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“Microcapsules with a high content of solid UV absorbers made in silk-silicone hybrid polymers facilitate O/W sunscreen formulations”

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1. Introduction

Ultraviolet (UV) rays are known to have adverse effects on human skin, including photoaging such as blemishes and wrinkles, and promoting the development of skin cancer [1]. Sunscreens are commonly used as a protection against UV damage and contain UV-scattering agents, which are inorganic metal oxide powders, and organic UV-absorbing agents as UV-protective ingredients. Many organic UV absorbers have been developed that have different morphologies, absorption wavelengths, and characteristics, and by combining multiple UV absorbers, it is possible to create sunscreens with high UV protection capabilities [2, 3]. However, in recent years, some studies have suggested that UV absorbers may have adverse effects on the marine environment, and some regions and countries have restricted the use of certain UV absorbers [4]. One of those, octyl methoxycinnamate (OMC), has a high UV absorption capacity and is a good solvent for solid UV absorbers, and has been widely used around the world [5]. UV absorbers with high photostability and UV protection ability, which have been increasingly used recently, are often solids that are difficult to dissolve in the oils commonly used in cosmetics. Therefore, it is believed that the restrictions on the use of OMC have made it difficult to incorporate high amounts of solid UV absorbers into formulations and to impart high UV protection capabilities. In addition, several problems with UV absorbers, such as stickiness, oiliness, and skin irritation, have been reported [6, 7].

We previously reported a microencapsulation technology for UV absorbers using a hybrid polymer of hydrolyzed silk peptide and silicone [8, 9]. With those microcapsules, the UV absorber does not mix with other oils in the formulation, so solid UV absorbers can be incorporated into the formulation while maintaining their solubility. In addition, since the UV absorbers do not come into direct contact with the skin, it may be possible to improve the unpleasant feel and to reduce skin irritation [6, 7, 10]. In this study, to solve the problems of UV absorbers mentioned above, we investigated a composition that can be highly incorporated with poorly soluble solid UV absorbers without using OMC, and developed water-dispersed microcapsules that encapsulate these UV absorbers (UVMC). We also report on sunscreen formulations that incorporate UVMC into O/W gel formulations, that have more limited amounts of oil.

2. Materials and Methods

2.1. Study of UV absorber composition

Four different UV absorbers (ethylhexyl salicylate (EHS), diethylamino hydroxybenzoyl hexyl benzoate (DHHB), bisethylhexyloxyphenol methoxyphenyl triazine (BEMT), and ethylhexyl triazone (EHT)) were mixed in various ratios, then dissolved by heating, and stored at 5°C for two months to observe whether precipitation occurred.

2.2. Absorbance measurement

The absorbance of each UV absorber was measured using a UV-vis spectrophotometer (UV-1900, Shimadzu Corporation). The UV absorber solution was diluted with ethyl acetate to 8 ppm.

2.3. Preparation of microcapsules

The mixture was dissolved at 70°C in a ratio of EHS:DHHB:BEMT:EHT=45:20:20:15. The UV absorber solution was added to the silk-silicone hybrid polymer aqueous solution, and the mixture was stirred with a homomixer, causing a silicone condensation reaction at the O/W interface to obtain a UVMC dispersion [8]. 10% of the UVMC was the capsule membrane, and 90% was the UV absorbers. A 60% aqueous dispersion containing 4% pentylene glycol was used for the experiment.

2.4. Optical microscope observation

The UVMC dispersion was appropriately diluted for easy observation and placed on a slide glass, covered with a cover glass, and observed using an optical microscope.

2.5. Particle size distribution

The particle size distribution of the UVMC dispersion was measured using a laser diffraction particle size distribution analyzer (SALD-2300, Shimadzu Corporation).

2.6. Stability test

Stability tests were conducted for temperature, pH, and salt concentration. After storing samples adjusted to each condition shown in Table 1 for a certain period of time, the UV absorber outside the capsule was extracted with hexane and the BEMT concentration was measured [11]. From these results, the BEMT concentration in the UVMC was calculated and its change was confirmed.

Table 1. Conditions for the stability test

Temperature	5°C↔40°C (every other day)	
pH	4.5	8.0
Salt concentration	5%	20%

2.7. Application to sunscreen formulations

2.7.1. Combined use with UV absorbers

O/W gel sunscreen formulations containing UVMC and non-encapsulated UV absorbers were prepared using an emulsifying thickener. The blending ratio of UVMC and non-encapsulated UV absorbers was adjusted so that the amount of UV absorbers contained in the formulation was constant, and changes in physical properties and usability were confirmed. The formulations used are shown in Table 2.

