

**A novel powder-dispersing system for skin-friendly cosmetics:
Designing a polymer gel network that boosts and maintains UV protection
without UV absorbers and surfactants**

Ikuya Ohshima*; Takashi Takeshita; Ryo Hagino; Yuji Masubuchi

Research Laboratories, KOSÉ Corporation, Tokyo, Japan

* Ikuya Ohshima, 48-18, Sakae-cho, Kita-ku, Tokyo 114-0005, Japan, +81-3-3919-6131,
ikuya_ohshima@kose.co.jp

Abstract

Regardless of gender, generation, race, and ethnicity, everyone has an essential need for UV protection with a skin-friendly formulation. Conventional formulations have aimed to achieve high UV protection and durability using chemical UV absorbers and surfactants, in combination with rigid silicone film formers. However, this strategy results in stress on the skin. To overcome this limitation, we have developed a novel powder-dispersing system that utilizes a unique hybrid silicone/polyurethane elastic polymer gel network (SIPU). The monomer ratio and the molecular weight of SIPU are optimized to provide an excellent ability to disperse UV scattering agents leading to enhanced UV protection, an appropriate hardness level to immobilize UV scattering agents leading to durability, and good elasticity so as not to stress the skin. Our SIPU-based W/O type foundation shows excellent UV protection, durability, and skin-friendliness that are unachievable with combinations of conventional materials.

Keywords: UV protection; surfactant free; durability; powder dispersion; polyurethane film former

Introduction.

As the negative effects of UV rays on skin have become common knowledge, people around the world are demanding higher UV protection regardless of gender, generation, race, or ethnicity. Furthermore, people are demanding not only high and durable UV protection, but also skin-friendly formulations made without UV absorbers.

Conventional UV-protective formulations are often water-resistant W/O types. These formulations contain large amounts of UV scattering agents, large amounts of silicone surfactants to sufficiently disperse the agents, and a rigid silicone film former to immobilize the agents on the skin in order to achieve high UV protection without using UV absorbers [1]. However, the large amount of surfactants in the formulation can cause a decrease in durability of makeup by the sebum. In addition, the rigid silicone film former in the formulation can cause stress on the skin, because it cannot readily adapt to facial movements.

In a previous study, a surfactant-free formulation technology was reported in which the UV scattering was achieved using a Pickering Emulsion treatment technology [2]. This formulation was able to achieve high UV protection. However, it was difficult for the Pickering Emulsion to contain sufficient film former, again, resulting in insufficient durability.

To address the limitations of previous formulations, here, we set out to develop a novel powder-dispersing system that combines high UV protection and durability with skin-friendliness by designing an original film forming material. Our film former had the following requirements:

Requirement 1: The UV scattering agents should be highly dispersed without the use of surfactants.

Requirement 2: The film former should combine hardness to immobilize the UV scattering agents and elasticity to flexibly follow repeated face movements.

In order to satisfy Requirement 1, we considered that the film former should have surface wettability and adsorption on the UV scattering agent which closely related to the ability to

disperse UV scattering agents [3]. To improve wettability, solubility in the solvent is necessary, and for adsorption, a highly polar functional group that strongly interacted with the surface hydroxyl groups of the UV scattering agents is required.

In order to satisfy Requirement 2, the film former needs to be sufficiently hard which requires increasing the molecular weight and crystallinity by introducing cross linking. Although static cross linking with covalent bonds improves hardness, it makes the material brittle [4]. This is problematic from the viewpoint of elasticity. Therefore, we considered that a dynamic cross-linking structure exemplified as hydrogen bonds formed between urethane bonds is necessary.

Based on the above, we hypothesized the material design of a silicone/polyurethane hybrid gel (SIPU). In general, polyurethane exhibits elasticity and hardness derived from the coexistence of soft segments that occupy the major space within the polymers and are capable of deforming the gel without collapse, together with hard segments that work as high-strength bridging points [5]. In SIPU, we chose soft segments to be comprised of silicone segments derived from dimethiconol, which contribute to solubility in various kinds of the outer oil phase. For the hard segments, we used ethylene glycols, which formed dynamic cross-linking points due to hydrogen bonds between urethane bonds as well as the surface adsorption points of the UV scattering agents. It was most important to clarify the relationship between the ratio of ethylene glycol and the physical properties of SIPU, and also the relationship between the ratio of ethylene glycol and dispersing ability in order to develop a novel powder-dispersing system satisfying all the requirements.

