The ultimate solution for an ideal non-chemical sunscreen: "A novel spherical zinc oxide renders unsurpassed transparency and texture"

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Abstract

The importance of protection from ultraviolet rays (UV) has been spreading among consumers, and the sunscreen market is growing worldwide. Many organic materials are used as UV filters in the sunscreen products currently on the market, but there are concerns about the safety of such materials in the human body and their adverse effects on the marine environment. Hence, the demand for inorganic materials such as zinc oxide and titanium dioxide has been increasing in recent years. However, non-chemical sunscreens that use only inorganic materials as UV filters have issues with unsatisfactory transparency and texture, and one cannot say that they are fully satisfying consumers. To solve these problems and to achieve an ideal non-chemical sunscreen, we developed spherical zinc oxide (S-ZnO) with super-dispersibility.

Common inorganic materials, including zinc oxide, are prone to particle aggregation. Excellent transparency and UV-protection effects cannot be obtained when particles aggregate. The newly developed S-ZnO suppresses aggregation of particles to the utmost limit and has extremely high dispersibility in oil. Therefore, S-ZnO can exhibit the transparency and UV-protection effect inherent to zinc oxide at a high level. Water in Oil emulsions containing S-ZnO exhibit higher transparency and UV-protection effects than those containing conventional zinc oxide, even under conditions of low dispersion strength and short dispersion times. S-ZnO can solve two major problems that non-chemical sunscreens have had to date, namely, unsatisfactory transparency and texture, and can enable the development of higher-quality cosmetics.

Keywords: Zinc oxide; Sunscreen; inorganic; UV; SDGs

1. Introduction

Ultraviolet rays (hereinafter referred to as UV) are the main cause of photoaging of skin [1], and the importance of UV protection is now recognised by consumers worldwide. The use of a sunscreen is effective for protecting the skin from UV, and UV absorbers, which are organic compounds, and UV scatterers, which are inorganic metal oxides, are used as UV filters.

Many sunscreen products use organic materials as UV filters. However, in February 2019, the FDA issued a new rule for UV protectants [2], indicating that some organic materials are unsafe, and that inorganic materials, such as zinc oxide and titanium dioxide, exhibit superior UV-protection efficacy and safety. In addition, there are concerns that some organic materials may have adverse effects on coral reefs and other marine environments [3], and the sale and distribution of sunscreens containing such materials have been banned in Hawaii and other states in USA. Given this background, the development of non-chemical sunscreens that use only inorganic materials as UV filters is expected to accelerate.

However, when a sunscreen is designed using only inorganic materials, there is a major issue of whiteness upon application and a creaky texture unique to inorganic powders [4], which reduce the cosmetic value. This challenge is the main reason why organic materials, rather than inorganic materials, have been used extensively in sunscreen products. Therefore, we have started to develop a new zinc oxide to solve these problems in preparation for the coming era of non-chemical sunscreens using mainly inorganic materials.

Zinc oxide is called a "UV scattering agent," but it actually provides UV protection not only by scattering but also by absorbing UV rays; its crystalline structure does not change before and after absorption, making it very safe [5]. In addition, zinc oxide specifically absorbs UVA due to its band gap energy of 3.3 eV and is a highly transparent oxide for visible light [6]. When designing a non-chemical sunscreen, zinc oxide, which exhibits excellent UVA protection and high transparency, is often used as the main ingredient, and the deficiency in the target SPF value is often made up using titanium dioxide, which exhibits excellent UVB protection.

The "primary particle size" and "dispersibility" of inorganic materials have a great influence on the transparency and texture of non-chemical sunscreens. The "primary particle size" of inorganic materials affects the scattering and absorption efficiency of visible light and UV, and significantly affects the transparency and UV-protection effect of the sunscreens in which they are blended. Next, "dispersibility" is described. The smaller the primary particle size of an inorganic material, the higher the particle surface energy and the likelier it is to aggregate. Generally, inorganic materials used for UV-protection purposes have primary particle sizes in the nanometre order, which means that the gravitational force between particles is larger than that applied to the particles, and their aggregation is extremely high [7, 8]. When such particles aggregate, the UV scattering and absorption efficiency significantly reduces and the transparency decreases, making it impossible to prepare excellent sunscreen formulations. In other words, optimising the primary particle size of zinc oxide, which is the main component in non-chemical sunscreens, and controlling particle aggregation and high dispersion in the formulation will enhance the UV-protection effect. In addition, the amount of inorganic material required to achieve the target SPF specification can be reduced, and the issues of unsatisfactory transparency and texture that non-chemical sunscreens have can be solved.

