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Published in: Skin Research and Technology

Link to article, DOI: 10.1111/srt.13115

Publication date: 2022

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

Keshavarzi, F., Knudsen, N. Ø., Komjani, N. M., Ebbesen, M. F., Brewer, J. R., Jafarzadeh, S., & Thormann, E. (2022). Enhancing the sweat resistance of sunscreens. *Skin Research and Technology*, *28*(2), Article 225-235. https://doi.org/10.1111/srt.13115

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DOI: 10.1111/srt.13115

ORIGINAL ARTICLE



Enhancing the sweat resistance of sunscreens

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Funding information Innovation Fund Denmark, Grant/Award Number: #6151-00007B

Abstract

Background: While sunbathing of performing outdoor sport activities, sunscreens are important for protection of uncovered skin against ultraviolet (UV) radiation. However, perspiration negatively affects the performance of a sunscreen film by weakening its substantivity and uniformity through the activation of two mechanisms, namely sunscreen wash-off and sunscreen redistribution.

Material and methods: We used a perspiring skin simulator to investigate the effect of sunscreen formulation on its efficiency upon sweating. Specifically, we modified the sunscreen formulation by incorporating a hydrophobic film former and adding waterabsorbing particles. Sunscreen performance before and after perspiration is assessed by in vitro sun protection factor measurements, direct detection of changes in the sunscreen distribution using UV reflectance imaging, and by coherent anti-Stokes Raman scattering (CARS) microscopy for microscopic characterization of the UV filter relocation.

Results: The results show that incorporating a hydrophobic film former can decrease sunscreen wash-off due to sweating, while an excessive amount of film former might negatively affect the sunscreen distribution. The addition of water-absorbing particles, on the other hand, had either a negative or positive impact on the sunscreen substantivity, depending on the particle properties. While the addition of large waterabsorbing particles appeared to increase sunscreen redistribution, smaller particles that could form a gel-like structure upon contact with water, appeared to change sunscreen wetting and sweat droplet spreading, thereby decreasing sunscreen wash-off and sunscreen redistribution.

Conclusions: We find that using a combination of hydrophobic film formers, which increase water resistance, and small water-absorbing particles, which change the wetting behavior, can make sunscreen formulations more sweat-resistant and less runny.

KEYWORDS

film former, gelatin, perspiring skin simulator, sunscreen, sweat resistance, water-absorbing particles

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1 | INTRODUCTION

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Overexposure to ultraviolet (UV) radiation from the sun can cause serious damage to the skin, such as sunburn, skin pigmentation, and DNA damage, which eventually increases the risk of skin cancer.^{1–3} One of the well-known methods of avoiding the harmful effects of UV radiation is the application of sunscreen on the exposed skin. An effective sunscreen should form a continuous and uniform film that covers the skin to provide UV protection by mainly absorbing but also reflecting and scattering the light over the broad UV spectrum.⁴ A sunscreen should naturally also be nontoxic, photostable, and durable and have good spreadability and sensorial properties.^{4,5}

Different factors and activities such as friction from toweling and wearing clothes, water exposure due to swimming or the influence of sweating can affect sunscreen performance after application on the skin.⁶⁻¹² However, despite the fact that sweating is highly probable in many situations where sunscreen is used, such as during outdoor sports activities, and sunbathing, the effect of sweating on the substantivity of sunscreens is rarely directly addressed. Our previous study, which involved an in vitro perspiring skin simulator, showed that the water released from the skin underneath the applied sunscreen film will have a distinct negative impact on the efficiency of the sunscreen.¹³ Specificator (SPF) by two mechanisms: (1) direct sunscreen wash-off, which leads to reduced film thickness and (2) redistribution of the sunscreen, which results in less uniformity. Both mechanisms negatively affect sunscreen substantivity and result in lower UV protection.

While the direct effects of sweating are widely neglected, the ability of a sunscreen to maintain high efficiency upon exposure to water (during swimming and bathing) is one of its documented and wellknown properties.^{14–16} Generally, water exposure can lead to wash out of UV filters and breaking down of sunscreen films, resulting in a reduction of UV protection.^{8,11,17-25} However, retention of the sunscreen upon exposure to water naturally depends on the type of sunscreen and its ingredients.^{4,16,23,26} Enhancing the sunscreen-skin adhesion (i.e., bonding between the sunscreen and the uppermost layer of the skin) or increasing the hydrophobicity of the formulation in order to repel water is known methods of improving the water resistance of a sunscreen.^{26,27} However, it is not well-known whether the same approach can be used to maintain high sunscreen efficiency upon perspiration, where sweat is released from the skin underneath the sunscreen affecting the sunscreen-skin adhesion and where the water cannot just be repelled by a hydrophobic sunscreen formulation.

