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"Novel hair cleansing technology

~Compatibility of cleansing and care functions at high level by lamellar liquid crystal structure~"

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1. Introduction

Humans have been dying and styling their hair since a long time ago, and even today, hair is as much a part of self-expression as fashion and makeup. However, the inner and outer conditions of hair can change not only with chemical treatments such as coloring and perming and heat of hair iron, but also with washing with shampoo that we do daily to cleanse and care for hair and scalp. The repetition of these hair care behaviors causes hair problems such as tangling and stiffness, which have not been completely solved.

Hair is composed mainly of proteins, lipids, and water. Although lipid's content is less than 10%, hydrophobic substances such as lipids are essential for hair to prevent and solve hair problems. For example, 18-MEA can be easily removed by hair coloring and perming and that makes hair surface hydrophilic and increase friction [1]. To solve this, it has been reported that the combination of 18-MEA and stearoxypropyl dimethylamine (SPDA) can form a persistent 18-MEA layer on hair surface after bleaching [2]. In addition, repeated hair coloring and washing causes loss of lipids inside the hair, resulting in coarse and stiff hair. Treatment of such damaged hair with a ceramide functional substance restores hair softness and flexibility [3].

Thus, since supplying lipids helps prevent and solve hair problems, hair conditioners usually contain hydrophobic substances. It is generally perceived that "shampoo: removes dirt and excess sebum from hair and scalp; hair conditioner: cares for hair," but repeated shampooing also washes away lipids from the hair [4,5]. In other words, it would be ideal if shampoos had both cleansing and care functions, but conventional shampoos cannot contain effective amounts of hydrophobic substances such as lipids due to problems of lather and stability, so shampoos are insufficient as a care function in the sense of supplying lipids. On the other hand, since cleansing conditioners are based on hair conditioners, they can contain lipids, but they do not lather well and are insufficient as a cleansing function. Therefore, in this study, we challenged the development of a novel hair cleansing technology that achieves both cleansing and care functions at a high level.

One of the hair properties that can be changed by lipid removal or supplementation is "stress relaxation property" [5]. Stress relaxation property of hair is "the ease of deformation when external forces are applied to hair," and an increase of stress relaxation improves hair style-ability and leads to various benefits, well alignment, reducing frizz, volume up, volume down, and creating beautiful curly styles [6,7]. As mentioned earlier, when lipids are removed from healthy hair, the stress relaxation property of hair decreases, resulting in worse alignment and frizz. However, treatment with fatty acid glycerides such as olive oil restores stress relaxation property [5]. Therefore, in this study, we selected olive oil as the care ingredient and attempted to formulate effective amount of olive oil in shampoo stably.

First, we reviewed the solution structure of shampoo in order to develop a novel cleansing technology that combines the lathering ability of shampoo with the lipid retention ability of hair conditioner. Conventional shampoos are capable of lathering because anionic surfactants of the cleansing ingredients form micelles, and the monomer of the surfactants is supplied from these micelles during dilution. On the other hand, hair conditioners form a lamellar structure with cationic surfactants and higher alcohols and the structure contain overlapping oil and water layers, and a large amount of lipids can be retained in the lamellar structure. From these two functions, we considered constructing a lathering lamellar structure. We investigated the construction of a lathering lamellar structure using an anionic surfactant used in shampoo and a fatty acid known to form a lamellar structure with anionic surfactants. In addition, we formulated olive oil in shampoo with lamellar structure and evaluated its lathering ability, stability, and effects on hair.

2. Materials and Methods

2.1. Hair samples

In order to evaluate and analyze the effectiveness of shampoos easily and clearly, delipidated hair was used.

Unless otherwise stated, the hair samples used in this study were prepared as follows:

Delipidated hair

Chemically virgin hair from Japanese women was delipidated by immersing in chloroform/ethanol/water = 18/9/1 (wt.) for 24 hours at room temperature.

2.2. Shampoo formulation

The typical procedure was as follows: For the lamellar structure shampoo formulation, a 25% ammonium laureth sulfate aqueous solution and lactic acid were dissolved in water and stirred at 70 °C. A hot-melted oil phase containing lauric acid (and olive oil if needed) was added in the solution to form a lamellar structure.