We herein report the synthesis of SIPU, the physical properties corresponding to the requirements, and the functionalities and skin-friendliness in use of our model foundation with SIPU. Our results show that SIPU can be effectively utilized in a novel powder-dispersing system that brings out the high UV protection, durability, and skin-friendliness.

Materials and Methods.

1-1. Synthesis of SIPU

Dimethiconol was selected for the soft segments, and ethylene glycol (EG) was selected for the hard segments. Polyurethane was obtained by reacting dimethiconol and EG with alkyl isocyanate in dimethicone by addition polymerization. Three types of SIPU (SIPU 1~3) with different molar ratios of EG in the polyurethane were synthesized. Then, ethanol was added to terminate the reaction. The weight-average molecular weights (M_w) of the synthesized SIPUs were measured by GPC using polystyrene standards.

1-2. Physical properties of SIPU

1-2-1. Ability of SIPU to disperse UV scattering agents

Three types of dispersions of zinc oxide with SIPU1~3 were prepared (Dispersions 1~3). The composition of Dispersion-1 was 20% zinc oxide (average particle size 25 nm, non-surface treated), 6% SIPU-1, and 74% dimethicone, while Dispersions-2 and 3 were prepared by replacing SIPU-1 with SIPU-2 and 3, respectively, otherwise with the same composition. To prepare Dispersions 1~3, SIPUs were diluted in dimethicone and heated at 90 °C, to which zinc oxide was added and dispersed with a roll-mill. The obtained dispersions were cooled to 25 °C.

In addition, in order to compare the ability of SIPUs to disperse UV scattering agents with conventional dispersants, Dispersion-4 was prepared by replacing SIPUs with PEG-9 polydimethylsiloxyethyl dimethicone, otherwise with the same composition as Dispersions 1~3, and dispersed with a roll-mill at 25 °C.

Then, SPF tests were conducted using SPF analyzer (UV-2000S, Labsphere Co.) to evaluate the ability of SIPU to disperse zinc oxide in accordance with ISO 24443. Dispersions 1~4 were applied on a 5 cm square substrate made from polymethyl methacrylate (HELIOPLADE™ HD Helioscreen Co.) at the application amount of 1.3 mg/cm² and spread

with a finger. After drying for 30 min, the applied films of the dispersions were irradiated with solar-simulating UV light within a wavelength range from 290 to 450 nm. During the irradiation, the amount of transmitted UV light was detected. A total of 27 measurements per dispersion sample were conducted across three films at nine locations per applied film to calculate the average values and standard errors (SE).

1-2-2. Hardness of SIPU

SIPU 1~3 were diluted to 20% in dimethicone, heated at 90 °C, and then poured into jar containers with a thickness of 1 cm. After cooling to 25 °C, the hardness of the samples was measured by a rheometer (FUDOH Rheometer, Rheotech Co.) using a disc-shaped adapter with a diameter of 20 mm, with an insertion speed of 2 cm/min as the maximum load value obtained, at an insertion depth of 2 mm.

1-2-3. Elasticity of SIPU

Trimethylsiloxy silicate or (acrylates/dimethicone) copolymer was used as the conventional silicone film former. These materials and SIPU 1~3 were coated on artificial leather at a thickness of 400 µm using a bar coater. After drying for a day, the uniaxial tensile test was conducted using a texture analyzer (Eko Instruments Co.) at a tensile length of 5 mm with a speed of 2 cm/s, and repeated twice per measurement. The elasticity of the materials was measured from the stress value applied to the artificial leather coated with each material.

1-3. Structural analysis of SIPU

The microstructure of SIPU was observed using transmittance electron microscopy (TEM, HT7800, Hitachi High-Tech Co.) at 80 kV. SIPU with a 30% polymer solid content swollen in dimethicone was stained with ruthenium tetroxide and sliced into thin sections using a microtome and then used for TEM observations.