In the current study, we used our perspiring skin simulator to investigate how certain ingredients in an ethanol-based sunscreen formulation may affect its ability to offer high UV protection after sweating. As a first approach, we added different concentrations of a hydrophobic film former, typically used to induce high water resistance, to study the effect of this parameter on the efficiency of the sunscreen upon perspiration. Second, we added a low concentration of a number of selected water-absorbing polymeric microparticles to determine whether a localization of the water by these particles can reduce the wash-off and redistribution of the sunscreen. For both cases, the efficiency of the



FIGURE 1 Schematic illustration of the perspiring skin simulator setup and a picture of the skin-mimicking substrate during perspiration

sunscreen formulations was evaluated by in vitro SPF measurements, direct detection of the UV filters distribution (UV reflectance imaging), and coherent anti-Stokes Raman scattering (CARS) microscopy for real-time observation of UV filter relocation on a microscopic scale.

2 | MATERIALS AND METHODS

2.1 | Materials

To prepare the sunscreen formulations, the UV filters diethylamino hydroxybenzoyl hexyl benzoate (Uvinul A Plus from BASF), ethylhexyl salicylate (Parsol EHS from DSM Nutritional Products Europe Ltd), and octocrylene (Uvinul N 539 T from BASF) were used. The oils in the formulations were a combination of phenoxyethyl caprylate from Evonik Nutrition & Care GmbH, C15-19 alkane from SEPPIC, ethylcellulose from Ashland, dibutyl adipate from BASF, and lastly a hydrophobic film former acrylate/octylacrylamide copolymer from Nouryon Surface Chemistry LLC was incorporated. Four water-absorbing polymer particles, polyacrylate crosspolymer-6 (PAC-6 from SEPPIC), crosslinked sodium polyacrylate (NaPA from Stewart Superabsorbents LLC), hydrophobically modified (cetyl) hydroxyethylcellulose (HMHEC from Ashland), and a core-shell particle (Core-Shell from Momentive Performance Materials Inc.) with a shell of polysilicone-34 and a core of isononyl isononanoate and water, were used as additives in the sunscreen formulation.

2.2 Perspiring skin simulator

In this study, we used a perspiring skin simulator, which is described in detail elsewhere.¹³ Briefly, the setup comprises a multilayer skinmimicking substrate, a chamber located underneath the substrate, a syringe pump, and connecting tubes, as illustrated in Figure 1. The

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TABLE 1 Overview of the used sunscreen formulations

Sunscreen	Evaluation
Basic sunscreen prepared with different concentration of film former (0%, 0.75%, 3%)	In vitro SPF and visualization by UV reflectance imaging on the perspiring skin simulator
Basic sunscreen prepared with 0.75% film former and different particles (no particles, NaPA, PAC-6, HMHEC, and Core-Shell)	In vitro SPF and visualization by UV reflectance imaging on the perspiring skin simulator
Model sunscreen – only containing one UV filter (20% octocrylene) with 0% and 1% PAC-6 particles	Visualization by CARS microscopy on the perspiring skin simulator

Abbreviations: CARS, coherent anti-Stokes Raman scattering; PAC-6, polyacrylate crosspolymer-6; SPF, sun protection factor; UV, ultraviolet.