To suppress the aggregation of particles, it is important to reduce their surface energy and the contact area with other particles, and we hypothesised that the shape that satisfies this is a sphere. Therefore, we succeeded in spheroidizing zinc oxide and found that spheroidization suppressed particle aggregation and improved dispersibility, as expected. By blending the spherical zinc oxide (hereinafter referred to as S-ZnO), we succeeded in developing an ideal non-chemical sunscreen formulation with high transparency and excellent texture.

In this report, we present the results of our investigation into the development of S-ZnO, which exhibits ultra-easy dispersibility and enables both high transparency and a high UV-protection effect.

2. Materials and Methods

2.1. Preparation of surface treatment samples

The primary particle size of S-ZnO was adjusted to 40 nm to protect from a wide range of wavelengths, from UVB to UVA, and to allow excellent transmission of visible light. Triethoxycaprylylsilane was selected as the lipophilic treatment agent to achieve high dispersion in any oil used in cosmetics.

For surface treatment, zinc oxide and triethoxycaprylylsilane were homogeneously mixed with isopropyl alcohol, wet-milled using a sand grinder mill, and then vacuum-distilled to remove isopropyl alcohol. The treated product was placed in a dryer and dried at 105 °C for 12 h, and then milled in a jet mill to prepare S-ZnO.

Conventional zinc oxide (C-ZnO; irregular shape) with a primary particle size of 35 nm was selected as a benchmark product and prepared using the same treatment agent and process. The electron micrographs of S-ZnO and C-ZnO are shown in Figure-1. The aspect ratio of S-ZnO is 1.18 and that of C-ZnO is 1.32. S-ZnO was more rounded than C-ZnO and was confirmed to be spherical in shape.

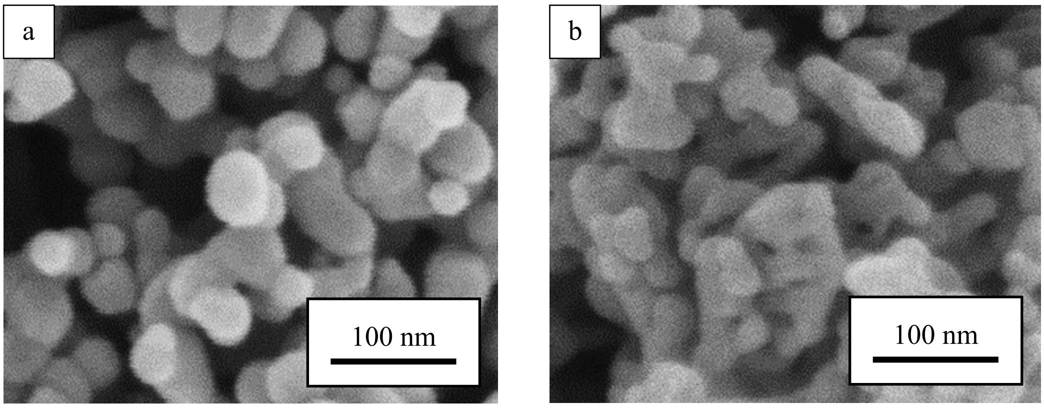


Fig-1 SEM images of (a) S-ZnO, (b) C-ZnO

2.2 Dispersibility evaluation of zinc oxide base material

Dispersibility of zinc oxide without surface treatment was evaluated. Each zinc oxide powder was dispersed in a solvent containing nitrocellulose at 20 wt.% concentration using glass beads, and the resulting dispersion was homogeneously applied to polypropylene films and dried at room temperature for 12 h. The absorbance and transmittance of the dried coating films were measured using an SPF analyser (UV2000S, Labsphere).

2.3. Preparation of water in oil (W/O) emulsion

S-ZnO or C-ZnO was mixed with oil and emulsifier and dispersed in a Disper mixer at 3000 rpm for 10 min to obtain an oil-phase dispersion. Water and butylene glycol were then added and emulsified with a Disper mixer at 3000 rpm for 5 min to make a W/O emulsion. Cyclopentasiloxane was selected as the oil and PEG-9 polydimethylsiloxyethyl dimethicone as the emulsifier.

2.4. Evaluation of W/O emulsion

The prepared W/O emulsions were homogeneously applied to polypropylene films and absorbance was measured using an SPF analyser.

2.5 Particle size distribution measurement

Particle size distribution was measured to confirm the aggregated particle size of each zinc oxide in the oil phase. The measurement was carried out using a concentrated particle size analyser (FPAR-1000, Otsuka Electronics Co., Ltd.) at a powder concentration of 0.5 wt.% in cyclopentasiloxane medium.

