Surface Structures of Cosmetic Standard Poly Methyl Methacrylate UV Evaluation Plates and their Influence on the in vitro Evaluation of UV Protection Abilities of Cosmetic Sunscreens

Akihiro Kuroda¹,², Karin Sakai², Shoichi Yahagi³, Tsubasa Mukawa⁴, Nobumasa Sato⁴, Naoki Nakamura⁴, Daisuke Maezawa⁴,², Hitoshi Masaki⁵, Taisuke Banno², and Kouichi Asakura²*

¹ Yokohama Research Center, Kuroda Consulting Inc., 85 Nakayama-cho, Midori-ku, Yokohama 226-0011, JAPAN
² Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, JAPAN
³ Department of Efficacy and Safety Evaluation, NIKKOL Group Cosmos Technical Center Co., LTD., 3-24-3 Hasune, Itabashi-ku, Tokyo 174-0046, JAPAN
⁴ R & D Center, Para Hermosa Co., Ltd., 2-12-1 Fukuura, Kanazawa-ku, Yokohama 236-0004, JAPAN
⁵ School of Bioscience and Biotechnology, Tokyo University of Technology, 1404-1 Katakura-cho, Hachiouji-shi, Tokyo 192-0982, JAPAN

Abstract: Cosmetic standard poly methyl methacrylate (PMMA) UV evaluation plates, i.e., roughened PMMA plates, are used in the EU and the US for the in vitro evaluation of UV protection abilities of sunscreen, such as in vitro UVA-PF and critical wavelength for the Broad-spectrum approval. In our previous studies, inhomogeneity in the thickness of a pseudo-sunscreen layer applied on a flat quartz plate was observed to alter UV transmission. Thus, the surface roughness of the standard plates should have a significant influence on the in vitro evaluation. In the present study, we have analyzed the surface structures of three cosmetic standard PMMA UV evaluation plates: Helioplates HD6 (Sa = 6 µm) and ISO plates (Ra = 2 and 5 µm). A decamethylcyclopentasiloxane and 2-propanol-mixed solvent solution of acrylsilicone resin was prepared, and the solution was added dropwise onto the plates. After the evaporation of the solvents, the plates were cut and the cross section was analyzed using SEM-EDS. The distribution of silicon atoms at the cross-section suggested that the maximum depth of penetrating of acrylsilicone resin was larger than Ra for all the standard plates, and the surface structure was significantly different for each standard plate. In addition, cracks into which the acrylsilicone resin deeply penetrated were observed on the surface of some plates. Clear-solution-type pseudo-sunscreen samples in which UV absorbers and acrylsilicone resin were dissolved were deposited on the standard roughened PMMA plates. It was observed that the addition of acrylsilicone resin drastically changed the net UV transmission. The degree to which the hollows of the roughened surface were filled with the pseudo-sunscreen samples determined the variation of UV transmittance.

Key words: in vitro evaluation of UV protection abilities, surface roughness, cosmetic standard PMMA UV evaluation plates, SEM/EDX, SPF analyzer

1 INTRODUCTION

The establishment of a reliable and reproducible in vitro evaluation method of the UV protection ability of sunscreens is required, as it provides results more quickly, is less expensive, and is more ethical¹⁸. For the evaluation of in vitro UVA-PF by ISO 24443¹³ and critical wavelength for the Broad-spectrum approval by US FDA’s Final Sunscreen Rule¹⁰, roughened cosmetic standard poly methyl methacrylate (PMMA) UV evaluation plates are used¹¹-¹⁸.

In our previous studies, it was shown that spontaneous pattern formation by viscous fingering¹⁴-¹⁸ on the sunscreen layer during the process of its application onto a flat...
substrate alters the UV transmission to change the value of the *in vitro* SPF \(^{20}\) and critical wavelength for Broad-spectrum approval \(^{30}\). When patterns are formed on the sunscreen layer, the generation of the thinner part reduces the UV absorption, whereas the thicker part increases the UV absorption. However, the degree of reduction of the UV absorption by the thinner part is larger than the degree of increase in UV absorption by the thicker part, resulting in a decrease in the net UV absorbance. In addition, the UV absorbance largely decreased through pattern formation at a certain wavelength demonstrating larger UV absorbance for the flat layer.

