

Characterization of carbon black nanoparticles using asymmetrical flow field-flow fractionation (AsFIFFF)

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Abstract High viscosity carbon black dispersions are used in various industrial fields such as color cosmetics, rubber, tire, plastic and color filter ink. However, carbon black particles are unstable to heat due to inherent characteristics, and it is very difficult to keep the quality of the product constant due to agglomeration of particles. In general, particle size analysis is performed by dynamic light scattering (DLS) during the dispersion process in order to select the optimum dispersant in the carbon black dispersion process. However, the existing low viscosity analysis provides reproducible particle distribution analysis results, but it is difficult to select the optimum dispersant because it is difficult to analyze the reproducible particle distribution at high viscosity. In this study, dynamic light scattering (DLS) and asymmetrical flow field-flow fractionation (AsFIFFF) analysis methods were compared for reproducible particle size analysis of high viscosity carbon black. First, the stability of carbon black dispersion was investigated by particle size analysis by DLS and AsFIFFF according to milling time, and the validity of analytical method for the selection of the optimum dispersant useful for carbon black dispersion was confirmed. The correlation between color and particle size of particles in high viscosity carbon black dispersion was investigated by using colorimeter. The particle size distribution from AsFIFFF was consistent with the colorimetric results. As a result, the correlation between AsFIFFF and colorimetric results confirmed the possibility of a strong analytical method for determining the appropriate dispersant and milling time in high viscosity carbon black dispersions. In addition, for nanoparticles with relatively broad particle size distributions such as carbon black, AsFIFFF has been found to provide a more accurate particle size distribution than DLS. This is because AsFIFFF, unlike DLS, can analyze each fraction by separating particles by size.

Key words: High Viscosity, Carbon black (CB), Asymmetrical flow field-flow fractionation (AsFIFFF), Dynamic light scattering (DLS), Size distribution

1. Introduction

Carbon black is a color pigment with high blackness, and because of its excellent colorability, electrical

conductivity, weather resistance, and chemical resistance, it has broad range of applications, including as a reinforcing agent and filler for plastics and elastomers¹ and a shading agent for a black matrix.²⁻⁴

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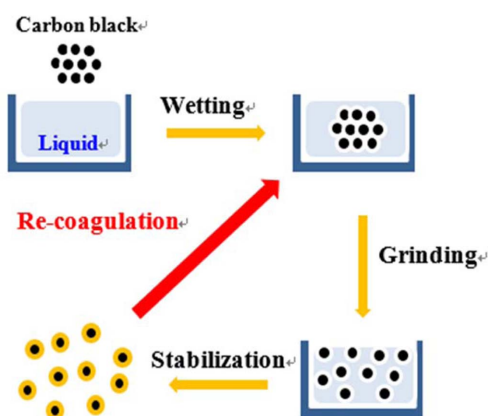


Fig. 1. Three stages of pigment dispersion.

However, carbon black has limitations such as a very small primary particle diameter, high porosity, a large specific surface area, and a strong tendency to form agglomerates owing to strong affinity for each other, which results in its poor dispersion stability. Moreover, as carbon black is hydrophobic, it has poor wettability for water, making it very difficult to disperse high concentrations in aqueous systems.⁵⁻⁸

An effective method for dispersing pigment particles is to use the electrostatic repulsion of electrically charged particles dispersed in a solution.^{4,9,10} Alternatively, an adsorbed surface layer can provide steric hindrance¹¹⁻¹⁴ to maintain a certain spacing between the pigment particles in order to prevent them from agglomerating.^{15,16} Fig. 1 shows the three basic stages of pigment dispersion.

Stage 1 (Wetting): This process involves removing air and moisture present on the surface of the pigment and replacing them with a solution. Here, the solution penetrates into the space between agglomerates.

Stage 2 (Grinding): In this stage, the pigment agglomerates are ground to appropriate size. The particles become smaller in size as the pigment agglomerates are ground by mechanical force (impact and shear force). As the particles become smaller, the surface area of the pigment increases to create instability.

Stage 3 (Stabilization): In this stage, precipitation and re-agglomeration of dispersed particles are prevented. The force that prevents agglomeration

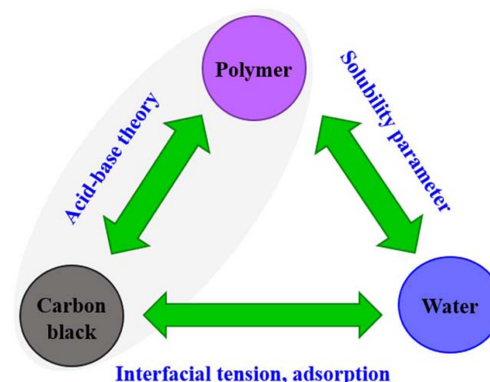


Fig. 2. Three-component system of carbon black dispersion.