skin-mimicking substrate consists of a gelatin-based skin layer (gelatin, glycerol, and formaldehyde), with a thickness of 250 μ m and a surface roughness of 100–200 nm.¹³ The gelatin-based film was applied to a polymethylmethacrylate (PMMA) (Plexiglas Film 0F058, thickness: 200 μ m, provided by Evonik [Germany]) by the aid of a casting knife film applicator (Elcometer 3580/4, Elcometer Ltd., UK). The backside of the PMMA substrate was then stacked with a low UV adsorbing double-sided acrylic adhesive (Tesa 4900, thickness: 50 μ m, Tesa [Germany]), and the three-layered structure (gelatin, PMMA substrate, and double-sided adhesive) was then laser-drilled to make funnel-like holes to mimic sweat pores. The holes had a pore size of 110–120 μ m on the gelatin side and 40–60 μ m on the adhesive side and a hole density of 200 cm^{-2} , which is similar to the density of sweat pores in the human skin.²⁸ Finally, the other side of the double-sided adhesive was attached to a track-etched hydrophilic membrane (PCT0220030, pore size: 0.2 μ m, pore density: 3 \times 10⁸ cm⁻², thickness: 10 μ m, obtained from Sterlitech [USA]) responsible for controlling the pressure drop and then providing a uniform flow through the sweat pores. To perform a perspiration experiment, the skin-mimicking substrate was mounted and fixed on the chamber (see Figure 1), and deionized water was pumped at a rate of 1.5 μ l min⁻¹ cm⁻² (corresponding to moderate sweating on the untreated human forehead).²⁸ To this end, it should be noted that pure water was used as the sweat mimicking liquid, since large amount of salt in the liquid significantly challenges post-sweating studies of sunscreen performance due to the scattering of light from salt crystals.

2.3 Sunscreen formulations

Basic sunscreen formulations were prepared as one phase ethanolbased solutions by dissolving the ingredients in ethanol using a homogenizer (Silverson L5T, Silverson Machines Ltd., England). Based on the UV filter composition (30% wt.), an SPF of 28 was calculated using a sunscreen simulator software (BASF).²⁹ To evaluate the effect of the concentration of the film former, three formulations containing 0, 0.75, and 3% wt. of the acrylic-based film former were prepared. To investigate the effect of water-absorbing particles, the concentration of the film former was kept constant at 0.75% wt., and four formulations containing 1% wt. water-absorbing particles were prepared. For the purpose of CARS microscopy, two model sunscreens with 0 and 1% wt. water absorbing PAC-6 particles were prepared. These formulations contained the same vehicle as the basic sunscreen formulation, but the number of UV filters was reduced to one, which was added in high concentration (20% octocrylene). This simplification of the formulation was done in order to get better contrast using CARS microscopy and to avoid overlap between spectroscopic peaks from multiple filters. An overview of the different formulations is provided in Table 1.

2.4 | In vitro SPF measurements

The efficiencies of the sunscreens in protecting against UV radiation were measured using a UV transmittance analyzer (Labsphere UV-2000S, Labsphere Inc., North Sutton, NH, USA) and were subsequently converted to in vitro SPF values using the formula below:

$$SPF = \frac{\sum_{290}^{400} E(\lambda) S(\lambda)}{\sum_{290}^{400} E(\lambda) S(\lambda) T(\lambda)}$$
(1)

where $E(\lambda)$ is the erythema action spectrum, $S(\lambda)$ is the spectral irradiance of the UV source, and $T(\lambda)$ is the measured transmittance of the light through a sunscreen film applied on a UV-transparent substrate. In this study, $T(\lambda)$ was recorded through the bare skin-mimicking substrate placed on a molded PMMA plate (Helioplates HD2; Helioscreen, Creil, France) as the reference for SPF measurements. A quantity of 0.6 mg cm⁻² of sunscreen was applied on the skin-mimicking substrate using a pipette and was subsequently spread by light circular strokes over the whole surface with a latex finger cot, pre-saturated with the sunscreen. The sample was then kept in a dark place at room temperature for 15 min to self-level and dry before the initial SPF measurement. The final SPF value was measured after the perspiring procedure.

2.5 | Procedure for perspiration studies

The skin-mimicking substrate was placed on an HD2 plate to record the blank $T(\lambda)$ spectrum using the UV transmittance analyzer. The sunscreen was then applied on the skin-mimicking substrate, and after drying for 15 min, the initial SPF was measured. Afterward, the sunscreentreated skin-mimicking substrate was mounted on the chamber, and the perspiration was started at a rate of 1.5 μ l min⁻¹ cm⁻² continuing for 30 min using a syringe pump. Once the perspiration was stopped, the chamber was drained, the excess amount of water on

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FIGURE 2 Schematic illustration of skin-mimicking substrate in which only the upper side is able to sweat. (A) Untreated substrate, and (B-D) Substrate with applied sunscreen on the upper side: (B) before onset of perspiration, (C) during perspiration, and (D) after drying. The chamber is kept in a vertical position during perspiration and drying, enabling sweat to flow from the sunscreen-treated area to the untreated area

the substrate surface was off-loaded, and the sample was allowed to dry for 30 min. Subsequently, the skin substrate was removed from the chamber, and post-perspiration in vitro SPF was measured. For each sunscreen formulation, we have applied the sunscreen on five newly prepared artificial skin models. The size of each of these samples further allowed for in vitro SPF measurements on nine different spots (see Supporting Information, Figure S1). Thus for each sunscreen formulation, we have performed two sets of 45 SPF measurements (45 measurement before and after running the sweating experiments, respectively) distributed in nine different locations on five individual samples.