1-4. Functionalities of SIPU-based W/O type foundation

1-4-1. UV protection

Two W/O type foundations (Foundation A and B) were prepared. Both formulations contained equal amounts of zinc oxide (average particle size 25 nm, non-surface treated), iron oxide (non-surface treated), and titanium oxide (average particle size 250 nm, non-surface treated). Additionally, Foundation A contained PEG-9 polydimethylsiloxyethyl dimethicone as a surfactant and trimethylsiloxysilicate as a film former, as well as Dimethicone/vinyl dimethicone crosspolymer as a thickener to match the viscosity of Foundation B. Here, we consider Foundation A to be representative of a conventional formulation. In Foundation B, SPU was added without these materials.

The SPF tests were conducted using the same procedure as in 1-2-1.

1-4-2. Durability

First, an evaluation of the durability of SPF was conducted. After conducting the SPF tests shown in 1-4-1, polymethyl methacrylate substrates were prepared. These were immersed in a flowing pseudo-sebum made from triglyceride and agitated for 80 min. Subsequently, the SPF measurements were taken again to evaluate the durability of the UV protection.

Second, an evaluation of makeup durability was conducted. Foundation A and B were applied on the artificial leather using the same procedures for the SPF measurement as shown in 1-2-1. Next, their color was measured by a colorimeter (SE-7700, Nippon Denshoku Co.). Then, the durability of the makeup was evaluated by measuring the color after immersion in pseudo-sebum and agitation for 80 min.

1-4-3. Analysis of applied film

First, to macroscopically evaluate the dispersion of metal oxides in the applied films, Foundation A and B were applied on glass plate at a thickness of 50 µm using a bar coater and observed by optical microscopy (VHX-8000, KEYENCE Co.).

Second, to microscopically analyze the dispersion of the metal oxides in the applied films on actual human skin, the applied films of Foundation A and B obtained by using the replica method [6] were observed by scanning electron microscopy (SEM, JSM-7800F Prime, JEOL Co.) at 15 kV. In addition, Energy dispersive X-ray spectroscopy (EDS) was used for elemental maps. The detection targets were Zn and Ti as UV scattering agents.

1-5. Skin-friendliness of SIPU-based W/O type foundation

The sensory evaluations of Foundation A and B were conducted through a questionnaire survey of 11 cosmetic specialist evaluators. Each evaluator rated the foundations on a 7-point scale using the criteria, "No rigidity of the applied film" at 5 hours after application, and "No stress on the skin" at the end of the test. The mean score for these three questions was calculated, and significance was determined using Student's *t*-test (*p*<0.05).

Results.

2-1. Synthesis of SIPU

Figure 1 shows the synthetic scheme of SIPUs. SPU 1~3 with different molar ratios of EG were obtained as shown in Table I. From the results of GPC measurements, the molecular weight of SPU 1~3 was estimated to be 60,000.

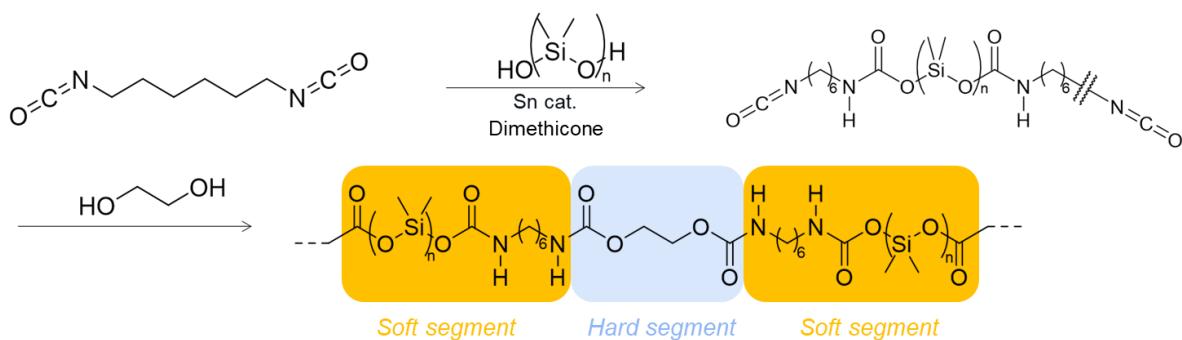


Figure 1. Synthetic scheme of SIPU (n=41~68)

2-2. Physical properties of SIPU

2-2-1. Ability of SIPU to disperse UV scattering agents

To confirm the Requirement 1, SPF values of three dispersions of zinc oxide with SIPU 1~3 (Dispersions 1~3) evaluated to verify the hypothesis that the EG ratio is an important determinant of the adsorption on UV scattering agents and is related to the dispersing ability. The SPF values of the Dispersions 1~3 are shown in Table I. SIPU-2 and SIPU-3 had the higher SPF values among all the samples, and there was no significant difference between SIPU-2 and SIPU-3 (Student's *t*-test, *p*<0.05).