The Formulas described in Table 1 were used in evaluations in this study. It contains Shampoo A: lamellar structure shampoo w/ olive oil, Shampoo B: conventional soluble shampoo w/ olive oil, Shampoo C: lamellar structure shampoo w/o olive oil, and Shampoo D: conventional soluble shampoo w/o olive oil. Shampoo B is not stable since olive oil cannot be formulated in it.

Table 1. Shampoo formulas used in this study.

[wt.%]

INCI name	Shampoo A lamellar structure shampoo w/ olive oil	Shampoo B conventional soluble shampoo w/ olive oil	Shampoo C lamellar structure shampoo w/o olive oil	Shampoo D conventional soluble shampoo w/o olive oil
Ammonium laureth sulfate	13.5	←	←	←
Lauric acid	7.0		7.0	
Olive oil	3.0	←		
Lactic acid	adjusted	adjusted	adjusted	adjusted
Water	Balance	Balance	Balance	Balance
pH of formula (5% aqueous)	3.6	3.6	3.6	3.6

2.3. Repeated washing method

2 g of hair were rinsed by tap water for 30 s. 0.5 g of the shampoo were applied to the hair and wash it for 60 s, which was later rinsed using tap water for 30 s. Then, the hair was dried with hair dryer for 60 s. These treatments were repeated 30 times.

2.4. Confirmation of shampoo structures

The lamellar structures were confirmed by polarizing microscope, small-angle/wide-angle X-ray scattering measurement (SAXS/WAXS), and Cryo-scanning electron microscope (Cryo-SEM). The measurement conditions are below.

Polarizing microscope observation

Nikon ECLIPSE E800 was used for polarizing microscope observation to evaluate the structure is solubility/liquid crystal/crystal.

SAXS/WAXS measurement

Anton Paar SAXSess mc2 was used for SAXS/WAXS measurements.
Detector: Imaging plate (IP) (small to wide angle range)
Cell: Liquid cell (quartz glass)
Measurement time: 60 min/sample Measurement temperature: 25 °C

Cryo-SEM measurement

JEOL JSM-7600F was used for Cryo-SEM measurement.
Sublimation: -180 °C → -100 °C for 30 min → -180 °C holding
Sample stage temperature: -180 °C
Deposition: No deposition Accelerating voltage: 1 kV Current value: 117.0 µA (No.7)
Detector: Lower secondary electron W.D.: 10 mm

2.5. Performance evaluations of shampoos

Lathering ability evaluation

We applied 1 g of each shampoo to 20 g of a hair tress (bundle), hold the tress with both hands, fold it, moved the hands as if rubbing them together. After 30 strokes of this action of lathering, the foam was squeezed from the tress and the volume was measured to evaluate lathering ability.

Stability evaluation

The appearance of each formulated shampoo was visually observed immediately after formulation. In addition, approximately 100 mL was filled into a 110 mL clear glass bottle, sealed, and stored at -5 °C, room temperature (25 °C), and 50 °C for one month. The appearance after the storage was visually observed and evaluated by judging soluble/separated/stable.

2.6. Evaluation of the effects of shampoos on hair

Alignment evaluation

After washing each untreated and shampoo-treated hair tress, each hair was towel-dried, combed once, shaken three times, and air-dried overnight. After the air-dry, the appearance photograph was taken to evaluate its alignment.

Untreated hair was washed with a plain shampoo.

Tensile stress relaxation measurement

Using the automatic hair tensile tester (MTT680, Dia-Stron), each hair fiber was hold at 1% tension for 3 minutes. The initial stress value of the stretch was used as the standard, and the stress relaxation ratio was calculated from the relative stress value after 3 min (Figure 1). The sample size was 30 mm, the stretching speed was 18 mm/min (1 %/sec), and n=20. All samples were humidified for 24 hours at 20 °C, 65 %RH, and measured under the same conditions.