In order to help understanding the active mechanisms that underlie sunscreen failure during perspiration, we prepared skin-mimicking substrates in which only half of the surface (semi-circle area) contained sweat pores, and the other half was the plain gelatin-based skin-like layer. Sunscreen was applied solely on the area with sweat pores. After mounting the substrate on the chamber, perspiration started and continued for 20 min while the chamber was kept in a vertical position with the sunscreen treated area on the upper side. The distribution of UV filters was monitored before the onset of perspiration, immediately after stopping the perspiration, and after 20 min and 2 h of drying, using UV reflectance imaging. Figure 2 shows a schematic view of the skinmimicking substrate on the vertical chamber at different stages of the experiment.

2.6 UV reflectance imaging

During perspiration, the chamber was placed in a box in which an area scan camera (acA4024-29um, Basler AG, Germany) equipped with a UV band-pass filter (365 nm, F/BP365-CMOUNT) and a high-resolution lens (Fujinon HF-1218-12 M, Fujifilm, Japan) was fixed perpendicular to the sweat chamber. The box was also equipped with light-emitting diode UV lamps emitting UVA radiation to provide suitable light to allow the camera to detect the changes in the sunscreen distribution (with UV absorption at wavelength 365 nm corresponding to the UVA filters) during perspiration.

2.7 | CARS microscopy

CARS spectra of the ingredients used in the simplified sunscreen formulations (containing only one UV filter, octocrylene, without and with 1% wt. of PAC-6 particles) and the skin-mimicking substrate were obtained in order to identify a unique vibration peak for CARS imaging (TCS SP8 CARS microscope, Leica Microsystems, Germany). The pump laser (PicoEmerald, APE, Germany) wavelength was varied from 787 to 877 nm with 1-nm increments (wavenumbers ranged from 3313 to 2009 cm⁻¹) with a Stokes laser fixed at 1064 nm. A distinct peak at wavenumber 2210 cm⁻¹, attributed to the nitrile group in the UV filter, octocrylene, did not overlap with the peaks of the other ingredients, PAC-6 particles, and the skin-mimicking substrate. Thus, it could be used as a unique peak to provide good chemical contrast between the active component of the sunscreen and the skin-mimicking substrate (see Supporting Information, Figure S2).¹³ By further obtaining images at different cross-sections, 3D-images with a z-resolution of approximately 10 μ m were obtained. For real-time monitoring of the sunscreen/sweat interaction and redistribution of the octocrylene UV filters, the sunscreen was applied at a quantity of 2 mg cm⁻². After selfleveling and drying of the sunscreen, the substrate was mounted on the sweat chamber. The chamber was then placed upside down on the sample stage of the CARS microscope, and perspiration was initiated. The field of view for the images was $1550 \times 1550 \,\mu\text{m}^2$ with a pixel size of $3.033 \times 3.033 \,\mu\text{m}^2$, and the images were acquired at 2210 cm⁻¹ (pump laser: 861.8 nm).

3 | RESULTS AND DISCUSSION

As previously demonstrated, perspiration can affect the ability of sunscreen films to provide protection from UV through different mechanisms (sunscreen wash-off or sunscreen redistribution), which lead to SPF reduction.¹³ Here, we have investigated how these mechanisms could possibly be altered, first by changing the concentration of the hydrophobic film forming polymer in the formulation and second by introducing water-absorbing particles into the formulation.