Additionally, the SPF values of the Dispersions 1~3 were significantly higher than that of Dispersion-4 (8.7 ± 0.5) prepared with the conventional dispersant (Student's *t*-test, *p*<0.05).

Table I. Characterization of the synthesized SIPUs and physical properties of the compositions using SIPUs

	SIPU-1	SIPU-2	SIPU-3
EG molar ratio (-)	1.5	2	2.4
$M_w (\times 10^4)$	6	6	6
SPF \pm SE value of dispersion (-)	15.1 ± 2.4	23.3 ± 4.7	20.3 ± 0.4
Hardness of the 20% gel (N)	No gelation	0.01	0.17

2-2-2. Hardness of SIPU

To confirm the Requirement 2, the hardness and elasticity of SIPUs were evaluated to verify the hypothesis that the EG ratio is an important determinant of the physical property to immobilize the UV scattering agents.

The hardness of SIPU gels with a solid content of 20% in dimethicone are shown in Table I. SIPU-1 did not gelatinize, so the hardness could not be measured. SIPU-3 formed the hardest oil gel without phase separation. It was found that the hardness of the gels depended on the EG ratios, with increased EG ratio leading to increased hardness. Thus, SIPU-3 was the most suitable in terms of hardness.

2-2-3. Elasticity of SIPU

Since SIPU-3 was the hardest among SIPU 1~3, the elasticity of SIPU-3 was compared with that of trimethylsiloxy silicate and (acrylates/dimethicone) copolymer, which represent conventional hard silicone film formers. Figure 2 shows the maximum difference in stress from the first to second tensile. Smaller values of difference in stress indicate higher elasticity because the difference reflects the breakage of the coating film due to the first tensile. The difference in SIPU-3 was smaller than that in the conventional film formers, indicating that SIPU-3 was the most elastic.

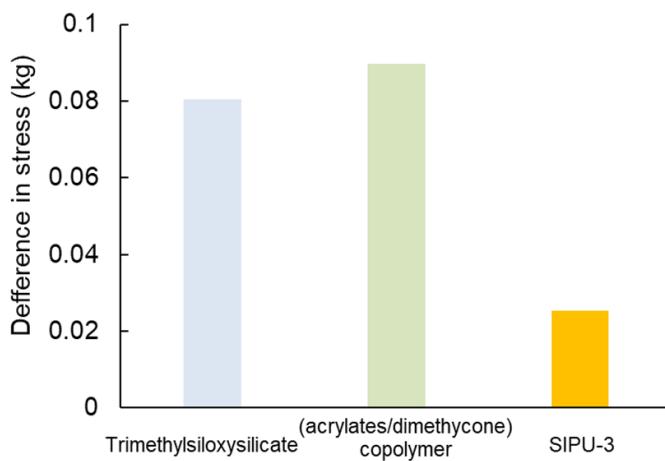


Figure 2. Profiles of the differences in stress from the first to second tensile

With the results of 2-2, we confirmed that SIPU-3 successfully met requirements 1 and 2 and could be expected to exhibit high UV protection, durability, and skin-friendliness in the UV-protective formulations.

2-3. Structural analysis of SIPU

In order to further investigate why SIPU-3 combines hardness and elasticity and exhibits superior physical properties compared to conventional film formers, the microstructure of SIPU-3 was analyzed. Figure 3 shows an exterior view of the 10% SIPU-3 gel in dimethicone and a TEM image of the microstructure. As shown in Figure 2, SIPU-3 formed an island-in-sea structure. This structure was similar to that observed in oil gels with the dynamic cross-linking structure with the intermolecular hydrogen bonds between urethane bonds [7].