2.6. Film characterisation

The prepared W/O emulsions were uniformly applied on polyethylene films and the surfaces of the resulting coated films were observed using a scanning electron microscope (S-4800, Hitachi High-Technologies Corporation).

2.7. Haze assessment

W/O emulsions were coated on polypropylene films, and the haze of the resulting coated films was measured using a turbidimeter (NDH-2000, Nippon Denshoku) irradiated with light at 550–560 nm wavelength.

2.8. UV protection

In vitro UV protection was evaluated using an SPF analyser. The obtained W/O emulsions were applied to PMMA plates (HELIOPLATE HD6, HelioScreen) at 1.3 mg/cm^2 according to ISO 24443 and allowed to dry in the dark at 25 °C for 30 min. The absorbance curve for wavelengths between 290 and 450 nm was then measured to obtain SPF, UVAPF, and critical wavelength (CW). Albuquerque data were used for solar irradiance.

3. Results

3.1 Effect of particle shape on optical properties

The specific surface area of zinc oxide was unified to about 20 m^2/g and the particle shapes were adjusted to spherical, irregular, and plate-like. These zinc oxide powders were dispersed in a solvent containing nitrocellulose at a concentration of 20 wt.% using glass beads, and the resulting dispersions were uniformly applied to polypropylene films. The absorbance and transmittance of the obtained coated films were measured using an SPF analyser, and the results are shown in Figure-2.

S-ZnO exhibited higher absorbance in the UVB-UVA region and higher transmittance in the visible light region compared to the irregularly shaped and plate-shaped zinc oxides. These results indicate that the dispersibility of zinc oxide depends on its shape. As expected, the dispersibility improved upon controlling the shape of zinc oxide as spherical compared to other shapes, which is considered to be due to the decrease in surface energy and contact area with other particles.

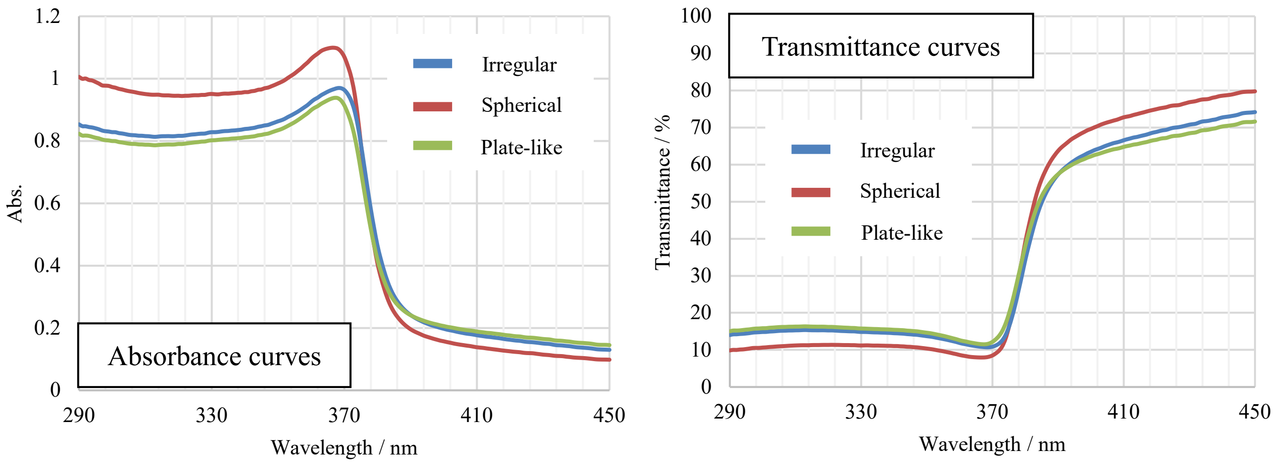


Fig-2 Absorbance and transmittance curves of zinc oxide with different particle shapes

3.2 Effect of primary particle size on optical properties

The primary particle size of S-ZnO was adjusted to 20, 40, and 50 nm, and coating films were prepared using the method described in Section 3.1. The absorbance and transmittance of the coated films were measured using an SPF analyser, and the results are shown in Figure-3.

