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Effect of particle size of TiO_2 and octyl-methoxycinnamate (OMC) content on sun protection factor (SPF)

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Abstract Exposure to UV light, i.e., UV-A (320-400 nm) or UV-B (290-320 nm) radiation, can cause skin cancer. Titanium dioxide (TiO_2) effectively disperses UV light. Therefore, it is used as a physical UV filter in many UV light blockers. Usually, the TiO_2 content in commercialized UV blockers is 25 % at most. To block UV-B, a chemical UV blocker, octyl-methoxy cinnamate (OMC) is used. OMC is commonly used in combination with TiO_2. In this study, TiO_2 and OMC were mixed in different proportions to produce UV blockers with different compositions. Also the changes in the sun protection factor (SPF) based on the composition and TiO_2 particle sizes were investigated. In order to analyze the TiO_2 particle size, dynamic light scattering (DLS) and asymmetrical flow field-flow fractionation (AsFlFFF) were used. The results showed that the SPF was influenced by the proportion of TiO_2 and OMC, where the proportion of TiO_2 induced a more significant influence. In addition, changes in the TiO_2 particle size based on the proportion of OMC were observed.

Key words: Titanium dioxide (TiO_2), Octyl-methoxy cinnamate (OMC), Sun protection factor (SPF), Asymmetrical flow field-flow fractionation (AF4), Dynamic light scattering (DLS)

1. Introduction

Sunlight consists of infrared light, visible light, UV rays, X-rays and γ-rays. UV light accounts for 6 % of the total sunlight, which is much lower as compared to visible light and infrared light. However, the human body is the most sensitive to UV light, and UV light can induce skin cancer and skin-aging. UV light is classified as UV-A (320-400 nm), UV-B (290-320 nm), and UV-C (200-290 nm) based on the wavelength.[1] UV-C destroys mono-cellular organisms through chromosomal abnormalities, which leads to hazardous effects on the body, such as damage of the cornea. However, most of the UV-C light is absorbed by the ozone layer and does not reach the ground surface or come in contact with the human skin. On the other hand, UV-A and UV-B radiations are not absorbed by the ozone layer and hence have hazardous consequences on the body, such as skin cancer and skin-aging. In particular, UV-A has the longest wavelength and most of the UV-A emitted by the sun reaches the ground surface. Therefore, it accounts

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for 90-95 % of the UV light coming into contact with the skin. Since the content of UV-A is high during the day and at night, and the amount that reaches the ground is constant, UV-A is also called "everyday UV light." UV-A can penetrate into dermis and is known as a main factor that leads to skin-aging by causing pigmentation, decreasing skin elasticity, and causing wrinkles.[2,3] UV-B has a relatively shorter wavelength and higher energy levels. Hence, UV-B can reach the dermis in a shorter span of time.[4] UV-B is responsible for skin burns during the summer, and it can inhibit nucleic acid and protein synthesis in skin cells and cause pigmentation. Moreover, UV-B can lower the immune system, increase the possibility of bacterial infections, and induce cancer.[3,5,6] Since different types of UV light have different penetration levels and frequencies, their effects on the skin are also different.

UV blockers are usually used to protect the skin from UV light.[7] UV blockers absorb, reflect and disperse sunlight, and consequentially, block UV light. UV blockers are usually available in the form of as creams, lotions, and sprays.[8] Commercialized UV blockers are marked with their corresponding sun protection factor (SPF), which reflects the ability of the product to block UV-B. A higher SPF means a higher degree of protection from UV-B. For example, when the amount of sunlight is 1, a product with SPF 15 would decrease the sunlight to 1/15. Further, the protection grade of UV-A (PA) is usually shown along with SPF, where PA can be either +, ++ or +++. A Higher number of + signs indicates a higher degree of protection from UV-A.[9,10] Based on the ingredients, UV blockers are classified as organic blockers, inorganic blockers, and organic/inorganic blockers. The most widely used inorganic UV blockers are titanium dioxide (TiO_2) and zinc oxide (ZnO). TiO_2 is sub-classified into anatase and rutile forms, where the latter is the most commonly used UV blocker.[11] Organic UV blockers include octyl-methoxy cinnamate (OMC), octocrylene, benzophenone, octyl salicylate, and oxybenzone.[12,13] Organic/inorganic blockers are produced by combining organic and inorganic UV blockers.