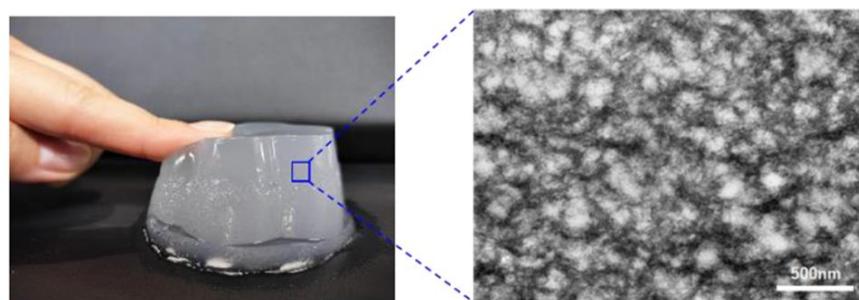


Figure 3. Exterior view of 10% SIPU-3 gel in dimethicone and TEM image

2-4. Functionalities of SIPU-based W/O type foundation

2-4-1. UV protection

Table II shows the formulations and SPF values for Foundation A (conventional) and B (SIPU). The SPF value of Foundation B was twice as high as that of A, even though they contained an equal amount of UV scattering agents.

Table II. Formulations and SPF values of W/O type foundations

	Foundation A /wt%	Foundation B /wt%
Trimethylsiloxysilicate	6	
PEG-9 polydimethylsiloxoxyethyl dimethicone	6	
Dimethicone/vinyl dimethicone Cross Polymer	7.2	
SIPU-3		6
Zinc oxide	20	20
Titanium oxide	6	6
Iron oxide	2	2
Dimeticone	29.8	40.5
Triethylhexanoin	4	5.25
Cetyl Ethylhexanoate	4	5.25
1,3-butylene glycol	3	3
Phenoxy Ethanol	0.3	0.3
Water	11.7	11.7
TOTAL	100	100
SPF ± SE	30.0 ± 11.9	59.0 ± 12.6

2-4-2. Durability

Figure 4(a) shows the change in SPF values of Foundations A (conventional) and B (SIPU) after exposure to the sebum. Foundation A showed a significant decrease in SPF value, while Foundation B maintained its SPF value without significant difference (Student's *t*-test, *p*<0.05).

The color change of Foundation A and B after sebum exposure is shown in Figure 4(b). The $|\Delta L|$ and $|\Delta E|$ values of Foundation B showed no change after exposure to the sebum.

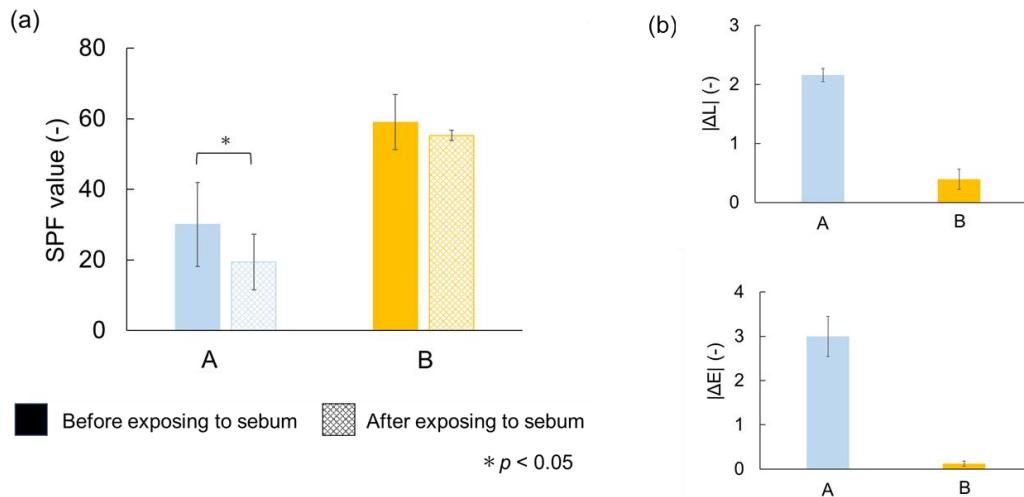


Figure 4. Evaluation of resistance to the sebum

(a) SPF values (Student's *t*-test, n=27), (b) $|\Delta L|$ and $|\Delta E|$ values

2-4-3. Analysis of applied film

Figure 5 shows the transmitted light images of the applied films of Foundation A (conventional) and B (SIPU). Black and red aggregates indicating iron oxide were observed in Foundation A, but not in Foundation B.

