A novel O/W sunscreen formulation with enhanced UV protection when subjected to water

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Abstract

Background

Whilst highly water-resistance sunscreens consist generally of W/O formulations, the drawbacks are their sticky and oily texture. Therefore, it would be ideal to develop an O/W sunscreen formulation that is devoid of the sticky and oily texture of its W/O counterpart, whilst maintaining its water-resistance with further enhancement of UV protective performance when subjected to water. We sought to achieve this through combining a soft-textured film polymer and an alkylene oxide derivative as a film enhancer.

Material and Methods

O/W sunscreen formulations with and without film enhancer (polyoxyalkylene glyceryl ethers) were prepared. The formulation was applied onto a PMMA plate and then subjected to an SPF analyzer to measure its in vitro SPF value. The PMMA plate was then submerged in tap water, and dried after which it was subjected to the SPF analyzer to confirm the improvement of UV protective performance compared to prior to subjecting it to water.

Result

The water resistance of O/W sunscreen formulations were found to improve through the addition of a film enhancer. The combination of PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether as film polymer and PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin as film enhancer was found to be most effective in terms of both water resistance and excellent texture.

Conclusions

A revolutionary O/W sunscreen formulation was developed that is devoid of sticky and oily texture with excellent water-resistance and further enhancement of UV protectivity when subjected to water.

Keywords: sunscreens, film polymer, film enhancer, polyoxyalkylene glyceryl ethers, polyurethane emulsifiers

Introduction

With the advancement of studies on damages induced by UV to the skin, sun protection products are being worn routinely by not just women but men and children as well. Whilst a variety of highly protective sun care products are available today, they are practically used mainly in a water-rich environment such as the seaside and swimming pools [1]. As highly water-resistance sunscreens are generally W/O formulations, their drawbacks at the summer leisure scene are their sticky and oily texture. It is also true that many of the O/W formulations too claim to be water-resistance, many of which are made effective through the usage of a coating film. However, an oil-based coating film gives rise to a heavy texture similar to that of a W/O formulation, whereas a water-based coating film lacks in absorptivity to the skin, and hence prone to be washed away by water. Addition of more water-based coating film to prevent this can negatively affect its texture. Hence, it is difficult to satisfactorily achieve both good texture and UV protectivity, even when water-based coating film with high water repellency is used.

Alkylene oxide derivatives are used for the purpose of improving texture, not only in sunscreens but in a variety of cosmetic formulations [2]. As they are reported to have improved the uniformity of the coated film when applied to sunscreen formulations, we can also expect them to enhance UV protectivity [3]. The availability of alkylene oxide derivatives in different structural analogs with diverse functions, has led us to believe that water-repellency could be one of such functionalities.

We attempted to individually look for a “Film Polymer” of soft texture and an alkylene oxide derivative “Film Enhancer” that when combined could offer a water-repellent coat in an O/W sunscreen formulation, whose functionalities were evaluated. The status of the surface of the coat was evaluated using various instrumentations along with how it behaved when exposed to water.

Materials and Methods

Materials

The O/W sunscreen formulation on which the current study is conducted is shown in Table 1. Film polymers and film enhancers contained in this formulation were evaluated. The film polymers were those widely used in O/W cosmetic formulations.

Their INCI names and corresponding quantities generally used in O/W sunscreens are shown below[4]~[8].

1), PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether (1%)
2), Acrylates/C10-30 Alkyl Acrylate Crosspolymer (0.2%)
3), Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer (1%)
4), Carbomer (0.2%)
5), Microcrystalline Cellulose (0.2%)
6), Alcaligenes Polysaccharides (0.03%)
7), Bentonite (0.5%)
8), Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer (1%)

The following ingredients were evaluated as film enhancers.
1), PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin
2), Glycereth-26
3), Polybutylene Glycol/PPG-9/1 Copolymer
4), PPG-9 Diglyceryl Ether
5), PPG-30-Buteth-30