Table 2. Compositions (w/w%) of the formulations containing encapsulated UV absorber and non-encapsulated UV absorbers in various ratios.

Formulation No.	1	2	3	4	5
encapsulated UV absorbers / non-encapsulated UV absorbers	100/0	75/25	50/50	25/75	0/100
Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer, Polyisobutene, PEG-7 Trimethylolpropane Coconut Ether, Water	2	2	2	2	2
Butylene Glycol	10	10	10	10	10
Olea Europaea (Olive) Fruit Oil	1	1	1	1	1
Glycerin	1	1	1	1	1
Phenoxyethanol	0.3	0.3	0.3	0.3	0.3
Water	65.7	68	70.3	72.6	74.9
UVMC-dispersion	20	15	10	5	0
Ethylhexyl Salicylate, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Ethylhexyl Triazone	0	2.7	5.4	8.1	10.8

2.7.2. Viscosity measurement

The viscosity of formulations was measured using a Brookfield viscometer (Tokyo Keiki). Samples were stored at 0°C, 25°C, and 40°C, and were returned to 25°C for measurement.

2.7.3. In vitro Sun Protection Factor (SPF) measurement

The in vitro SPF of each formulation was measured using an UV transmittance analyzer (Labsphere UV-2000S, Labsphere Inc.). Samples were applied to surgical tape (BlendermTM, 3M) at a concentration of 2 mg/cm^2 and were dried for 15 minutes before measurement. Four measurements of each sample were performed to calculate the mean and standard error (n = 4).

2.7.4. Sensory assessment

The sensory evaluation was performed by a panel of 10 people using formulations No. 1, 3, and 5. Each formulation was given a score of 2, 1, or 0, in order of best to worst, and the total score for each formulation was calculated. The evaluation was conducted in seven categories: "Non-sticky feeling," "Non-oily feeling," "Ease of blending," "Ease of spreading," "Moist feeling," "Smoothness," and "Preference."

2.7.5. Combined use with UV scattering agent

O/W gel sunscreen formulations were prepared using a surface-treated zinc oxide slurry in combination with UVMC or non-encapsulated UV absorbers. The formulations used are shown in Table 3.

Table 3. Compositions (w/w%) of the formulations using zinc oxide in combination with encapsulated or non-encapsulated UV absorbers.

Formulation No.	6	7	8
Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer, Polyisobutene, PEG-7 Trimethylolpropane Coconut Ether, Water	2	2	2
Phenoxyethanol	0.3	0.3	0.3
Water	87.7	67.7	76.9
Zinc Oxide, Isostearic Acid, Polyhydroxystearic Acid, Hydrogenated Polyisobutene	10	10	10
UVMC-dispersion	0	20	0
Ethylhexyl Salicylate, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Ethylhexyl Triazone	0	0	10.8

3. Results

3.1. Solubility test of UV absorbers

When three solid UV absorbers (DHHB, BEMT, EHT) were dissolved in the liquid UV absorber EHS, the solubility was DHHB: 30%, BEMT: 15%, and EHT: 10%. However, when all of these UV absorbers are mixed, the solid absorbers could be blended at a higher concentration (Table 4). Composition B was adopted because it has high UV absorption ability (Fig. 1) and stable solubility.

Table 4. Solubility of UV absorbers with various compositions when stored at 5°C for 2 months.

UV absorber composition (w/w%)	A	B	C
EHT	15	15	20
BEMT	15	20	15
DHHB	20	20	20
EHS	50	45	45
Solubility	Dissolved	Dissolved	Precipitated

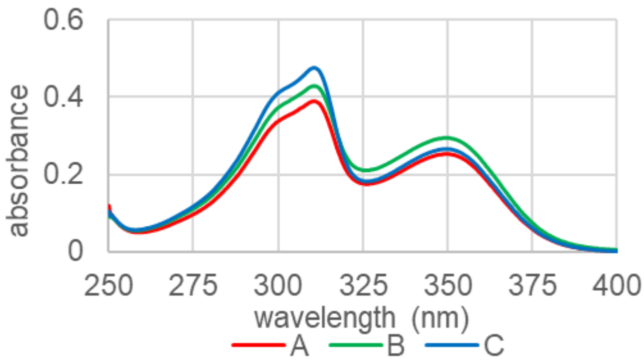

Figure 1. Absorbance of each UV absorber solution.