Previous studies have investigated the effects of optical properties such as UV absorption rate and UV reflection rate on SPF and PA, based on different forms of TiO_2. Studies confirming the TiO_2 concentration, particle size, and distribution in commercially available UV blockers, as well as changes in the SPF based on different TiO_2 particle sizes, have been conducted.[14-16] A previous study has investigated the synergic effects of organic and inorganic UV blockers mixed together.[17]

Field-flow fractionation (FFF) is widely used to analyze the characteristics of colloids and to separate colloids (ex. nanoparticles, protein, DNA, etc.) based on their sizes. FFF has a wide range of analysis, from a few nanometers to hundreds of micrometers.[18-21] Based on the type of external field, FFF is classified as asymmetrical flow field-flow fractionation (AsFlFFF), sedimentation field-flow fractionation (SdFFF), and thermal field-flow fractionation (ThFFF).[18]

In this study, commonly used methods for size analysis, i.e., microscopy and dynamic light scattering (DLS), as well as the relatively unknown AsFlFFF, were used. The changes in TiO_2 particle sizes based on the proportion of organic/inorganic UV blockers were observed, and the correlation between the physical/chemical characteristics of organic/inorganic UV blockers and the SPF was studied. The appropriate proportion of organic and inorganic UV blockers required for a high SPF was also investigated.

2. Theory

2.1. Theory of AsFlFFF

AsFlFFF can be used to directly calculate the hydraulic diameter (d_H) using retention time (t_r), as shown in Eq. (1).[21,22]

$$d_H = \frac{2kTV^0}{\pi\eta w^2 V_c t^0} t_r \tag{1}$$

Here, k is the Boltzmann constant, T is the absolute temperature (K), V^0 is the void volume of the channel, η is the carrier liquid viscosity, w is the width of the channel, V_c is the intensity of the external field, and t^0 is the void time of the channel. In Eq. (1), all variables with the exception of t_r are constants based on the experimental conditions. Therefore, determination of t_r of a sample using AsFlFFF can yield the sample size and size distribution.

3. Experimental

3.1. Materials

TiO_2 used in this study to manufacture UV blockers was of rutile form, and was purchased from Ishihara Sangyo Kaisha, Ltd. (Tokyo, Japan). OMC was purchased from BASF SE (Mannheim, Germany). The ingredients required to manufacture UV blockers (purified water, oil, emulsifier, etc.) were purchased from Ecofactory (Seongnam, Korea). To disperse the manufactured UV blocker, Tween 80 (Sigma-Aldrich, St. Louis, USA) was used. The FL-70 (Fisher Chemical, New Jersey, USA) and sodium azide (NaN_3, Sigma-Aldrich, St. Louis, USA) were used to prepare the FFF carrier liquid.

3.2. Instruments

The homogenizer used for manufacturing the UV blocker was MS-280D (MTOPS, Yangju, Korea). The SPF and monochromatic protection factor (MPF) were measured with an SPF analyzer-290As (Solar Light, Glenside, USA). The range of measured wavelength was 290-400 nm, at the interval of 5 nm. A total of 12 measurements were carried out, and the measurement site was changed each time. The average value was calculated and reported. The SPF and MPF of the manufactured UV blocker were measured after the UV blocker was spread on Schonberg PMMA plates. The spread amount was determined based on the "UV blocker measurement method and standard" of notice 2012-88 from the Ministry of Food and Drug Safety.[23]