Table1: O/W sunscreen formulation

INCI	
Ethylhexyl Methoxycinnamate	8.00%
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00%
Dodecane	2.00%
Cetyl Alcohol	0.50%
Tocopherol	0.05%
Zinc Oxide, Hydrogenated Polyisobutene, Polyhydroxystearic Acid, Hydrogen Dimethicone	18.0%
Phenoxyethanol	0.50%
Magnesium Aluminum Silicate	1.00%
Agar, Xanthan Gum	0.50%
Trisodium EDTA	0.05%
Sorbitan Stearate	0.50%
Silica	1.00%
Propanediol	3.00%
Film Polymer	-
Film Enhancer	-
Water	Up to 100%

Methods

1. Investigation of film polymers

O/W sunscreen samples containing various film polymers in the base formulation as described above were prepared, after which their water resistance was evaluated by means of an SPF analyzer (Labsphere; UV-2000S). Each sample was applied to the PMMA plate (Labsphere; HELIOPLATE HD 6) amounting to 1.33 mg/cm^2 of material, and thereafter dried naturally. The PMMA plate coated with the sample was subjected to the SPF analyzer to measure the “SPF value prior to immersion in water”. The PMMA plate was then placed in a petri dish, immersed in tap water of room temperature and shaken for 20 minutes using a shaker (AS ONE; Rocking mixer RM-80). After the procedure was repeated twice replacing new tap water each time, the PMMA plate was left for over 30 minutes to dry. This was measured using the SPF Analyzer providing the “SPF value after immersion in water”. The degree of water resistance can be described as “SPF change rate” using the following equation.

SPF change rate (water resistance) (%) = (SPF value after immersion in water) / (SPF value prior to immersion in water) × 100

2. The amount of film enhancer and its effect

The effect of the film enhancer on water resistance was evaluated by varying the concentration of the film enhancer PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin from 0 to 10% stepwise. This was conducted on the base formulation using PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether as the film polymer. The water resistance was evaluated using the method as described above.

3 -1. Observation of the surface of the coated film (the surface roughness)

The surface status of sunscreens applied to PMMA plate was observed and compared before and after immersing in water using a digital microscope (Keyence; VHX-6000) at 100-fold magnification. The roughness of the surface was evaluated via image processing. The sample was applied to PMMA plate, immersed in water, and dried as described above in “1. Investigation of film polymers”.

3 -2. Observation of the surface of the coated film (the roughness of the cross section and measurement of absorbance)

The roughness of the cross section of O/W sunscreens applied to SPFMASTER-PA01(FUJI KASEI) was observed and compared before and after immersing in water using a digital microscope. Conditions for measurement and water immersion were identical to those described above. Absorbance was measured using the SPF analyzer, where a change was confirmed when comparing before and after immersion in water.

4 . Evaluation of in vivo SPF water resistance

An in vivo SPF water resistance test was conducted in accordance with ISO 18861[9]. Along with measuring SPF values before and after immersion in water, the status of how the

O/W sunscreens were coated on the skin was also observed. The samples used for comparison were the control that is devoid of film enhancer and a formulation containing 2% of film enhancer. The tested formulations are shown in Table 2.

