Novel Multifunctional SPF Booster by Advanced Disperse Technology: Spherical Silica Encapsulating Dispersed Titanium dioxide for Mineral Sunscreen with Excellent UV protection

Toru Tanaka, Daisuke Osaki, Isao Shimizu

Okayama Research Laboratory, Tayca Corporation
50-1, Osegi, Akaiwa-shi, Okayama, Japan

Abstract (Maximum of 200 words)

Inorganic materials such as Titanium dioxide (TiO_2) and Zinc Oxide (ZnO) are safe, protect the skin against ultraviolet (UV) rays, and have low environmental impacts. Hence, the demand for mineral sunscreens with excellent UV protection is increasing worldwide. However, enhancing the sun protection factor (SPF) by using large amounts of these inorganic materials in the formulation may leave the skin to appear white with an unsatisfactory texture and transparency. To solve these problems, a raw material that can achieve an excellent UV protection effect with small amounts of UV scattering agent is required. Combining our proprietary spherical silica (SiO_2) synthesis technology with TiO_2. This spherical SiO_2 enables to reduce the amount of UV scattering agents in mineral sunscreen and simultaneously has high SPF, pleasant texture, and satisfactory transparency. Furthermore, because it provides the same smooth texture as spherical SiO_2, it can also be used as an alternative raw material for microplastic beads. Our efforts can reduce adverse effects on the human body and lessen environmental impact.

Keywords: Mineral Sunscreen; SPF Booster; Texture improvers; SiO_2; Microplastic beads

Introduction.

Approximately 150 million km away, the Sun releases energy from the nuclear fusion reaction of hydrogen, which becomes light and illuminates the surrounding stars and Earth. Ultraviolet (UV) rays, which are a part of sunlight, are divided into UVC (100-280 nm), UVB (280-320 nm), and UVA (320-400 nm) according to the wavelength. UVC has the greatest impact on the human body; however, because it is blocked by the ozone layer, only UVB and UVA rays reach the Earth’s surface. Although the impact of UVB and UVA on the human body is smaller than that of UVC, they cause photoaging and skin cancer [1, 2].

One of the ways to minimize the adverse effects of UVB and UVA on the human body is to use sunscreen [3]. The main active ingredients of sunscreen are organic UV absorbers and inorganic UV scattering agents. In recent years, the need for sunscreens has been increasing year by year, and the use of sunscreens is becoming more common around the world. As a result, not only is there a demand for improved Sun Protection Factor (SPF), which indicates the degree of UV protection effect, but also for formulations with a pleasant texture and satisfactory transparency. UV absorbers provide high UV protection in a small amount; therefore, they are often used in sunscreens that focus on texture and transparency [4].

However, in February 2019, the United States Food and Drug Administration (FDA) issued a draft of the new rule on UV protection agents,[5] which included concerns about the safety of UV absorbers; however, the UV scattering agents TiO_2 and ZnO were shown to have high UV protection abilities and are safe. In addition, there are concerns that some UV absorbers, such as octinoxate and benzophenone-3, may have a negative impact on coral reefs and other marine environments because of their runoff into the ocean [6]. Hawaii and other states in the USA have banned the sale and distribution of sunscreens containing these UV absorbers. Against this background, there is a growing demand for mineral sunscreens that use only UV scattering agents. However, when making mineral sunscreens with high SPF, large amounts of UV scattering agents are used, which results in poor transparency and texture [7]. Therefore, there is a demand for SPF boost materials (SPF boosters) that can provide high SPF with a small amount of UV scattering agents. SPF boosters do not have UV protection effects themselves but act as auxiliary agents to enhance the protection effects of UV protection agents. Specifically, extracts from natural resources [8] and synthetic polymers [9] are being developed and considered; however, in recent years, there has been a demand for the development of multifunctional and sustainable raw materials that not only improve SPF but also improve the texture of the product [10]. Notably, mineral sunscreens have a unique powder-like squeaky texture; therefore, there is a demand for improving the product's texture when used. To improve the texture of the product when used, microplastic (MP) beads with a particle size of approximately 5 μm are generally used as a texture improver. However, in recent years, it has been shown that these MP beads can invade ecosystems and become carriers of harmful chemicals [11,12]. Therefore, proposals to regulate MP beads are being considered in various countries around the world, and the use of MP beads is scheduled to be restricted in Europe in 2029 [13]. Among these, inorganic spherical SiO_2 is being considered as an alternative raw material for MP beads from the perspective of preventing marine pollution [14]. This material is highly pure and chemically stable, making it one of the sustainable raw materials available in our daily lives. We thought that by imparting an SPF boost effect to this material, we could create a mineral sunscreen that combines excellent texture with a high SPF.