The spontaneous pattern formation on the sunscreen layer during the process of its application as well as any factors that make the sunscreen layer become spatially inhomogeneous alter the UV transmission to change the values of *in vitro* UV protection abilities. Thus the surface roughness of the cosmetic standard PMMA UV evaluation plate should have a significant influence on the values of *in vitro* UV protection abilities. In addition, some groups have suggested the influence of surface roughness on bad reproducibility for the *in vitro* evaluations of UV protection abilities \(^{21, 22}\). However, no detailed regulation has been established for the roughness of the surface structure so far. This situation motivated us to analyze the surface roughness of the standard PMMA evaluation plates and its influence on the *in vitro* evaluations of UV protection abilities.

Analyses were performed for three standard plates having different roughness averages (Ra): Helioplates HD6 (Sa = 6 µm) and ISO plates (Ra = 2 and 5 µm). Acrylsilicone resin solution was prepared and its penetrating behavior into the hollows of the roughened surface of the plate was analyzed using scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) to investigate the surface structure. In addition, clear-solution-type pseudo-sunscreen samples were prepared by dissolving UV absorbers and acrylsilicone resin into hexane. They were added dropwise onto the cosmetic standard PMMA UV evaluation plates and the solvent was evaporated. UV absorbance of the substrates was measured using an SPF analyzer at the wavelengths ranging from 290 to 400 nm to study the influence of surface roughness on the UV transmission.

### 2 EXPERIMENTAL PROCEDURES

#### 2.1 Standard roughened PMMA plates

Three types of cosmetic standard PMMA UV evaluation plates, Helioplates HD6 (Sa = 6 µm) (HeliopScreen), HD6, and ISO plates (Ra = 2 and 5 µm) (Solar Light Company, Inc.), ISO2 and ISO5, were purchased. All the plates were square-shaped with a side of 5 cm.

#### 2.2 Materials

Acrylsilicone resin (ASR), Silicone Acrylates KP-541 (40% 2-propanol solution of acrylsilicone resin), was supplied by Shin-Etsu Chemical Co., Ltd. It was diluted with decamethyldicyclopinoloxiane (D5) to prepare sample solutions for analyzing the surface roughness of the standard PMMA plates.

UV absorbers, diethylamino hydroxybenzoyl hexyl benzoate (DHHB) and 2-ethylhexyl methoxycinnamate (EHMC), were purchased from BASF Japan Ltd., and butyl methoxydibenzyilmethane (BMDM) was purchased from DSM Nutrition Japan K. K. A cosmetic oil, 2-ethylhexyl methoxycinnamate (EH-O-HAS) \(^{23}\), exhibiting a hydroxyl value \(^{24}\) of 29.26 mg KOH/1g of oil, indicating that its degree of oligomerization was 6.33 \(^{25}\), was supplied by National Mimatsu Co., Ltd. According to our recent finding of the strong coexistence effects of DHHB and BMDM on their solubility in EHMC in the presence of EH-O-HAS \(^{26}\), DHHB, BMDM, and EH-O-HAS were dissolved in EHMC to prepare a UV absorber solution in which the weight ratio was DHHB : BMDM : EHMC : EH-O-HAS = 0.220 : 0.217 : 0.470 : 0.096. It was subsequently dissolved in a hexane solution of ASR to prepare three types of pseudo-sunscreen solutions 1, 2, and 3 (Table 1). All the solutions wetted a flat PMMA plate so that the contact angle could not be measured using a contact angle meter (DropMaster 500, Kyowa Interface Science Co., Ltd.), and the viscosity was determined as 25.9 x 10^{-3} Pa s, 11.0 x 10^{-3} Pa s, and 8.0 x 10^{-3} Pa s, respectively for pseudo-sunscreen solutions, 1, 2, and 3 using the NDJ-8S digital viscometer (Shanghai Changji Geological Instrument Co., Ltd.).