Table 2: The tested formulations

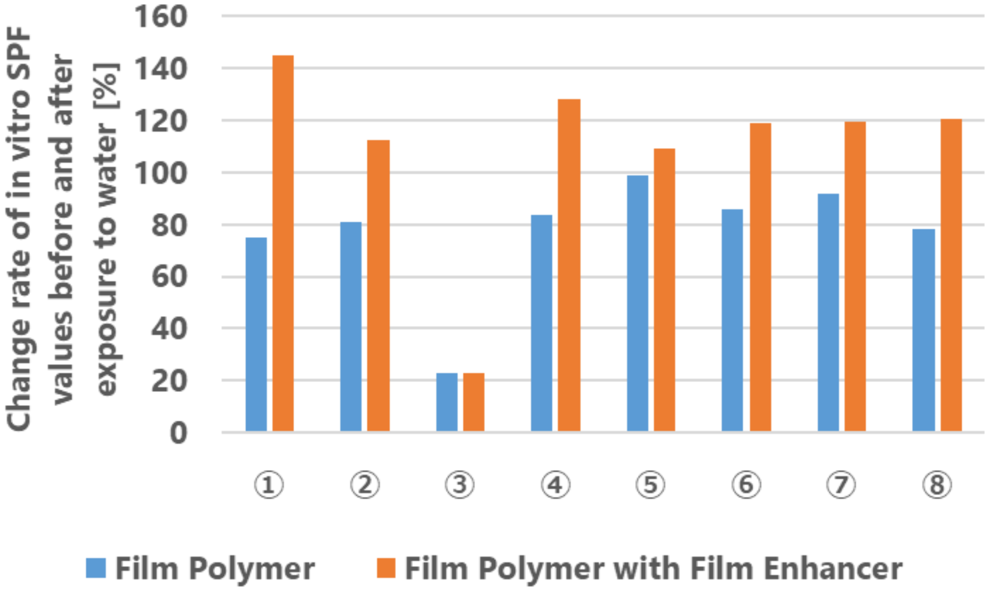
INCI	
Ethylhexyl Methoxycinnamate	10.0%
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.00%
Diethylamino Hydroxybenzoyl Hexyl Benzoate	2.00%
Cetyl Alcohol	0.50%
Tocopherol	0.05%
Zinc Oxide, Hydrogenated Polyisobutene, Polyhydroxystearic Acid, Hydrogen Dimethicone	14.0%
Squalane, Titanium Dioxide, Aluminum Hydroxide, Stearic Acid, Dextrin Palmitate	8.00%
Phenoxyethanol	0.50%
PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether, Trideceth-6	1.00%
Magnesium Aluminum Silicate	1.00%
Agar, Xanthan Gum	0.50%
PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin	0% or 2.0%
Trisodium EDTA	0.05%
Sorbitan Stearate	0.50%
Silica	1.00%
Propanediol	3.00%
Water	Up to 100%

Results and Discussion

1. Investigation of film polymers and the effect of film enhancers

We first confirmed the water resistance of the film polymers and how it could be improved through the addition of film enhancers. As depicted in Fig. 1, whilst most film polymers show certain water resistance on their own, the addition of a film enhancer will improve water resistance of some of them to a great extent. Especially noteworthy was PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether, whose water resistance almost doubled due to the addition of a film enhancer. The film enhancers under study varied significantly in terms of water resistance, texture and stability due to the diverse chemical structures that they possess. In this study, PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin was found to be the material of choice as it was most water resistant with dewy texture and high stability.

We therefore chose “PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether” as the film polymer and “PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin” as the film enhancer for further studies. Furthermore, from the perspectives of texture and stability, the amount of PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether in the formulation was fixed to 1%. The structures of the two materials are shown in Fig. 2.



①PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether

②Acrylates/C10-30 Alkyl Acrylate Crosspolymer

③Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer

④Carbomer

⑤Microcrystalline Cellulose

⑥Alcaligenes Polysaccharides

⑦Bentonite

⑧Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer

Fig. 1: The results of water resistance test

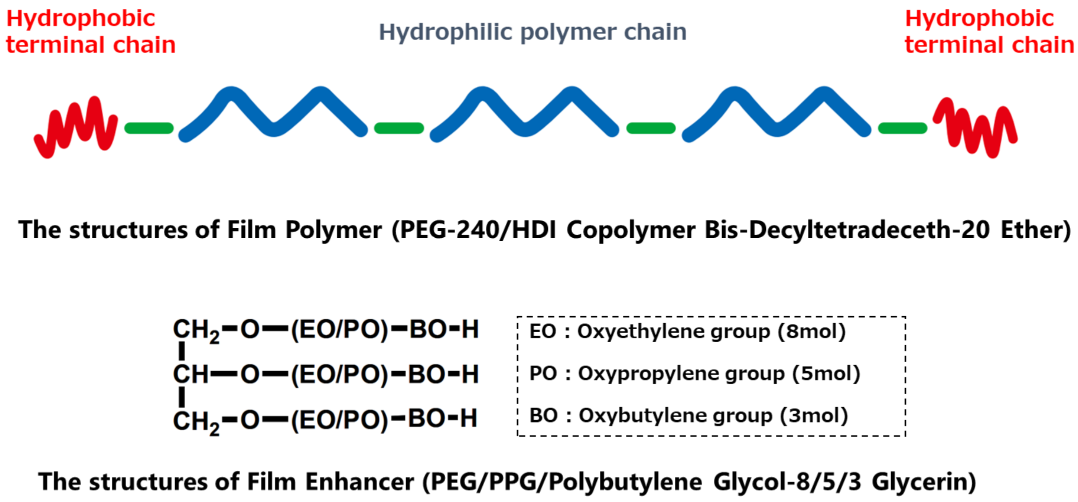


Fig. 2: The structures of Film Polymer and Film Enhancer

2. The amount of film enhancer

The relationship between the amount of film enhancer and water resistance is shown in Fig. 3. The film enhancer shows effect with as little as 0.5% improving water resistance. However, on the contrary, the water resistance declines at amounts of more than 7%. This probably owes to the interaction between the film polymer and film enhancer with an optimum concentration somewhere in between. By further adding 2% of film enhancer, it was possible to moderate the squeakiness and stickiness that are characteristic of sunscreens, thereby imparting a dewy and refreshing texture. The amount of film enhancer will be fixed to 2% as maximum water resistance was confirmed at this concentration.

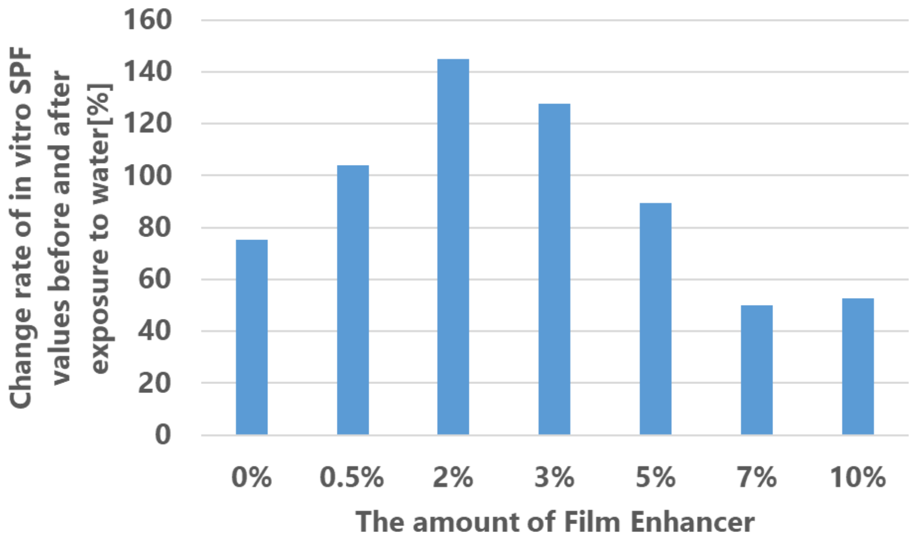


Fig. 3: The relationship between the amount of Film Enhancer and water resistance

3. Observation of the status of the coated film

To observe the effect of the film enhancer on the coated film as compared before and after immersion in water, we looked into the roughness of its surface (Fig. 4). A formulation without a film enhancer tends to be abundant in areas with dents implying that portions of the coated film have exfoliated. Contrarily, the coated film of a formulation with a film enhancer remains more or less consistent even after immersion in water with less dented areas.