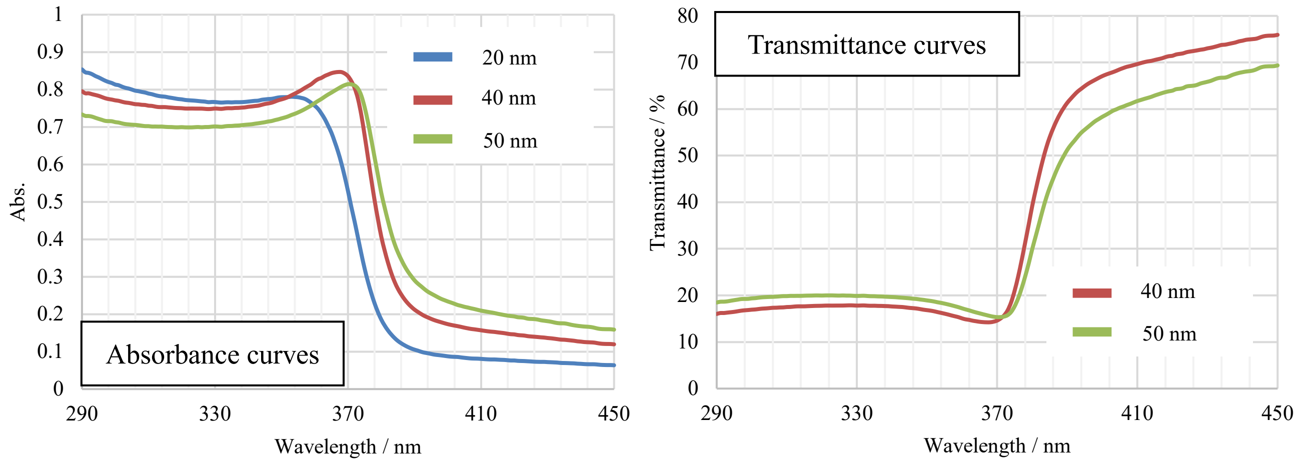
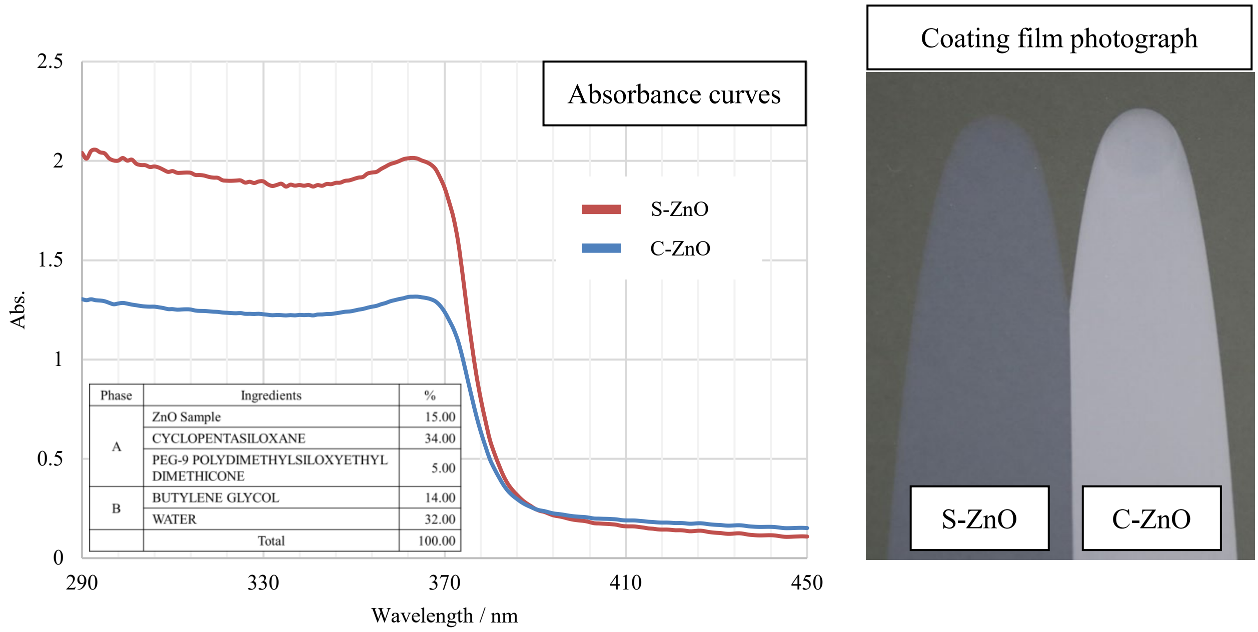


Fig-3 Absorbance and transmittance curves of spherical zinc oxide with different primary particle sizes

In the UVB region (290–320 nm), the absorbance of the 20 nm primary particle size was the highest and that of 50 nm was the lowest. On the other hand, in the UVA region (320–400 nm), the absorption edge of 20 nm was on the lower wavelength side than those of other particle sizes, and it was confirmed that the UVA-protection effect was low. Therefore, the 20 nm S-ZnO was considered not optimal for UVA protection, which is required for zinc oxide as a UV filter, and was excluded from the candidates. The transparency in the visible light range was higher at 40 nm than at 50 nm, and hence 40 nm was judged to be the optimal primary particle size for S-ZnO, which exhibits both transparency and UVA-protection effects.