Figure 6 shows the EDS maps of the cross section of the applied films of Foundation A and B obtained by the replica method. Both the elements Zn and Ti in Foundation B were distributed more homogeneously in the applied film than in Foundation A.

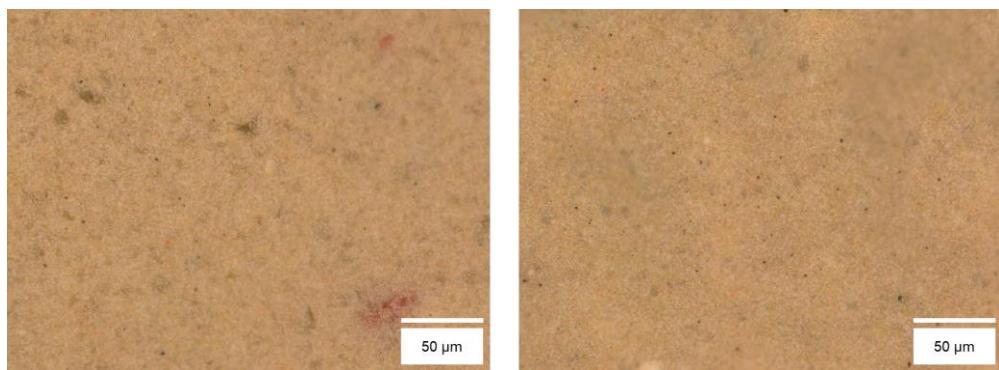


Figure 5. Transmitted light images of applied films

Left: Foundation A, Right: Foundation B

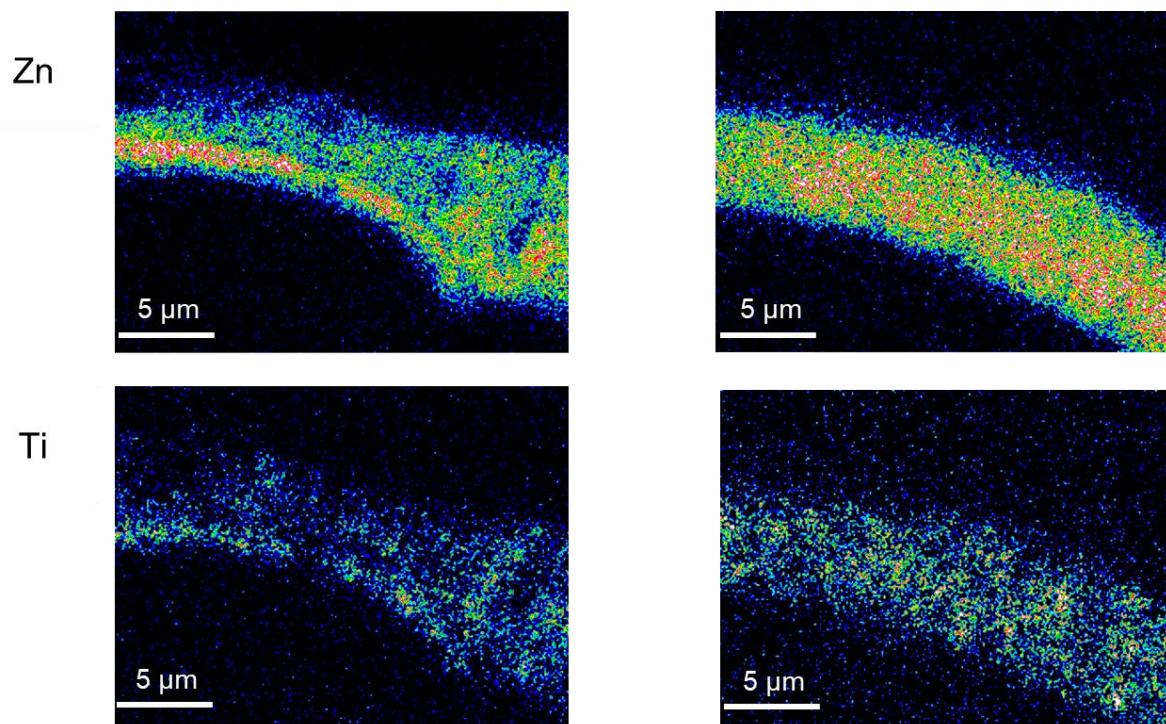


Figure 6. EDS maps of cross sections of the applied films

Left: Foundation A, Right: Foundation B

2-5. Skin-friendliness of SIPU-based W/O type foundation

To verify the skin-friendliness of SIPU-based foundation, rigidity of the applied film and stress on the skin were evaluated. Figure 7 shows the results of the questionnaire. Higher scores indicate no rigidity of the applied film and no stress on the skin. For both questions, Foundation B (SIPU) scored significantly higher than Foundation A (conventional).