To impart the SPF boost effect to spherical SiO_2, it is necessary to give it the ability to reflect UV radiation. Generally, as shown below, the greater the difference in refractive index at the interface between materials, the more easily UV radiation is reflected.

$$F=((n^1-n^2)/(n_1+n_2))^2$$

F: Reflectance of the boundary surface,

n_1: Refractive index of material 1, n_2: Refractive index of material 2

Among the inorganic materials used in cosmetics, TiO_2 has the largest refractive index. Therefore, we selected TiO_2 as the composite material with the largest refractive index difference.

In this study, we attempted to impart an SPF boost effect to spherical SiO_2, by encapsulating TiO_2 in a highly dispersed state within spherical SiO_2 particles which has a texture-improving effect. By comparing the UV protection effects of mineral sunscreen formulations, the factors that contribute to the boost effect will be discussed. Furthermore, we will report a mineral sunscreen that uses this material to simultaneously have a high SPF (above SPF50), pleasant texture, and satisfactory transparency.

Materials and Methods.

2.1 Preparation

By combining our unique spherical SiO_2 synthesis technology with advanced TiO_2 dispersion technology, we synthesized spherical SiO_2 (spherical SiO_2 encapsulating dispersed TiO_2: SCAP-dT) that encapsulates dispersed TiO_2 within the particles. Figure 1 shows a scanning electron microscope (SEM) image of SCAP-dT, which was a spherical particle with an extremely uniform particle size.

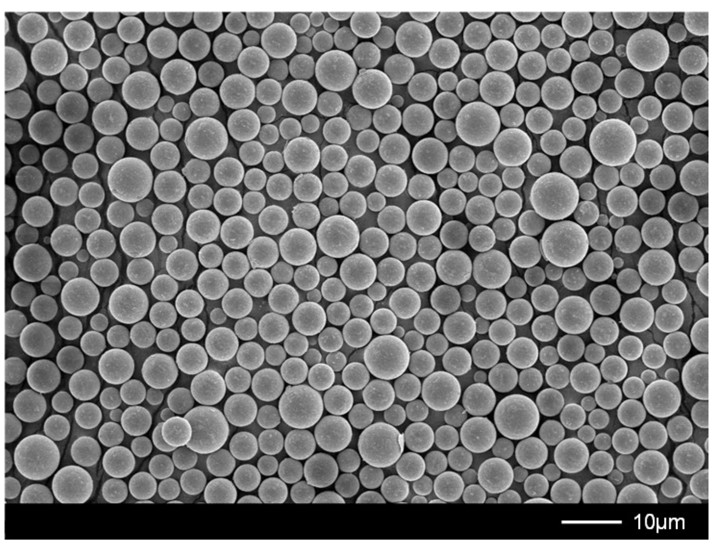

Fig. 1 SEM image of SCAP-dT

For comparison, we also prepared spherical SiO_2 coating with TiO_2 (SSCT), spherical SiO_2 encapsulating aggregated TiO_2 (SCAP-aggT) by a conventional dispersion method, and spherical SiO_2 (SS) without TiO_2 encapsulation.

2.2 Measurement of the dynamic friction coefficient of powder

To quantitatively evaluate the smoothness of each of the prepared spherical SiO_2 samples alone, the dynamic friction coefficient was measured using a friction tester (KSE-SE, Kato Tech Co., Ltd.). Measurements were performed by applying 0.2 mg/cm^2 of each spherical SiO_2 to artificial leather under a load of 50 g and a constant speed of 1.0 mm/s.

2.3 SEM observation

SiO_2 samples were observed using a scanning electron microscope (S-4800, Hitachi High-Technologies Corporation). For the particle cross-section observation, the sample was embedded in thermosetting resin and stored in a thermostatic chamber at 80°C for 12 h. After hardening, the resin was cut using a microtome, and the particle cross-section exposed on the cut surface of the resin was observed.

2.4 Measurement of particle size distribution of TiO_2 in spherical SiO_2 precursor

To evaluate the dispersibility of TiO_2 in the spherical SiO_2 particles, the particle size distribution of TiO_2 in the SiO_2 particle precursor was measured by DLS (FPAR-1000, Otsuka Electronics Co., Ltd.).