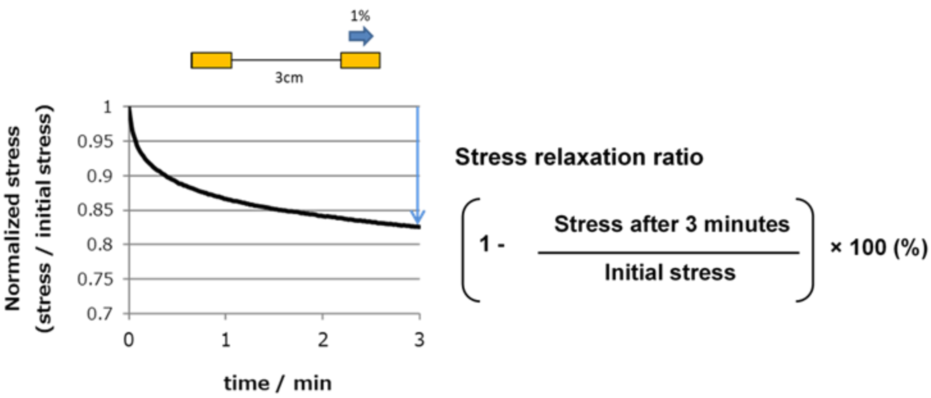


Figure 1. Method for calculation of stress relaxation ratio.

3. Results

3.1. Investigation of the construction for the shampoo with lamellar structure

We investigated the construction of lathering lamellar structure shampoos using three components: ammonium laureth sulfate (ES) as an anionic surfactant, lauric acid (LA), a fatty acid, as a lamellar structuring agent, and water, at different component ratios. The phase diagram created from the results is shown in Figure 2. As a result of the study, the shampoo was soluble in the region (I) where the amount of LA was less than 3~4 %, and formed a structure when the amount was higher than that. However, in the region (II) where the amount of LA was between 3~4% and 5~6%, it was found to separate during one month of storage and the structure was unstable. It was also found that as the amount of LA increased, a crystalline structure formed, resulting in poor lathering (regions (IIII, V)). In region (III), which exists between region (II) where the structure is unstable and region (III) where crystals precipitate, it was found that shampoo with sufficient lathering ability and a stable structure was formed. SAXS/WAXS analysis of the shampoo solution in this region (Shampoo C in Table 1.) revealed a lamellar liquid crystal structure with regular spacing of 12.0 nm (Figure 3).

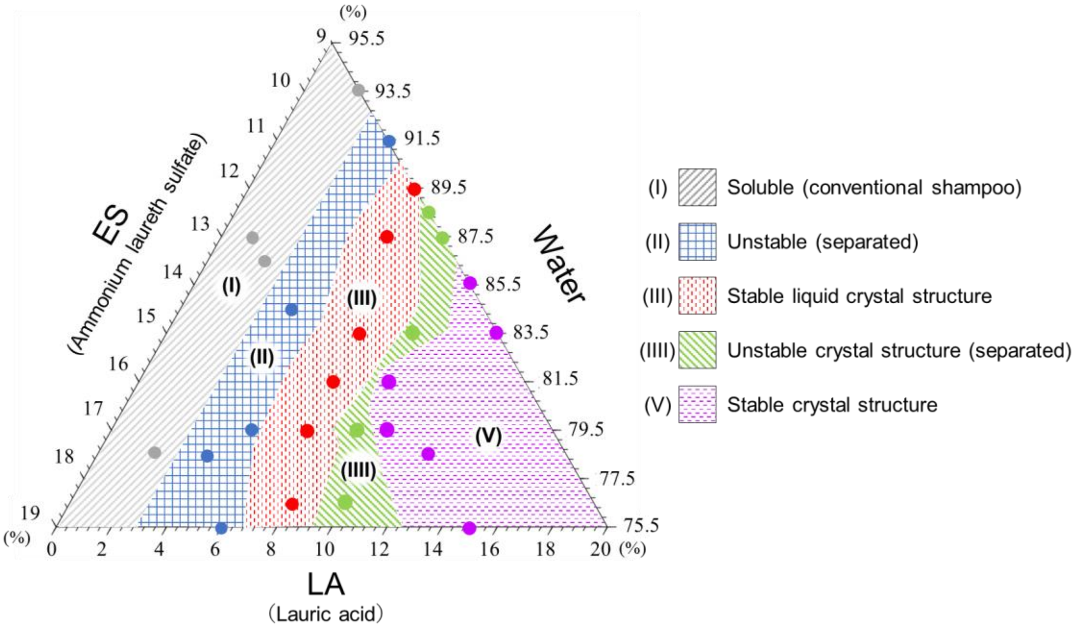


Figure 2. Relationship between the component ratio of water, lauric acid, and ammonium laureth sulfate and the shampoo solution structure.

