

양이온 폴리머와 음이온/양쪽성 계면활성제로 형성된 코아세르베이트 건조 필름 특성이 샴푸 건조 후 사용감에 미치는 영향

손성길[†] · 전현욱 · 이인호 · 장석윤

LG생활건강 기술연구원

(2012년 3월 14일 접수, 2012년 5월 15일 수정, 2012년 6월 16일 채택)

Surface Properties of the Dried Coacervate Film Affect Dry Feel of the Shampoo Composed of Cationic Polymer and Anionic /Amphoteric Surfactant

Seong Kil Son[†], Hyun Wook Jeon, In Ho Lee, and Sug Youn Chang

LG Household & Health Care / Research Park, #84, Jang-dong, Yuseong-gu, Daejeon 305-343, Korea

(Received March 14, 2012; Revised May 15, 2012; Accepted June 16, 2012)

요약: 본 연구는 건조된 코아세르베이트 필름의 물리적 특성이 샴푸 건조 후 모발 사용감에 미치는 상관관계를 조사하기 위하여 실시하였다. 단순 샴푸 조성물은 동일한 조성의 계면활성제에 양이온 전하 밀도가 서로 다른 두 종류의 양이온 폴리머를 사용하여 제조하였다. 이 단순 조성물을 물에 희석하여 코아세르베이트(Coacervate)를 형성되도록 하였고, 3000 rpm, 30 min 조건으로 원심 분리하여 형성된 코아세르베이트를 얻었다. 얻어진 코아세르베이트를 유리판 위에 균일한 두께로 도포하고 50 °C 건조기에서 1 h 건조하여 코아세르베이트 필름을 얻었다. 이렇게 얻어진 코아세르베이트 필름의 접촉각과 코아세르베이트의 SEM 이미지 조사를 수행하였고, 코아세르베이트의 수분 보유량과 수분 유지력을 동시에 조사하였다. 샴푸 후 건조된 모발의 부드러움과 보습감은 모발타래를 이용하여 전문 미용 패널이 평가를 수행하였다. 본 실험결과 건조된 코아세르베이트 필름의 특성이 샴푸 후 건조된 모발의 부드러움 및 보습감에 영향을 주는 것으로 확인되었다.

Abstract: The purpose of this study was to examine the correlation between physical properties of dried coacervate films and dry feel for shampoo composition. Simple shampoo compositions were made of two different cationic charge density polymers in the same surfactant compositions. The simple shampoo compositions were diluted with distilled water to make coacervate. Formed coacervate was collected by centrifuge (3,000 rpm, 30 min). Coacervate was coated on the glass plates and dried in drying oven (for 1 h, 50 °C) to make the thin film. We carried out an experiment on measurement of contact angle, moisture loss ratio and SEM image analysis of the dried coacervate film. Dry feelings of the shampoos were evaluated by panel using hair tresses. Results show that the properties of dried coacervate films affect the dry feel of the after shampooing.

Keywords: coacervate, film, shampoo, dry feel, polymer

1. Introduction

Conventional shampoos are composed of anionic / amphoteric surfactants for cleansing and foaming, and cationic polymers for hair conditioning, stabilizing, in-

creasing viscosity, foam stabilizing and deposition of other conditioning materials[1-3]. Anionic / amphoteric surfactants and cationic polymers coexisted by mixed micelle or structured micelle in the shampoo. But, in specific composition, these make polymer-surfactant complex coacervate that separates as a distinct phase during the rinse stage of the shampoo process[4-7].

[†] 주 저자 (e-mail: skson@lgcare.com)