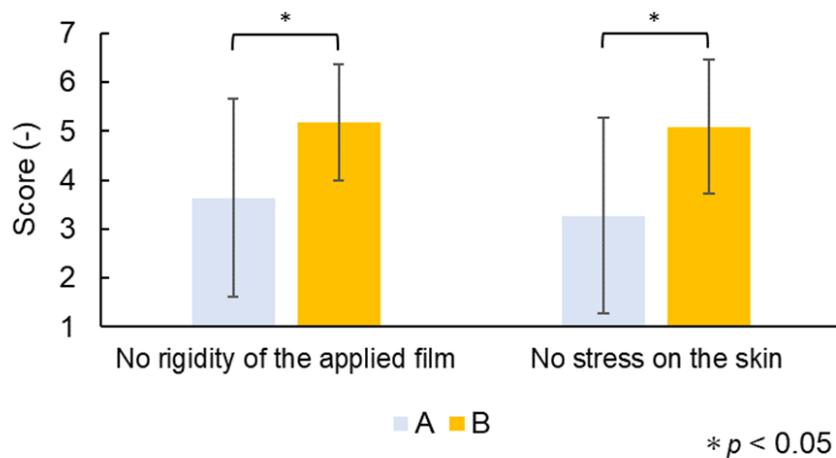


Figure 7. Sensory evaluations of Foundations A and B (student's *t*-test, n-11)

With the results of 2-4 and 2-5, we confirmed that SIPU-based foundation successfully met requirements 1~2 and exhibited high UV protection, durability, and skin-friendliness.

Discussion.

Relationship between the EG ratio and the powder-dispersing ability of SIPU

First, we discuss the ability to disperse UV scattering agents (2-2-1). The UV protection increased with an increase in the EG molar ratios. Since the M_w of SIPU 1~3 was equal, an increase in the EG molar ratio implied an increase in the number of urethane bonds. Thus, the enhanced UV protection suggests that a strong interaction was formed between the urethane bonds of SIPU and the hydroxyl groups on the surface of the UV scattering agents, and the UV scattering agents dispersed in the gel network.

Relationship between the EG ratio and the physical properties of SIPU

Next, we discuss the hardness (2-2-2) and elasticity (2-2-3) of SIPU-3. In the TEM image in Figure 2, the black tone (sea) was considered to indicate polymer networks of SIPU since the ruthenium tetroxide tends to selectively stain amorphous areas. The gray tone (island) was considered to be dimethicone swelling SIPU. These results shows that intermolecular hydrogen bonds reported in the previous literature are formed between the hard segments, forming a pseudo-crosslinked gel network, and consequently the hardness and elasticity of SIPU-3 reported in 2-2-2 and 2-2-3 were demonstrated.

Effect of powder dispersion states in the applied film on functionalities of foundations

Next, we discuss how SIPU-based foundation exhibited UV protection and durability of SPF and color by the structure of the applied film (2-4-3). The formation of the gel network and powder-dispersing mechanism discussed in the previous paragraph were also demonstrated in the model foundation. The transmitted light images of applied films showed that the aggregation of iron oxide was more suppressed in Foundation B (SIPU) than in A (conventional), suggesting that not only the UV scattering agents but also the iron oxide was highly dispersed in the SIPU gel network. The EDS maps showed that in Foundation A, Zn and Ti, which reflect the distribution of UV scattering agents, were localized, forming a non-uniform applied film, as shown in Figure 8(a). As a result, the UV scattering agent was unable to provide sufficient UV protection, and the film former was unable to sufficiently immobilize the UV scattering agents, which we consider to have reduced the durability of the UV protection against the sebum. In Foundation B, on the other hand, Zn and Ti were both delocalized and formed a uniform applied film, as shown in Figure 8(b). Both zinc oxide and titanium oxide have hydroxyl groups on their powder surfaces, which are considered to interact with the urethane bonds of SIPU. As a result, they were dispersed in the gel network of SIPU, and spread uniformly in the applied film. Furthermore, the urethane bonds were considered to immobilize

the applied film to the skin, resulting in a higher UV protection and durability than Foundation A. The immobilization of titanium oxide and iron oxide was also considered to have increased the color durability of Foundation B.