2.5 Preparation of W/O emulsion

To formulate a mineral sunscreen with excellent UV protection, ZnO was selected as the UV scattering agent, which has the potential to independently protect against a wide range of UV rays, ranging from UVA to UVB. In addition, since a formulation that has issues with texture and transparency in the sunscreen market is W/O, which contains a high amount of UV scattering agents, therefore, we attempted to consider a W/O formulation. 25% triethoxycaprylylsilane-treated ZnO (primary particle size: 25 nm) was mixed with 5% of each spherical SiO_2, oil, and emulsifier and dispersed at 3000 rpm for 10 min in a dispersing mixer (LABLUTION, PRIMIX Corporation) to obtain an oil phase. Then, an aqueous phase consisting of water and butylene glycol was added and emulsified for 5 min in a homo-mixer to produce a W/O emulsion. In addition, for comparison, a W/O emulsion without spherical SiO_2 but with an increased amount of oil and a W/O emulsion without ZnO but with only SCAP-dT were also formulated.

2.6 SPF Boost effect evaluation

The *in vitro* UV protection effect was evaluated using an SPF analyzer (UV-2000S, Labsphere). The obtained W/O emulsion was applied at 1.3 mg/cm^2 to a PMMA plate (HELIOPLATE HD6, HelioScreen) based on ISO 24443 and dried in the dark at 25°C for 30 min. The absorbance curve was then measured at wavelengths of 290-450 nm, and the SPF and UVAPF values were calculated. In addition, a formulation without spherical SiO_2 was used as the reference formulation, and the ratio of the SPF value of the test formulation containing spherical SiO_2 to that of the reference formulation was calculated as the SPF boost index.

SPF boost index = (SPF value of test formulation) / (SPF value of the reference formulation)

2.7 Observation of the application films

The application films of each W/O emulsion applied to the PMMA plate were observed and compared using a shape analysis laser microscope (VK-X1100, KEYENCE Corporation). The surface roughness Ra of each application film was calculated using software (Multi-File Analysis Application, KEYENCE Corporation).

2.8 Evaluation of UV protection ability

SPF and UVAPF values were tested *in vivo* based on ISO 24444 and ISO 24442.

Results.

3.1 Dynamic friction coefficient of powder

The lower the dynamic friction coefficient, the smoother the surface. Comparing the dynamic friction coefficients of each spherical SiO_2, SSCT had the highest dynamic friction coefficient at 0.19. The dynamic friction coefficients of SCAP-dT and SCAP-aggT were 0.17, which was as low as that of SS without TiO_2 composite.

3.2 SEM observation of the particle shape

SEM images of each spherical SiO_2 are shown in Figure 2. The TiO_2-surface-treated SSCT had uneven TiO_2 surfaces, but SCAP-aggT and SCAP-dT, which contain TiO_2 inside, were spherical particles equivalent to untreated SS, with a particle diameter of approximately 5 µm.

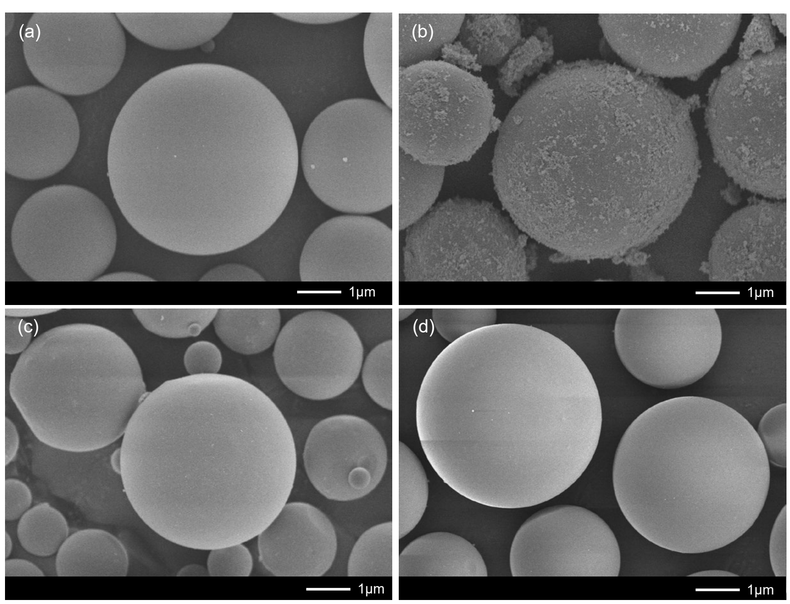

Fig. 2 SEM images of (a)SS, (b)SSCT, (c)SCAP-aggT, and (d)SCAP-dT

3.3 Evaluation of TiO_2 in spherical SiO_2 particles

An SEM image of the cross-section of a SCAP-dT particle is shown in Figure 3(a), and the particle size distribution of TiO_2 in the precursors of SCAP-dT and SCAP-aggT is shown in Figure 3(b). In the observation of the particle cross-section, irregularities and gaps thought to be derived from TiO_2 were observed on the cross-section of the SiO_2 particles containing TiO_2, confirming the presence of TiO_2 in the SCAP-dT particles. In addition, the particle size distribution of TiO_2 in the SiO_2 particle precursor was narrower in SCAP-dT than in SCAP-aggT, and the dispersed particle size was smaller, indicating that TiO_2 was dispersed.