The roughness of the cross section as deconvoluted vertically is shown in Fig. 5. The maximum height difference of the coated film of the formulation without a film enhancer prior to exposure to water was 171 μm which expanded to 239 μm after immersion in water. The height difference is believed to have expanded due to the partial exfoliation of the coated film on exposure to water. Contrarily, the maximum height difference of the coated film of the formulation containing a film enhancer was 127 μm prior to exposure to water which this time reduced to 101 μm after immersion in water. Furthermore, as the UV absorption curve of the coated film depicts in Fig. 6, the formulation without a film enhancer shows an overall decline in absorption implying from this result too that exfoliation of the coated film has occurred. On the other hand, no decline in absorption was observed in a formulation containing a film enhancer after exposure to water. In fact, the absorption in the UV-B range was even found to increase. By comprehensively examining the results obtained from Fig. 4, 5 and 6, it can be speculated that the addition of a film enhancer makes the coated film thicker and more uniform after exposure to water than it was before. A possible reason is the water-soluble nature of the film enhancer that absorbs water whilst immersed in water, thereby reconstituting the coated film to bring about uniformity.

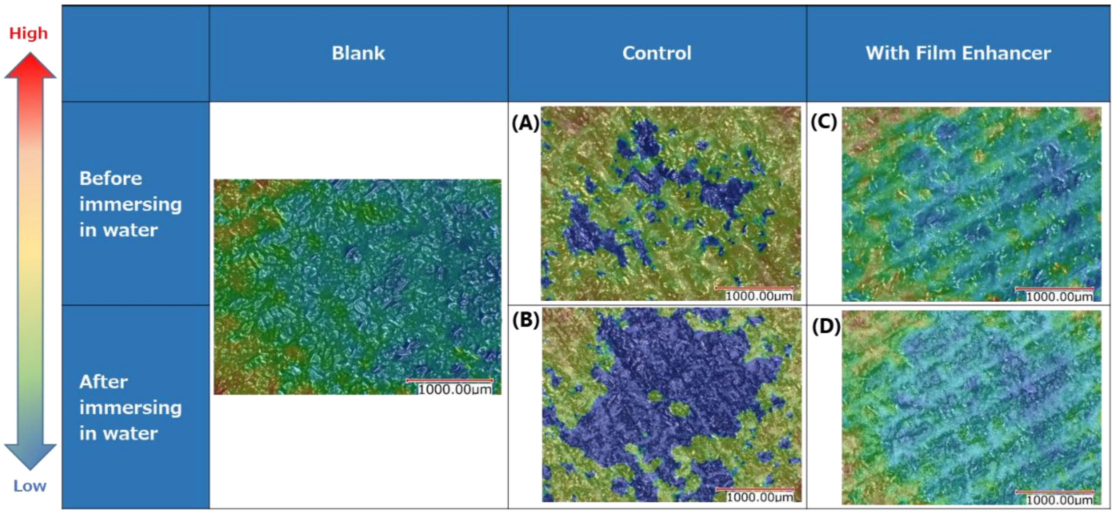