This phase separations are a well-known phenomenon called coacervation or "Lochhead Effect"[8]. The coacervation is very important phenomenon for conditioning shampoo (or 2 in 1 shampoo), especially during the wet and rinsing stage of the shampoo process[9]. Coacervate can effectively deposit onto the hair surface, providing multiple benefits to hair[10-15]. Most conditioning shampoos depend on deposition of polymer-surfactant coacervate to confer good wet combing and manageability[16,17]. Coacervate is also associated with dry feel of the shampoo by forming thin films with insoluble active ingredients dispersed in shampoo to the hair surface. Coacervate can make a co-aggregate with water insoluble suspended material in the shampoo solution during the rinsing process. And then, the co-aggregate is deposited to the hair surface [18,19]. When the hair is dried, the surface of hair is coated with a thin film composed of polymersurfactant coacervate and insoluble active ingredients dispersed in the shampoo. Thus, Coacervate plays a crucial role in determining the dry feel of the shampooing[20]. But, physical properties of dried coacervate film are not clearly defined so far. We studied correlation between hydrophilic and hygroscopic properties of dried coacervate film and dry feel of shampoo composed of cationic polymer and anionic / amphoteric surfactant. In this studies, we hope to examine the correlation between physical properties of dried coacervate films and dry hair feel of a simple shampoo composition composed of cationic polymer and anionic / amphoteric surfactant.

2. Material and Method

2.1. Hair Tresses

Tress of virgin dark hair for panel test from DeMeo Brothers Inc. (New York, USA). To get hair damaged, hair tress was placed in a bleaching solution composed of 4 wt% of Monoethanolamine (MEA), 0.28 wt% of Ammonia, and 5 wt% of Hydrogen Peroxide for 1 h, then rinsed thoroughly with water and dried in air. Each tress for this hair, weighing 12 g and approximately 17 cm in length, was washed with 3.0 wt%

Sodium Lauryl Sulfate (SLS) aqueous solution for 3 min and then rinsed with tap water for 5 min. Afterward, they were dried at constant humid and temperature (25 °C, 50 % RH).

2.2. Materials

A simple formulation, we are made two types of cationic cellulosic polymers (Polyquaternium-10) were used in this study including the same molecular weight but different cationic charge densities. Polymer LR400 (% nitrogen 0.8 ~ 1.1) and Polymer JR400 (% nitrogen 1.5 ~ 2.2) were obtained from Amerchol Corporation (USA). Cocamidopropyl Betaine (CAPB) was used in this test. Amphoteric surfactant CAPB (30 wt% in Water) was obtained from Miwon Corporation (Korea). Sodium Laureth Sulfate (SLES) was also used in this test. Anionic surfactant SLES (3EO, 28 wt% in Water) was obtained from LG Household & Healthcare (Korea).

2.3. Simple Shampoo Composition

Each formulation was simply prepared with one of the polymers (1.0 wt% active), SLES surfactant (7.5 wt% active), and CAPB (6.0 wt% active) in distilled water.

2.4. Making and Gathering of Coacervate

The simple composition was diluted (9X) with distilled water. We consider 9X dilution which is approximately the same as concentration of shampoo during foaming and massage on hair fiber. Formed coacervate was collected by centrifuge (3,000 rpm, 30 min).

2.5. Making of Dried Coacervate Film

Coacervate were coated 2 μ m thickness on the glass plate using film applicator. Then glass plates dried in drying oven (for 1 h, 50 °C) to make the thin film.

2.6. Measurement of Contact Angle

Kruss, Easy Drop (DSA2 Software) instrument was used to measuring of contact angle for coacervate film. Contact angles were obtained for 5 drops on the same glass plate. 7 glass plates were used to measure contact

angles for each coacervate film.

2.7. Measurement of Electric Moisture Balance

HR-83, Mettler Toledo Co. Ltd., was used to measure moisture loss ratio of hair fiber. Each hair tress was washed with simple composition and rinsed with tap water repeating three times for the same sample. An electric moisture balance was employed to measure the moisture content of hair. A 1 g of hair sample was placed on balance dishes, and the weight change with heating was recorded every 1 min. The tress was heated for 30 min at 65 °C to evaporate surface water from hair.

2.8. Analyze of Cryo-scanning Electron Microscopy

JSM-840A cryo-scanning electron microscopy (cryo-SEM), Jeol Ltd., was used to analyze image of coacervate. Alto 2500 cryo-transfer equipment, Gatan Inc., was used to treatment of the test sample. The pre-treatment and prepare of cryo-SEM sample was perform freezing, cutting, etching, coating and investigate. The analyzed condition of image was 20 KV of accel voltage and 1×10^{-9} Am of probe current.

2.9. Panel Test

Simple shampoo compositions were tested by sensory panels (n = 7) for softness and moist feel of the hair tresses (12 g of 17 cm bleached hair).

