

샴푸의 모발 손상에 대한 코아세르베이트 시스템의 영향

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Effect of the Coacervate Systems in Shampoo Formulation on Hair Damage

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요약: 코아세르베이트의 구조는 모발의 침착에 매우 큰 영향을 줄 수 있다. 본 연구의 목적은 모발의 표면 성질과 모발 손상에 미치는 영향에 대해 상대적으로 미세하고 균일한 구조를 갖는 코아세르베이트의 효과를 조사하였다. 본 연구에서는 10% 농도로 희석한 샴푸 용액에서 크기가 다른 코아세르베이트를 탐구하였다. 하나의 용액은 입자의 크기가 균일하지 않은 코아세르베이트(평균 10 - 300 μm)를 함유하고, 다른 용액은 미세하고 균일한 구조(평균 1 - 3 μm)의 코아세르베이트를 형성하였다. 샴푸가 모발의 물리적 성질과 모발 손상에 미치는 영향을 연구하기 위해 두 종류의 샴푸를 사용하여 모발 파괴 특성, 색 변화, 마찰 특성, 지질 함량 및 모발 표면을 조사하였다. 결과는 상대적으로 미세하고 균일한 크기의 코아세르베이트가 모발 표면에 고르게 침착되었음을 명확하게 보여주었다. 결과적으로, 코아세르베이트 계는 모발 마찰, 파손 특성 및 색상과 같은 모발의 표면 성질에 실질적으로 영향을 미칠 수 있다. 마찰력 역시 크게 감소하였다. 미세하고 균일한 크기의 코아세르베이트의 사용은 현저하게 모발 표면 특성을 향상시킬 수 있다. 결론적으로, 모발 파괴가 감소하였고 코아세르베이트의 모발 손상에 대한 영향은 현저하게 높았다.

Abstract: The structure of the coacervate can dramatically influence deposition on the hair. The purpose of this study was to investigate the effect of coacervate with a relatively fine and uniform structure on the surface properties of hair and its influence on hair damage. In this study, coacervates of different sizes were explored in 10% shampoo solutions; one solution contained coacervates with non-uniform sizes (10 - 300 μm average), and the other solution formed a coacervate with a fine and uniform (1 - 3 μm) structure. To study the effect of shampoo on the physical properties of hair and damage to the hair, the hair breakage characteristics, color changes, friction properties, lipid contents and hair surface were examined after using two different types of shampoo. The results clearly show that the relatively fine and uniformly sized coacervate was evenly deposited over the surface of the hair. As a result, the coacervate system can substantially influence the surface properties of the hair such as hair friction, breakage characteristics, and color. The frictional force was dramatically reduced. The use of a fine and uniformly sized coacervate can notably improve hair surface properties. Consequently, hair breakage decreased, and the effect of the coacervate on hair damage was remarkably high.

Keywords: hair treatment, polymers, shampoo, fine coacervate, hair damage

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1. Introduction

Conventional shampoos are composed of anionic / amphoteric surfactants for cleansing and foaming, and cationic polymers for hair conditioning, stabilizing, increasing viscosity, foam stabilizing, and deposition of other conditioning materials[1-3]. Anionic / amphoteric surfactants and cationic polymers coexist in the shampoo as mixed micelles or structured micelles. However, in specific formulations, these compounds can generate polymer-surfactant complex coacervates that separate into a distinct phase during the rinsing stage of the shampoo process[4-7]. This phase separation is a well-known phenomenon called coacervation or the “Lochhead Effect”[8]. The coacervation is very important for conditioning shampoos (also known as 2-in-1 shampoos), especially during the wet and rinsing stages of the shampooing process[9]. Coacervate can effectively be deposited onto the hair surface, providing multiple benefits to hair[10-15]. Most conditioning shampoos depend on the deposition of the polymer-surfactant coacervate to confer good wet combing and manageability to the hair[16,17]. Coacervate is also associated with the dry feel of the shampoo through the formation of thin films with insoluble active ingredients dispersed within the shampoo onto the surface of the hair. Coacervate can form a co-aggregate with suspended materials in the shampoo solution during the rinsing process. In addition, the co-aggregate can then be deposited on the surface of the hair[18,19]. When the hair dries, the surface of hair remains coated with a thin film composed of the polymer-surfactant coacervate and insoluble active ingredients that were dispersed within the shampoo. Thus, coacervates play a crucial role in determining the dry feel of the hair after shampooing[20,21]. Sara Llamas et al. reported that the adsorption, structure and properties of both the polyelectrolytes and the layers of the polyelectrolyte-surfactant complex are governed by a complex balance of interactions that determine the bulk conformation of the different chains/molecules/aggregates and consequently defines their partition between the bulk and the surface/interface. While charged homopolymers have