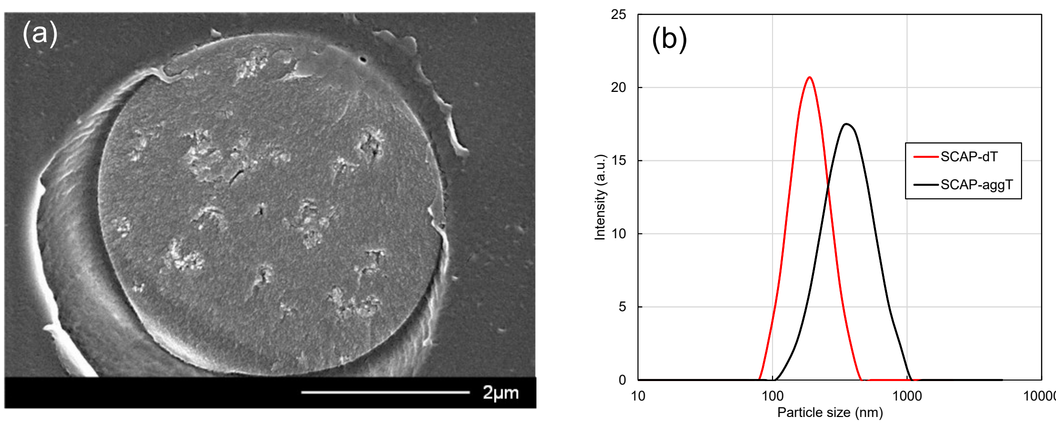

Fig. 3 (a)SEM image of particle cross section of SCAP-dT and

(b) the particle size distribution of TiO_2 in spherical SiO_2 precursors

3.4 Comparison of UV protection effects of each W/O emulsion

The results of the evaluation and comparison of the UV protection effect of each W/O emulsion containing spherical SiO_2 are shown in Figure 4. Compared with a W/O emulsion without spherical SiO_2 (None), the SPF values of the W/O emulsions containing SS and SCAP-aggT were approximately 10% higher. Furthermore, the SPF values of the W/O emulsions using SSCT and SCAP-dT were approximately 40% higher than None. Among these, the SPF value of the W/O emulsion containing SCAP-dT was approximately 60% higher than None, indicating the greatest UV protection effect.

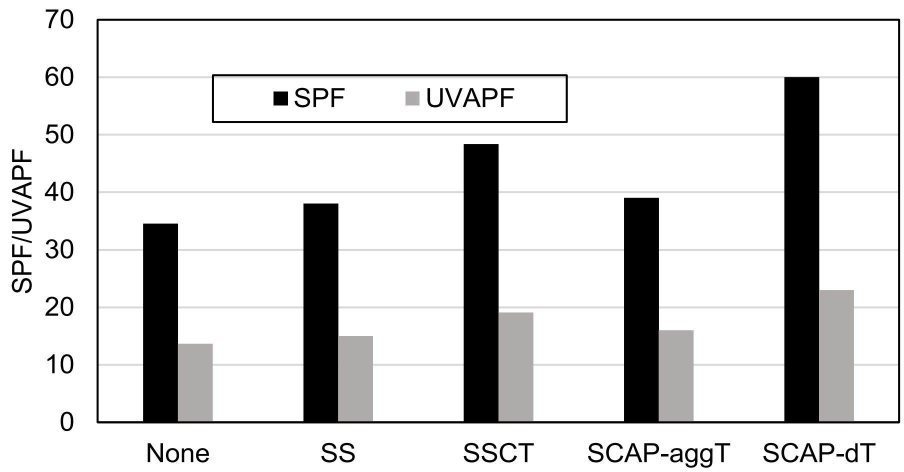

Fig. 4 *In vitro* SPF/UVAPF value of each W/O emulsion

3.5 Observation of W/O emulsion films on PMMA plate

Figure 5 shows the application film of None and W/O emulsion films containing SS and SCAP-dT. The top images are photographs of the appearance of the application films, and the bottom images show the degree of unevenness in the height direction of the application films by color. The higher the surface roughness Ra value shown in the photographs, the rougher the W/O emulsion film. The application films of SS and SCAP-dT, which contain spherical SiO_2, have Ra values of 6.6-6.9 µm, which is lower than the Ra value of 8.7 µm for None, indicating that the application films with spherical SiO_2 are smoother.