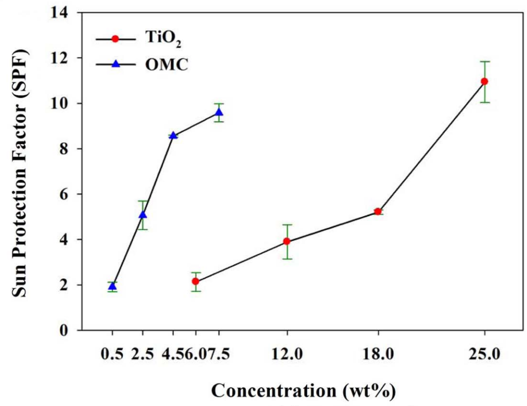
To confirm the sizes and shapes of the TiO_2 particles, transmission electron microscopy (TEM, Tecnai F30 ST, FEI Company, USA) and scanning electron microscopy (SEM, Magellan 400, FEI Company, USA) were used. The sizes and distributions were analyzed using a DLS system (DynaPro NanoStar, Wyatt Tech. Corp., Santa Barbara, USA) and an AsFlFFF short channel (Wyatt Tech., Europe GmbH, Dernbach, Germany) equipped with a cellulose membrane (Millipore, Bedford, USA) with 10 kDa molecular weight cut-off, and a 250-μm-thick Mylar spacer. The carrier liquid used in the AsFlFFF separation was deionized distilled water containing 0.1 % FL-70 and 0.02 % NaN_3. In order to remove impurities from the carrier liquid, a 0.45-μm membrane filter (Membrane Solutions, Plano, USA) was used for filtration before analysis. An HPLC pump (LC-20AD, Shimadzu Corp., Kyoyo, Japan) was used for injecting the carrier liquid, and an Optiflow 1000 Liquid Flowmeter (Agilent Technologies, Palo Alto, CA, USA) was used to measure the flow rate. A UV detector (Model 500, Chrom Tech, Minnesota, USA) was used to detect the samples assorted based on their sizes. 20 μL of the sample was injected using a syringe pump (Legato 100, KD Scientific Inc., Mendon, USA) at a flow rate of 0.2 mL/min. Each measurement was repeated 3 times to confirm reproducibility.

4. Results and Discussion

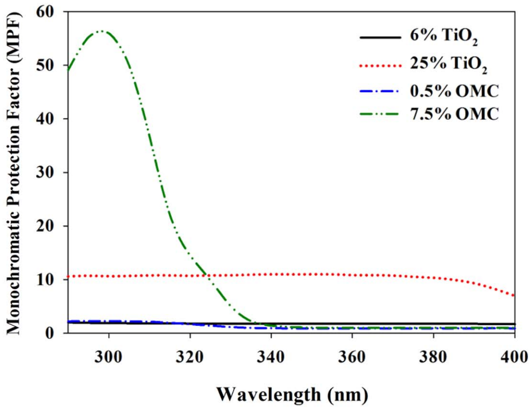
4.1. UV blocker effects of TiO_2 and OMC

Prior to preparing UV blockers, the UV blocking properties of TiO_2 and OMC were individually evaluated. In order to approximate the formulation of UV blockers without the effects of other added compounds, TiO_2 and OMC were mixed with Vaseline prior to SPF and MPF measurements. The measurements of pure Vaseline were then subtracted to calculate the SPF and MPF of pure TiO_2 and OMC. In order to determine the changes in the SPF and MPF with concentrations, the concentration of TiO_2 was set to 6, 12, 18 and 25 wt% and the concentration of OMC was set to 0.5, 2.5, 4.5 and 7.5 wt%, respectively. The concentrations were all within the permitted range for functional cosmetics.

Fig. 1 shows the SPF and MPF measured at various concentrations of TiO_2 and OMC. *Fig.* 1(a) shows that, as the TiO_2 and OMC concentrations increase, the SPF increases accordingly. When the rate of increase in the SPF with the concentration



(a)



(b)

Fig. 1. Results of sun protection factor (SPF) (a) and monochromatic protection factor (MPF) (b) for different concentration of TiO_2 and OMC.

was compared using the slope of the plot, TiO_2 was 0.45 and OMC was 1.11. These results indicate that OMC is twice as sensitive as TiO_2 in terms of changes in the SPF. Although the SPF was not measured for identical concentrations of the two compounds, the highest concentration was comparable to the upper limit of the permitted range in cosmetics. The SPF of pure TiO_2 and OMC in UV blockers can be estimated to be close to 10. *Fig.* 1(b) shows the range of UV light that TiO_2 and OMC can block. It was observed that TiO_2 effectively blocks UV light at 290-400 nm, which corresponds to both UV-A and UV-B. On the other hand, OMC effectively blocked UV light at 290-320 nm, which corresponds to UV-B. The results suggest that UV blockers solely composed of OMC can be specialized for protection from the UV-B range, while those solely composed of TiO_2 can block both UV-A and UV-B. Furthermore, it can be inferred that combination of organic and inorganic UV blockers result in more effective blocking of UV light.