FIGURE 3 In vitro SPF measurements for sunscreen formulations with different film former concentrations. (A) Individually measured in vitro SPF values measured on given positions after sweating versus initial SPF values measured on the exact same positions. The data for each formulation are obtained on five individual artificial skin samples and for nine positions on each sample. The dashed lines represent the location of the SPF values if there is no difference before and after sweating. (B) Statistical representation of the difference in measured SPF values before and after sweating. The colored area represents the interquartile range (IQR) showing the middle 50% of the data (25%-75%). The middle line represents the median, and the small white dot is the mean value. The mean value for each set of experiments is also shown. The upper and lower lines represent the maximum and minimum SPF change excluding the outliers. The dots outside the colored region indicate the outliers

3.1 | Effect of hydrophobic film former concentration

The film former assists the uniform distribution of UV filters on the skin and increases the film integrity during contact with water.³⁰⁻³² Different categories of film formers are used in sunscreen formulations, including water-repellent or water-dispersible materials.^{32,33} We selected an acrylic-based film former with hydrophobic properties and prepared three formulations containing 0%, 0.75%, and 3% of this

film forming polymer. These three formulations were tested on the perspiring skin simulator to assess the effect of the hydrophobic film former and its concentration on the sunscreen substantivity during perspiration.

Figure 3A, B outlines the results obtained from in vitro SPF measurements before and after sweating as described in Section 2.5. Here, it is seen that the SPF reduction for the sunscreens containing 0% and 3% of the film former was higher than that of the sunscreen with 0.75% film former (58% \pm 26% and 69% \pm 19%, respectively, compared to



FIGURE 4 Ultraviolet (UV) reflectance images of the skin-mimicking substrates. The images show how sunscreens with different concentrations of hydrophobic film formers are washed off and redistributed during perspiration. (A) After sunscreen application on the area with sweat pores, (B) after sweating for 20 min, (C) 20 min after the sweating was stopped, and (D) after complete drying of the samples

42% ± 24% SPF reduction). The results illustrate that the hydrophobic film former enhances the sunscreen substantivity, probably by bonding effectively to the substrate, entrapping the UV filters in the film former network, and repelling the water.^{31,32} However, increasing the concentration of the film former up to 3% did not amplify the aforementioned characteristics and, in contrast, resulted in a higher SPF reduction compared to the other two sunscreens. The exact reason for this observation is unknown. However, we noticed that adding 3% hydrophobic film former led to an ~70% increase in the viscosity of the sunscreen formulation, and the change in performance could simply be due to a reduced spreadability and self-leveling and thus give rise to a different initial film structure.

UV reflectance imaging was now used in an attempt to distinguish how the two SPF reducing mechanisms (sunscreen wash-off and sunscreen redistribution) are affected by altering the concentration of the film former, a skin-mimicking substrate with only artificial sweat pores on half of its area was used. Here, the sunscreens were applied only on the area with the sweat pores, and perspiration was started and continued for 20 min while the chamber was kept in a vertical position, with the treated area on the upper side (the schematic view is shown in Figure 2. and the treated substrates are shown in Figure 4A). Figure 4B,C shows the substrates 20 min after perspiration was started and 20 min after the perspiration was stopped, respectively. Figure 4D shows the completely dried samples (approximately 2 h after perspiration was stopped). Prior to the discussion of the individual cases, we will first provide a general interpretation for the observations in these experiments. Before the sweating experiment is started, the area covered with sunscreen appears black and rather homogenous, which suggests that the UV filters are evenly distributed after application of the sunscreens. However, when the sweating experiment is initiated two things occur. Firstly, UV filters (i.e., sunscreen) are running vertically

down to the part of the skin substrate, which is not originally covered with sunscreen, which is seen as black lines in column B-D in Figure 4. This is the phenomenon which we refer to as sunscreen wash-off. Secondly, after the sweating experiment is ended, the originally homogenously sunscreen covered part of the artificial skin surface no longer has an evenly black color. Instead, this region is demonstrating areas with an inhomogeneous UV filter distribution, which we interpret as a (negatively) redistribution of the UV filters due to first expansion of sweat droplets and secondly to running sweat. This is the phenomenon which we refer to as sunscreen redistribution.