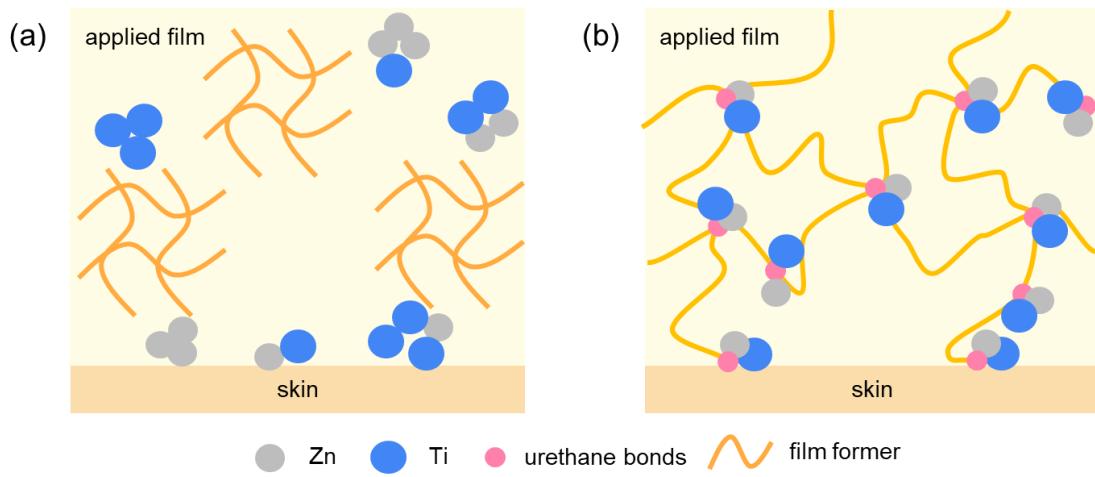


Figure 8. Schematic illustrations of cross sections of the applied films

(a) Foundation A, (b) Foundation B

Factors that improves skin-friendliness by using SIPU

Finally, we discuss why Foundation B (SIPU) was evaluated as more skin-friendly than Foundation A (conventional). As mentioned in 2-2-3, our SIPU was more elastic film former than conventional silicone film former formulated in Foundation A due to dynamic cross-linking of hydrogen bonds. Additionally, Foundation B was surfactant-free due to the powder dispersing-ability of SIPU. As a result, Foundation B was considered to be more skin-friendly than Foundation A, with less rigidity, stickiness, and stress on the skin.

Conclusion.

In this study, we established a novel powder-dispersing system by first defining the applied film requirements for a formulation that exhibits high UV protection, durability, and skin-friendliness, and then designing a silicone/polyurethane hybrid film former that met these requirements. We consider that the dispersion ability of SIPU was enabled by two factors, Firstly, the urethane bonds in SIPU adsorb to the surface of UV scattering agents. Secondly, SIPU immobilizes the powders in the polymer network by dynamic cross-linking through hydrogen bonds between urethane bonds. Our SIPU-based foundation shows excellent UV protection, SPF and color durability, as well as the skin-friendliness, which cannot be achieved with combinations of conventional materials.

Thus, SIPU is more than just a film former, but it works as a novel powder-dispersing system that can be utilized in a wide variety of item categories, such as sunscreens, daytime serums, primers, and foundations, which transcend the boundaries between skincare and makeup. This core technology was proven to boost and maintain UV protection, giving consumers comfort that their skin is protected even in the tough environments. Our technology can elevate the quality of cosmetics so that children with immature skin barriers and people who could not use cosmetics due to skin stress can use them comfortably, and expand the adaptability of cosmetics to all people around the world, contributing to the development of skin-friendly cosmetics so that no one is left behind.

Acknowledgments.

The authors wish to acknowledge the assistance of H. Ota, Safety and Analytical Laboratory, KOSÉ Corporation, for his technical support with electron microscope imaging.

Conflict of Interest Statement.

NONE.

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