been used to maximize the adsorption and perception of hair softness, other mechanisms, such as more complex polymer structures and compositions that may influence the surface structuring or the adsorption of non-charged or negatively charged polymers, are much less explored[22]. M. Miyake et al. showed the dissolved state and physicochemical properties of oppositely charged polymer/surfactant complexes in a dilute deposition system[23]. There is great interest in reducing hair damage because human hair can be easily damaged by chemical treatments (including bleaching and permanent waving), ultraviolet radiation, heat exposure and physical treatments including hair drying and combing[24-28]. In addition, hair damage can occur during daily grooming including combing and shampooing. Specifically, the surfactants in shampoo can damage hair[29-32]. In fact, changes in hair properties caused by chemical and physical factors and methods to treat/reduce hair damage have been widely studied. However, it is challenging to investigate the structure of the coacervates formed during the shampooing process and the effects of coacervates of different sizes and volumes on hair properties. Herein we demonstrate the great deposition properties of coacervation with fine and uniform structures compared to non-uniformly sized coacervation and its dramatic effects on the physical and sensory properties of hair.

2. Materials and Methods

2.1. Materials

All materials were used as received.

Anionic surfactants. Disodium laureth sulfosuccinate (3-EO, 30%), ammonium laureth sulfate (3-EO, 25%) and ammonium lauryl sulfate (26% solution) were all purchased from Miwon Commercial Co., Ltd. (Korea). Sodium lauryl sulfate (30%) was obtained from LG Household & Health care (Korea).

Cationic polymers. Guar-hydroxypropyltrimonium chloride (100%) was purchased from Rhodia (France), and polyquaternium-7 (9%) was purchased from Lubrizol (USA).

Hair damaging agents. Monoethanolamine (98%), am-

Table 1. The Composition of the Simple Shampoos Used in This Study

Ingredient	Shampoo A	Shampoo B
D.I. Water	87.7	87.7
Polyquaternium-7	-	0.3
Guar-Hydroxypropyltrimonium Chloride	0.3	-
Ammonium Laureth Sulfate (3-EO)	8.5	-
Ammonium Lauryl Sulfate	3.5	-
Disodium Laureth Sulfosuccinate (3-EO)	-	12.0
Total	100.0	100.0
pH	5.0-5.5	5.0-5.5

monia solution (25%), and hydrogen peroxide (30%) were purchased from Sigma-Aldrich. Ammonium thioglycolate (50%) was purchased from Junsei (Japan). Reagents for adjusting the viscosity and pH of the shampoo formulation such as sodium chloride, citric acid, and sodium citrate were purchased from Sigma-Aldrich.

2.2. Preparation of Normal and Damaged Hair Tresses

Tresses of virgin dark hair were purchased from DeMeo Brothers Inc. (New York, USA). The hair tresses were chemically damaged by perming using a 1 M solution of ammonium thioglycolate at pH 9.5, and sodium hydroxide was used to adjust the pH. The hair tresses were wetted with twice as much of the prepared solution by weight and stored for 10 min at a constant temperature of 25 °C to reduce the disulfide bonds in the hair. Treated hair tresses were rinsed with tap water for 5 min and then dried on paper towels at room temperature. The disulfide bond-reduced hair tresses were wetted with 3 wt% hydrogen peroxide solution with pH 7 and then stored at a constant temperature of 25 °C for 10 min to allow the tresses to be oxidized. After that, the treated tresses were cleansed twice with 15 wt% SLS then dried at 25 °C at a relative humidity of 50 RH%.