3.2. Microscopic observations of UVMC

When the prepared UVMC dispersion was observed using an optical microscope, the capsules were dispersed in water without agglomeration. In addition, the particle size distribution was measured, and the average particle size was 2.056 ± 0.140 μm. The micrograph and particle size distribution are shown in Fig. 2.

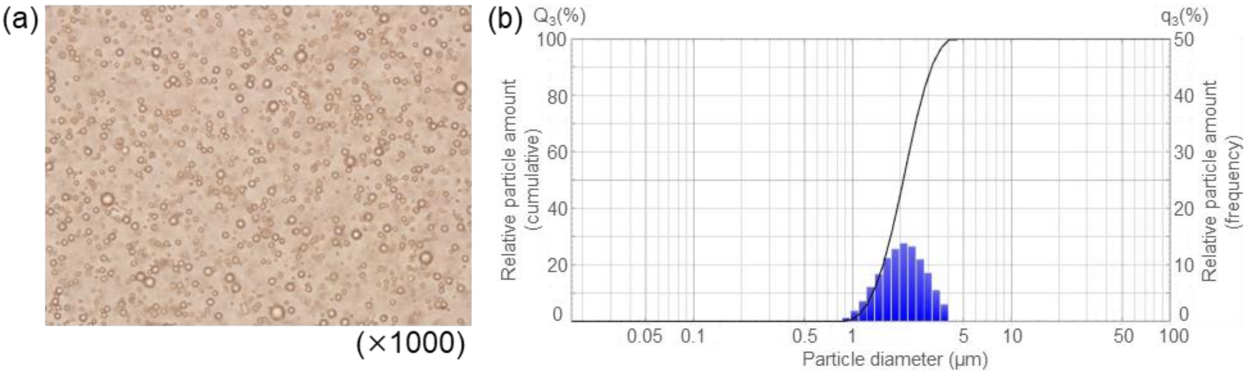

Figure 2. (a) Optical microscope image and (b) particle size distribution of UVMC-dispersion.

3.3. Stability test

The UVMC dispersions were stored at different temperatures, pHs, and salt concentrations, after which the amount of BEMT in each UVMC was measured. There was almost no change under any of the conditions, confirming that the capsules stably encapsulated the UV absorbers (Fig. 3).

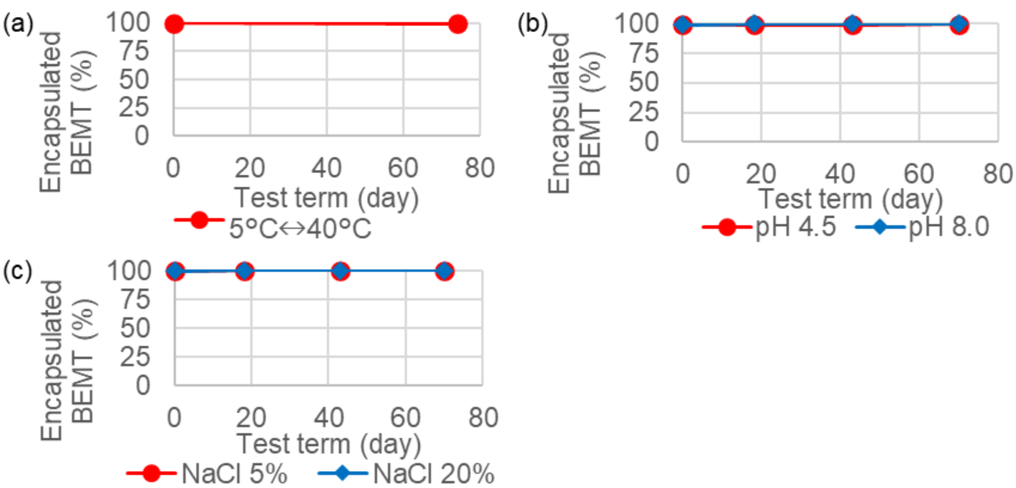

Figure 3. Stability of UVMC (a) temperature, (b) pH, (c) salt concentration.

