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"Characterization of unique hybrid surface treated cellulose spherical powder"

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1 Introduction

Currently, spherical microplastic powders used in cosmetics, such as Nylon and Polymethyl methacrylate (PMMA) are becoming significant concerns in the environment. In October 2023, the Scientific Committee on Consumer Safety (SCCS) in EU published the roadmap towards banning their use in cosmetics within the next 10 years [1]. For these backgrounds, cellulose beads were featured as one of promising alternatives, which shows biodegradability according to SCCS criteria [2]. While cellulose spherical powder has been utilized in cosmetic formulations for approximately two decades, due to its very smooth feeling in application, it shows hydrophilic property against lipophilic powders like Nylon and PMMA. It is easy to be got in water phase of water-in-oil (W/O) formulations, and sometimes making aggregation. This difference makes it difficult to replicate characteristics of conventional formulation, or achieve desired performance, in formulating cellulose spherical powder instead of traditional microplastics beads, such as Nylon and PMMA beads. To overcome this challenge, the surface of cellulose powder is necessary to be modified into hydrophobic. Surface treatment of the salt of saturated fatty acid (SFA) is widely known as a method make cellulose spherical powder hydrophobic property. Although SFA treatment imparts certain water repellency to cellulose beads, it is not enough to be lipophilic property, such as less dispersibility in oil and make aggregations in oil.

In this study, to improve dispersibility in oil, we focused on using salts of gemini-type acylated amino acids (ASL), which possess a unique molecular structure. We developed a novel hybrid surface treatment combining ASL and SFA. Furthermore, this study investigates the effects of precipitation conditions on the composition and structure of the surface treatment agents, as well as how these conditions influence the dispersibility of the treated cellulose powders.

2 Materials and Method

2.1 Materials and evaluation

Spherical cellulose beads with a median diameter of 8–15 μm were used in this study. The surface treatment of the cellulose beads involved magnesium salts of a gemini-type acylated amino acid surfactant (ASL; Figure 1), and magnesium salts of fatty acid (SFA). The concentration of the treatment was set to 5% by weight. Processing combined treatment ASL and SFA, it was prepared in both ASL: SFA= 1: 4 by weight. Furthermore, analysis of thermal property (DSC) and Infrared spectroscopy (IR spectrum) were assessed as characterization of treatment agents. In addition, as cosmetics formulated surface treated cellulose powder, prepared W/O cream formula and lipstick formula, it evaluated usability and sustainability.

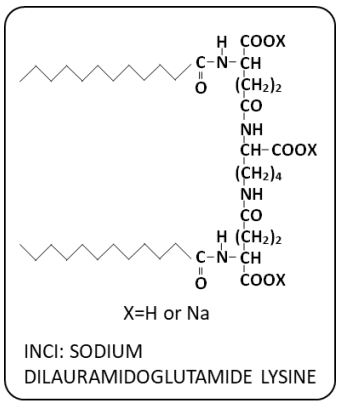

Figure 1: Structure of gemini type acylated amino acid

2.2 Preparation of treatment agents for characterization

Samples of the treatment agents for characterization (IR, DSC) were prepared without cellulose beads, using procedures analogous to those applied for the surface treatment of the beads, as described in a later section. The combined ASL+SFA18 treatment agents were obtained under four different pH conditions: below pH 5.3 (condition ‘a’), pH 5.3–5.7 (condition ‘b’), pH 6.0–6.5 (condition ‘c’), and pH 6.5–7.0 (condition ‘d’). All precipitated samples were isolated by filtration and thoroughly dried prior to analysis. These samples were utilized for the characterization of molecular structures using IR and DSC.

2.3 Characterization method for treatment agents

The prepared treatment agent samples were characterized using the following methods. Differential Scanning Calorimetry (DSC; DSC8230) measurements were performed over a temperature range of 0 to 150°C at a heating rate of 10°C/min. Infrared (IR) spectra（Nicolet Summit LITE FTIR Spectrometer） were recorded using a Fourier transform infrared spectrometer (FTIR) spectrometer via the Attenuated Total Reflectance (ATR) method.