2.3. Preparation of Simple Shampoo Formulations

Hair breakage characteristics, color changes, friction properties, lipid contents and hair surface images were examined after using the two different types of shampoo shown in Table 1.

2.4. Particle Size Distribution within the Coacervates

The shampoos described in Table 1 were diluted in water to form 10 wt% solutions to generate the coacervates and stirred at 50 rpm for 3 min to avoid precipitation. The particle size distribution was determined using a MASTERSIZER 2000 particle size analyzer (Malvern Instruments, UK).

2.5. Hair Breakage

Bleaching damaged hair tresses (5 g) were washed 3 times with 0.5 g of the shampoos described in Table 1. The washed hair tresses were stored in a constant temperature room at 25 °C and 50 RH% for 8 hours to dry completely and minimize the effect of humidity. The extent of hair breakage was examined after combing 500 times by automatic combing machine.

2.6. Hair Color Change

The initial hair color of the virgin hair tresses (5 g) and perm-damaged hair tresses (5 g) was measured by a color meter (Labscan XE, Hunter Lab, USA). The hair tresses were washed 30 times with the shampoos described in Table 1 and then stored in a constant-temperature room at 25 °C and 50 RH% for 8 hours to dry completely and minimize the effect of humidity. The difference in the colors (ΔE) of the initial hair tresses and the tresses washed 30 times was determined.

2.7. Hair Surface Friction

The perm-damaged hair swatch (5 g) was washed 30 times with the shampoos described in Table 1 and then

stored in a constant-temperature room at 25 °C and 50 RH% for 8 hours to dry completely and minimize the effect of humidity. The commercial XE-series atomic force microscope (AFM, XE-100, Park Systems, Suwon, Korea) was used for this study. All images were obtained using contact mode with an NSC36C Cr-Au cantilever (spring constant 0.60 N/m, tip radius 35 nm, Mikromasch, Germany). Topography images were obtained at 10 spots in 22 $\mu\text{m} \times 22 \mu\text{m}$ regions at a scan rate of 0.8 Hz, and lateral force mode (LFM) was also examined in situ. All AFM images were plane-flattened using XEI software (v. 4.3.4 build2), and Rq was calculated according to Equation 1:

$$R_q = \sqrt{\frac{\sum_{n=1}^N (z_n - z_m)^2}{N-1}}$$

2.8. Hair Surface Lipids

Virgin hair tresses (5 g) were washed 30 times with 0.5 g of the shampoos described in Table 1. To remove residual reagents during the shampooing process, each hair tress was washed with sodium lauryl sulfate (15% solution). The treated tresses were stored in a constant-temperature room at 25 °C and 50 RH% for 8 hours to dry completely and minimize the effect of humidity. The dried hair tresses were analyzed with an FT-IR spectrometer, and the spectra were used to determine the lipid contents on the hair by comparing the intensity of the CH₂ stretching band at 2925 cm⁻¹.

2.9. Cryo-Scanning Electron Microscopy

A JSM-840A cryo-scanning electron microscope (cryo-SEM, Jeol Ltd., JAPAN) was used to analyze the surface of the hair. Alto 2500 cryo-transfer equipment (Gatan Inc., US) was used to treat the test samples. The pretreatment and preparation procedures for the cryo-SEM samples included freezing, cutting, etching, coating and analyzing. The acquisition conditions for the cryo-SEM micrographs were an accelerating voltage of 20 kV and a probe current of 1 $\times 10^{-9}$ A.