2.10. Statistical Analysis

The data was treated statistically by mean \pm SD. Comparisons between groups were used to the *t*-test. Asterisk (*, $p < 0.01$) was considered to be statistically significant between each samples.

3. Result and Discussion

3.1. Contact Angle Results

The contact angles for the polymer and coacervate were measured using the film formed on the glass plate. Contact angle of coacervate films are lower than corresponding polymer films (Figures 1, 2). This result revealed that absorbed material on hair surface has dif-

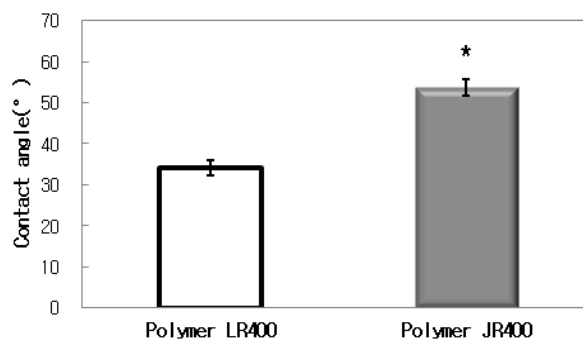


Figure 1. Contact angle of polymer film effect of charge density.

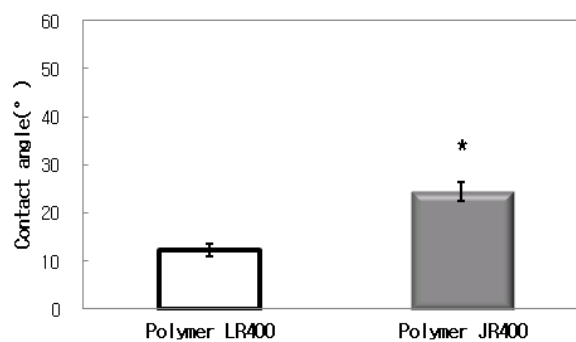


Figure 2. Contact angle of coacervate film effect of charge density.

ferent properties from the polymer itself. Because the coacervate film has coexisted small amount of surfactant molecules, which has lower contact angle than the polymer film. Polymer LR400 has lower cationic charge density than Polymer JR400. Polymer LR400 has a lower contact angle than Polymer JR400. We guess that result comes from structural properties of the polymers and coacervate.

3.2. SEM Image Analysis

The SEM images analysis was performed to the coacervate foamed by two different polymers those have different cationic charge densities. It is possible to observe the porous structure in the lower charge density Polymer LR400 coacervate. But the higher charge density Polymer JR400 coacervate is not a porous structure. Coacervate formed by lower charge density Polymer LR400 has many numbers of holes on the

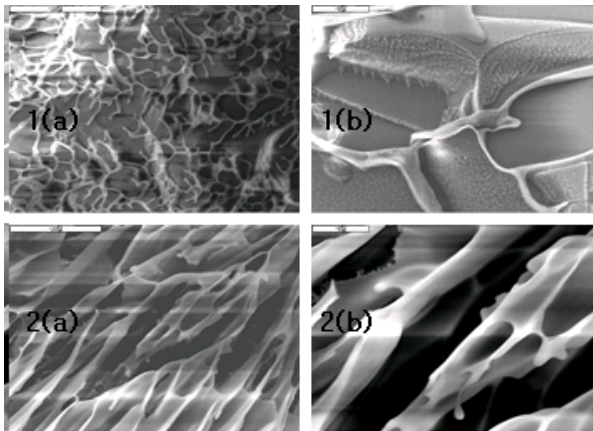


Figure 3. SEM images of coacervate film formed by two different Polymer JR 400 and LR 400, 1(a) : Polymer JR400 coacervate ($\times 2000$), 1(b) : Polymer JR400 coacervate ($\times 5000$), 2(a) : Polymer LR400 coacervate ($\times 2000$), 2(b) : Polymer LR400 coacervate ($\times 5000$).

structure (Figure 3). This porous structure is similar to a sponge. We believe the structural differences of coacervate in the SEM images were related charge density of cationic polymers. Structural difference can be related holding capacity of water from the coacervate films.