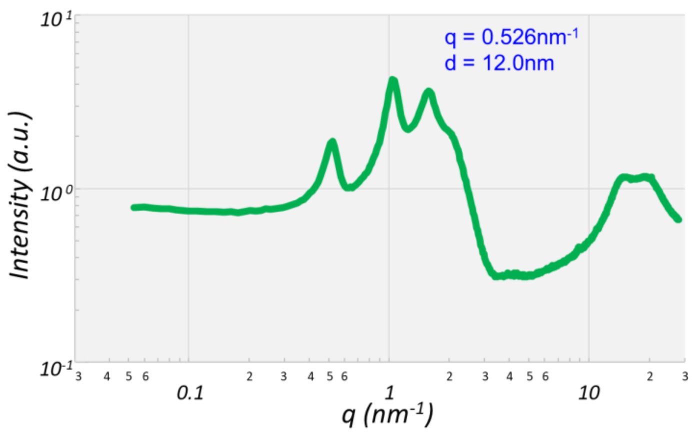


Figure 3. SAXS/WAXS measurement result of lamellar liquid crystal shampoo (Shampoo C).

Furthermore, when 3% of olive oil, which has the effect of improving stress relaxation of hair, was added to the shampoos in region (III), which has a stable lamellar liquid crystal structure, it was found that olive oil could be stably formulated in an even narrower region (Figure 4). All of these shampoos had sufficient lathering ability despite the inclusion of lipids. Hereafter, the shampoo with a lamellar liquid crystal structure is referred to as "lamellar shampoo."

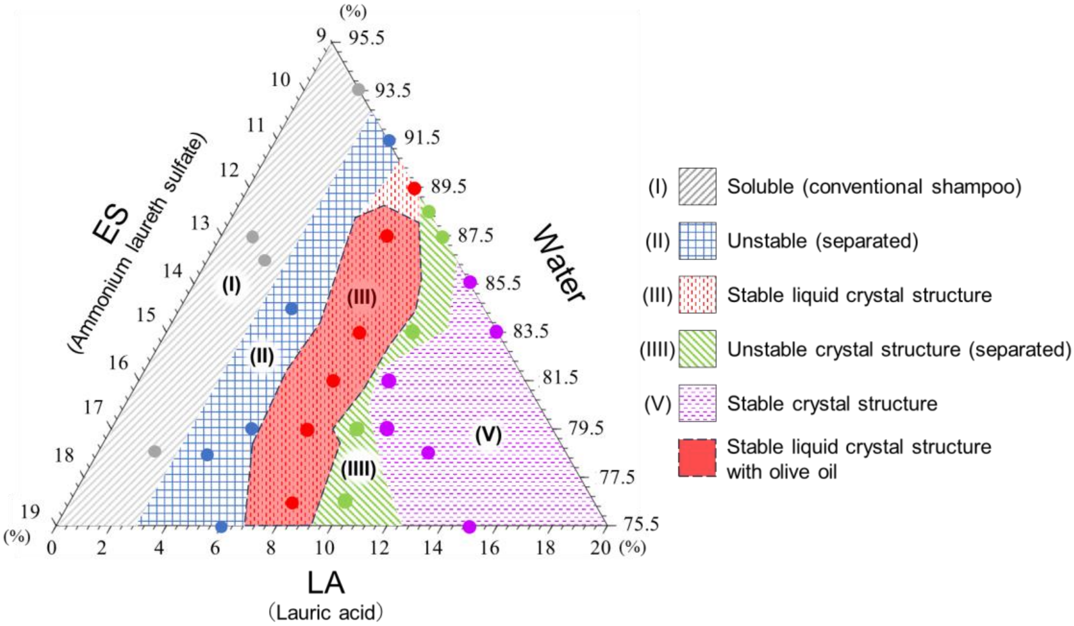
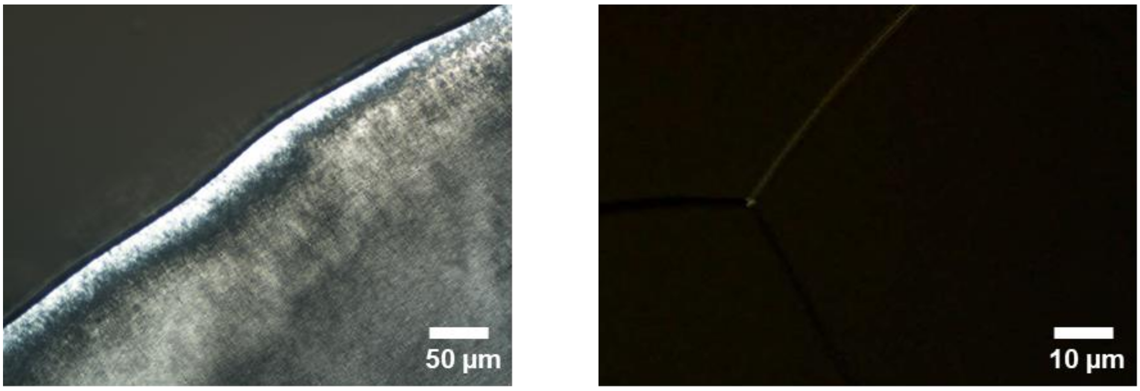