3.4. Application to sunscreen formulations

3.4.1. Combinations with UV absorbers

We prepared O/W gel sunscreens containing UVMC and non-encapsulated UV absorbers in various ratios. Although there were differences in the initial viscosity, no differences were observed in the stability over time (Fig. 4), but the formulations with a high non-encapsulated UV absorbers content had many large emulsion droplets, while the higher the proportion of UVMC, the more small emulsion droplets there were (Fig. 5). When measuring the SPF, the formulation with a 50/50 ratio of encapsulated UV absorbers/non-encapsulated UV absorbers had the highest SPF (Fig. 6).

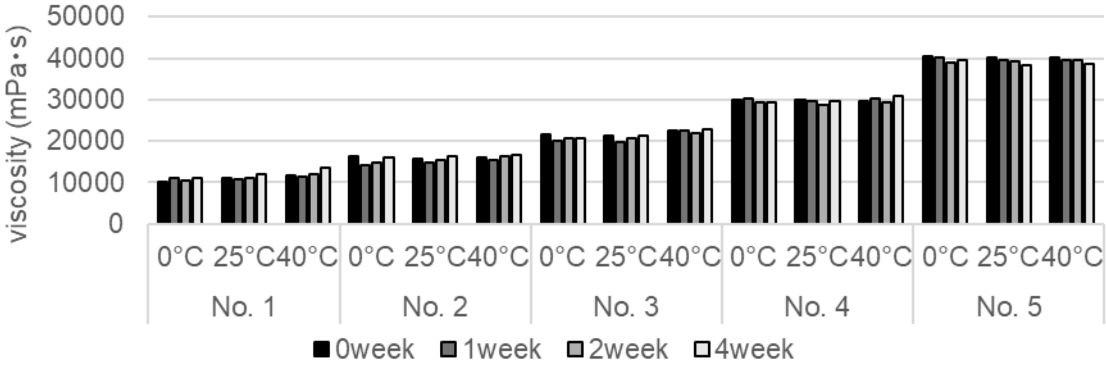

Figure 4. Viscosity change of formulations No. 1 – 5 over time.