originates either from electrostatic repulsion between charged particles or the steric hindrance effect of a polymer adsorption layer.^{17,18}

Fig. 2 shows a simple depiction of three components in carbon black dispersion. For stable dispersion, it is important to achieve a balance between the three components of dispersion: pigment, solvent, and dispersant. Among these three components, the acid–base affinity between the carbon black particles and the dispersant is especially important.^{19,20}

Generally, dispersants are divided into low molecular weight (LMW) and high molecular weight (HMW) types. LMW dispersants typically lack effectiveness on organic pigments consisting of carbon, hydrogen, oxygen, and nitrogen atoms. Accordingly, HMW dispersants are generally used and they usually have an adsorption group with a chain that can be adsorbed on the surface of an organic pigment particle.¹⁰

In the present study, mechanical disruption²¹ was used to analyze the size of particles in a carbon black dispersion according to the type of dispersant and dispersion time. Moreover, styrene maleic acid (SMA) dispersant, a HMW dispersant with excellent thermal stability, was used to prepare the carbon black dispersion. The thermal stability at high temperatures was assessed to verify the stability of the prepared black carbon dispersion. In addition, the study investigated the feasibility of an analytical method using scanning electron microscopy (SEM), dynamic light scattering (DLS), and asymmetrical flow field-flow fractionation (AsFFFF)²² for particle size

analysis to determine the appropriate dispersant and dispersion time for carbon black particles.

2. Theory of AsFIFFF

Field-flow fractionation is a system that separates materials based on the differences in the diffusion coefficient of materials passing through a hollow channel. An AsFIFFF channel separates particles by releasing the fluid into space created by placing a spacer in between two plates. Because of the structural characteristics of the channel, a parabolic flow is formed, where the flow rate in both sides of the plates is slow owing to the surface tension formed inside the channel with the flow rate increasing toward the center of the plate. Consequently, elution occurs in the order of smaller particles to larger particles over time, whereby separation by particle size also occurs. By altering the rate of cross-flow that acts perpendicularly to the channel over time, the sample retention time could be adjusted to increase the separation capability (field-programming).²³

One of the key features of AsFIFFF (AF4) is that the hydrodynamic diameter (d_H) can be calculated directly by measuring the sample retention time (t_r) (refer to Eq. (1)).²⁴⁻²⁶

$$d_H = \frac{2kTV^0}{\pi\eta w^2 V_c t^0 t_r} \quad (1)$$

In Eq. (1), k is the Boltzmann constant; T is the absolute temperature (K); V^0 is the void volume of the channel; η is the viscosity of the carrier liquid; w is the channel thickness; V_c is the cross-flow rate; and t^0 is the time required to pass through the channel volume (void time). In Eq. (1), all the variables, except t_r , are constants under the given experimental conditions, and the t_r of the sample can be measured by AF4 to determine the particle size and size distribution of the sample directly.^{19,27,28}

3. Experimental

3.1. Materials

Carbon black (S.A. 75 m²/g, Bulk density 80-120 g/

L, Alfa Aesar, USA) was used to prepare the carbon black dispersion. For the synthesis of the dispersant, deionized water (Milli Q PLUS), SMA-1000 (styrene maleic anhydride 1000), SMA-2000 (styrene maleic anhydride 2000), and SMA-3000 (styrene maleic anhydride 3000, SARTOMER Co. Ltd, Pennsylvania, USA) were used, along with ammonia water (25-28%, DUKSAN, KOREA) for acidification. Moreover, FL-70 (Fisher Chemical, New Jersey, USA) and sodium azide (NaN₃, Sigma-Aldrich, St. Louis, USA) were used to prepare the AF4 carrier liquid.

3.2. Analytical instruments

A digital overhead stirrer (HT-50DX, DAIHAN-brand, Korea) was used to prepare the carbon black dispersion, and a heating mantle (DH.WHM 12214, DAIHAN-brand, Korea) was used to apply heat during stirring. The physical properties and stability of the prepared carbon black solution were assessed using a pH and conductivity meter (OHAUS Corp, OHAUS STARTER 3100C, USA) and a viscosity meter (Brookfield, LVDVE 230, USA). To measure the color of carbon black, a colorimeter (CR-400 Chroma meter, Konica Minolta, USA) was used.