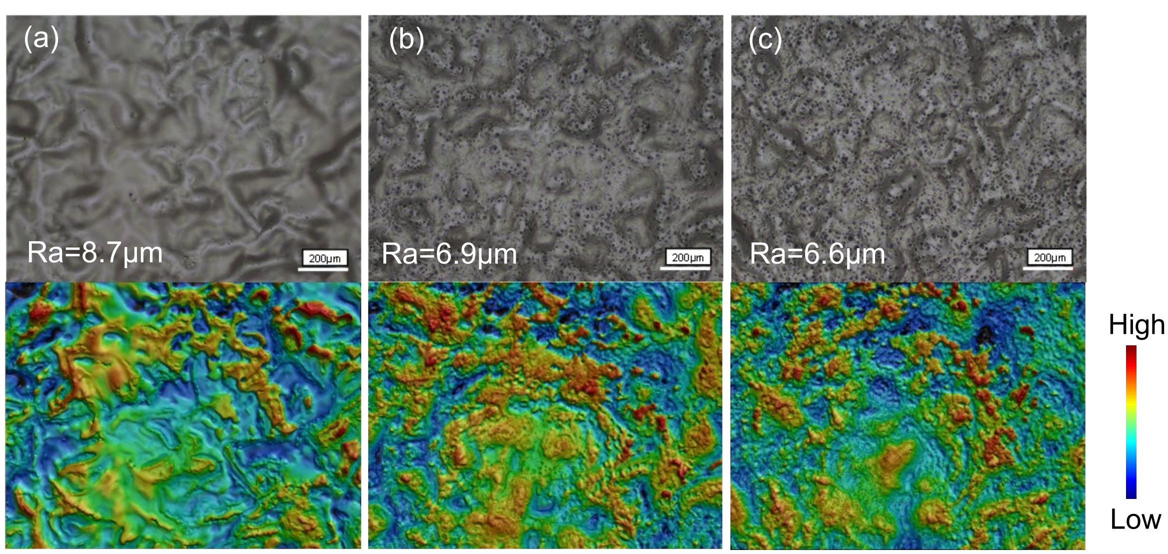

Fig. 5 Laser microscope images of W/O emulsion films : (a)None, (b)SS and (c)SCAP-dT

3.6 Absorbance curve of W/O emulsion

The absorbance curves of a formulation containing ZnO and SCAP-dT in combination, and a W/O emulsion containing only ZnO, and W/O emulsion containing only SCAP-dT alone are shown in Figure 6. Figure 6(c) shows that SCAP-dT alone has no UV protection effect. Compared with Figure 6(b), the absorbance in Figure 6(a) is improved from the UVB region to the UVA region at a wavelength of approximately 380 nm, indicating that the incorporation of SCAP-dT enhances the entire UV protection range of ZnO. In addition, in the visible light region around 400 nm, the absorbance of SCAP-dT is approximately the same as that of SS, indicating high transparency.

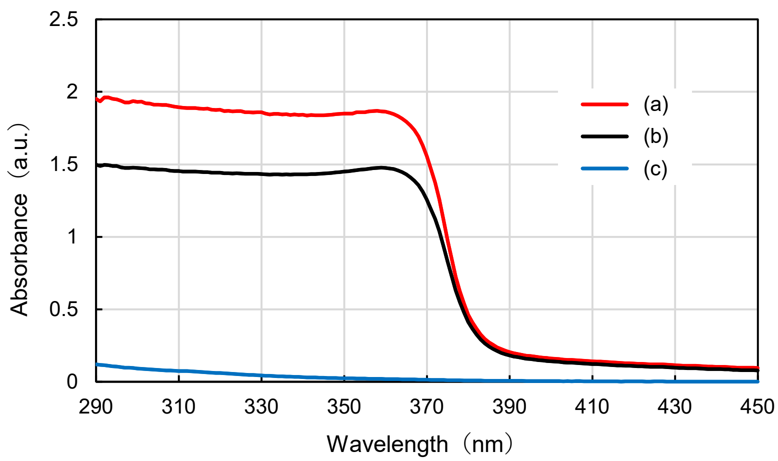

Fig. 6 Absorbance curves of each W/O emulsion (a) 5% SCAP-dT + 25% ZnO, (b) 25% ZnO (c) 5% SCAP-dT

3.7 Varying the SPF boost due to differences in the amount of ZnO or SCAP-dT

Figure 7(a) shows the SPF boost index of the W/O emulsion when the amount of SCAP-dT is fixed at 5% and the amount of ZnO is varied to 15%, 20%, 25%, and 30%, and Figure 7(b) shows the SPF boost index of the W/O emulsion when the amount of ZnO is fixed at 25% and the amount of SCAP-dT is varied to 1%, 2%, 3%, 4%, 5%, 7%, and 10%. The SPF boost index was highest when the amount of ZnO was around 20-25%, then decreased at

30%. It also increased with the amount of SCAP-dT, significantly increasing from 4% or more, and saturating at around 7%.