#### 2.3 Preparation of samples for SEM/EDS analysis

Cutting scathes were carved at two lines on a rear side of the cosmetic standard PMMA UV evaluation plates, HD6, ISO2, or ISO5. With the use of a Pasteur pipette, the D5 and 2-propanol-mixed solvent solution of ASR was slowly added dropwise onto the plate, which was thereafter stored at room temperature for 5 days followed by storing at 35°C in an air supply dryer for 2 days to evaporate the solvents completely. The completion of evaporation of the solvent was confirmed by the fact that there was no weight

| Table 1 | Pseudo-sunscreen solutions prepared by dissolving ASR and UV absorbers solution containing DHHB, BMDM, EHMC, and EH-O-HAS. |
|---------|-------------------------------------------------|
| Sample  | ASR / mg | UV absorbers solution / mg | Hexane / mL |
| 1       | 400      | 10.0                        | 8.0         |
| 2       | 200      | 10.0                        | 8.0         |
| 3       | 0        | 10.0                        | 8.0         |
change of the sample during the last day of storing in the air supply dryer. ASR was deposited on the PMMA plate to make its amount per unit area as 0.75, 1.3 and 2.0 mg cm$^{-2}$, respectively for the aforementioned three plates, i.e., HD6, ISO2, and ISO5. The plate was broken into three pieces at the lines of the cutting scathe.

2.4 SEM/EDS analysis

The broken sample plate was placed on an SEM sample holder to observe the cross-section. The distribution of silicon atoms at the cross-section was evaluated using SEM/EDS (JSM-6010LA, JEOL) mapping images. SEM/EDS observations were conducted under low vacuum condition (30 Pa), and the acceleration voltage was 10 kV, whereas it was 20 kV when the point analysis was conducted for Si atom ratio. No vapor deposition was performed for each sample. SEM observations were also conducted on the original HD6, ISO2, and ISO5.

2.5 Deposition of the pseudo-sunscreen samples and measurements of their UV transmission by SPF analyzer

The cosmetic standard PMMA UV evaluation plate, HD6, ISO2, or ISO5, was placed in a petri dish, which was placed on an electronic balance. By using a Pasteur pipette, 0.80 mL of the pseudo-sunscreen solution was slowly added dropwise onto the PMMA plate without spilling the solution over the edge of the plate. Subsequently, it was left until the weight became constant upon the completion of evaporation of hexane. As the pseudo-sunscreen solution containing 1.0 mg of UV absorbers was added dropwise in all experiments and the area of all plates was 25 cm$^2$, the amount of UV absorbers solution per unit area was constant at 4.0 × 10$^{-3}$ mg cm$^{-2}$, whereas that of ASR was 1.60, 0.80, and 0 mg cm$^{-2}$ for 1, 2, and 3, respectively. The UV absorbance of the plate on which the pseudo-sunscreen sample was deposited was measured using an SPF analyzer (SPF-290S, Optometrics Corporation) in the range 290 to 400 nm. The diameter of the path of the beam was 16 mm, and the measurement was conducted at five points to calculate the average. The analyzer collected all the transmitted UV light into the integrating sphere to determine the net UV absorbance.