Moreover, a transmission electron microscope (TEM; JEM-F200, JEOL Ltd., Japan) and field-emission scanning electron microscope (FE-SEM; JEOL-7800F, JEOL Ltd., Japan) were used for the identification of the morphology and size of the carbon black particles, whereas dynamic light scattering (DLS; ELSZ-2000, Otsuka, Japan), AF4 short channel (Wyatt Tech, Europe GmbH, Dembach, Germany), cellulose membrane with cut-off MW of 10 kDa (Millipore, Bedford, USA), and a Mylar space with the thickness of 250 μ m were used for the measurement of particle size and size distribution. The carrier liquid used in AF4 analysis was an aqueous solution containing 0.1% FL-70 and 0.02% NaN₃. The flow of the carrier liquid was generated using a high-performance liquid chromatography (HPLC) pump (P-6000, FUTECS Co., Ltd, Korea), whereas an Optiflow 1000 Liquid Flowmeter (Agilent Technologies, Palo Alto, CA, USA) was used to measure the flow rate. A UV detector (Spectra SERIES UV 150, THERMO SEPARATION

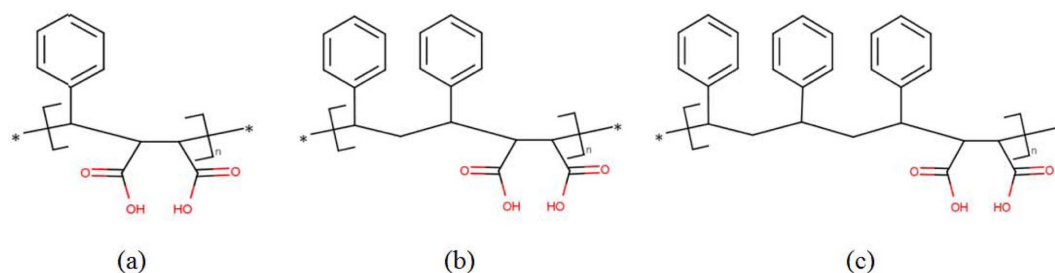


Fig. 3. Structure of synthesized SMA dispersant. (a) SMA1000, (b) SMA 2000, (c) SMA 3000.

PRODUCTS, USA) was used to detect the samples eluted after being separated by particle size from AF4. The analysis was performed with a channel flow of 0.8 mL/min and cross-flow of 0.3 mL/min. The samples were injected using a syringe pump (Legato 110, KD Scientific Inc., Mendon, USA), with 50 μ L being injected at a rate of 0.2 mL/min. To evaluate the reproducibility of the analysis results, all the measurements were repeated thrice.

3.3. Synthesis of dispersant

For the dispersion of carbon black particles, three types of dispersants were synthesized.²⁹ First, after adding 42 g of SMA powder to a three-neck flask, 42 g of DI water was added and mixed by stirring. Here, a heating mantle was used to raise the temperature of the solution up to 80 °C. Once the temperature of the solution reached 80 °C, 24 g of ammonia water was added and mixed by stirring for 2 h to synthesize the dispersant. As there were three different types of SMA powder, three different types of dispersant were prepared. Fig. 3 shows the structure of the synthesized SMA 1000, SMA 2000, and SMA 3000.

3.4. Preparation of high-viscosity carbon black dispersion

For the preparation of carbon black dispersion, a basket mill (HSX0502251, Hyosung, Korea) was used. Accordingly, 75 g of SMA dispersant and 420 g of distilled water were added to 5 g of carbon black. The size of the beads used was 0.8 mm and a total of 350 g of beads were used to perform milling at 1,500 rpm.

4. Results and Discussion

4.1. Storage stability analysis of carbon black dispersion

High-viscosity carbon black dispersion requires an accurate size analysis method for the optimization of dispersion time and dispersant. DLS, which is currently used, shows reproducibility for the particle distribution of a low-viscosity dispersion, but it has the disadvantage of not being able to produce reproducible results with a high-viscosity dispersion owing to the decline in particle mobility. Owing to such a reason, high-viscosity carbon black dispersions have limited industrial application. In the present study, different types of dispersants and milling times were used to assess storage stability over 11 days at 60 °C. Figs. 4, 5, and 6 show the changes in pH, viscosity, conductivity, and particle size over time in the carbon black dispersion prepared using SMA 1000, SMA 2000, and SMA 3000 dispersants, respectively. In all the cases, the milling time was 1–3 h. It was confirmed that, after 3 h, the particles became bigger owing to overdispersion. For the confirmation of stability, measurements were obtained over 11 days at 60 °C. It was also confirmed that most cases showed slight changes after 11 days. The results shown in Figs. 4, 5, and 6 are summarized in Tables 1, 2, and 3, respectively. All the subsequent experiments showed the results from three repeated measurements.