2.4 Surface Treatment method for cellulose spherical powder

The surface treatment of cellulose spherical beads was conducted using the following method. The cellulose beads are dispersed in aqueous solution dissolved fatty acid or gemini type acylated amino acid. Next, Magnesium chloride solution added, and prepared pH conditions. The magnesium salt of fatty acid (SFA) or magnesium salt of acylated amino acids (ASL) were precipitated on surface of cellulose beads in this process.

2.5 Evaluation of Dispersibility in simple W/O emulsion system

To evaluate dispersibility in W/O emulsion of treated cellulose spherical powder, we have prepared very simple system in Table 1. For example, lipophilic beads, such as silicone elastomer, are generally localized in the oil phase, and the emulsion viscosity tends to become lower. On the other hand, hydrophilic beads like cellulose spherical powder are easily localized in the water phase, increasing the emulsion viscosity. The procedure to make this simple elusion was as follows: C9–12 alkane and a W/O emulsifier (Polyglyceryl-3 diisostearate and Polyglyceryl-3 polyricinorate) were mixed in a 50 mL centrifuge tube using a vortex mixer for 20 seconds until a uniform solution was obtained. Subsequently, the surface-treated cellulose beads were added to this oil phase and mixed by vortexing for an additional 20 seconds. Next, deionized water colored with Blue 1 was added to the oil–bead mixture, followed by vortex mixing for another 20 seconds to form a W/O emulsion. The resulting emulsion was then observed using a digital microscope to evaluate the localization of the beads and the characteristics of the emulsion.

Table 1: formula of simple W/O

Ingredients	%
C9-12 Alkane	48.0
Polyglyceryl-3 diisostearate, Polyglyceryl-3 polyricinorate	4.0
treated cellulose beads	8.0
Water(colored by Blue 1)	40.0

2.6 Evaluation in Cosmetics

In order to make clear the unique functionality of surface treated cellulose spherical powder, the evaluations of formulations of W/O cream and lipstick containing surface treated cellulose spherical powder were carried out. I

2.6.1 Preparation of W/O cream formulation (Table 2)

Phase A was prepared by mixing in condition of 1,500 rpm for 1minute. Then, Phase B was added to Phase A and mixed in 1,000 rpm for 1 minute. Phase C was dissolved separately with heating, and after cooled down to 50 °C. It was added to the A+B mixture. The entire mixture was then homogenized in 3,000 rpm for 3 minutes to obtain the W/O cream formulation.

Table 2: formula of W/O cream formulation

Phase	Ingredients	(%)
A	POLYGLYCERYL-6 POLYRICINOLEATE, POLYGLYCERYL-2 ISOSTEARATE, DISTEARDIMONIUM HECTORITE	4.50
	SORBITAN SESQUIISOSTEARATE	1.00
	C9-12 ALKANE	12.60
	COCO-CAPRYLATE/CAPRATE	5.50
	ETHYLHEXYLGLYCERIN	0.50
B	TREATED CELLULOSE BEADS	6.00
C	DE-IONIZED WATER	60.35
	PRESERVATIVE	0.30
	SODIUM CHLORIDE	0.50
	GLYCERIN	3.00
	PROPANEDIOL	5.00
	XANTHAN GUM	0.75
	Total:	100.00

2.6.2 Preparation of Lip stick formulation (Table 3)

Phase A was completely mixed while heating at 80 °C. Separately, Phase B was mixed until this got to completely uniform. The prepared Phases B and C were then added to Phase A and mixed in 1,500 rpm for 1 minute. After degassing the mixture under vacuum to remove air bubbles, it was poured into a mold to prepare the lipstick formulation.