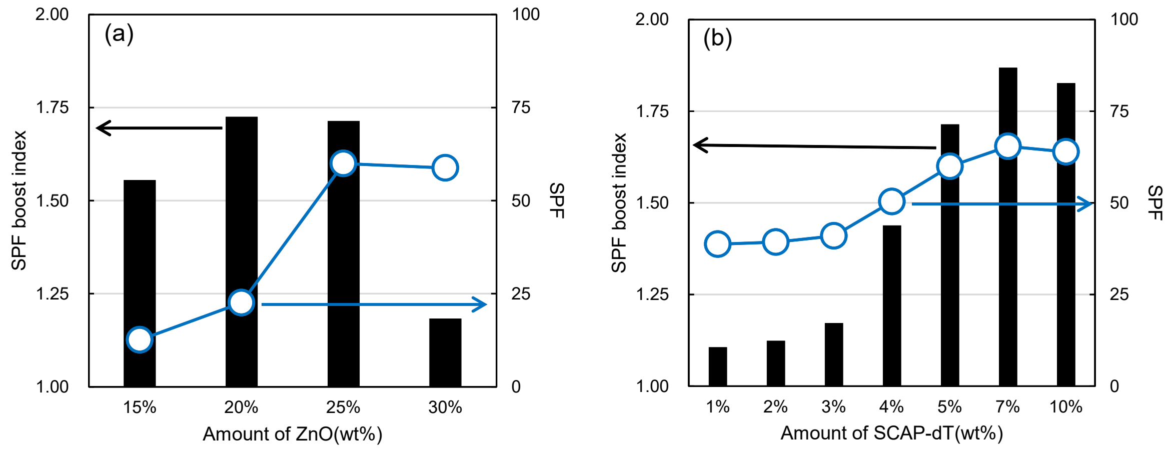

Fig. 7 Relationship between SPF boost index and ZnO or SCAP-dT content

Discussion.

4.1 Relationship between the particle surface and dynamic friction coefficient

Because of the ball-bearing effect, spherical particles provide a smooth texture when applied to the skin. In other words, rolling the spherical particles on a smooth surface can reduce the resistance of fingers and the contact area between particles, thus minimizing frictional resistance. From the measurement results in Section 3.1, the friction resistance of the SSCT is the highest because of its surface roughness. As can be seen from the electron microscope image in Fig. 2(b), there are irregularities on the particle surface caused by TiO_2. these irregularities on the particle surface inhibit the rolling properties of the spherical particles, preventing the ball-bearing effect from being fully exerted, and resulting in increased friction resistance.

4.2 Order of the SPF boost effect

As shown in Fig. 4, the order of the UV protection effect was None, SS, SCAP-aggT, SSCT, and SCAP-dT. This could be due to (1) the homogenization of the application film by the addition of spherical SiO_2 and (2) the difference in the dispersion state of TiO_2 in the SiO_2 particles.

4.2 (1) Homogenization of the application film by the addition of spherical SiO_2

Sunscreen is applied to uneven skin surfaces using fingers or palms; however, when considering the actual application method, it is difficult to form a uniform application film. Figure 8 shows the schematic illustration of the state in which a W/O emulsion is applied to an uneven PMMA substrate. Figure 8(a) shows the ideal state for a substrate with regular unevenness. The film thickness is uniform, resulting in higher UV protection. However, the substrate has irregular unevenness, which causes non-uniformity in the film thickness, as shown in Figure 8(b), resulting in lower UV protection. On the other hand, by adding spherical SiO_2, the application film thickness is uniformized by accumulation in the concave portions of the substrate, as shown in Figure 8(c). Therefore, it is inferred that the UV protection effect of SS with the addition of spherical SiO_2 is improved by approximately 10% compared with that of None, as shown in Figure 4.