Figure 4. Stable area with olive oil in lamellar shampoo.

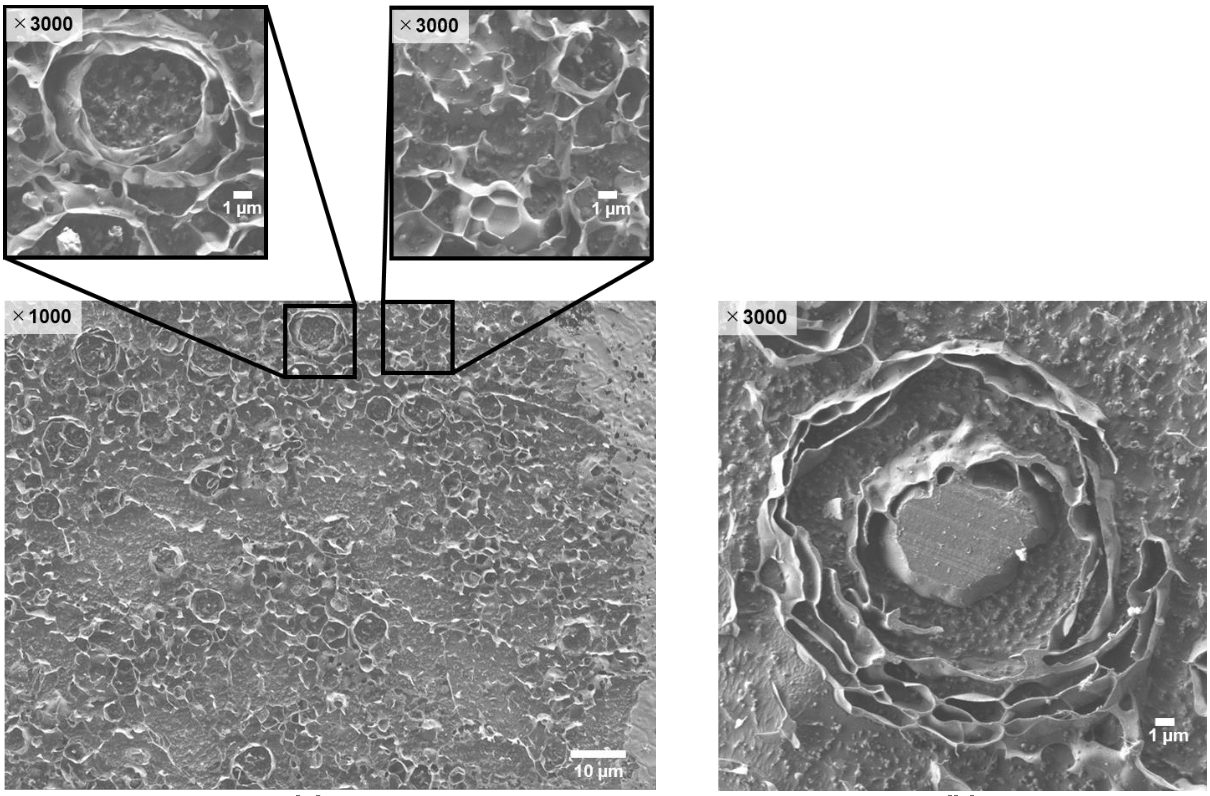
3.2. Solution structure of the lamellar shampoo