Table 3: formula of lipstick formula

Phase	Ingredients	(%)
A	PARAFFIN, MICROCRYSTALLINE WAX, HYDROGENATED MICROCRYSTALLINE WAX, ETHYLENE/PROPYLENE COPOLYMER, POLYETHYLENE, SYNTHETIC WAX, POLYGLYCERYL-2 TRIISOSTEARATE, OCTYLDODECANOL, ISONONYL ISONONANOATE, DIPENTAERYTHRITYL TETRAHYDROXYSTEARATE/TETRAISOSTEARATE	74.90
	HELIANTHUS ANNUUS (SUNFLOWER) SEED WAX, RHUS SUCCEDANEA CERA, ORYZA SATIVA (RICE) BRAN WAX, ORYZA SATIVA (RICE) BRAN OIL, VEGETABLE (OLUS) OIL	10.00
	POLYGLYCERYL-2 TRIISOSTEARATE	5.00
	PRESERVATIVE	0.10
B	TITANIUM DIOXIDE, ALUMINUM HYDROXIDE, ISOPROPYL TITANIUM TRIISOSTEARATE, SODIUM LAUROYL ASPARTATE, ZINC CHLORIDE	1.40
	IRON OXIDES, ISOPROPYL TITANIUM TRIISOSTEARATE, SODIUM LAUROYL ASPARTATE, ZINC CHLORIDE	1.00
	IRON OXIDES, ISOPROPYL TITANIUM TRIISOSTEARATE, SODIUM LAUROYL ASPARTATE, ZINC CHLORIDE	2.20
	IRON OXIDES, ISOPROPYL TITANIUM TRIISOSTEARATE,SODIUM LAUROYL ASPARTATE, ZINC CHLORIDE	0.40
C	TREATED CELLULOSE BEADS	5.00
	Total :	100.00

3 Results and Discussion

3.1 Characterization of combined treatment agents in preparation in different pH conditions

The salt of a gemini type acylated amino acid (ASL) has been reported to exhibit oil dispersibility and ability to stabilize Pickering emulsion in the treatment of pigments. In this study, we aim to improve the dispersibility of SFA -treated cellulose beads in oil. Therefore we have proposed the combined ASL and SFA surface treatment. We have thought that to obtain the desired complex of ASL and SFA, the pH in process would be very important factor. Figure2 shows the DSC measurement results with changing pH in process. The ratio of ASL and SFA is 1:4. As seen in this figure, the DSC features are different depending on the pH during precipitation of the combined treatment agents. Therefore, pH conditions were initially examined, and magnesium stearate (SFA18) was used as the SFA participants.

The features of DSC for each sample depending on pH in process are following:

*Agent (a) [below pH 5.3] detected a single endothermic peak at 67-72°C.

*Agent (b) [pH 5.3-5.7] detected three endothermic peaks at 67-72°C, 80-90°C and 110-125°C.

*Agent (c) [pH 6.0-6.5] detected three endothermic peaks at 67-72°C, 100-110°C 110-125°C.

*Agent (d) [pH 6.5-7.0] showed a single endothermic peak at 110-125°C.

These results suggest that the interaction and forming structure of complex of ASL and SFA are affected depending on pH conditions in complexation process. Fatty acid (in this case Stearic acid (pKa = 4.85)) is easy to exist as free acid under acidic pH condition, so that it is considered a peak at 67-72°C shows melting point of stearic acid in Agent (a). Furthermore, we suggest that the peak at 110-125°C is attributable to SFA18 in Agents (b), (c), and (d). While ASL mainly precipitates under weak acidic conditions (pH 5.3-5.7), the ASL agent itself does not show a clear peak in DSC measurements (data not shown). The peak seen in Agent (b) at 80-90°C is unique. This peak would be showing the complex compound of ASL and SFA18 consisting of the process. Depending on the pH in process the structure of surface