3.3 Evaluation of W/O emulsion of S-ZnO and C-ZnO

S-ZnO and C-ZnO W/O emulsions were prepared, the optical properties of each were evaluated, and the coated films were observed. The absorbance measurement results of each W/O emulsion and photographs of the coating films are shown in Figure-4. The absorbance curves show that in the UVB-UVA region, the absorbance of the S-ZnO W/O emulsion was better by up to 78% compared to that of C-ZnO, confirming a high UV-protection effect.



Phase	Ingredients	%
A	ZnO Sample	15.00
	CYCLOPENTASILOXANE	34.00
	PEG-9 POLYDIMETHYLSILOXYETHYL DIMETHICONE	5.00
B	BUTYLENE GLYCOL	14.00
	WATER	32.00
	Total	100.00

Fig-4 Absorbance curves and coating film photographs of S-ZnO and C-ZnO W/O emulsions

The transparency of the W/O emulsion with S-ZnO was much higher than that with C-ZnO, and the difference was clearly confirmed using the photograph of the coated film.

4. Discussion

4.1 Improvement in transparency of S-ZnO

The difference in transparency of W/O emulsions containing S-ZnO and C-ZnO was predicted to be due to the difference in dispersibility and aggregate particle size of each surface-treated zinc oxide in the formulation, which changed the scattering efficiency of visible light. The relationship between particle size and light scattering efficiency is explained below. As shown in Figure-5, the light scattering efficiency depends on particle size and is maximum in the Mie region, where the particle size is around half the targeted wavelength of light [9]. This applies not only to primary particles but also to aggregated particles. When the target is visible light (400–700 nm), the particle size that scatters most effectively is 200–350 nm.

The particle size distributions of S-ZnO and C-ZnO were measured in cyclopentasiloxane at 0.5 wt.% concentration. S-ZnO was more highly dispersed in this solvent.

Applying this particle size distribution measurement result to the relationship between light scattering efficiency and particle size, the madian size (D50) of S-ZnO is 115 nm, and hence the scattering effect of visible light is low. On the other hand, the D50 of C-ZnO is 218 nm, and hence the scattering effect of visible light is high. Therefore, the transparency of the films was different, as shown in Figure-4.