4.2. Effects of TiO_2 and OMC proportions on SPF

In order to systematically confirm the effects of organic and inorganic UV blocker proportions on the SPF and MPF, the permitted limits in cosmetics were disregarded. The TiO_2 and OMC concentrations were set to 0 %, 4.5 %, 9 % and 13.5 %, and the standard method provided by the Ministry of Food and Drug Safety was used for the manufacturing UV blockers.[23]

Table 1 shows the proportions of the organic and inorganic UV blockers, concentrations, and the measured SPF.

The SPF for Sun-1 and Sun-2, UV blockers prepared with single compounds, were measured to be 10.6 ± 1.6 and 18.0 ± 0.3, respectively, which are higher than those shown in *Fig.* 1. It can be inferred that

Table 1. Compositions of organic-inorganic sunscreen formulations and their SPF values

Number	TiO_2 concentration (wt%)	OMC concentration (wt%)	TiO_2 : OMC Mixing ratio	SPF ± SD
Sun-1	0	4.5	0 : 1	10.6 ± 1.6
Sun-2	4.5	0	1 : 0	18.0 ± 0.3
Sun-3	4.5	4.5	1 : 1	18.2 ± 1.3
Sun-4	4.5	9.0	1 : 2	20.3 ± 1.7
Sun-5	4.5	13.5	1 : 3	23.7 ± 1.8
Sun-6	9.0	4.5	2 : 1	23.9 ± 1.5
Sun-7	13.5	4.5	3 : 1	26.5 ± 1.2

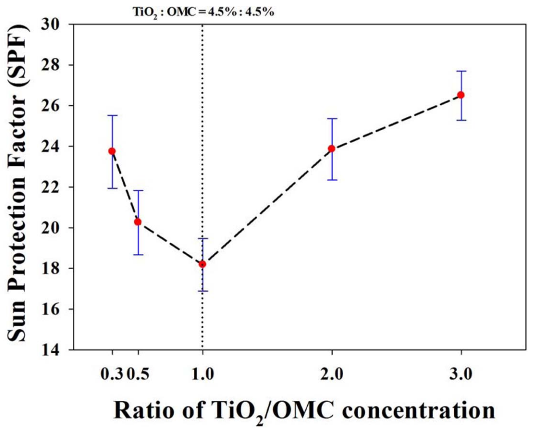


Fig. 2. SPF of sunscreen formulations for compositions of TiO_2 and OMC.

these values are due to the added compounds such as emulsifiers and oils during the manufacturing process. These added compounds led to relatively higher synergic effects with inorganic compounds such as TiO_2 as compared to organic compounds such as OMC. In addition, UV blockers manufactured by mixing TiO_2 and OMC (Sun-3) had an SPF of 18.2 ± 1.3, which was higher than that of Sun-1 and Sun-2, as shown in *Table* 1.

Fig. 2 shows the changes in the SPF based on the composition of TiO_2 and OMC. The results were computed by fixing the concentration of one compound and increasing the concentration of the other compound two- or threefold. *Table* 1 shows the changes in the SPF in the plots of Sun-3, 4, 5, 6 and 7.

The SPFs were similar when the OMC concentration was tripled (Sun-5, SPF=23.7 ± 1.8) and the TiO_2 concentration was doubled (Sun-6, SPF=23.9 ± 1.5). This observation indicates that TiO_2 has a greater effect on the SPF in UV blockers than does OMC. However, this result contradicts those shown in *Fig*. 1, because of the added compounds and the difference in blocking mechanisms between the two compounds.[24,25] The UV blocking mechanism of OMC is based on the absorption of UV light, while that of TiO_2 is based on a complex process involving the absorption and reflection of UV light, followed by dispersion. Therefore, it is inferred that these differences in mechanisms lead to different outcomes. However, further studies should be conducted to determine the exact reason for the aforesaid difference. *Fig*. 2 shows that the changes in the SPF are the greatest when the OMC concentration is fixed at 4.5 % and the TiO_2 concentration is increased. As predicted earlier, use of a combined organic/inorganic UV