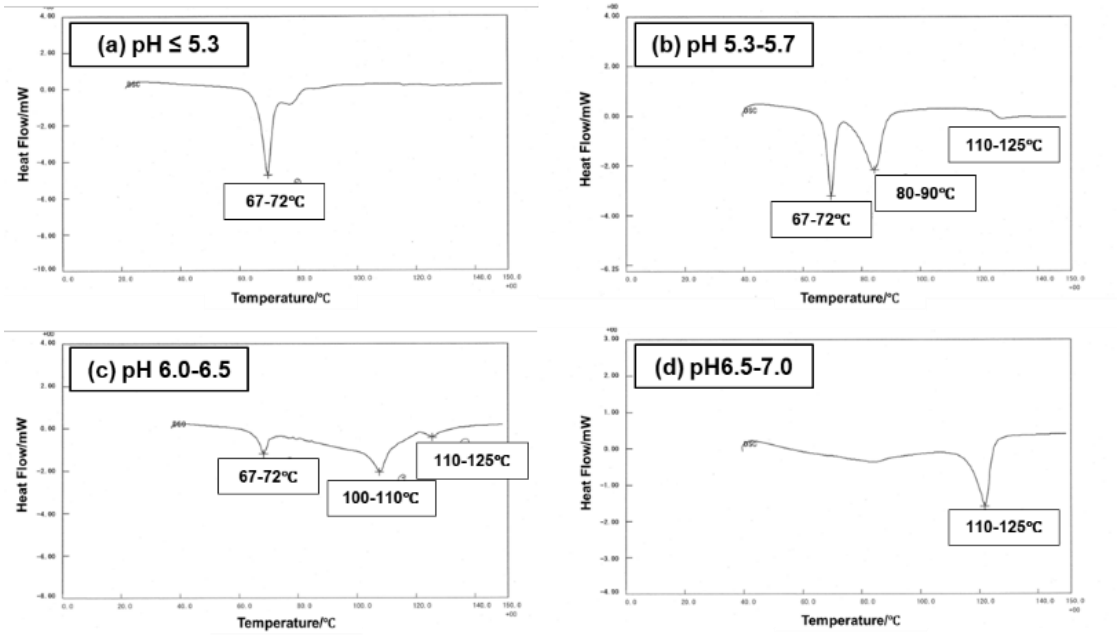

Figure 2: Influence of Precipitation pH on ASL+SFA18 Agent Characteristics (DSC)

treatment agents participates differently. We needed to define suitable pH conditions for the process.

3.2 The dispersibility of surface treated cellulose beads

The surface of the cellulose spherical beads treated with the ASL-SFA complex were prepared in conditions of the pH, as same process as described in Section 3.1, (total treatment concentration of 5 wt% (ASL:SFA=1:4)). Each surface treated beads were subsequently formulated into a simple water-in-oil (W/O) system (Table 1), and their dispersion behavior was observed with microscope (Figure 3).

As a result, the surface treated cellulose beads under condition (b) was almost completely and uniformly dispersed in the oil phase, demonstrating excellent oil dispersibility. While (a) treated beads were mainly present in the oil phase, some were also distributed in the oil-water interface. And exfoliated stearic acid crystals were also observed in this emulsion. (c) treated beads were mainly distributed in the oil phase, however some were also distributed in the water phase. Although it is expected that SFA18 is the main component, (d) treated beads were entirely transferred into the water phase and agglomerated. This (d) treated beads behavior was considered that it was caused treatment layer is exfoliated from cellulose surface, because the adsorbing force of SFA layer would be weak with shear stress in the process of emulsification. The excellent dispersibility of (b) treated beads suggests that the complex of ASL-SFA formed under pH 5.3-5.7 is stably absorbed on cellulose surface, and it imparts both effective hydrophobicity and dispersibility.

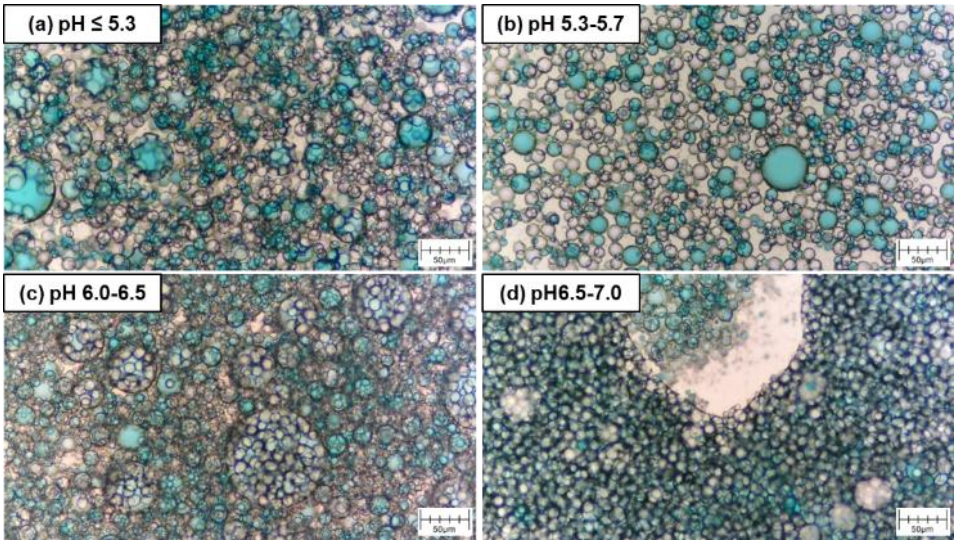

Figure 3: Influence of Precipitation pH on ASL+SFA18 treated Cellulose beads Dispersibility