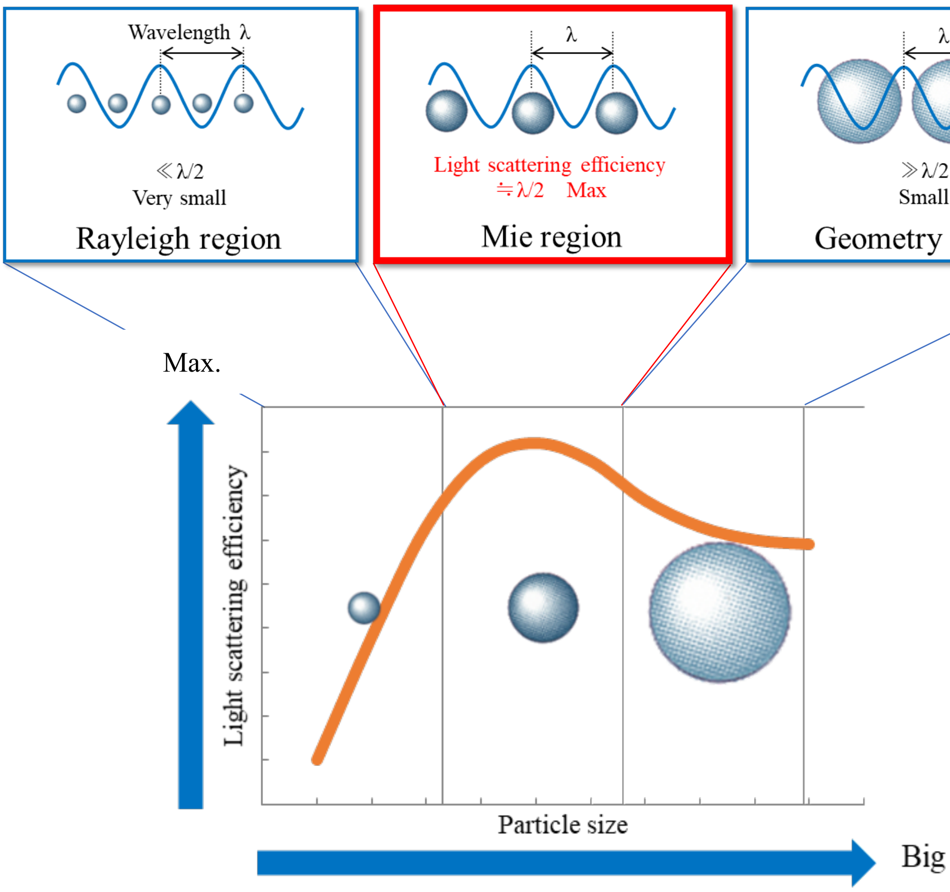


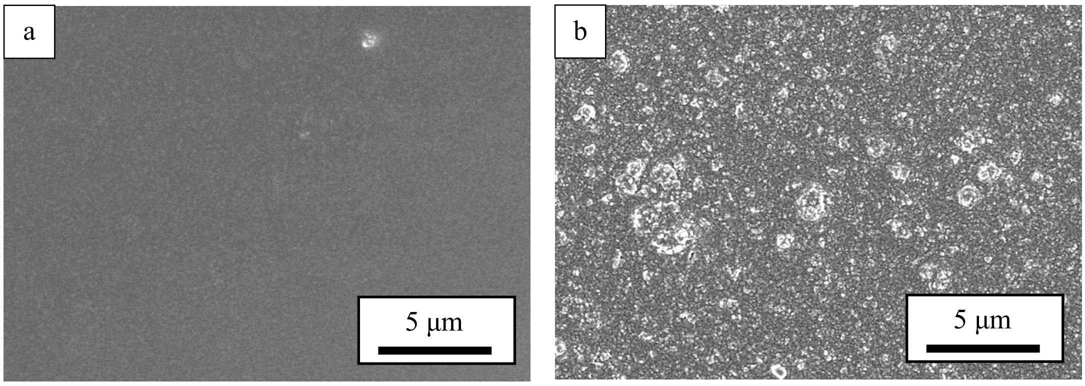
Fig-5 Particle size and light scattering efficiency

The surface of the coated film shown in Figure-4 was observed using scanning electron microscopy, and the optical properties were measured as shown in Figure-6. Figures-6(a) and 6(b) show that the surface of the S-ZnO film is smooth, whereas that of the C-ZnO film has many irregularities. Figure-6(c) shows that S-ZnO has a low haze value and high transparency. Haze and total light transmittance are expressed using the following equations.

Haze [%] = (Diffuse transmittance [%] / Total light transmission [%]) × 100
Total light transmittance [%] = Diffuse transmittance [%] + Linear transmittance [%]

The total light transmittance of S-ZnO and C-ZnO was similar, but the diffuse transmittance of C-ZnO was higher than that of S-ZnO, whereas the linear transmittance of S-ZnO was higher than that of C-ZnO. Based on the above equation, diffuse transmittance has a significant effect on the haze value; S-ZnO has high transparency because the coated film is smooth and the diffuse transmission of visible light is small. On the other hand, C-ZnO has high diffuse transmittance due to the presence of unevenness caused by aggregation, and thus the transparency of the coating film is lower.

In other words, the transparency of W/O emulsions containing S-ZnO is higher than that of emulsions containing C-ZnO because of both the smaller aggregated particle size of S-ZnO and the higher smoothness of the coating film.



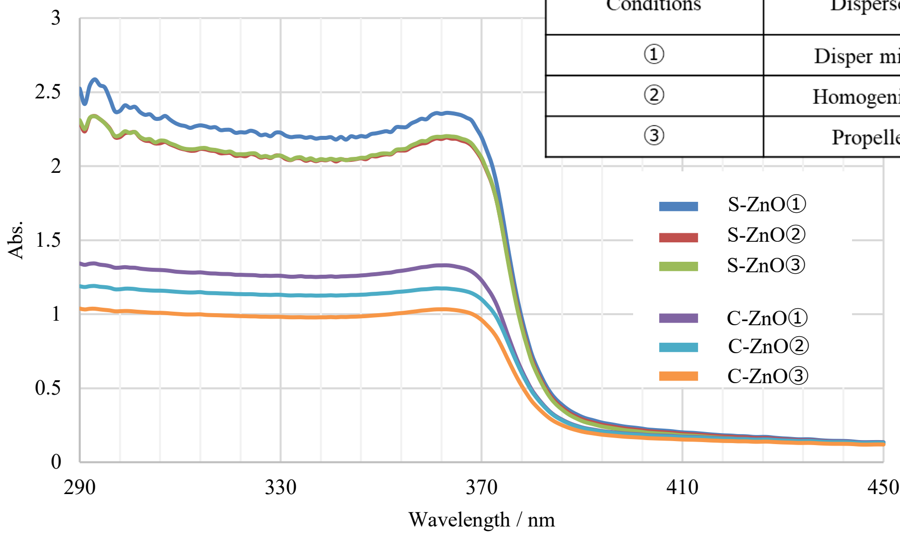
c	S-ZnO	C-ZnO
Haze [%]	9.2	54.9
Total light transmittance [%]	90.0	91.8
Diffuse transmittance [%]	8.3	50.4
Linear transmittance [%]	81.7	41.4