Figs. 4, 5, and 6 and Tables 1, 2, and 3 showed that the pH and viscosity remained constant without significant change. However, the carbon black dispersion

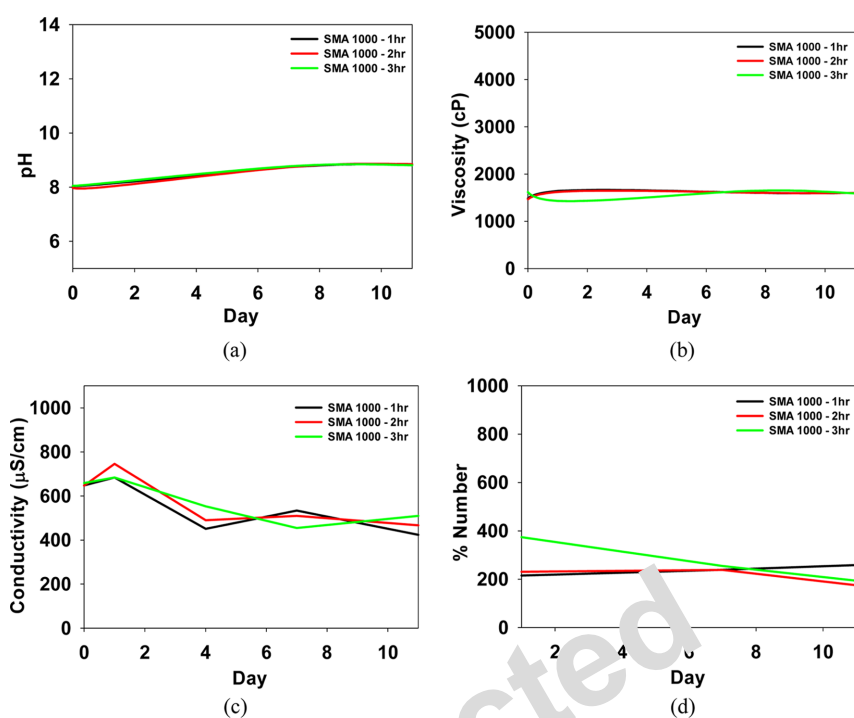


Fig. 4. The pH change of carbon black dispersion prepared by using SMA 1000 according to milling time (1~3 hr) at 60 °C, 11 days (a), viscosity (b), conductivity (c), particle size (d).

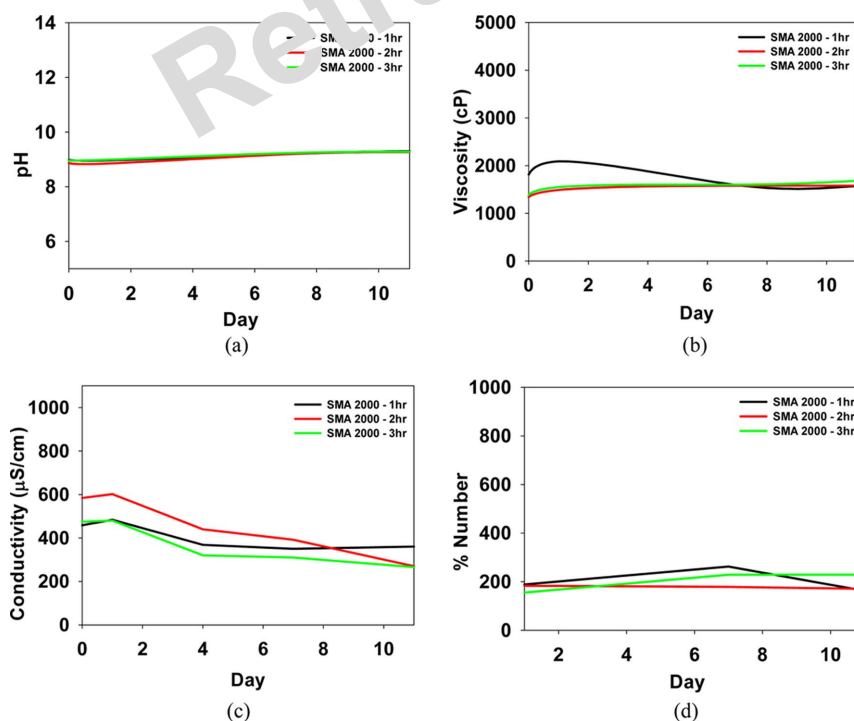


Fig. 5. The pH change of carbon black dispersion prepared by using SMA 2000 according to milling time (1~3 hr) at 60 °C, 11 days (a), viscosity (b), conductivity (c), particle size (d).