Using the polarizing microscope, we observed the undiluted solution of lamellar shampoo (Shampoo C) and confirmed that it formed a lamellar liquid crystal structure as shown in Figure 5(a). On the other hand, when the solution was diluted 10 times, the structure could no longer be confirmed as shown in Figure 5(b). This suggests that the lamellar structure composed of an anionic surfactant and lauric acid is easily broken by dilution. Therefore, we analyzed the detailed structure by Cryo-SEM measurement, and found two structures in the 10-fold diluted solution: a fragmented structure and a spherical structure (Figure 6(a)). In the spherical structure, a structure not observed in the shampoo without olive oil, was observed inside the spherical structure (Figure 6(b)), suggesting that olive oil is contained inside the spherical structure.



(a) (b)

Figure 5. Polarizing microscope images of (a) lamellar shampoo (Shampoo C) undiluted solution and (b) lamellar shampoo (Shampoo C) 10-fold diluted solution.



(a) (b)

Figure 6. Cryo-SEM images of (a) Shampoo C (lamellar shampoo w/o olive oil) 10-fold diluted solution and (b) shampoo A (lamellar shampoo w/ olive oil) 10-fold diluted solution.

3.3. Lathering ability evaluation

The results of the evaluation of the lathering ability of each shampoo are shown in Figure 7. As can be seen by comparing Shampoo C and D, the lamellar shampoo showed lathering ability comparable to that of the soluble shampoo. Comparing Shampoo B and D, the soluble shampoo showed a significant decrease in lathering ability when lipids were added. On the other hand, the results of Shampoo A and C showed that the lamellar shampoo maintained its high lathering ability even when lipids were added. Therefore, it was confirmed that lamellar shampoos have good lathering ability despite the presence of a liquid crystal structure and lipids.

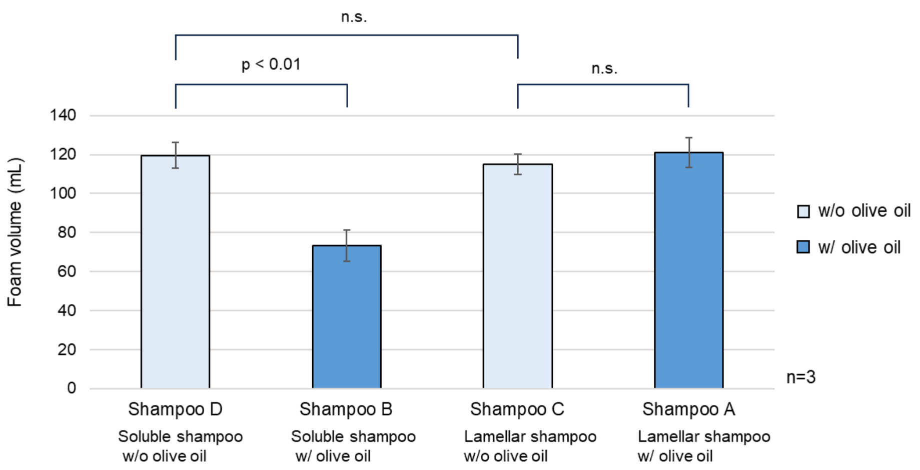


Figure 7. Lathering evaluation of conventional soluble shampoo and lamellar shampoo.