Fig-6 SEM images of coating films of (a) S-ZnO and (b) C-ZnO W/O emulsions, and (c) optical property evaluation results of the coating films

4.2 Effects of super-easy dispersibility of S-ZnO

So far, we have shown the evaluation results using a disper mixer; however, in actual cosmetic manufacturing, devices with dispersion strength lower than that of a disper mixer, such as homogenizers and propellers, are often used.

The absorbance of C-ZnO was higher in the order of disper mixer, homogenizer, and propeller. On the other hand, although the same tendency was seen with S-ZnO, the absorbance of the W/O emulsion prepared using the homogenizer and the propeller was similar, and the absorbance of S-ZnO was much higher than that of the C-ZnO dispersion prepared using the disper mixer. In other words, S-ZnO was found to be an extremely versatile and super-easy-dispersible zinc oxide that could be used in any dispersing apparatus.



Conditions	Disperser	Rotation speed [rpm]
①	Disper mixer	3,000
②	Homogenizer	3,000
③	Propeller	800

Fig-7 Absorbance curves of W/O emulsions prepared by changing dispersion conditions

The absorbance of each zinc oxide at a wavelength of 330 nm was checked when the dispersion and emulsification were carried out using a disper mixer with a rotation speed fixed at 3000 rpm and the dispersion time varied from 1 to 10 min. The absorbance of S-ZnO reached the highest point in only 1 min, whereas that of C-ZnO took more than 5 min to reach the highest point. Therefore, S-ZnO is a very eco-friendly raw material because the time and energy required for dispersion can be reduced to less than one-fifth of those required for C-ZnO.

4.3. Evaluation of W/O formulation of S-ZnO achieving SPF > 50, UVAPF > 16, and CW > 370 nm

W/O formulations were prepared using S-ZnO and C-ZnO with the compositions shown in Table-1(a) satisfying SPF > 50, UVAPF > 16, and CW > 370 nm. To achieve high transparency while providing sufficient SPF, both formulations were prepared with aluminum hydroxide and stearic acid surface-treated titanium dioxide with a primary particle size of 8 nm. The results of *in vitro* measurements of SPF and UVAPF of both W/O formulations are shown in Table-1(b).

Table-1 (a) Formulations of W/O emulsions satisfying SPF > 50, UVAPF > 16, and CW > 370 nm, and (b) SPF and UVAPF of W/O formulations

a

Ingredients*	S-ZnO W/O [%]	C-ZnO W/O [%]
S-ZnO	20.0	
C-ZnO		25.0
Titanium dioxide treated with Aluminum Hydroxide and Stearic Acid	5.0	5.0
Lauryl PEG-9 Polydimethylsiloxyethyl Dimethicone	3.0	3.0
PEG-9 Polydimethylsiloxyethyl Dimethicone	1.5	1.5
Diphenylsiloxy Phenyl Trimethicone	2.0	2.0
Hydrogenated Polyisobutene	7.5	7.5
Cyclopentasiloxane	37.0	32.0
Polymethylsilsesquioxane	5.0	5.0
Water	15.0	15.0
Butylene Glycol	3.0	3.0
Sodium Chloride	1.0	1.0

*All ingredients were commercially available cosmetic-grade materials

b

Sample	SPF	*in vitro* UVAPF	CW
S-ZnO W/O formulation	52	19	373
C-ZnO W/O formulation	63	18	371

Table-1(a) shows that the amount of inorganic material required to satisfy SPF > 50, UVAPF > 16, and CW > 370 nm for S-ZnO was 25.0%, whereas 30.0% was required for C-ZnO. In other words, the amount of inorganic material blended with S-ZnO was successfully reduced by 16.7% compared with that for C-ZnO. This was attributed to the improved UV-protection effect of S-ZnO due to its super-easy dispersibility. The results of the usability evaluation of W/O emulsions containing S-ZnO and C-ZnO conducted by nine monitors are shown in Figure-8. The five evaluation items were transparency, non-squeakiness, lightness, good spreadability, and smoothness. The S-ZnO W/O emulsion was found to be superior to the C-ZnO emulsion in all the items due to the lower amount of inorganic ingredients used.