3 RESULTS and DISCUSSION

3.1 Roughness of the standard roughened PMMA plates

No significant difference was observed among the surface structure of HD6, ISO2, and ISO5 by SEM observation of their cross-section (Fig. 1), whereas SEM/EDS analysis of the plates on which ASR was deposited provided important information on the structural differences among each cosmetic standard PMMA UV evaluation plate. SEM and EDS mapping images of the cross-sections shown in Fig. 2 represent the case of ASR deposited on each cosmetic standard PMMA UV evaluation plate. The yellow part in the EDS mapping image is the region consisting of a high density of Si atoms. As no Si atom is incorporated in the PMMA molecules, the yellow part indicates the regions in which the ASR solution penetrated. The maximum depth of penetrating of ASR was observed to be larger than Ra for all plates. ISO2 and ISO5 had mainly simple roughness, whereas the cross-section of HD6 had relatively large isolated domains containing a high density of Si atoms apart from the surface. Thus, the Si atom ratio in O, C, and Si determined via the point analysis did not always asymptotically decrease from the surface, indicating the presence of many small cracks on the surface of HD6. For example, in the case shown in Fig. 3, the Si atom ratio at Point 3 was larger than that at Point 2. HD6 was manufactured by melting PMMA at 195-200°C for injection into the mold, and the molding and drying temperatures were 50-60°C and 2-4°C, respectively. As the coefficient of linear thermal expansion of PMMA is approximately 7 × 10$^{-5}$ K$^{-1}$, the volume shrinkage ratio during the cooling process after the injection can be calculated as 1-[(1-(7 × 10$^{-5}$ K$^{-1}$ × 195K)]$^3$ = 4.0%. This volume shrinkage of PMMA may lead to the generation of cracks on the surface.

The degree of penetrating of ASR into the hollows of HD6 was observed to depend on the amount of deposition. With increase in the amount of ASR, Si atoms contained in ASR were more likely to penetrate into the deeper part from the surface of the plate (Fig. 4). Near a relatively

![Fig. 1](image-url) SEM images of the cross section of cosmetic standard PMMA UV evaluation plates, HD6, ISO2, and ISO5.
large crack on the surface of HD6, a part of the surface that was scarcely covered with ASR was observed (Fig. 5). In this case, a large amount of ASR penetrated into the deeper part of the crack. If the volume at 200 µm from the surface of HD6 was shrunk by 4.0% to generate cracks, the total volume of the cracks per unit area became 0.80 mm³. It indicates that almost two-fifths of sunscreens penetrate into the cracks and are ineffective for UV protection when the sunscreen has a specific gravity of 1.0 and the amount of deposition is 2.0 mg cm⁻².
When the sample sunscreens are applied on these cosmetic standard PMMA UV evaluation plates, their surface roughness should make the sample sunscreen layer spatially inhomogeneous to influence the UV transmission. Thus, changing the volume of the sample should change the UV transmission, although the amount of UV absorbers in the sample is identical.

3.2 Influence of surface roughness on the UV transmission of the pseudo-sunscreen layer

All the cosmetic standard PMMA UV evaluation plates, HD6, ISO2, and ISO5, without the deposition of pseudo-sunscreen samples, exhibited a nonzero value of UV absorbance determined using an SPF analyzer when a flat quartz plate was used as a reference (Fig. 6). However, UV absorption by PMMA was scarce. In these cases, decline in UV intensity upon passing through the plates was mostly due to diffuse reflection at the roughened surface, which led to the nonzero "UV absorbance" value.

Although all the pseudo-sunscreen samples 1, 2, and 3 contained identical amounts of UV absorbers, their UV absorbance determined using the SPF analyzer was significantly different for all the cosmetic standard roughened PMMA evaluation plates (Fig. 7). Sample 3 did not contain ASR, and the UV absorbers were more likely to localize at the vicinity of the bottom of the hollows. Thus, the trans-
mitted UV intensity did not decrease at the rest of the part of the plate, and consequently, the net UV absorbance scarcely increased. On the other hand, samples 1 and 2 contained ASR, whose deposition fills the hollows of the roughened surface. Thus, the UV absorbers were more likely to extend on a relatively larger part of the roughened surface of the plate. The degree of spatial extension of the UV absorbers increased with increase in the amount of ASR. Sample 1, which contained the largest amount of ASR, exhibited the highest net UV absorbance among all the cosmetic standard roughened PMMA evaluation plates. Filling the hollows of the roughened surface by the sample containing ASR decreased the diffuse reflection. The value of "UV absorbance" at the wavelength at which the UV absorption by the UV absorbers was scarce thus became close to zero when sample 1 and 2 was deposited on all the cosmetic standard PMMA UV evaluation plate.