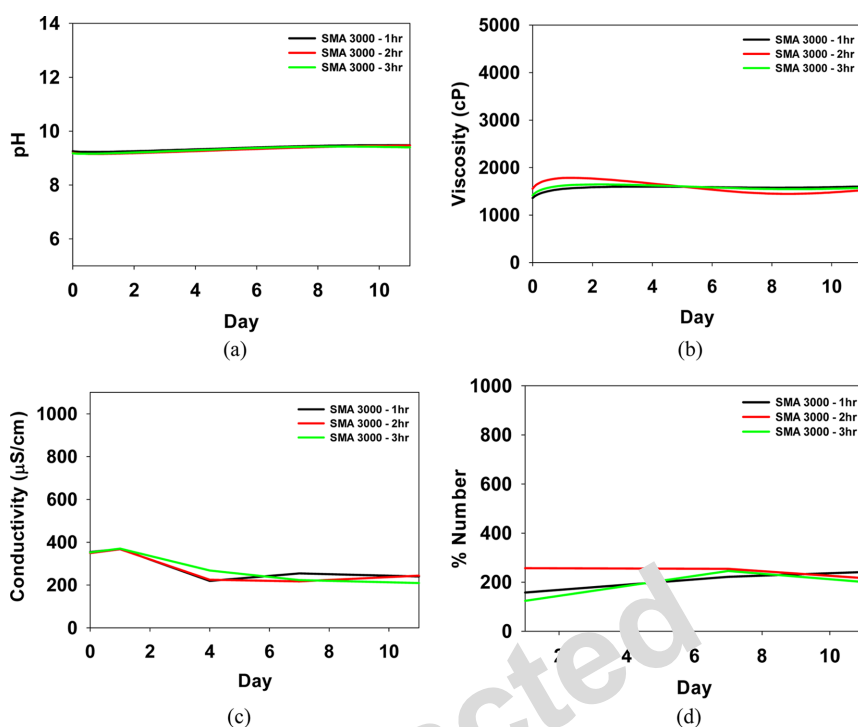


Fig. 6. The pH change of carbon black dispersion prepared by using SMA 3000 according to milling time (1~3 hr) at 60 °C, 11 days (a), viscosity (b), conductivity (c), particle size (d).

Table 1. The storage stability of carbon black dispersion prepared by using SMA 1000 according to milling time (1~3 hr) at 60 °C, 11 days

SMA 1000	pH	Conductivity (μS/cm)	Viscosity (cP)	DLS (nm)
1 hr	8.46±0.39	573±118	1,520±199	238±21.7
2 hr	8.43±0.42	593±128	1,510±200	215±34.7
3 hr	8.45±0.39	577±112	1,660±232	274±91.6

Table 2. The storage stability of carbon black dispersion prepared by using SMA 2000 according to milling time (1~3 hr) at 60 °C, 11 days

SMA 2000	pH	Conductivity (μS/cm)	Viscosity (cP)	DLS (nm)
1 hr	9.14±0.15	413±168	1,620±358	204±51.9
2 hr	9.08±0.19	462±159	1,450±214	178±65.6
3 hr	9.12±0.15	385±111	1,490±241	204±42.4

Table 3. The storage stability of carbon black dispersion prepared by using SMA 3000 according to milling time (1~3 hr) at 60 °C, 11 days

SMA 3000	pH	Conductivity (μS/cm)	Viscosity (cP)	DLS (nm)
1 hr	9.14±0.15	304±66.6	1,450±259	207±43.8
2 hr	9.08±0.19	294±74.8	1,470±280	243±22.6
3 hr	9.12±0.15	289±84.5	1,460±258	190±61.5

prepared using SMA 1000 dispersant showed the largest decrease in conductivity i.e., 77.4 % on day 11, as compared with the baseline. This decrease was larger than that observed when other dispersants were used. It is suspected that the surface charge values of the particles gradually decreased owing to the cohesive force between the particles. Moreover, the 2 h dispersion data of SMA 2000 and SMA 3000 remained consistent over 11 days, which indicated that dispersion for 2 h had the highest stability.

4.2. Morphology of carbon black particles

SEM images were examined to check the morphology

of the prepared carbon black particles.

An examination of the SEM images showed that the primary particle diameter of carbon black was within the range of 30–40 nm. Moreover, the particles were present as irregularly shaped agglomerates, but not spherical ones. These results demonstrated that the dispersion process stably maintained the appearance of the carbon black particles without any deformation.