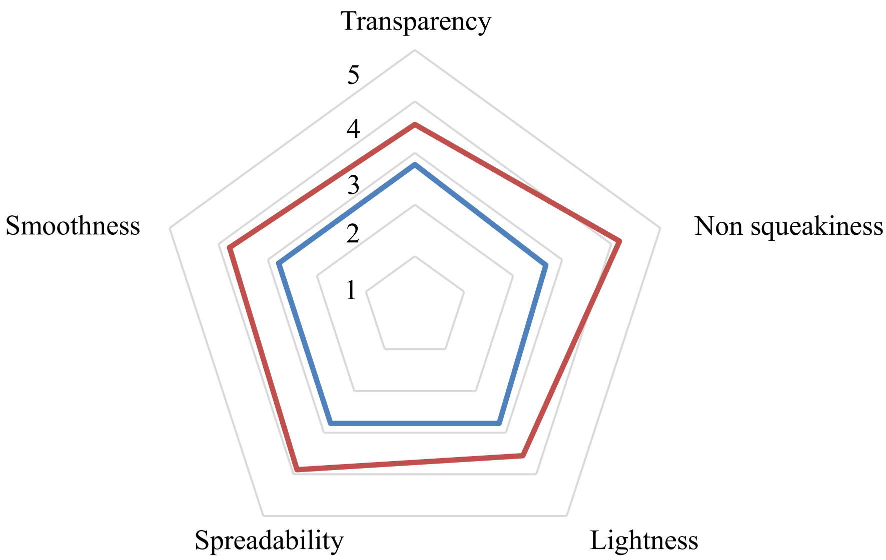


Fig-8 Usability evaluation results of S-ZnO (-) and C-ZnO (-) W/O formulations

Figure-9 shows the results of W/O emulsions applied to paper imitating each skin tone to confirm the blendability of the emulsions to skin. It is apparent that the C-ZnO emulsions look conspicuously white on any skin tones, the S-ZnO counterparts blend in naturally regardless of the skin tone.

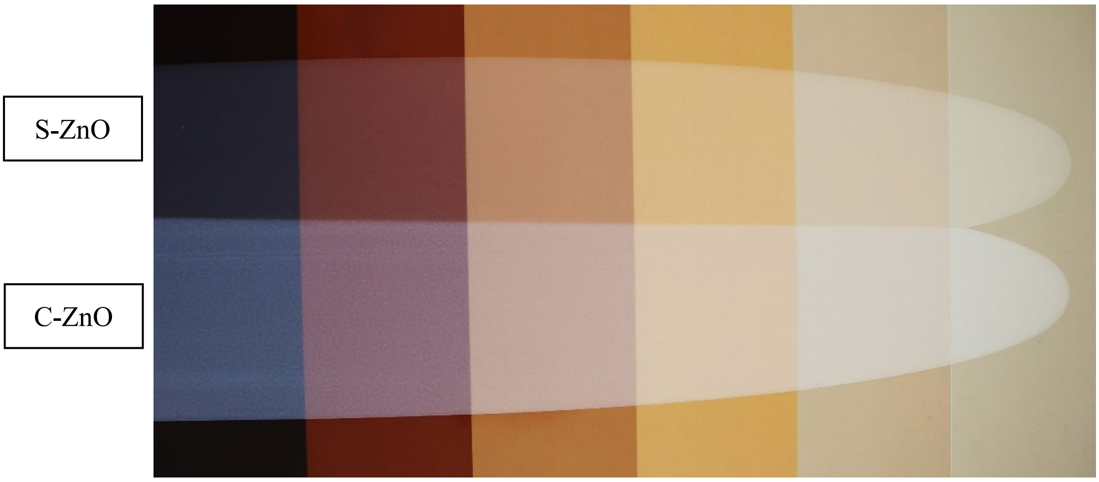


Fig-9 Skin compatibility test of W/O formulations

5. Conclusion

In this study, we found that S-ZnO improves dispersibility in oil and exhibits excellent transparency and UV-protection properties. The dispersibility of S-ZnO also improved upon treatment with triethoxycaprylylsilane, which has a primary particle size of 40 nm. Thus, high transparency and UV-protection effects could be obtained. S-ZnO is highly versatile because it can be dispersed in any dispersion equipment, and even a short dispersion time provides a high UV-protection effect; therefore, it is an eco-friendly raw material that can reduce energy costs. In addition, S-ZnO provides the highest transparency and naturalness for all skin tones.

The S-ZnO developed in this research can solve the issues of transparency and texture that non-chemical sunscreens have had, and will enable new possibilities for the development of higher-quality cosmetics, as well as contribute to the achievement of many SDGs.

Conflict of Interest Statement

NONE

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