Furthermore, to confirm the structure of treatment agent (b), the IR spectrum of the complex treatment agent (b) itself was measured compared with stearic acid, SFA18 and ASL (Figure 4). The inherent peaks around 1500cm^{-1} can be seen differently from Stearic acid, SFA18 and ASL. This will also mean that the unique complex of ASL+SFA will be constructed in this pH process.

From the above results, this combined complex treatment of SFA and ASL, is extremely important for the desired properties.

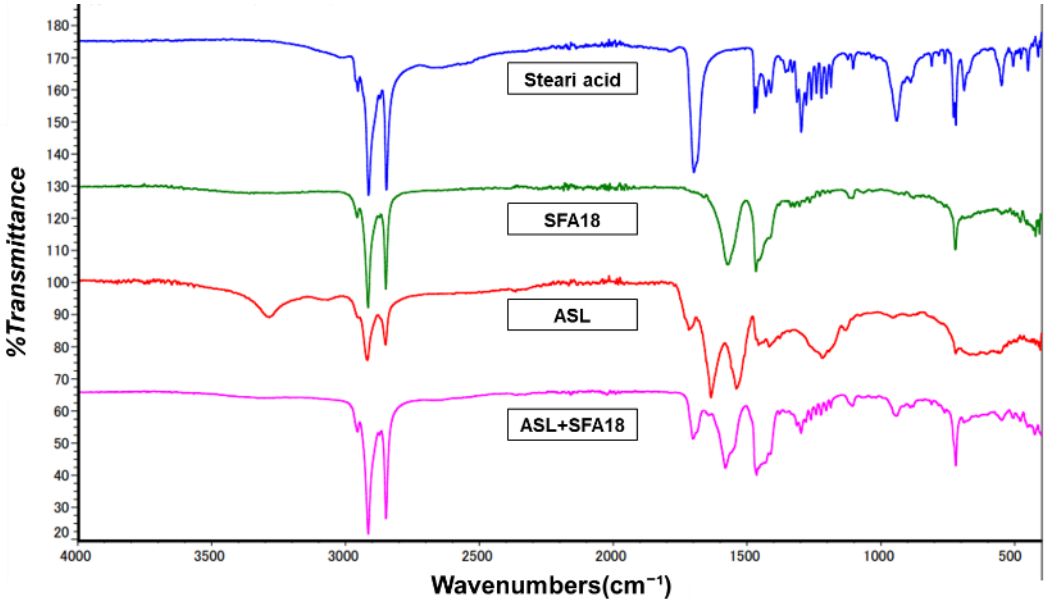

Figure 5: IR spectra of ASL+SFA18 agent

3.3 Influence of the carbon chain length

The effect of the carbon chain length of SFA used in the complex treatment on the dispersibility of the treated beads was evaluated. Specifically, fatty acids with carbon chain lengths of 14 (myristic acid), 18 (stearic acid), and 22 (behenic acid) were used. Cellulose spherical beads were treated with ASL and above each fatty acid, (ASL+SFA14 (magnesium myristate), ASL+SFA18 (magnesium stearate) and ASL+SFA22 (magnesium behenate)). For comparison, beads treated with each SFA itself (SFA14, SFA18, SFA22) and beads treated with ASL itself were also prepared in a similar manner. The hydrophobicity and dispersibility were evaluated in the formulation (Table 1).

In Figure 5, each surface treated cellulose beads were put in water, then observed after a few minutes. ASL treated one does not show good hydrophobicity. On the other hand, SFA14, 18 and 22 treated ones show better hydrophobicity gradually increasing the hydrocarbon chain.