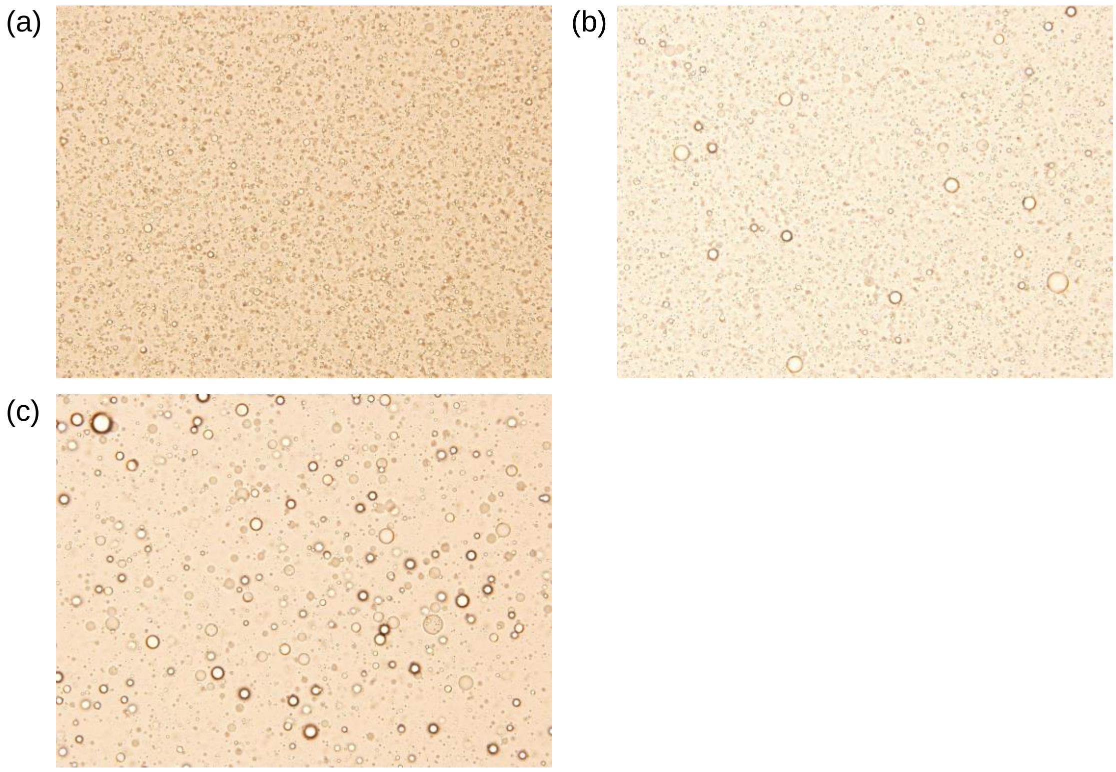

Figure 5. Optical microscope images of formulations (a) No. 1, (b) No. 3, and (c) No. 5. The magnification is 400x.

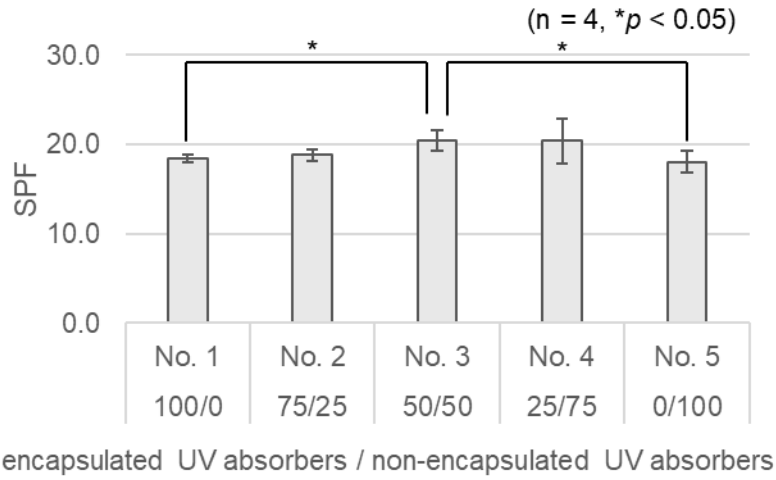

Figure 6. In vitro SPF of formulations No. 1 – 5; bars indicate means ± S. D. of SPF (n = 4); significance *$p < 0.05$ (Student's *t*-test).

Fig. 7 shows the results of sensory evaluations of the three formulations, No. 1, 3, and 5. The non-encapsulated UV absorbers were superior in terms of "Moist feeling," while UVMC was superior in terms of "Non-oily feeling" and "Smoothness." Formulation No. 3 had the highest score for "Preference," suggesting that the texture of the formulation can be adjusted by changing the blending ratio of UVMC and the non-encapsulated UV absorbers.

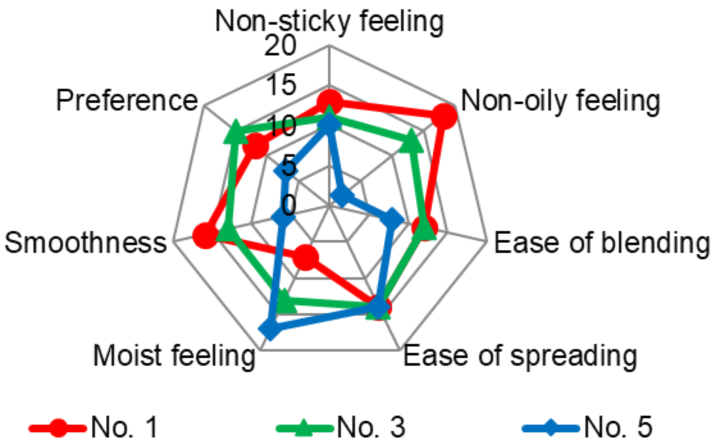

Figure 7. Sensory evaluation results of formulations No. 1, 3, and 5.

3.4.2. Combination with UV scattering agents

Three types of formulations were prepared: zinc oxide only (No. 6), zinc oxide + UVMC (No. 7), and zinc oxide + non-encapsulated UV absorbers (No. 8). Viscosity measurements showed that the viscosity of formulation No. 8 increased and became unmeasurable after two weeks at 40°C, while the viscosity of formulation No. 7 remained stable over time (Fig. 8a). Optical microscopy confirmed that zinc oxide was dispersed in the emulsion droplets and UVMC was dispersed in the external phase (Fig. 8b, 8c). SPF measurements confirmed that the combination of zinc oxide slurry and UVMC significantly increased the SPF (Fig. 9). The SPF was also higher when used in combination with UVMC than when used in combination with non-encapsulated UV absorbers.