4.3. Particle size analysis of carbon black dispersion

Particle size analysis of the prepared carbon black

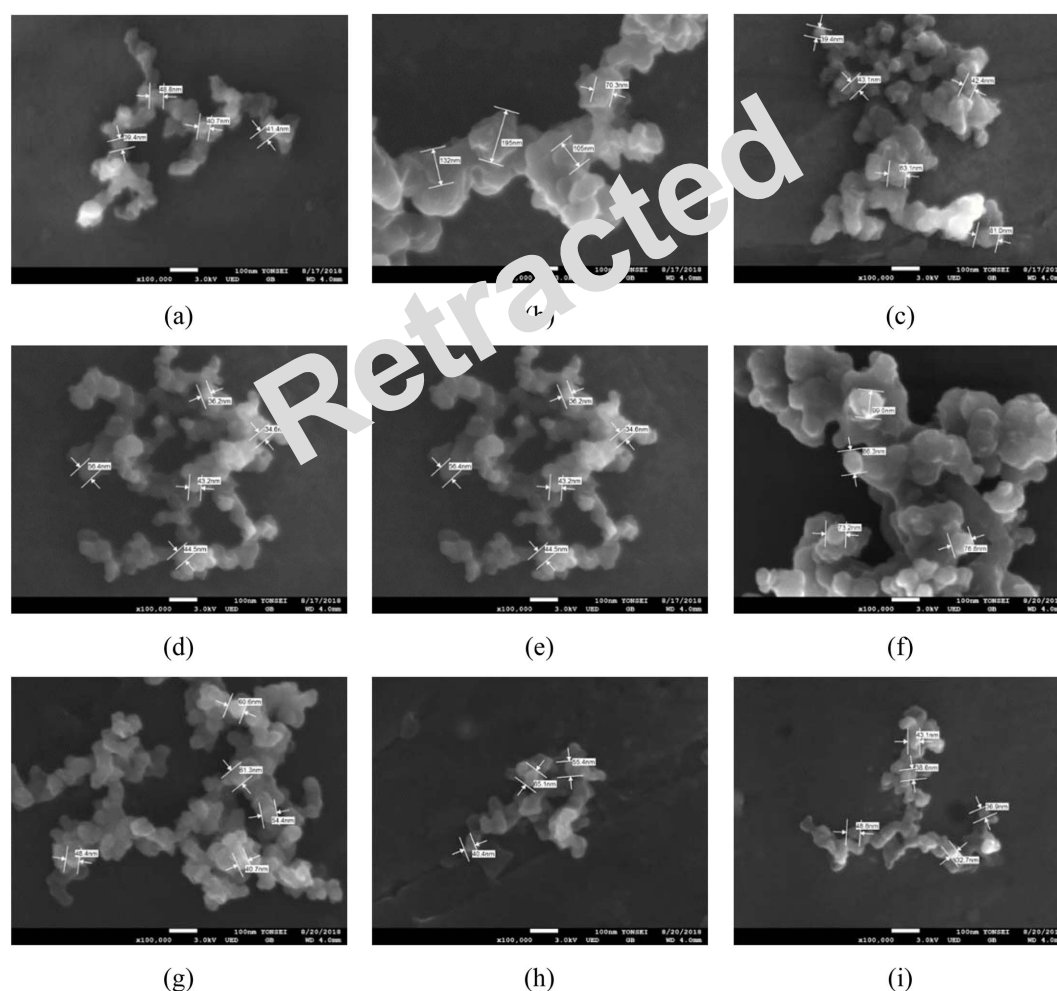


Fig. 7. SEM image of carbon black particles according to dispersant and milling time (X 100,000). (a) SMA 1000, milling 1 hr, (b) SMA 1000, milling 2 hr, (c) SMA 1000, milling 3 hr, (d) SMA 2000, milling 1 hr, (e) SMA 2000, milling 2 hr, (f) SMA 2000, milling 3 hr, (g) SMA 3000, milling 1 hr, (h) SMA 3000, milling 2 hr, (i) SMA 3000, milling 3 hr.