Next, we will now discuss the specific cases with sunscreen formulations containing 0%, 0.75%, and 3% film former, respectively. For the sunscreen with 0% film former, a drastic redistribution of UV filters and massive wash-off occur during perspiration. Here, we speculate that the film former acts as a network that holds the sunscreen film together, and in its absence, the water released underneath the film could significantly disturb the UV filter distribution. For the sunscreen with 0.75% film former, sunscreen wash-off and redistribution of UV filters are still visible, while increasing the film former concentration up to 3% appears to effectively prevented sunscreen wash-off. However, while the effect film former on the sunscreen wash-off phenomenon is rather obvious from Figure 4, the relative effects on the sunscreen redistribution is more difficult to rank based on the UV reflectance images alone. However, from the in vitro SPF measurements, the formulation containing 0.75% hydrophobic film former was observed to provide a higher protection after sweating compared to the protection of the formulation containing 3% hydrophobic film former. We interpret this as if a higher degree of redistribution mostly has occurred for the formulation containing 3% film former. This further suggests that sunscreen redistribution has a more pronounced effect on SPF than sunscreen wash-off. We note, however, that in addition to SPF changes,

running sunscreen might create other types of discomfort such as eye irritation or staining on clothes, and a higher amount of hydrophobic film former seems to be able to prevent such events.

3.2 | Effect of water-absorbing particles

In the next experiment, where the effects of introducing waterabsorbing particles into the formulation were studied, we fixed the concentration of the film former at an intermediate level (0.75%) and added 1% of the water-absorbing particles. The selected particles possess different characteristics in terms of chemistry, particle size, polydispersity, water-absorbing kinetics, and water uptake capacity. Here, we will focus mainly on the particle size and water uptake capacity. NaPA and PAC-6 are both superabsorbent particles with water uptake capacities >300 g/g, whereas HMHEC and Core-Shell possess more moderate water uptake capacities of ~20-30 g/g. With respect to size, NaPA and HMHEC are relatively large particles with diameters of approximately 10–40 and 30–180 μ m, respectively, which means that NaPA and HMHEC particles will act as large water-absorbing domains in the sunscreen film. On the contrary, PAC-6 and Core-Shell particles are smaller with diameters of approximately $1-10 \mu$ m. This means that PAC-6 and the Core-Shell particles will be embedded in the sunscreen film and that for the same weight fraction, the particles will be more homogenously distributed laterally in the sunscreen film compared to the larger particles. The Core-Shell particles, which is a translucent microgel particle comprising a water-absorbing polyacrylic core covered by a protective silicone copolymer shell, has a special feature that allows it to scatter UV light and is thus boosting the SPF when included in a sunscreen formulation (see Supporting Information, Table S1). However, upon exposure to water, the polyacrylate core will moderately swell and thus change the particle shape, leading to an expected alteration in its ability to scatter UV light. Thus, adding the Core-Shell particles to our sunscreen formulation will, therefore, enable us to explore an additional effect of perspiration on sunscreen efficiency, which is different from the two previously documented effects (sunscreen wash-off and sunscreen redistribution).

Figure 5A presents the in vitro SPF values measured after perspiration versus the initial SPF values for the sunscreens with and without 1% of the water-absorbing particles, and Figure 5B shows the associated average SPF values measured before and after perspiration. For the sunscreen formulation without water-absorbing particles, the average SPF reduction was 42% \pm 24%. For sunscreen formulations containing NaPA and HMHEC particles (the larger particles), the average SPF reductions were 49% \pm 19% and 61% \pm 21%, respectively, which means that the addition of these particles has either a negative or no impact on the sweat resistance of the sunscreen film. However, for the sunscreen formulation containing PAC-6 particles, the SPF reduction was only $13\% \pm 20\%$, indicating that these particles successfully increased the sweat resistance of the sunscreen. For the sunscreen formulation containing the Core-Shell particle, the initial SPF was as expected boosted to a considerably higher value than for the other formulations; however, after perspiration, the SPF was reduced



FIGURE 5 In vitro sun protection factor (SPF) measurements for sunscreen formulations with and without water-absorbing additives before and after sweating. (A) Individually measured in vitro SPF values measured on given positions after sweating versus initial SPF values measured on the exact same positions. The data for each formulation are obtained on five individual artificial skin samples and for nine positions on each sample. The dashed lines represent the location of the SPF values if there is no difference before and after sweating. (B) Statistical representation of the difference in measured SPF values before and after sweating. The colored area represents the interquartile range (IQR) showing the middle 50% of the data (25%-75%). The middle line represents the median, and the small white dot is the mean value. The mean value for each set of experiments is also shown. The upper and lower lines represent the maximum and minimum SPF change excluding the outliers. The dots outside the colored region indicate the outliers



FIGURE 6 Ultraviolet (UV) reflectance images of the skin-mimicking substrates. The images show how sunscreens with and without water-absorbing particles are washed off and redistributed during perspiration. (A) After sunscreen application on the area with sweat pores, (B) after sweating for 20 min, (C) 20 min after the sweating was stopped, and (D) after complete drying of the samples

drastically to a value that was similar to the post-perspiration values observed for the other sunscreen formulations. This clearly shows that the Core-Shell particles do not recover their SPF boosting ability after the water evaporates, indicating an irreversible change in their shape. However, based on these results alone, it is difficult to identify any connection between the influence of the Core-Shell particles and the sunscreen substantivity.