Each sample deposited on ISO2 exhibited a larger UV absorbance than that of a sample deposited on ISO5. In our previous studies, it was shown that the spatial inhomogeneity in the thickness of the pseudo-sunscreen layer reduces the UV absorbance. If a quasi-one-dimensional system having a coordinate x is considered, the thickness of the layer and the intensity of the transmitted UV light are the functions of the position, \( h(x) \) and \( I(x) \), respectively, and their relation is as follows

\[
I(x) = I_0 10^{-\frac{\alpha c h(x)}{\ln 10}}
\]

where \( I_0, \alpha, \) and \( c \) are the intensity of incident light, absorption coefficient, and concentration of the UV absorber, respectively. If the spatial inhomogeneity in the thickness of the layer is spatially periodic such as the viscous fingering pattern generated during the sample application, the net intensity of the transmitted UV light and the corresponding net absorbance, \( I \) and \( A \), respectively, are represented as functions of the characteristic length of the spatial periodicity, \( l \), as follows.

\[
I = \frac{I_0}{l} \int_0^l \int_0^l 10^{-\frac{\alpha c h(x)}{\ln 10}} \, dx
\]

\[
A = \log \frac{I_0}{I} = \log \left[ \frac{I_0}{l} \int_0^l \int_0^l 10^{-\frac{\alpha c h(x)}{\ln 10}} \, dx \right]
\]

Fig. 6 Value of UV absorbance of HD6, ISO2, and ISO5 without deposition pseudo-sunscreen measured by SPF analyzer using a flat quartz plate as a reference.

Fig. 7 Value of UV absorbance of HD6, ISO2, and ISO5 on which pseudo-sunscreen sample was deposited determined by SPF analyzer using a flat quartz plate as a reference. Amount of the UV absorbers solution per unit area was \( 4.0 \times 10^{-2} \) mg cm\(^{-2} \) for each measurement.
spatial inhomogeneity reduced the UV absorbance, and the UV absorbance of the layer depending on the spatial inhomogeneity determined experimentally was quantitatively reproduced by a mathematical simulation\textsuperscript{19,20}. However, in the present study, the pseudo-sunscreen layer deposited on the cosmetic standard PMMA UV evaluation plate does not possess a spatially periodic structure. Quantitative reproduction of the UV absorbance through mathematical simulation is impossible for such a random spatially inhomogeneous layer. Nevertheless, the qualitative tendency of the relation between spatial inhomogeneity and the UV absorbance still holds for a random spatially inhomogeneous layer. Thus the lower UV absorbance observed in the case of using ISO5 is considered to be due to its larger surface roughness, which enhances the spatial inhomogeneity of the deposited pseudo-sunscreen sample. Although cracks were observed on the surface of HD6, the UV absorbance of the sample deposited on HD6 was relatively high. If cracks are developed perpendicular to the surface, the UV absorbance should have a lower value. However, the real cracks have bent shapes to develop parallel to the surface. The pseudo-sunscreen sample penetrated into the cracks of HD6 thus becomes involved in UV absorption to some extent.

4 CONCLUSION

In this study, we have analyzed the surface structures of three cosmetic standard PMMA UV evaluation plates: Helioplates HD6 (Sa = 6 μm) and ISO plates (Ra = 2 and 5 μm), for the \textit{in vitro} evaluation of UV protection abilities used in the EU and US. As these plates have a roughened surface, their surface structures were analyzed by observing the penetrating behavior of ASR solution into their hollows of the surface using SEM-EDS. It was observed that the maximum depth of penetrating was larger than Ra for all the standard plates, and the surface structure was significantly different for each standard plate.