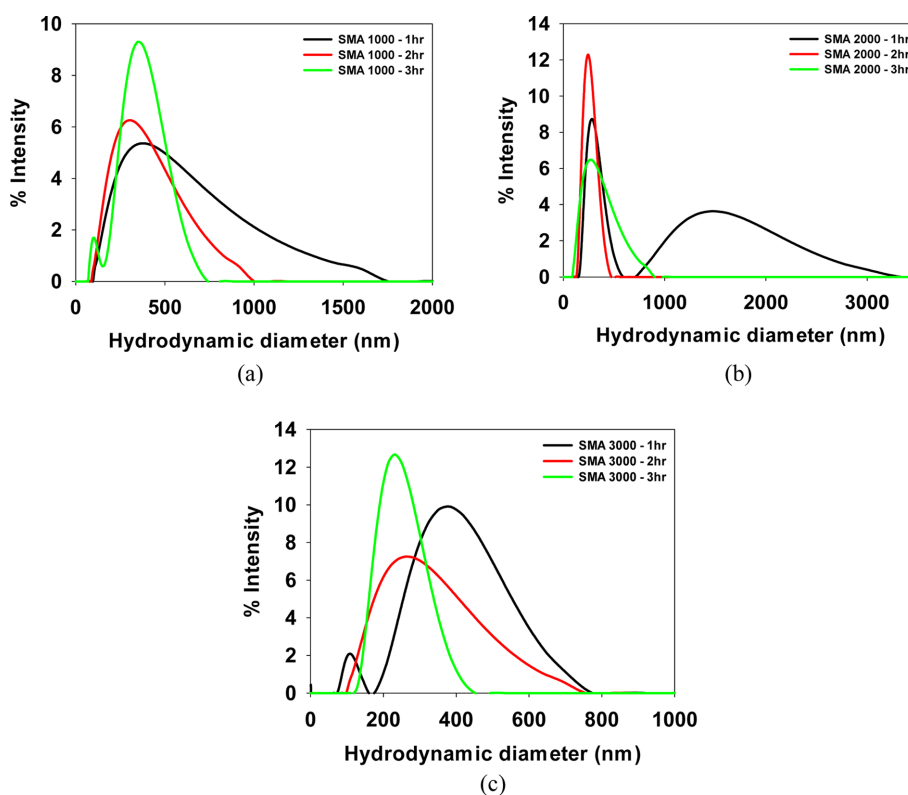


Fig. 8. DLS particle size analysis of carbon black suspension according to milling time. SMA 1000 (a), SMA 2000 (b), SMA 3000 (c).

Table 4. DLS particle size analysis of carbon black suspensions

Milling time	1 hr	2 hr	3 hr
SMA 1000	472±292	340±168	104±17.2 359±109
SMA 2000	257±66.1 1,070±335	252±61.6	307±146
SMA 3000	110±17.2 390±111	292±121	240±58.2

dispersion was performed using DLS and AF4. The sample analyzed was carbon black dispersion stored for 11 days at 60 °C. Fig. 8 and Table 4 show the results from DLS.

As shown in Fig. 8, the DLS particle size analysis results showed the progression of agglomeration owing to overdispersion after 3 h of milling, regardless of the type of dispersant. Moreover, based on the appearance of two peaks after 1 h of milling, an undispersed state was suspected. Accordingly, it was

determined that 2 h of milling was the optimal dispersion time. Considering the aforementioned conductivity results and DLS results, a stable dispersion of carbon black particles may be difficult to achieve with the SMA 1000 dispersant. It is suspected that this is because the SMA 1000 dispersant is desorbed from the surface of carbon black because of the heat owing to the lack of styrene groups within the SMA 1000 dispersant covalently bonded to carbon black. However, the DLS results showed that, as the range of error was too large, it was still difficult to determine the optimal dispersant and dispersion time.

Fig. 9 and Table 5 show the AF4 results for the same sample.

Unlike the DLS results, the AF4 measurement results showed a tendency of gradual decrease in the particle size according to an increase in milling time when the SMA 1000 and SMA 2000 dispersants were used, whereas the particle size tended to increase