We again also performed UV reflectance imaging on substrate with sweat pores on half of its surface area in order to investigate the effect of the water-absorbing particles on the two different mechanisms for SPF reduction. For the sunscreen without water-absorbing particles, moderate redistribution and considerable wash-off were observed. For the sunscreen formulations containing the large particles (NaPA and HMHEC), a significant sunscreen redistribution was observed. The sunscreen containing NaPA was also extensively washed off. These observations are in agreement with the negative impact of these particles on sweat resistance, which was observed through the SPF measurements. Here, we suggest that the significant redistribution is related to the large size and swelling of these particles. When water is absorbed by NaPA particles, their volumes increase significantly, and we speculate that they start moving within the sunscreen film whereby they could push the sunscreen aside or disturb its uniformity. Simultaneously, NaPA particles become so heavy that, as a result of gravity, these water-rich particles are likely pulled downward, dragging the sunscreen along. This phenomenon is referred to as sunscreen washoff. In sunscreens containing HMHEC, the water-rich particles move within the sunscreen film, leading to a redistribution of UV filters. However, owing to their low water-absorbing capacity, the particles appear to be less affected by gravity.

For sunscreen formulations containing smaller particles (PAC-6 and Core-Shell), we observed very limited sunscreen wash-off, and for the formulation containing PAC-6 particles, a minor sunscreen redistribution was also observed. For the formulation containing PAC-6 particles, this observation is in agreement with the relatively low SPF reduction. For the formulation containing Core-Shell particles, our observation confirms that the large reduction in SPF is rather a consequence of the lost SPF boosting effect than a disturbed sunscreen film. However, Figure 6D, which shows a sunscreen containing the Core-Shell particles, illustrates that a UV filter redistribution could occur as a result of particle expansion. A provisional conclusion based on the size of water-absorbing particles is that small water-absorbing particles appear to better prevent sunscreen wash-off compared to larger particles, while the actual water uptake capacity seems to play a less significant role. Moreover, the water responsive behavior of large





FIGURE 7 $1.5 \times 1.5 \,\mu\text{m}^2$ coherent anti-Stokes Raman scattering (CARS) images showing the growth and merging of sweat droplets on the sunscreen-treated skin-mimicking substrate. (A) Sunscreen formulation with no water-absorbing particles. The z-axis here shows an elevation up to 250 μ m. (B) Sunscreen formulation with 1% wt. PAC-6 particles. The z-axis here shows an elevation up to 100 μ m

particles, that is, the significant increase in the volume and the movement of these particles, could negatively affect the distribution of the sunscreen.

Even though both PAC-6 and NaPA particles have high water uptake capacity (which, according to our expectation, would result in the ability to localize the sweat droplets), only PAC-6 seems to increase the substantivity of the sunscreen formulation. Based on the water responsive behavior of these two particles and their corresponding sunscreens, observed using an optical microscope (see Supporting Information, Figure S3), PAC-6 particles appear to form a gel-like structure when exposed to water, which seems to strengthen the integrity of the sunscreen film and prevent or delay the movement of UV filters by localizing water. On the other hand, when the large NaPA particles absorb water, they expand and move toward neighboring particles but do not merge to form a network. As seen in Figure 6, the massive expansion of the NaPA particles, however, disturbed the sunscreen

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distribution and intensified the sunscreen wash-off. Moreover, when the sweating was stopped and the drying process started, we observed that the NaPA particles moved toward each other to form small clusters, which affected the distribution of UV filters inside the sunscreen formulation (see Supporting Information, Figure S4). In contrast, PAC-6 particles seem to maintain the network structure upon evaporation of the sweat.

