, France) (Figure 1). MS-DWS uses DLS and analyzes drying dynamics through the Brownian motion of the particles.24,25 A camera without a lens detects speckle images caused by the interference of backscattered light. At the same time, the dynamics of the particles are evaluated by the intensity difference between these images. In MS-DWS, the intensity difference is analyzed by a vectoral distance (\(d_2\)) between two images (eq 5).

\[
d_2 = \sqrt{\sum (I(x, y) - I(x, y))^2}
\]  

(5)

From the set of speckle images, the interimage distance between each image and the reference one is plotted as a function of time. The correlation function has approximately an exponential shape, and from the correlation function, the SR representing the dynamics of the particles is obtained. A high SR means the fast movement of particles. More detailed information on the instrument and operating principle can be found in literature.20,24,25

Figure 12 illustrates the measurement scheme. The instrument uses a laser with a 655 nm wavelength. It can take images with resolutions of 320 × 240 pixels, and the maximum frame rate was 30 images/s. For the measurement, the wet coating layer was applied to the glass plate using a film-casting doctor blade. Drying conditions were controlled to have constant temperature and humidity (23.0 ± 0.5 °C, RH 50 ± 3%). Simultaneously, the weight change during the process was monitored using an analytical balance (Radwag, Poland). The resolution of the balance was 0.1 mg.

4.5. Structure of the Coating Layer. The images of the surface structure were obtained by a field-emission scanning electron microscope (AURIGA, Carl Zeiss). The pore structure of the coating layer was investigated using a focused ion beam microscope (AURIGA, Carl Zeiss) and a mercury porosimeter (AutoPore IV, Micromeritics Instrument Corp., USA). The coating color was applied to a 100 μm thick polyethylene terephthalate film using a four-sided gap applicator and dried at room temperature.

The porosity of the coating layer was also measured using a mercury porosimeter and by the silicon oil saturation method. In mercury porosimetry, the porosity was calculated by the intrusion volume per coating layer volume (eq 6). The diameters of the pores ranged from 10 to 100 nm, and they were assumed to have a cylindrical shape. When the porosity was checked with silicon oil, the same film used in the mercury porosimeter measurement was used as a coating substrate, but a bar coater was used to apply the coating.

\[
\text{Porosity} (\%) = \frac{\text{intrusion volume (mL)}}{\text{coating layer volume (cm}^3\text{)} \times 100}
\]  

(6)

4.6. Shrinkage Rate. The shrinkage rate of the coating layer was determined from the volumetric data obtained from the drying kinetics and porosity measurements. First, the volume of the coating layer before drying was calculated using the coating color formulation and density of each component. The volume of solids in the coating layer was obtained from the coating color formulation, solid content, and density data of each component. Next, the volume of the coating layer at the immobilization point was obtained from the total weight of the coating layer at the FCC and the dried coating layer. The volume of water at the FCC was calculated from the mass of the coating layer at the FCC and the solid weight of the coating layer. The volume of the fully dried coating layer was obtained from the porosity data and the solid volume of the coating layer.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: lhakl@snu.ac.kr. Phone: +82 2 880 4786.*

**ORCID**

Hak Lae Lee: 0000-0002-2365-4133

**Notes**

The authors declare no competing financial interest.

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