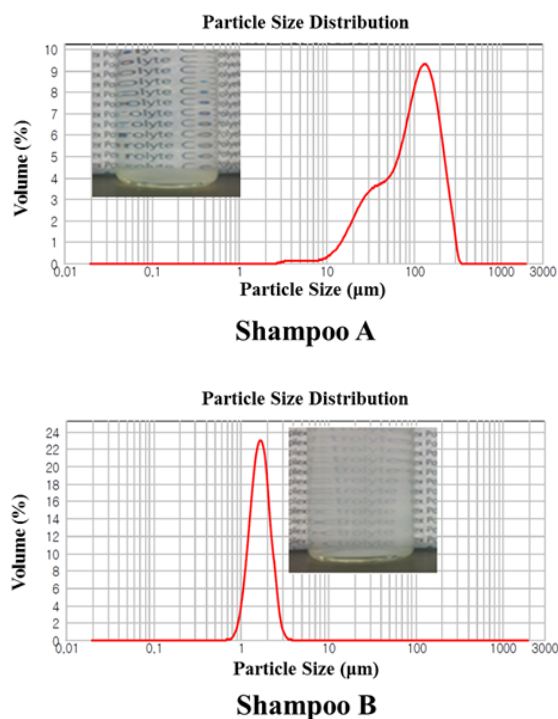


Figure 1. The particle size distribution of coacervates prepared from shampoos A and B.

3. Results and Discussion

3.1. Particle Size Distribution within the Coacervates

The particle size distributions within the coacervates prepared with 10 wt% solutions of Shampoo A and B were compared. The coacervate formed with shampoo A had a relatively higher and broader range of sizes (10 - 300 μm). Interestingly, the coacervate prepared with shampoo B was more uniform in size (1 - 3 μm). The results show that the anionic surfactant and the cationic polymer composition have strong influences on the coacervation profiles. Specifically, the differences in the coacervation size distributions can be attributed to the structure of the anionic surfactant and cationic polymer used in the formulations of shampoo A and B. As for the structures of the cationic polymers, polyquaternium-7 has a more flexible backbone than guar-hydroxypropyl-trimonium chloride. Regarding the anionic surfactants, disodium laureth sulfosuccinate (3-EO) has two anionic

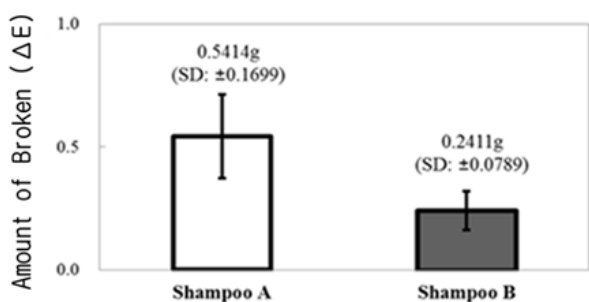


Figure 2. The amount of broken hair (g) in the bleached tresses caused by combing after washing 30 times with shampoos A and B.

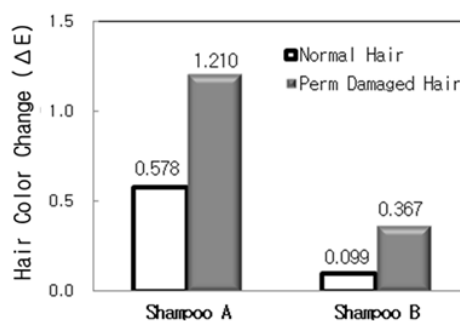


Figure 3. The color change (ΔE) for normal and perm-damaged hair after washing 30 times with shampoos A and B.

head groups unlike ammonium laureth sulfate (3-EO) and ammonium lauryl sulfate which only have one anionic head group. Coacervation with a relatively fine and uniform size can be prepared with shampoo B because the flexible cationic polymer backbone and two anionic heads of the surfactant creates very dense and small polyelectrolyte complexes called loop-crown structures. The loop-crown polyelectrolyte complex has relatively lower cationic charge density, which prevents these complexes from easily aggregating. As a result, coacervation with a small and uniform size can be prepared without aggregation.

As shown in Figure 1, the particle size distributions were measured on a particle size analyzer. The inset pictures in Figure 1 were obtained 24 hours after formation of the coacervation. The coacervate prepared with shampoo A precipitated out of solution; in contrast, the coacervate prepared with shampoo B remained evenly dispersed in the test tube due to the influence of the particle size distribution.