3.3. Moisture Content and Sustainable Effect

The moisture contents and sustainable effect test were performed to the hair fiber tresses treated by two kinds of simple cleansing compositions. Moisture existing in human hair can be divided into two phase. The 1st phase is primary transpiration moisture which means the surface moisture of hair. And the 2nd phase is transpiration moisture means inner, bound moisture of hair. We only use the primary transpiration moisture value. Because of that the coacervate film can be formed just only on the hair surface. Surface moisture content is more important than inner, bound moisture of hair in this test. The surface moisture content of hair was observed by the electric moisture analyzer. It is possible to observe a high moisture content in lower charge density Polymer LR400 coacervate. But high charge density Polymer JR400 coacervate is less moisture content then (Figure 4). As mentioned above, Coacervate formed by lower charge density Polymer LR400 has

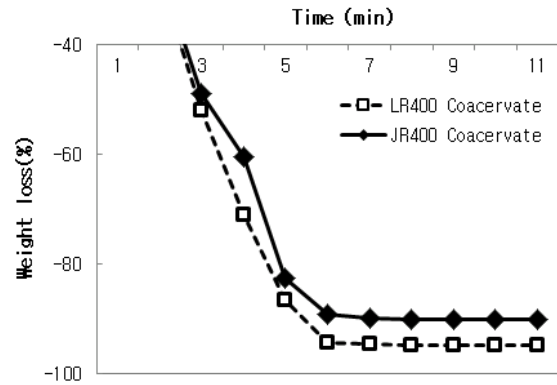


Figure 4. Moisture content and loss of bleached hair treated with Cationic polymer / SLES / CAPB (7.5 / 1.0 / 6.0 wt%) solution for drying in ambient condition.

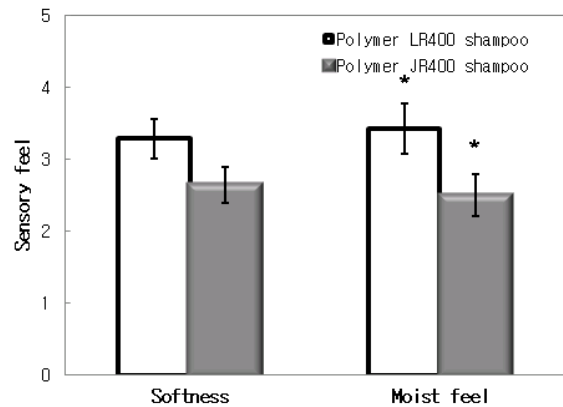


Figure 5. Panel test result of softness and moist feel of hair tresses treated for Cationic polymer / SLES / CAPB (7.5 / 1.0 / 6.0 wt%) solution (n = 7, Hair professionalist).

many numbers of holes on the structure. This porous structure can hold much more moisture like a sponge. Structural difference has related holding capacity of water from the coacervate films. According to the test result for moisture loss ratio, we can see that the coacervate formed by lower charge density Polymer LR400 is more water content capacity than the coacervate formed by the higher charge density Polymer JR400. We think that the result is due to the structural difference of the coacervate foamed.

3.4. Panel Test of Dry Hair Feel After Shampooing

The sensorial test of the hair softness and moist feel

were performed by 7 persons of hair specialist ($n = 7$). It is possible to observe simple shampoo composition using the Polymer LR400 is better than the Polymer JR400 in sensorial results to the hair softness and moist feel on dried hair. We can see that the sensorial results actually correlated with the moisture content of the coacervate films and the structural properties of the coacervate (Figure 5).

4. Conclusion

The results from examining the correlation between physical properties of dried coacervate films and dry feel properties for a shampoo show that the contact angle of coacervate films are lower than corresponding polymer films. Polymers with lower charge density make more porous coacervates. High porous coacervates can hold more water in its structure. Properties of dried coacervate film affect dry feel of the shampoo.

Acknowledgment

The authors thank Mr. Hyun-seok Park for consulting formulation and test method and Mr. Sung-hyun Im for his advice on SEM analyze.