Clear-solution-type pseudo-sunscreen samples were prepared by dissolving UV absorbers and ASR in hexane. They were added dropwise onto the plates, and the UV absorbance of each plate was measured using an SPF analyzer after the completion of evaporation of the solvent. The amount of ASR in the pseudo-sunscreen samples drastically influenced the net UV transmission. The degree of filling of the hollows of the roughened surface with the pseudo-sunscreen samples determined the variation of UV transmittance.

The results of this study suggest the strong necessity for more strict regulation on the surface structure of cosmetic standard PMMA UV evaluation plates. If the surface roughness is carved on the surface of the plates in order to correlate the values of \textit{in vitro} UV protection abilities with the corresponding \textit{in vivo} value, the surface structure should be a precise mimic of human skin.

ACKNOWLEDGMENT

This work was supported in part by Cosmetology Research Grants from The Cosmetology Research Foundation and the fund from Keio Leading-edge Laboratory of Science and Technology.

References
1) Stokes, R.P.; Diffey, B.L. \textit{In vitro} assay of high-SPF sunscreens. \textit{J. Soc. Cosmet. Chem.} \textbf{48}, 289-295 (1997).
2) Diffey, B.L.; Tanner, P.R.; Matts, P.J.; Nash, J.F. \textit{In vitro} assessment of the broad-spectrum ultraviolet protection of sunscreen products. \textit{J. Am. Acad. Dermatol.} \textbf{43}, 1024-1035 (2000).
3) Gers-Barlag, H.; Klette, E.; Bimczok, R.; Springob, C.; Finkel, P.; Rudolph, T.; Gonzenbach, H.U.; Schneider, P.H.; Kockott, D.; Heinrich, U.; Tronnier, H.; Bernklau, R.; Johncock, W.; Langner, R.; Driller, H.J.; Westenfelder, H. \textit{In vitro} testing to assess the UVA protection performance of sun care products. \textit{Int. J. Cosmetic Sci.} \textbf{23}, 3-14 (2001).
4) Heinrich, U.; Tronnier, H.; Kockott, D.; Kuckuk, R.; Heise, H.M. Comparison of sun protection factors determined by an \textit{in vivo} and different \textit{in vitro} methodologies: a study with 58 different commercially available sunscreen products. \textit{Int. J. Cosmetic Sci.} \textbf{26}, 79-89 (2004).
5) Ferguson, J.; Brown, M.W.; Hubbard, A.W.; Shaw, M.I. Determination of sun protection factors. Correlation between \textit{in vivo} human studies and \textit{in vitro} skin cast method. \textit{Int. J. Cosmetic Sci.} \textbf{10}, 117-129 (1988).
6) Diffey, B.L.; Robson, J. A new substrate to measure sunscreen protection factors throughout the ultraviolet spectrum. \textit{J. Soc. Cosmet. Chem.} \textbf{40}, 127-133 (1989).
7) Kelley, K.A.; Laskar, P.A.; Ewing G.D.; Drongoole, S.H.; Lichtin, J.L.; Sakr, A.A. \textit{In vitro} sun protection factor evaluation of sunscreen products. \textit{J. Soc. Cosmet. Chem.} \textbf{44}, 139-151 (1993).
8) Soruce, S.R.; Hewitt, J.P. \textit{In vitro} SPF, methodology and correlation with \textit{in vivo} data. \textit{Eur. Cosmet.} \textbf{6}, 14-20 (1995).
9) International Standards Organization, Cosmetics -Sun protection test methods- Determination of sunscreen UVA photoprotection \textit{in vitro}. ISO 24443 (2012).
10) U. S. Food Drug Administration and (FDA), Sunscreen drug products for over-the-counter human uses; Final
rules and proposed rules. *Federal Register* **76**, 35623-35665 (2011).

11) Miksa, S.; Lutz, D.; Guy, C. Improvement of *in vitro* sunscreen testing inter-laboratories reproducibility by means of reference absorbance curve. *H&PC Today* **9** (2), 32-35 (2014).