3.2. Evaluation of Hair Breakage after Washing

Figure 2 shows the amount of broken hair (g) after washing 30 times with shampoos A and B. This test was designed to evaluate the breakage of hair during brushing automatically carried out with a brushing machine. Figure 2 shows the amount of hair broken during the brushing process. Under these conditions, hair breakage was reduced by 44.5% after treatment with shampoo B. There was a statistical difference between two amounts with $p < 0.01$.

The formulations for two shampoos are different at the conditioning polymer and the surfactant, resulting in different physical property. The formulation with cationic polymer and anionic surfactant allows a phase separation phenomenon, known as coacervation. The formulation of the shampoo B involves disodium laureth sulfosuccinate, contains two negatively charged head group, generates more adhesion for the polymer to the surfactant than the adhesion in the shampoo A. The backbone chain of a polyquaternium-7 in the shampoo B possesses higher flexibility in comparison to the cellulose polymer in the shampoo A. Taken together, the coacervation in the shampoo B seems to be formed with high density in comparison to that in the shampoo A. As a result, the shampoo B forms a fine and uniformly sized coacervate with a large surface area, which causes it to be uniformly deposited on the surface of the damaged hair. Thus, the frictional force of the hair surface was dramatically reduced and hair breakage decreased.

3.3. Evaluation of the Change in Hair Color due to Washing

The change in hair color (ΔE) after washing the tresses 30 times with shampoos A and B is presented in Figure 3. The ΔE of the virgin hair washed with shampoo A was 0.578 and that of shampoo B was 0.099. In the case of perm-damaged hair tresses, the ΔE when using shampoo A was 1.210 and that of shampoo B was 0.367. Notably, perm-damaged hair showed a substantial color change after washing. Treatment with shampoo B

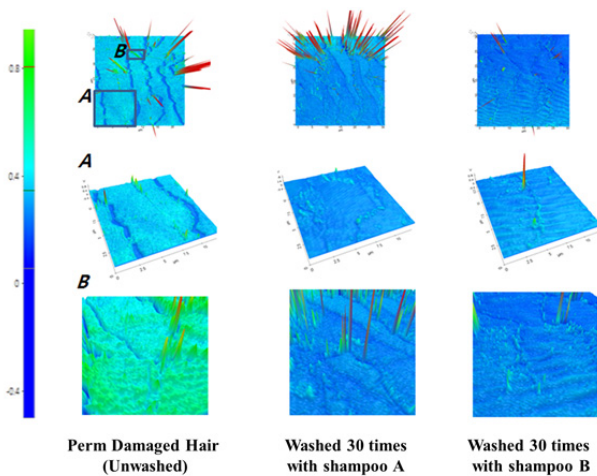


Figure 4. The results of LFM surface friction analysis on the perm-damaged hair and after washing 30 times.

caused less color change than treatment with shampoo A. Because shampoo B forms a small and uniformly sized coacervate, it evenly covers the hair to protect it from color change.

3.4. Alteration of the Surface Friction of the Perm-damaged Hair After Shampooing

Lateral force measurements in combination with AFM can provide fundamental information about the physical and chemical properties of a surface such as friction. Lateral force (mV) of the hair surface was examined with AFM, and the results are presented in Figure 4. The frictional forces of perm-damaged hair with no treatment and those of per-damaged hair washed 30 times with shampoos A and B were studied. The colors in Fig. 4 indicate the coefficients of friction, which increase from blue to green. The friction force of perm-damaged hair was much higher than that of shampoo washed hair, implying that the hair surface was coated with the cationic polymer during shampooing. The values of the root-mean-square surface roughness, R_q , of the surfaces of the hair samples were compared to identify the effect of shampoos A and B on surface roughness. The R_q 's of perm-damaged hair, shampoo A-treated hair and shampoo B-treated hair were 55, 18 and 14 mV respectively. The R_q value of perm-damaged hair was the highest, followed by shampoo

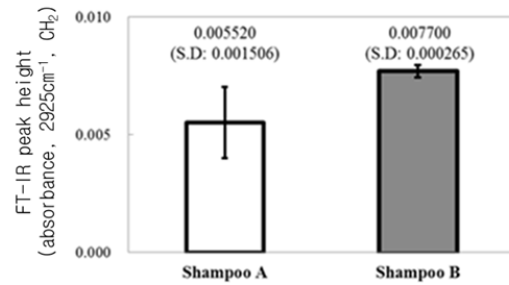


Figure 5. The change in the surface lipids for the virgin hair after washing 30 times.