3.4. Effects of lamellar shampoo with lipids on Hair

The alignment effect of the lamellar shampoo was evaluated. Each photograph of the untreated hair tress and the hair tress after 30 repeated shampoo treatments with the lamellar shampoo containing olive oil (Shampoo A) are shown in Figure 8(a). The tresses' alignment and manageability was improved in spite of repeated hair washing with the shampoo only. Furthermore, Figure 8(b) and Figure 8(c) show before and after photographs of the conventional soluble shampoo with olive oil (Shampoo B) and the lamellar shampoo without olive oil (Shampoo C), respectively. As can be seen, the presence of olive oil in the soluble shampoo did not improve the alignment of the hair, nor did the absence of olive oil in the lamellar shampoo.

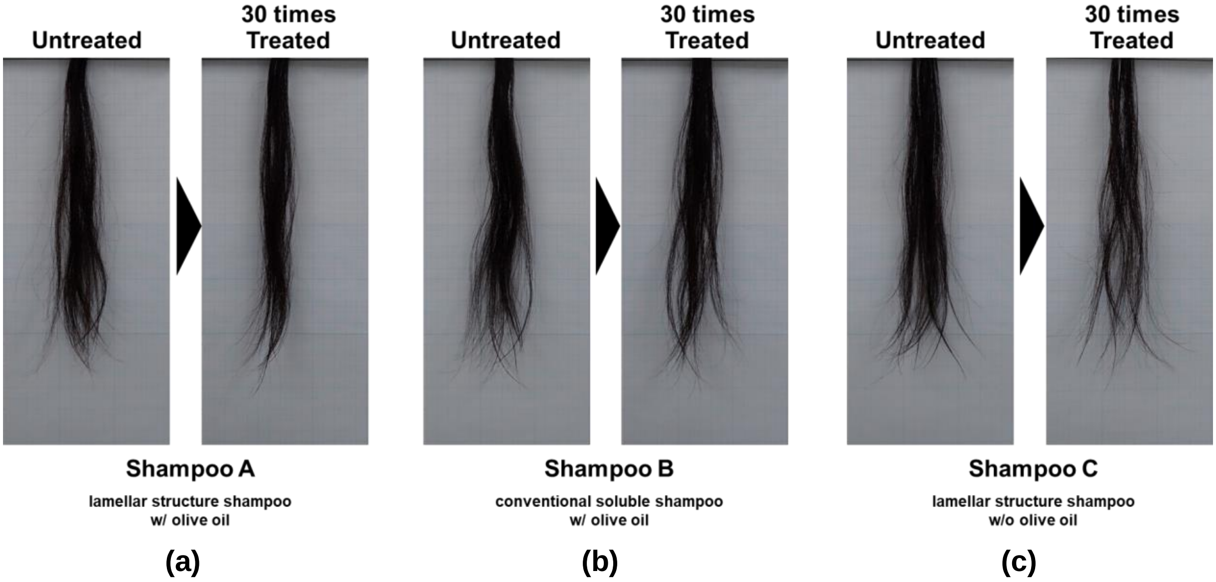


Figure 8. Change in appearance of hair tress before and after each shampoo treatment. (a) Shampoo A: lamellar structure shampoo w/ olive oil, (b) Shampoo B: conventional soluble shampoo w/ olive oil, and (c) Shampoo C: lamellar structure shampoo w/o olive oil.

Next, hair fibers were collected from each tress in Figure 8 and its tensile stress relaxation ratio was measured. Figure 9 shows the results. (The untreated values differed from tress to tress due to differences in the collection area, although the hairs were from the same person.) Shampoo A showed a significant increase in stress relaxation after 30 times treatments, while Shampoo B and C showed almost the same values before and after the treatments. In other words, only the lamellar shampoo containing olive oil improved the stress relaxation of the hair.