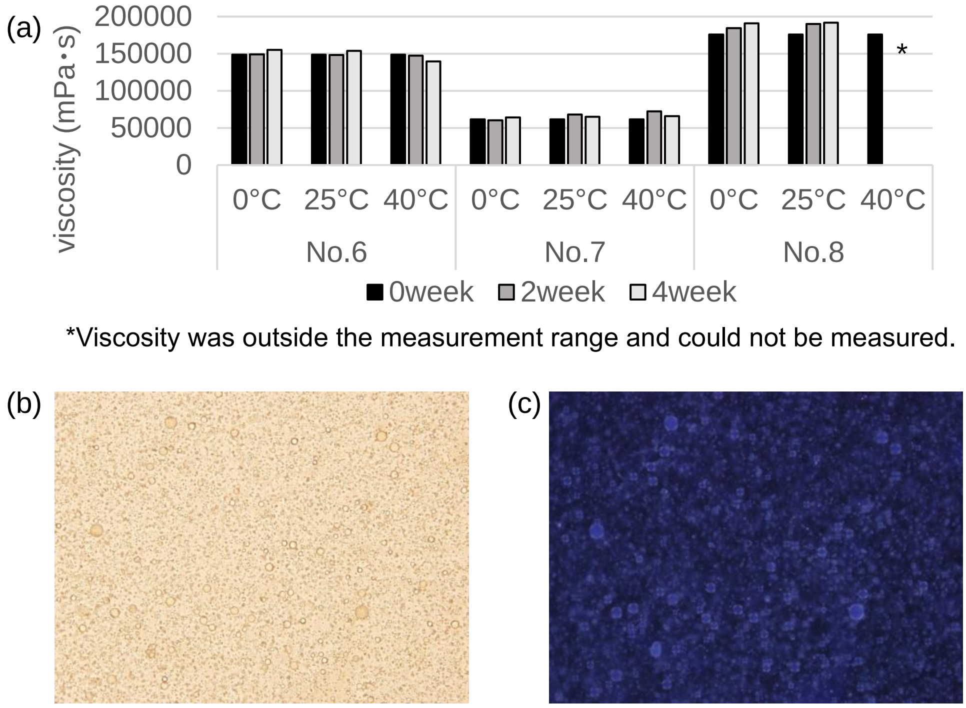

Figure 8. (a) Viscosity change of formulations No. 6 – 8; (b) Optical microscope image; (c) polarizing filtered image of formulation No.7. The magnification is 400x.

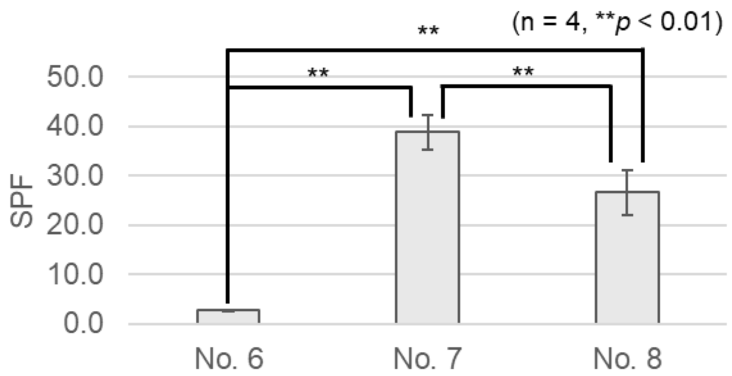

Figure 9. In vitro SPF of formulations No. 6 – 8; bars indicate means ± S. D. of SPF (n = 4); significance ***p* < 0.01 (Student's *t*-test).

4. Discussion

We investigated the development of water-dispersible microcapsules encapsulating solid UV absorbers, which are widely used these days, at high concentrations that can be easily incorporated into the aqueous phase.