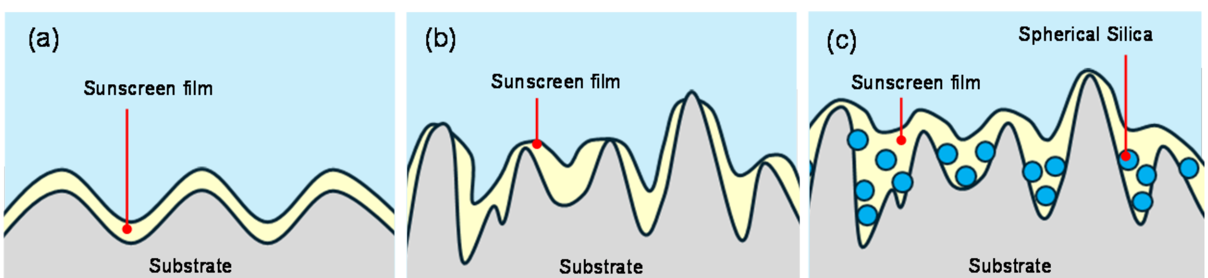

Fig. 8 Schematic illustration of the sunscreen distribution on surface substrates;
(a) Ideal state, (b) None, (c) SS

4.2 (2) Dispersion state of TiO_2 in spherical SiO_2 particles

In mineral sunscreens, the dispersibility of the UV protection agent has a large effect on UV protection[15]. We believe that the dispersion state also contributed greatly to the SPF boost effect of the SPF booster we synthesized. Figure 9 shows the schematic illustration of the differences in the dispersion state of TiO_2 in the particles and its effect. If the TiO_2 is aggregated, it cannot block UV radiation efficiently, so the SPF boost effect will be decreased. On the other hand, if the TiO_2 is dispersed within the spherical SiO_2 particle, the number of particles is large, so it is possible to scatter UV radiation efficiently, resulting in an excellent SPF boost effect.

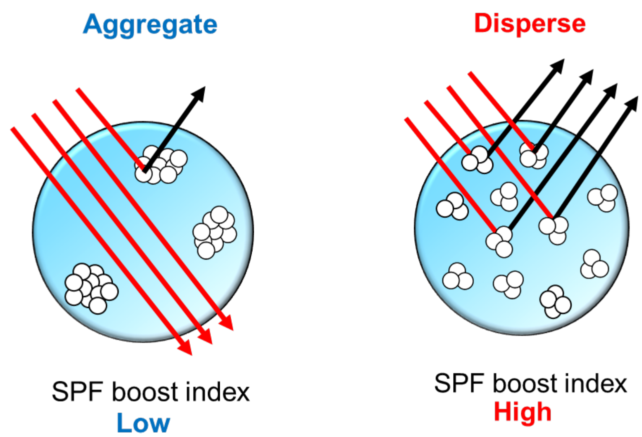

Fig. 9 Schematic illustration of the relationship between the dispersion state of TiO_2 in a spherical SiO_2 particle and the UV scattering effects

It is difficult to confirm the dispersion state of TiO_2 in spherical SiO_2 particles in a application film. Therefore, we observed the cross-section of the particle and measured the particle size distribution of the precursor. The particle cross-section photograph in Figure 3(a) shows that TiO_2 is present in the SCAP-dT particle, and the particle size distribution of TiO_2 in the SiO_2 precursor in Figure. 3(b) is narrower in SCAP-dT than in SCAP-aggT, and the dispersed particle size is smaller. This result indirectly shows that the dispersibility of TiO_2 in SCAP-dT particles is extremely high compared with SCAP-aggT, which indicates that the SPF boost effect obtained in Figure. 4 corresponds to the dispersibility of TiO_2 in the particles. Therefore, SCAP-dT, which contains TiO_2 in a dispersed state inside spherical SiO_2 particles, has the best SPF boost effect.

The above results show that SCAP-dT makes the application film uniform by blending it with a W/O emulsion and that differences in the dispersion state of TiO_2 have a significant effect on the SPF boost effect. In particular, since the SPF of SCAP-dT is about 60% higher than that of SS and SCAP-aggT, it is clear that the most effective way to increase the SPF boost effect is to encapsulate TiO_2 in a highly dispersed state.

4.3 The amount of mineral sunscreen to achieve a high SPF

From the studies so far, SCAP-dT scatters UV radiation and acts as a supplementary boost to the protective effect of UV scattering agents. The scheme by which the SPF boost effect works is shown in Fig. 10. When UV radiation is irradiated, not only the UV scattering agents but also SCAP-dT scatter the UV radiation as a supplement, and it is thought that the scattered UV radiation is collected by nearby UV scattering agents to be efficiently cut off.