Fig. 4: The roughness of its surface

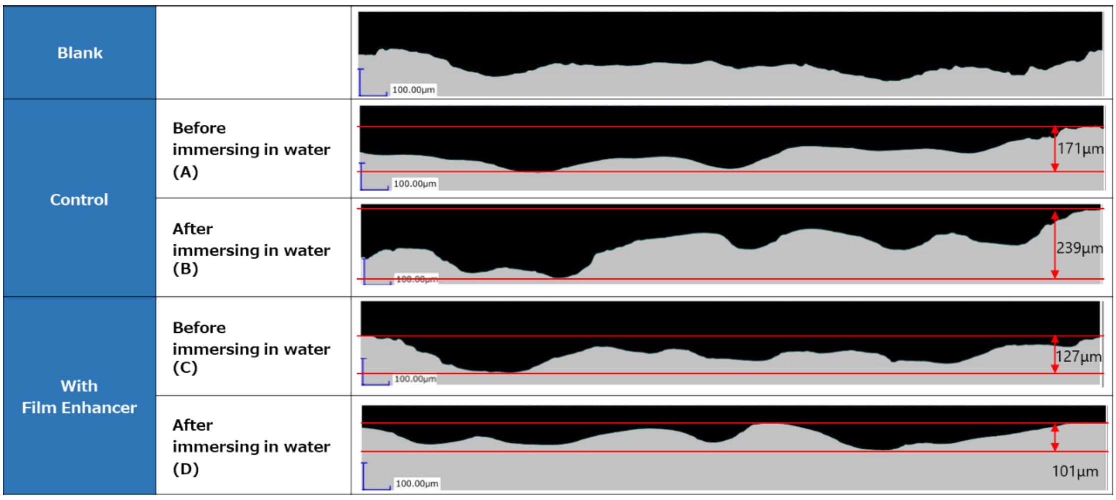


Fig.5: The roughness of the cross section

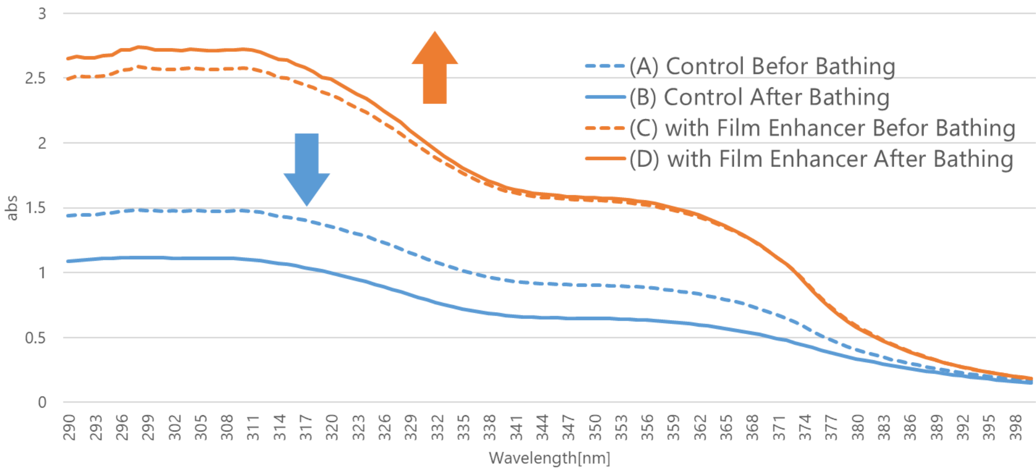


Fig.6: The UV absorption curve of the coated film

4. Evaluation of in vivo SPF water resistance

The status of the coated samples during an in vivo SPF water resistance test is shown in Fig. 7. The addition of a film enhancer made the coated film look clearly visible in water. This is due to the water-soluble nature of alkylene oxide derivatives that the film enhancer is made up of. It enables the coated film to take in water, making it thicker, and speculated to reconstituting and homogenizing it at the same time. Meanwhile, the dried state is less visible back to its natural appearance without a white cast. After exposure to water, the Control looks “worn-off”, hence the coated film is uneven with weaker UV protection.

The in vivo SPF water resistance test results are shown in Fig. 8. As with the in vitro test, the addition of a film enhancer was found to improve water resistance on human skin as well. Whilst the improvement was not as marked as that of the in vitro evaluation, this we speculate is due to the harsher water flow condition employed by ISO 18861 under which the in vivo test was conducted. None the less, the fact that the film enhancer strengthens the water resistance of the film polymer was demonstrated not only on plates but also on human skin.