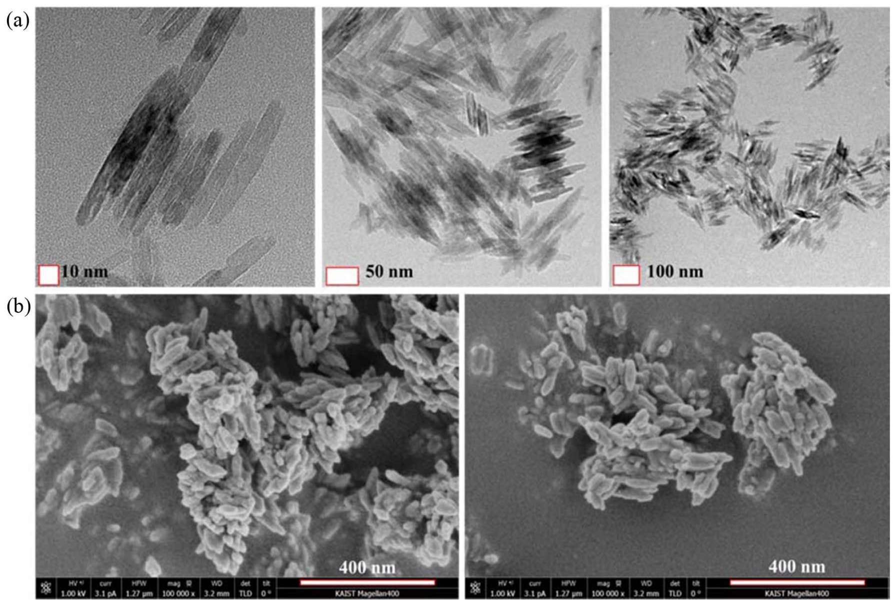


Fig. 3. Electron microscope images of TiO_2 powder. TEM (a) and SEM images (b).

blocker would increase the SPF more effectively and easily than using single UV blocker.

4.3. Changes in TiO_2 particle size

TEM and SEM observations were performed to confirm the particle size and shape of TiO_2 in the inorganic UV blocker used in this study. The results are shown in *Fig*. 3.

Overall, the TiO_2 particles are rod shaped rather than spherical, with lengths of 50-100 nm and widths of 5-10 nm, as shown in *Fig*. 3.

During the manufacture of the UV blocker, physical energy may be produced by the high temperature and the use of the homogenizer. In this case, the physical properties of TiO_2 (size, distribution, etc.) could be altered. The sizes and size distributions of TiO_2 in the manufactured UV blocker were measured using DLS and AsFlFFF.

In order to measure the particle size of TiO_2 in the manufactured UV blocker, each sample was diluted to 1 mg/mL in aqueous solution of 1 % Tween 80. The samples were dispersed for 15 min using a sonicator prior to the measurement. The particle size of TiO_2 in the UV blockers Sun-2, 3, 4, 5, 6 and 7 were measured using DLS. The results of size measurements for Sun-2 and 6 by AsFlFFF are shown in *Table* 2. Unlike the case of DLS, only 2 samples were chosen for the size analysis by AsFlFFF and the remaining 4 samples were not analyzed. The results showed that as the OMC and TiO_2 concentrations increased, the average size of the TiO_2 particles increased, leading to increased SPF.