References

1. P. Hössel, R. Dieing, R. Nörenberg, A. pfau, and R. Sander, Conditioning polymers in today's shampoo formulations - efficacy, mechanism and test method, *International Journal of Cosmetic Science*, **22**(1), 1 (2000).
2. G. Clera, New cationic conditioning polymers for hair care, *ASIA PACIFIC PERSONAL CARE*, September (2005).
3. R. Y. Lochhead and L. R. Huisinga, Advances in Polymers for Hair Conditioning Shampoos, *Cosmetics & Toiletries magazine*, **120**(5), 69 (2005).
4. E. D. Goddard, T. S. Phillips, and R. B. Hannan, Water soluble polymer-surfactant interaction part I, *J. Soc. Cosmet. Chem.*, **26**(9), 461 (1975).
5. J. Caelles, F. Comelles, J. SÁNCHEZ Leal, J. L. Parra, and S. Anguera, Anionic and cationic compounds in mixed systems, *Cosmetics & Toiletries*, **106**(4), 49 (1991).
6. E. D. Goddard, P. S. Leung, and K. P. A. Padmanabhan, Novel gelling structures based on polymer/surfactant systems, *J. Soc. Cosmet. Chem.*, **42**, 19 (1991).
7. S. Zhou, C. g Xu, J. Wang, P. Golas, and J. Batteas, Phase behavior of cationic hydroxyethyl cellulose-sodium dodecyl sulfate mixtures: Effect of molecular weight and ethylene oxide side chain length of polymers, *Langmuir*, **20**(20), 8482 (2004).
8. R. Y. Lochhead and L. R. Huisinga, A brief review of polymer/surfactant interaction, *Cosmetics & Toiletries magazine*, **119**(2), 37 (2005).
9. R. L. Schmitt, B. Brook, E. D. Goddard, and Edison, Investigation into the adsorption of cationic polymers, *Cosmetics & Toiletries magazine*, **109**(12), 83 (1994).
10. J. A. Faucher, E. D. Goddard, and R. B. Hannan, Sorption and desorption of a cationic polymer by human hair: Effect of salt solutions, *Textile Research Journal*, **47**(9), 616 (1977).
11. Y. K. Kamath, C. J. Dansizer, and H. D. Weigmann, Surface wettability of human hair. III. Role of surfactants in the surface deposition of cationic polymers, *Journal of Applied Polymer Science*, **30**(3), 937 (1985).
12. E. Terada, Y. Samoshina, T. Nylander, and B. Lindman, Adsorption of cationic cellulose derivatives/Anionic surfactant complexes onto solid surface. I. Silica Surfaces, *Langmuir*, **20**(5), 1753 (2004).
13. E. Terada, Y. Samoshina, T. Nylander, and B. Lindman, Adsorption of cationic cellulose derivatives/anionic surfactant complexes onto solid surface. II. Hydrophobized Silica Surfaces, *Langmuir*, **20**(16), 6692 (2004).
14. F. E. Antunes, E. F. Marques, R. Gomes, K. Thuresson, B. Lindman, and M. G. Miguel, Network formation of cationic vesicles and oppositely charged polyelectrolytes. Effect of polymer charge

- density and hydrophobic modification, *Langmuir*, **20**(11), 4647 (2004).
15. T. Nylander, Y. Samoshina, and B. Lindman, Formation of polyelectrolyte-surfactant complexes on surfaces, *Advances in Colloid and Interface Science*, 105, **123** (2006).
 16. S. Chiron, Performance and sensorial benefits of cationic guar in hair care applications, *Cosmetics & Toiletries magazine*, **119**(2), 47 (2004).
 17. L. Wing, G. Clara, A. Jennifer, J. Susan, T. Alan, and C. Davis, Maximising shampoo performance, *ASIA PACIFIC PERSONAL CARE*, July (2006).
 18. M. Gamez-Garcia, Controlling the deposition of insoluble actives to hair from shampoo systems, *ASIA PACIFIC PERSONAL CARE*, May (2002).
 19. Y. Hiwatari, K. Yoshida, T. Akutsu, M. Yabu, and S. Iwai, Polyelectrolyte micelle coacervation -Effect of coacervate on the properties of shampoo-, *International Journal of Cosmetic Science*, **26**(6), 316 (2004).
 20. R. Y. Lochhead, L. R. Huisinga, and Tara Waller, Deposition from conditioning shampoo: Optimizing coacervate formation, *Cosmetics & Toiletries magazine*, **121**(3), 75 (2006).