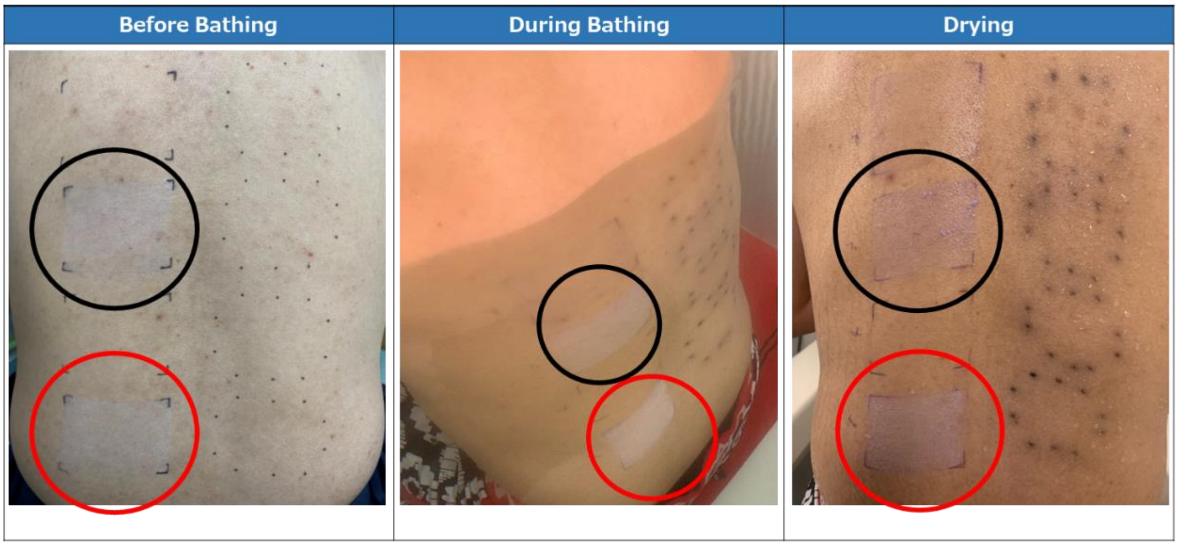
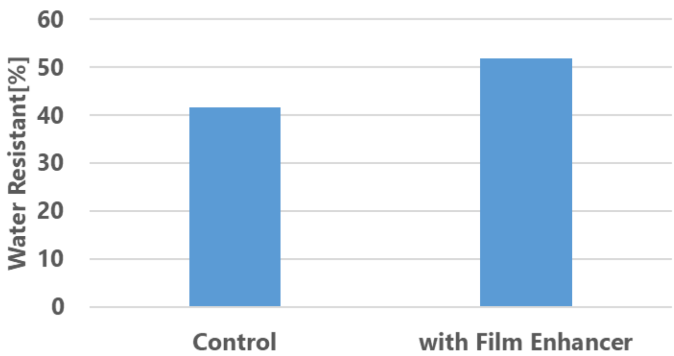


Fig. 7: The status of the coated samples during an in vivo SPF water resistance test (Black: Control, Red: With Film Enhancer)



	Control	With Film Enhancer
In vivo SPF	28.6	34.3

Fig. 8: The in vivo SPF water resistance test results

Conclusion

In order to impart water-resistance via conventional technologies, one has to either prepare a W/O type sunscreen formulation with an oil-based continuous phase or by using coating film in large quantities, both of which resulted in sacrificing satisfactory texture [10]. In this study, we combined "PEG-240/HDI Copolymer Bis-Decyltetradeceth-20 Ether" as film polymer and "PEG/PPG/Polybutylene Glycol-8/5/3 Glycerin" as film enhancer to create a formulation that simultaneously achieves both water-resistance and UV protectivity while maintaining the dewy texture characteristic of O/W sunscreen formulations. The current combination of film polymer and film enhancer does not form a rigid coat as would W/O formulations, but a flexible coat that is resistant to both water and the movement of the skin. This coat improves its thickness and uniformity as it comes into contact with water, giving it high water-resistance through a new mechanism that remains to be investigated.

This gives refreshing usage at water-rich environments such as swimming pools whilst providing sufficient UV protection which might even improve through sweating or other means of exposure to water. We proudly give birth to a revolutionary O/W sunscreen formulation that provides water-resistance, UV protection and excellent usability for the benefit of the consumers.

We need to further understand the mechanism through which this formulation improves its affinity with skin as it comes into contact with water, and how the coat thickens. This would allow us to look for a further effective "Film Enhancer", in turn providing us with a formulation of even higher UV protectivity.

Conflict of Interest Statement

NONE

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