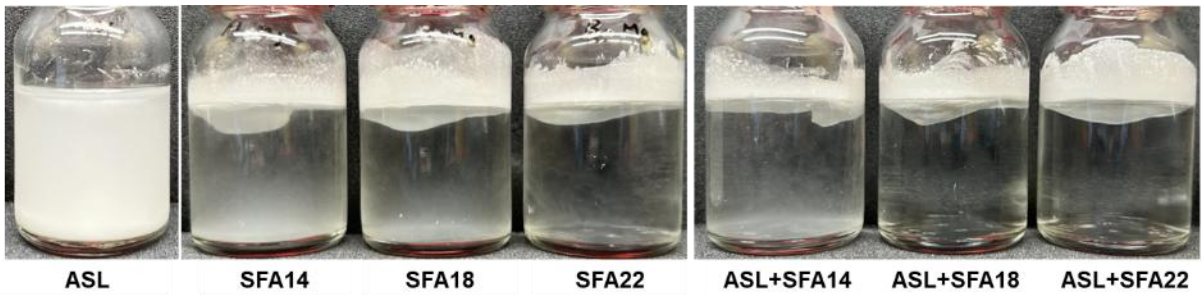

Figure 4: Evaluation of Water Repellency for Surface-Treated Cellulose Beads

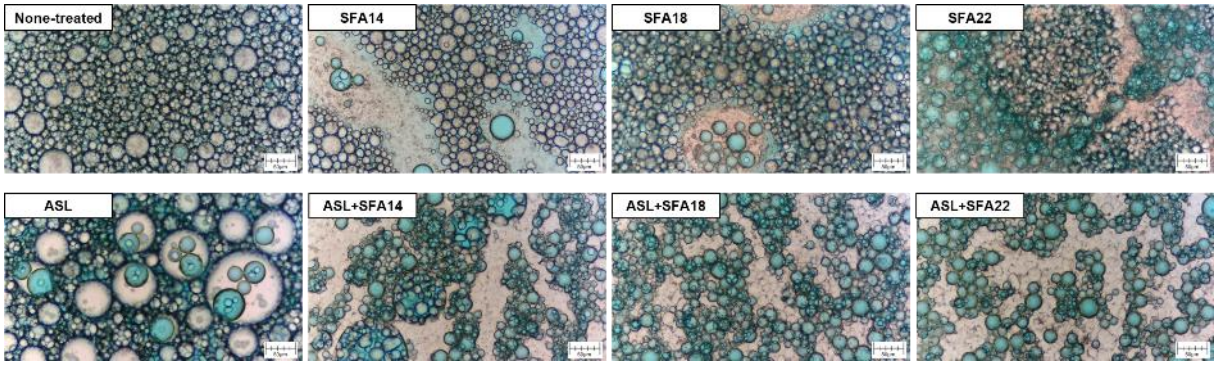

Figure 6: Dispersibility and Localization of Surface-Treated Cellulose Beads in a Simple W/O Emulsion System

This tendency will be seen for ASL+SFA14, ASL+SFA18 and ASL+SFA22. However, in the evaluation of simple W/O emulsion system, ASL+SFA18 shows the best dispersibility and stability (Figure 6). This suggests that ASL+SFA18 complex is the most suitable treatment for cellulose beads.

3.4 Evaluation in Cosmetics

We have evaluated the actual cosmetics formulations with ASL+SFA18-treated cellulose beads, which showed the best results (the pH condition (b)).

3.4.1 W/O cream formula

W/O cream formulations (Table 2) containing beads treated with SFA18 itself and beads treated with ASL+SFA18 were evaluated. As the results, the ASL+SFA18 treated beads were more uniformly dispersed in the formulation than the beads treated with SFA18 itself, as seen in Figure 7. These indicate the effect of improving dispersibility by the ASL+SFA18 combined treatment is effective not only in simple W/O systems but also in actual W/O creams.