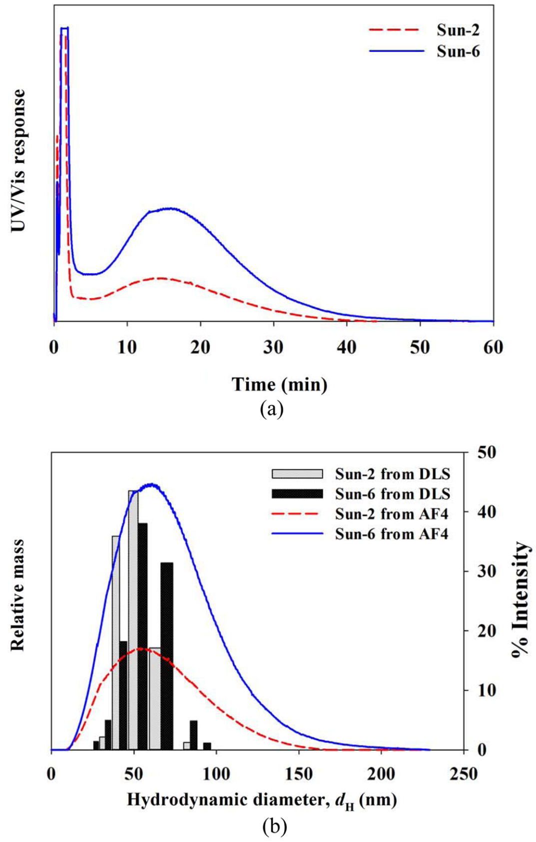


Fig. 4. AF4 fractograms of sunscreen formulations (a) and size distributions from DLS (bar) and AF4 (line) of sunscreen formulations (b). The AF4 channel and the cross flow rates were 1.0 mL/min, and the carrier liquid was water containing 0.1 % FL-70 and 0.02 % NaN_3.

Nanoparticles usually have high surface energy and easily cohere. Therefore, as the TiO_2 concentration increases, the collision rate between particles also increases and thus may lead to cohesion. The cohesion between the TiO_2 particles increases with an increase

Table 2. Mean diameter of TiO_2 in sunscreen formulations measured by DLS and AF4

Number	TiO_2 : OMC	SPF ± SD	Mean diameter from DLS ± SD (nm)	Mean diameter from AF4 ± SD (nm)
Sun-1	0 : 1	10.6 ± 1.6	-	-
Sun-2	1 : 0	18.0 ± 0.3	46 ± 4.9	66 ± 1.6
Sun-3	1 : 1	18.2 ± 1.3	53 ± 2.9	n.d*
Sun-4	1 : 2	20.3 ± 1.7	57 ± 3.5	n.d*
Sun-5	1 : 3	23.7 ± 1.8	63 ± 5.4	n.d*
Sun-6	2 : 1	23.9 ± 1.5	56 ± 5.0	71 ± 1.4
Sun-7	3 : 1	26.5 ± 1.2	65 ± 1.3	n.d*

n.d*: not determined

in the OMC concentration. It can be inferred that this is due to the increased degree of emulsification caused by the increased OMC concentration.[26,27] Further studies will be needed to identify the accurate correlation between the degree of emulsification and the cohesion between the TiO_2 particles. Light scattering also increases with the increase in particle size, which leads to light blocking and consequently affects the SPF.

Fig. 4(a) shows the AsFlFFF fractogram of Sun-2 and Sun-6. *Fig*. 4(b) shows the size distributions determined by DLS and AsFlFFF. The AsFlFFF size distribution was determined by applying Eq. (1). The distribution determined through AsFlFFF differed from that determined by DLS, which is due to the different measurement mechanisms in the two techniques. DLS usually does not separate particles based on their sizes and measures the average particle size. On the other hand, AsFlFFF separate particles according to their sizes and determines their average size and distribution. Therefore, AsFlFFF allows visualization of TiO_2 particles that are too small or too large to be measured by DLS.[28,29]

5. Conclusions

In this study, the effects of the organic UV blocker OMC and the inorganic UV blocker TiO_2 on the SPF were compared and analyzed using various methods.

A higher SPF was observed in the case of using pure OMC as compared to that with TiO_2. In the case of UV blockers manufactured by mixing the two compounds, the TiO_2 concentration had a greater effect (approximately 1.5 times greater) on the SPF than did the OMC concentration.

TiO_2 showed similar UV blocking properties in the wavelength ranges of UV-A and UV-B, while OMC showed greater UV blocking properties in the UV-B range than in the UV-A range.

TiO_2 particle analysis using DLS and AsFlFFF showed that as the concentration of TiO_2 and OMC increased in the UV blockers, the TiO_2 particle size increased. This increase in particle size led to a higher SPF in the UV blockers.

Thus, the correlation between the physical/chemical properties of TiO_2 and OMC and the SPF was investigated. Based on the results, it was confirmed that AsFlFFF and DLS had the potential to evaluate the SPF efficiency in UV blockers.

Acknowledgements

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