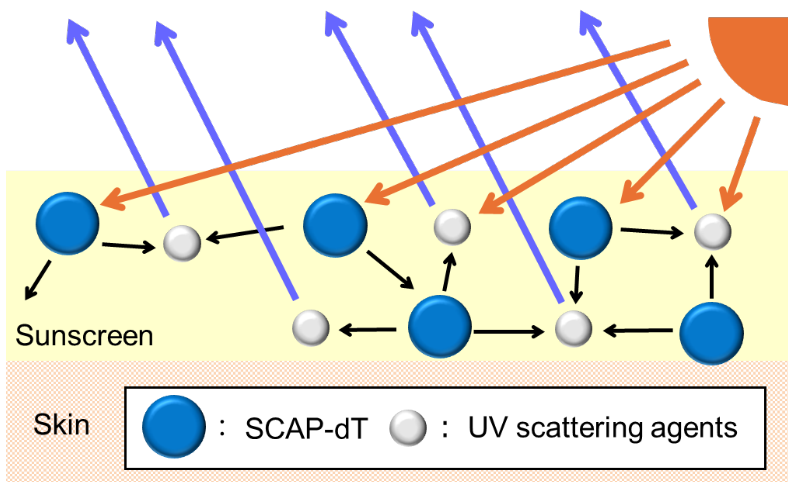

Fig. 10 Schematic illustration of the mechanism by which SCAP-dT improves the SPF of UV scattering agents in application film.

As a result of examining the conditions of the formulation that brings out a high UV protection effect, the SPF boost index decreases when the amount of ZnO is 30% in Figure 7(a) and tends to saturate when the amount of SCAP-dT is 7% or more in Figure 7(b). This is due to the mechanism in which ultraviolet light is scattered in SCAP-dT and blocked by ZnO present in the vicinity of the particles, as shown in Figure 10. When the ZnO content is 30%, the amount of ZnO present away from the vicinity of SCAP-dT increases. Hence, the boosting effect of SCAP-dT is not fully exerted resulting in a decrease in the SPF boost index. Also, when the amount of ZnO is 25% and the amount of SCAP-dT is 7%, SCAP-dT covers the entire application film, and when it exceeds that, SCAP-dT is layered, so the SPF boost index is thought to be saturated. From the above, to effectively bring out the SPF boost function in mineral sunscreen formulations, it is necessary to consider the balance between the amount of UV scattering agent and SCAP-dT.

Therefore, after careful consideration of the above balance, *in vivo* test was conducted on a W/O emulsion mineral sunscreen containing 25% ZnO and 5% SCAP-dT, the amounts needed to achieve the SPF value of over SPF 50. As a result, SPF of 51 and UVAPF of 18 was achieved *in vivo* test. Normally, to achieve SPF50+, approximately 33% ZnO alone is required. However, by using SCAP-dT, the amount of ZnO can be reduced to approximately 3/4. In addition, this material maintains the same high transparency as spherical SiO_2 while improving the blocking effect over a wide range of wavelengths from UVB to UVA as shown in Figure 6. This proves that a mineral sunscreen with a high SPF with satisfactory transparency can be achieved with only ZnO.

Conclusion.

To realize a mineral sunscreen with high UV protection, it is necessary to incorporate a high amount of UV scattering agents, which leads to problems such as impaired texture and transparency. To solve these problems, a raw material that can produce high UV protection effects with some UV protection agents is needed. After extensive research from the perspective of developing environmentally friendly and sustainable raw materials, we succeeded in developing a novel multifunctional SPF booster SCAP-dT that provides pleasant texture and high SPF boost effects by encapsulating TiO_2 in a highly dispersed state in spherical SiO_2 particles using our proprietary technology.

In this study, we concluded that SCAP-dT can smooth out the unevenness of the application film by blending it with a W/O emulsion and provides the highest SPF boost effect when combined with a UV scattering agent. Notably, the most effective way to increase the SPF boost effect is to encapsulate TiO_2 in a highly dispersed state within spherical SiO_2 particles. Not only this material can reduce the amount of UV scattering agents by approximately 3/4, but also increases the UV protection effect in a wide wavelength range from UVB to UVA. Making it possible to simultaneously have high SPF, pleasant texture, and satisfactory transparency, which was previously impossible with mineral sunscreens. Furthermore, because it provides a smooth texture like that of spherical SiO_2, it can also be used as an alternative raw material for microplastic beads.

Like a star shining in the vast universe, SCAP-dT shines together with the UV scattering agents in the application film, and if it becomes easier for people all over the world to use them in conventional mineral sunscreens, it will be one of the materials that will make the future of the Earth even brighter.

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Conflict of Interest Statement.

NONE.

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