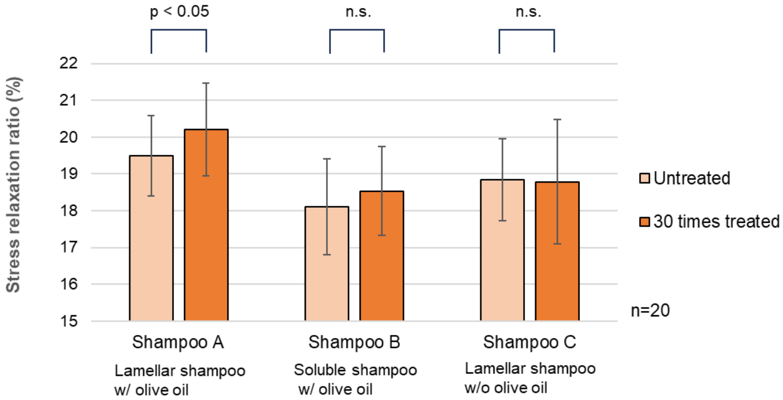


Figure 9. Stress relaxation ratio before and after 30 times treatments of each shampoo.

4. Discussion

We successfully developed the lamellar liquid crystal shampoo that contains ammonium laureth sulfate and lauric acid in a specific ratio and can contain an effective amount of olive oil. The lamellar shampoo with olive oil had a good lathering ability and improved the alignment and manageability of the hair with the shampoo treatment alone. Treatment with lamellar shampoo without olive oil and conventional soluble shampoo with olive oil did not improve hair alignment, suggesting that "the presence of olive oil in the lamellar shampoo" is a condition for improving hair alignment. Similarly, only the lamellar shampoo with olive oil increased hair stress relaxation ratio, indicating that the stress relaxation ratio results reflected changes in tress appearance. In other words, it is considered that when hair was washed with the lamellar shampoo containing olive oil, the olive oil penetrated into the hair, resulting in improved stress relaxation, which is styleability of the hair, and improved alignment as well.

In the undiluted shampoo solution, the liquid crystal structure could be seen in the polarized light microscope image, but not in the diluted solution, suggesting that this lamellar liquid crystal structure is easily broken by dilution. Further observation of the diluted solution of the lamellar shampoo with olive oil by Cryo-SEM revealed two structures: a fragmented structure and a spherical structure containing olive oil. It is considered that the fragmented structure provides the monomer, which is responsible for the lathering ability. In addition, the adsorption of the spherical structures on the hair surface may have allowed the olive oil to penetrate efficiently into the hair, resulting in improved stress relaxation of the hair. In other words, it is suggested that the spherical structure contains lipids, thereby expressing lipid supplying (care function) to the hair. Therefore, this novel technology is a lamellar structure control technology that changes into the two roles of cleansing and lipid retention by dilution, and thus enables both cleansing and care functions at a high level, which has not been possible with shampoos previously.

This technology can be designed for shampoo performance and functional effects by combining various anionic surfactants with various aliphatic derivatives. For example, rinsing smoothness and lathering performance can be further improved by combining fatty alcohols and fatty acid glycerides in addition to fatty acids [5]. Treating hair with a lipid-containing lamellar shampoo can control the lipids inside the hair and condition the hair's interior. In addition, since the shampoo can contain hydrophobic ingredients such as lipids as well as hydrophilic ingredients, various effects that could not be added with conventional shampoos can be added to the shampoo. Furthermore, since the appearance and viscosity can be controlled more widely than with conventional soluble shampoos, it is possible to create shampoos that have not only functional values but also sensory values. In other words, it is no exaggeration to say that this has the potential to change the world of in-bath hair care and people's hair care habits.

5. Conclusion

We have successfully developed a novel cleansing technology that have both cleansing and care functions at a high level by combining anionic surfactants and fatty acids. As a result, it is possible to supply lipids to hair by washing hair with the shampoo alone, thereby improving the stress relaxation and alignment of hair. The results suggest that this technology expresses both cleansing and lipid retention functions by dilution. The novel technology we developed enables shampoos to contain not only hydrophilic ingredients but also hydrophobic ingredients such as lipids, thereby expanding the range of ingredients that can be used in shampoos. In other words, we can expect to add various effects to shampoos that could not be added with conventional shampoos. This technology has the potential to revolutionize the history of shampoo and change the world of in-bath hair care and people's hair care habits.

6. References

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