A-treated hair, and then shampoo B-treated hair. As noted earlier the discussion of the particle size distribution of the coacervates, shampoo B forms small and uniformly sized coacervate. Therefore, it is apparent that the coacervate can be uniformly deposited on the hair surface, which results in relatively less roughness.

3.5. Change of Surface Lipids for the Virgin Hair

To compare the lipid contents on the hair surface, the virgin hair treated with shampoos A and B were analyzed with an FT-IR spectrometer. The intensity of the FT-IR absorbance peak at 2925 cm⁻¹ (CH₂ stretching band) was measured to compare the lipid contents. The intensity of the peak of the virgin hair washed 30 times with shampoo A was 0.005520 (S.D: 0.001506), and the corresponding peak with shampoo B was 0.007700 (S.D: 0.000265). The statistical difference was less than 0.01. The result shows that the amount of lipids on the surface of the hair treated with shampoo B was higher than that of the hair treated with shampoo A. This indicates that the composition of shampoo B caused less damage to the lipids on the hair surface.

3.6. Morphological Change to the Hair Surface for the Perm- and Bleach-damaged Hair after Washing

Figure 6 shows the SEM images of perm- and bleach-damaged hair without washing and after washing with shampoos A and B. In the case of perm-damaged hair, the cuticle edge is clearly damaged by washing with shampoo A (Figure 6-1b) compared to its initial state (Figure 6-1a).

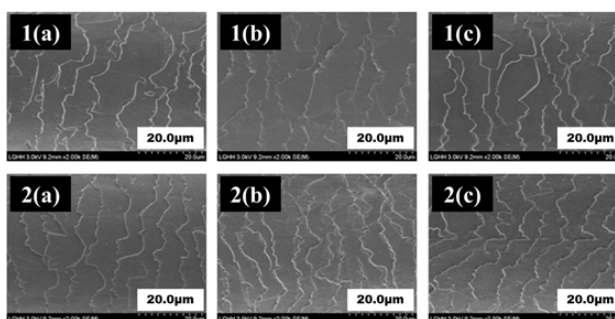


Figure 6. SEM micrographs of the surface of perm- and bleach-damaged hair after washing 30 times. 1(a): Perm-damaged hair-unwashed, 1(b): Perm-damaged hair-washed 30 times with shampoo A, 1(c): Perm-damaged hair-washed 30 times with shampoo B, 2(a): Bleach-damaged hair-unwashed, 2(b): Bleach-damaged hair-washed 30 times with shampoo A, 2(c): Bleach-damaged hair-washed 30 times with shampoo B.

However, when shampoo B was used, the cuticle structure remained similar to its initial state (Figure 6-1c), which shows that shampoo B caused less cuticle damage than shampoo A. Interestingly, the bleach-damaged hair showed similar results. Compared to the initial state (Figure 6-2a), the edges of the cuticle scales were worn away by washing with shampoo A 30 times. Partial cuticle peeling was observed upon cuticle. On the other hand, when shampoo B was used instead, the hair surface remained similar to its initial state (see Figure 6-2c). This demonstrates that shampoo B caused less cuticle damage than shampoo A during the shampoo washing procedure.

In future, it will be useful to identify a proper concentrations of the surfactant and polymer to increase deposition efficiency by coacervation. Finding uniformly formed coacervate in other cationic polymer and anionic surfactant will be helpful to develop personal care product for hair.

4. Conclusion

The results clearly show that the particle size distribution of the coacervation can substantially influence the hair surface properties. In conclusion, a relatively small and uniformly sized coacervate can be deposited more evenly over the surface of hair than a larger and less uniformly sized coacervate. Consequently, we have

demonstrated that using a fine and uniformly sized coacervate remarkably improves hair surface properties and protects hair from damage caused by various physical activities.

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