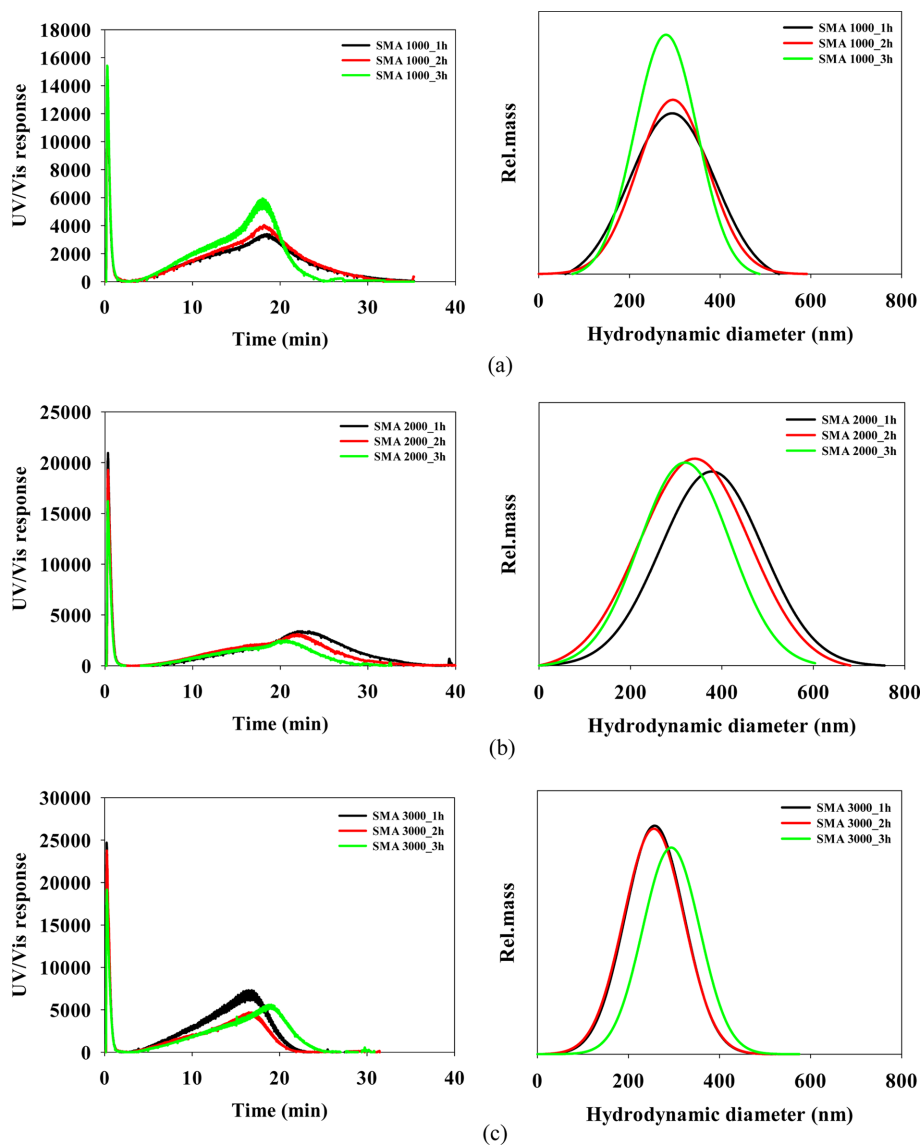


Fig. 9. AF4 fractograms of carbon black suspension according to milling time. SMA 1000 (a), SMA 2000 (b), SMA 3000 (c). The AF4 channel flow rate was 0.3 mL/min and the cross flow rates was 0.3 mL/min, and the carrier liquid was water containing 0.1% FL-70 and 0.02% NaN_3 .

Table 5. AF4 particle size analysis of carbon black suspensions

Milling time	1 hr	2 hr	3 hr
SMA 1000	291±79.1	295±77.1	286±85.4
SMA 2000	314±90.0	279±87.2	267±46.0
SMA 3000	274±22.9	275±25.3	295±70.3

according to the milling time when the SMA 3000 dispersant was used. As with the DLS results, this

indicated that, when SMA 3000 was used, 3 h of dispersion resulted in a gradual increase in the particle size owing to overdispersion. As shown in Table 5, the overall reproducibility of the AF4 particle size analysis appeared more consistent than that of DLS. Especially, when SMA 3000 is compared, AF4 showed a relative standard deviation (SD) of 34.8, whereas DLS showed a relative SD of 175, which was approximately 5 times higher.

Table 6. Colorimetric results of carbon black suspensions prepared using SMA 2000

SMA 2000	1 hr	2 hr	3 hr
L*	24.3±0.01	24.3±0.01	23.9±0.01
a*	0.34±0.03	0.34±0.02	0.33±0.04
b*	0.08±0.02	0.23±0.01	0.28±0.02

Table 7. Colorimetric results of carbon black suspensions prepared using SMA 3000

SMA 3000	1 hr	2 hr	3 hr
L*	23.3±0.01	24.6±0.01	24.1±0.01
a*	0.38±0.06	0.29±0.04	0.31±0.03
b*	0.23±0.02	0.12±0.02	0.25±0.02

4.4. Colorimetric analysis of carbon black dispersion

A colorimeter was used for the additional analysis of carbon black dispersion. A colorimeter provides the numerical values for brightness (L*), redness (a*), and yellowness (b*). Colorimetric measurements were performed using the stable dispersants SMA 2000 and SMA 3000. Tables 6 and 7 show the colorimetric measurement results of the carbon black dispersion obtained using the SMA 2000 and 3000 dispersants for the same samples as mentioned above (samples store for 11 days at 60 °C).

Colorimetric measurement results showed that, when the SMA 2000 dispersant was used, the lowest L* value was observed at the milling time of 3 h, whereas when the SMA 3000 dispersant was used, the lowest L* value was observed at the milling time of 1 h. The L* value represents brightness and luminosity, where a lower L* value is closer to black, indicating the smallest particle size. The results in Tables 6 and 7 showed similarity with the AF4 results shown in Table 5 with respect to the correlations of particle size.

Based on these results, it is believed that additional optimization studies are required to use the SMA 1000 dispersant for the dispersion of carbon black. AF4 and colorimetric analyses results confirmed that the preparation of stable carbon black dispersions would be possible with a milling time of 3 h when the SMA 2000 dispersant is used and 1 h when the

SMA 3000 dispersant is used.

5. Conclusions

The present study analyzed the characteristics of carbon black particles. Carbon black tends to agglomerate easily due to low thermal stability. In particular, the agglomeration of carbon black used as a pigment can cause color changes and product defects. Therefore, the selection of a stable dispersant and optimal dispersion time is important. In the present study, appropriate types of dispersant and milling times for the preparation of stable carbon black dispersions were identified through AF4 and colorimetric analyses.

In the particle size analysis of high-viscosity carbon black dispersions, conventional DLS results showed relatively low reproducibility, whereas AF4 results showed relatively high reproducibility. Moreover, the correlations of AF4 and colorimetric analyses results for the type of dispersant and milling time verified these as powerful analytical methods for determining the appropriate dispersant and milling time for high-viscosity carbon black dispersion.

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