3.3 | CARS microscopy

CARS microscopy was employed for label-free three-dimensional visualization of the local relocation of UV filters upon perspiration. Since incorporation of PAC-6 particles enhanced the sweat resistance of the sunscreen, we prepared model sunscreens (containing only one UV filter, i.e., octocrylene, see Section 2.3) without and with 1% of PAC-6 particles. Like for the UV reflectance images in Figures 4 and 6, the UV filters (in this case only octocrylene) provide the contrast in the CARS images in Figure 7. Here, the red color corresponds to an area with high concentration of octocrylene while the black color corresponds to an area with no or a little amount of octocrylene, and in the time resolved experiments, we observe systematic changes in the color distribution as sweating occur. For example, we are during a sweating experiment visually observe growing droplets of artificial sweat while we simultaneously in the CARS images see corresponding growing black areas surrounded by an intense red color. We generally interpret such an observation as if the growing sweat droplets are depleting octocrylene from the skin interface with a resulting concentration of octocrylene at the three-phase-line between sweat, air, and the sunscreen/skin interface. Figure 7A shows the CARS images of the growth of sweat droplets on the skin-mimicking substrate treated with sunscreen with no water-absorbing particles. Here, it is observed how the sweat droplet expands in all directions, and the sunscreen film surrounding the droplet thins out in the z-direction. Thus, the sweat droplets on the substrate surface push the sunscreen film around it away in the direction of the sweat droplet expansion. Consequently, when two water droplets move toward each other (as seen in Figure 7A), the concentration of UV filters on their common border increases transiently (Figure 7A, t = 289 s). In contrast, the CARS images of the sunscreen containing 1% of PAC-6 particles show a different droplet/sunscreen interactions. As discussed in relation to Figure 6, we know that the water-absorbing PAC-6 particles have an ability to absorb the water flowing through the sweat pore in order to form a gel-like structure (see also Supporting Information Figures S3 and S4). As seen in Figure 7B, this leads to some changes the sweat droplet shape. More specifically the droplet appears to have a more flat (or less semi-spherical) shape as compared to sweat droplets formed on the substrate treated with the sunscreen without PAC-6 particles (Figure 7B, and also see Supporting Information, Figure S5). We believe that this is because the gel-like structure strengthens the sunscreen film integrity and slows down the expansion of the sweat droplet in the z-direction and that this reduces the risk of sunscreen film rupture. Additionally, the process by which two neighboring droplets merge is also different for sunscreens

containing PAC-6 particles. Here, the concentrated ring of UV filters surrounding the expanding droplets is less pronounced, and when the droplets encounter each other, it seems like that the formation of the gel-like network structure can limit the UV filters redistribution.

4 CONCLUSION

The retention of sunscreen performance upon perspiration depends extensively on the ingredients used in the formulation. In this study, we evaluated the sweat resistance of sunscreens by changing the concentration of a hydrophobic film former and by introducing waterabsorbing particles. A perspiring skin simulator and three characterization techniques were employed to investigate the potential mechanisms that underlie the failure of sunscreens upon perspiration. The results illustrated that the presence of a hydrophobic film former enhances the sweat resistance of sunscreens by reducing sunscreen wash-off for formulations with high film former concentrations and reducing sunscreen redistribution for formulations with intermediate film former concentrations. This means that a sunscreen formulation applied on sweating skin can potentially provide better protection against UV light and be less runny. Therefore, it becomes more user-friendly when a hydrophobic film former is incorporated. The introduction of water-absorbing particles into sunscreen formulations was shown to have either a positive or negative impact on the sunscreen substantivity upon perspiration, depending on the properties of the particles. Generally, small particles with the ability to change the overall sunscreen wettability and to form a gel-like network appear to protect sunscreen integrity, while larger particles which are localizing large amounts of water upon swelling are leading to significant sunscreen redistribution and a decrease in SPF. Finally, as observed for Core-Shell particles, perspiration can have other formulation-specific effects on the UV-protecting performance of a sunscreen. Overall, a combination of hydrophobic film formers to increase water resistance and small water-absorbing particles to change the wetting behavior appears to be a promising approach for the development of more sweat-resistant sunscreens.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Innovation Fund Denmark through the Grand Solutions Project #6151-00007B. We also thank the Danish Molecular Biomedical Imaging Center (DaMBIC, University of Southern Denmark) for allowing us to use their CARS microscope.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

How to cite this article: Keshavarzi F, Knudsen NØ, Komjani NM, Ebbesen MF, Brewer JR, et al. Enhancing the sweat resistance of sunscreens. Skin Res Technol. 2022;28:225–235. https://doi.org/10.1111/srt.13115