12) Cariou, N.; Lutz, D. Sunscreen in-vitro SPF determination – Inter and intra comparison tests between several measurement instruments. *H&PC Today* **7**(3), 22-24 (2012).

13) Miksa, S.; Lutz, D.; Guy, C. New approach for a reliable *in vitro* sun protection factor method Part I: Principle and mathematical aspects. *Int. J. Cosmet. Sci.* **37**, 555-566 (2015).

14) Hakim, V.; Rabaud, M.; Thome, H.; Couder, Y. Directional growth in viscous fingering in *New Trends in Nonlinear Dynamics and Pattern-Forming Phenomena* (Coulet, P.; Huerre, P. ed.), Plenum Press, New York, p. 327 (1990).

15) Yamazaki, Y.; Toda, A. Dynamical-morphological property of adhesive tape in peeling. *J. Phys. Soc. Jpn.* **71**, 1618-1621 (2002).

16) Yamazaki, Y.; Toda, A. Stability of tunnel structure and relationship between peel load and spatiotemporal pattern by deformed adhesive during peeling. *J. Phys. Soc. Jpn.* **73**, 2342-2346 (2004).

17) Kuroda, A.; Ishihara, T.; Takeshige, H.; Asakura, K. Fabrication of spatially periodic double roughness structures by directional viscous fingering and spinodal dewetting for water-repellent surfaces. *J. Phys. Chem. B* **112**, 1163-1169 (2008).

18) Joly, P.; Kuroda, A.; Asakura, K. Preparation of highly water-repellent surface by spontaneous formation of double scale roughness pattern. *J. Oleo Sci.* **59**, 89-94 (2010).

19) Fujikake, K.; Tago, S.; Plasson, R.; Nakazawa, R.; Okano, K.; Maezawa, D.; Mukawa, T.; Kuroda, A.; Asakura, K. Problems on *in vitro* SPF measurements brought by viscous fingering generated during sunscreens applications. *Skin Pharmacol. Physiol.* **27**, 254-262 (2014).

20) Wakabayashi, M.; Okano, K.; Mukawa, T.; Maezawa, D.; Masaki, H.; Kuroda, A.; Asakura, K. Problems on the evaluation of the critical wavelength of sunscreens for “Broad Spectrum” approval brought by viscous fingering during sunscreen application. *Photochem. Photobiol.* **92**, 637-643 (2016).

21) Ferrero, L.; Pissavini, M.; Dehais, A.; Marguerie, S.; Zastrow, L. Importance of substrate roughness for *in vitro* sun protection assessment. *IFSCC Magazine* **9** (2), 1-13 (2006).

22) Fageon, L.; Moyal, D.; Coutet, J.; Can-dau, D. Importance of sunscreen product spreading protocol and substrate roughness for *in vitro* sun protection factor assessment. *Int. J. Cosmetic Sci.* **31**, 405-417 (2009).

23) Higaki, Y. *Jpn. Pat.*, S57-99332 (1982).

24) Hydroxyl value (Pyridine-acetic anhydride method). *Standard Methods for the Analysis of Fats, Oils and Related Materials 2nd English Edition* (Japan Oil Chem. Soc. ed.), 2.3.6.2-2013 (2013).

25) Sato, N. *US Pat.*, 8198335 B2 (2012).

26) Endo, M.; Mukawa, T.; Sato, N.; Maezawa, D.; Ohtsu, Y.; Kuroda, A.; Wakabayashi, M.; Asakura, K. Coexistence effect of UVA absorbers to increase their solubility and stability of supersaturation. *Int. J. Cosmetic Sci.* **36**, 546-552 (2014).

27) Helio Screen labs, HELIOPLEATE HD Guide (2008).

28) Timoshenko, S.P.; Young, D.H. *Elements of Strength of Materials*. 5th ed. D. Van Nostrand Co., Inc, Princeton (1968).

29) Sherman, S.; Zappe, H. Printable Bragg gratings for polymer-based temperature sensors. *Proc. Tech.* **15**, 702-709 (2014).