As a result of the investigation [12], when the solid UV absorbers DHHB, BEMT, and EHT were dissolved in various ratios in the liquid UV absorber EHS, which is currently considered to be in high use, the results showed that when EHS:DHHB:BEMT:EHT = 45:20:20:15, the solid UV absorbers could be stably dissolved at a high ratio of 55% in total while maintaining high UV absorption capacity (Fig. 1, Table 4). Furthermore, we developed microcapsules using a silk-silicone hybrid polymer that encapsulated the UV absorber mixture and was dispersed in water (Fig. 2). The capsule membrane is a polymer that combines hydrolyzed silk peptide and silicone resin, and the lipophilic silicone resin encases the UV absorbers, and the hydrophilic peptide is oriented on the outside of the capsule, which allows the UV absorbers to be dispersed in water [8]. Furthermore, UVMC was not destroyed by changes in temperature, pH, or salt concentration (Fig. 3), and it is believed that UVMC can be incorporated into cosmetics while stably encapsulating the UV absorbers.

Next, UVMC was incorporated into sunscreen formulations. As the harmful effects of UV rays have become widely known, sunscreens have become an item used daily, and the feeling of use is important. In particular, O/W gels tend to be more popular due to their fresh feel, and this time we investigated a blend of UVMC or non-encapsulated UV absorbers into O/W gels using an emulsifying thickener (Table 2). In general, when blending solid UV absorbers, it is necessary to heat and dissolve them in the oil before mixing them into the formulation, but when blending UVMC, there is no need to heat it. In the prepared sunscreen, the larger the amount of non-encapsulated UV absorber, the more large emulsified droplets there were, which suggests that oil containing a large amount of solid UV absorber may be difficult to emulsify (Fig. 5). Although there was no effect this time, depending on the oily ingredients used, it is possible that the solubility of the solid absorbent may be reduced, leading to a decrease in stability and the promotion of precipitation of the UV absorbers. In addition, the SPF was highest in the formulation containing a 50/50 ratio of encapsulated UV absorbers/non-encapsulated UV absorbers (Fig. 6). This is thought to be because UVMC is dispersed in the water phase and the non-encapsulated UV absorbers in the oil phase, allowing the UV protection agent to spread evenly over the applied film. In addition, sensory evaluation tests showed that UVMC was superior in terms of "Non-sticky feeling," "Non-oily feeling," and "Smoothness" (Fig. 7). If UV absorbers are added as is, the oily component comes into direct contact with the skin, making it sticky and oily, but encapsulating it makes it possible to have a smooth feel. Also, by changing the mixing ratio of UVMC and non-encapsulated UV absorbers, it is possible to adjust the smooth and moist feeling, which suggests that the feeling can be easily adjusted while maintaining the SPF.

We then investigated formulations in which the formula was used in combination with zinc oxide, an inorganic UV scattering agent. It has been reported that the combination of organic UV absorbers and inorganic UV scattering agents improves the SPF more than when used alone [2]. When the formulations in Table 3 were analyzed, the formulation that combined zinc oxide and UVMC showed a greater boost in SPF and was more stable than the formulation that combined non-encapsulated UV absorbers (Fig. 8(a), 9). The zinc oxide used in this study had a hydrophobic surface treatment and was dispersed in oil. Therefore, the dispersibility of zinc oxide was reduced by blending a solid UV absorber with low solubility in the same oil phase, which may have caused thickening and a decrease in UV protection. Furthermore, when used in combination with a non-encapsulated UV absorber, the UV protection agent is only present in the oil phase, but since UVMC disperses in the aqueous phase, when used in combination with zinc oxide, the UV protection agent can be present both in the oil and in the aqueous phases, which may provide more powerful protection against UV rays. There are reports that UV scattering agents are safer than UV absorbers, but due to poor compatibility with water-soluble polymers such as carbomer, and poor usability such as the white appearance and the squeaky feeling, it is not easy to develop a high SPF O/W gel with a high UV scattering agent content [13]. These results suggest that by using UVMC, it is possible to more easily develop formulations with high UV protection that are pleasant to the touch and can be used in combination with inorganic powders, while suppressing concerns about the safety of UV absorbers.

5. Conclusion

In this study, we investigated combinations of UV absorbers that can be highly loaded with solid UV absorbers without using OMC, and developed UVMC encapsulated in silk-silicone hybrid polymer. The results showed that UVMC is stably dispersed in water and does not break down due to changes in temperature, pH, or salt concentration. It was confirmed that applying UVMC to sunscreen formulations and combining it with UV absorbers and UV scattering agents improves the SPF. In addition, encapsulation gives the UV absorber a smooth feeling without stickiness or oiliness, suggesting that the feeling can be easily adjusted by incorporating it into the formulation.

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