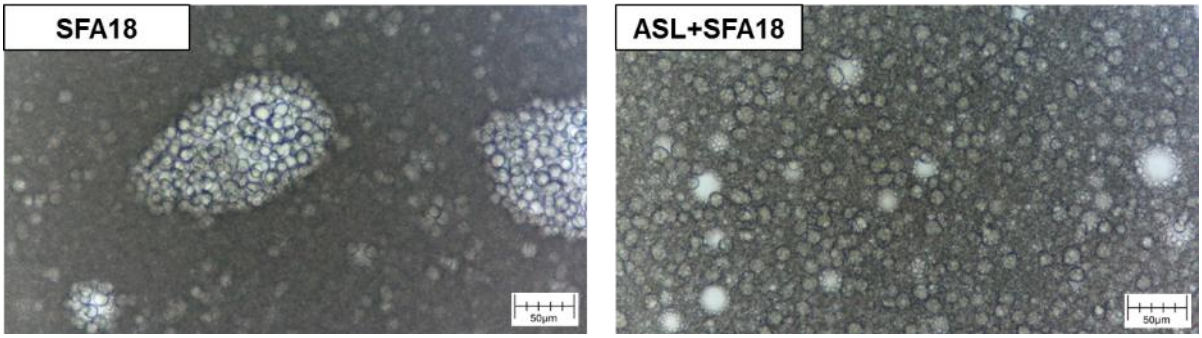

Figure 7: Dispersibility and Localization of Surface-Treated Cellulose Beads in W/O cream formula

3.4.2 Lipstick formula

As same manner, we evaluated the lipstick formulations (Table 3) with using same as in W/O foundations. No significant differences were observed in the appearance of the lipstick itself depending on the type of surface-treated cellulose beads (Figure 8 above).

However, in terms of the application feeling on skin (sensory test by human), by formulating cellulose beads it will become very smooth. This becomes even better in case of formulating ASL+SFA18 complex treatment one. This improvement suggests that the skin affinity is getting better because of ASL and creamier feeling by fatty acid segment. These results revealed that ASL+SFA18 complex-treated cellulose beads show good dispersibility not only in formulations containing water, such as W/O systems, but also in oil-based formulations like lipstick. Additionally, it provides the functionality of improved skin affinity, likely derived from ASL.

Figure 8: Effect of Cellulose Bead Surface Treatment on Lipstick Appearance and Skin Adhesion

From the results of this study, it revealed that for the ASL and SFA18 make unique complex treatment in pH process. This complex is very important to give suitable lipophilic property on cellulose beads.

This complex treatment is superior to ASL-itself or SFA-itself treatment for cellulose beads. Furthermore, it was confirmed that these complex-treated beads exhibit the expected functionalities, such as improved dispersibility and skin adhesion, when formulated into actual cosmetic formulations (W/O cream and lipstick).

Amphiphilic ASL provides particularly good dispersibility and affinity to skin. Furthermore, fatty acids, especially stearic acid (SFA18), impart particularly good hydrophobicity. However, in order to obtain a unique complex structure, it is very important to define the treatment conditions.

Namely, it is considered that the amphiphilic ASL controls the behavior of the beads at the oil-water interface, contributing to dispersion stability. On the other hand, the highly hydrophobic free stearic acid and SFA18 play a role in imparting hydrophobicity to the beads and promoting localization in the oil phase. Additionally, for the improved adhesion to the skin observed in the lipstick formulation, it is suggested that, in addition to the affinity of ASL's amino acid part for the skin surface, the flexibility derived from the molecular structures of stearic acid and SFA18 may contribute to suppleness and conformability during application.

4 Conclusion

The novel complex surface treatment technology developed in this study, which is ASL+SFA, enabled the efficient modification of hydrophilic cellulose bead surfaces, imparting both high hydrophobicity and excellent oil dispersibility. These properties are difficult to achieve with untreated cellulose beads or with ASL or SFA treatments themselves. These complex-treated beads not only show excellent oil dispersibility in W/O systems but also demonstrate additional functions in oil-based formulations like lipstick, such as improving skin application feel. This is thought to involve the skin affinity of the ASL-derived amino acid part and the flexibility provided by the fatty acid components. Since their main raw materials are of natural origin, the ASL+SFA complex treated cellulose beads obtained in this study, possess high potential as an alternative material to microplastic spherical powders, which are an environmental concern.
Finally, to obtain these properties, the treatment process conditions are very important. We have to define this. This study showed this process.

5 Reference

[1] Commission Regulation (EU) 2023/2055 of 25 September 2023 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards synthetic polymer microparticles (Text with EEA relevance)
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