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The Influencing Factors of the Impermeability of Water-resistant and Sun-protective Agents and Their Action Pathways

Zimeng Wang

Jinan New Channel -JUTES High School, Jinan, China.

Abstract: *Water-resistant sunscreens block ultraviolet rays through the construction of physical barriers and the synergistic effect of chemicals. Their anti-seepage performance is influenced by multiple factors such as the characteristics of film-forming agents, the compatibility of sunscreens, environmental conditions, and the physiological state of the skin. This article systematically reviews the molecular structure and film-forming mechanism of anti-water film-forming agents, analyzes the interaction pathways between physical and chemical sunscreens, reveals the destructive mechanisms of environmental factors such as humidity, temperature, and friction on the stability of the film layer, and explores the correlation between skin barrier function and the penetration of sunscreens. Research indicates that optimizing the molecular weight of film-forming agents, regulating the compounding ratio of sunscreens, and improving the hydrophilic and lipophilic balance value (HLB) of the formula are the key paths to enhance the efficacy of water-resistant sunscreens, providing a theoretical basis for the development of highly efficient and long-lasting sunscreen products.*

Keywords: *Water-resistant and sun-protective agent; Impermeability capacity; Film-forming mechanism; Sunscreen agent compatibility; Environmental adaptability.*

1. Introduction

The risks of skin photoaging, DNA damage and canceration caused by ultraviolet radiation have driven the development of sunscreen cosmetics towards high efficiency and long-lasting effects. As a core functional component, the water-resistant and sun-protective agent needs to maintain the integrity of the film layer in dynamic environments such as sweat, friction and water immersion to achieve continuous water resistance. According to market research, the proportion of water-resistant claimed products in the European and American markets exceeds 50%, and the Asian market has also shown a rapid growth trend in recent years. However, there are still technical bottlenecks in the stability of existing products under extreme environments. For instance, the film layer shedding rate can reach over 30% under high-temperature and high-humidity conditions. This article systematically analyzes the influencing factors and action paths of the impermeability of water-resistant sunscreens from three dimensions: the molecular design of film-forming agents, the interaction of sunscreens, and environmental adaptability, providing theoretical support for product development.

2. Molecular Structure and Film-forming Mechanism of Anti-water Film-forming Agents

2.1 Types and Molecular Design of Film-forming Agents

Water-resistant film-forming agents mainly include acrylic copolymers, polyurethanes, vinyl polymers and silicone resins. Acrylic acid copolymers (such as acrylate /C10-30 alkanol acrylate cross-linked polymers) bind to the keratin layer proteins of the skin through the carboxyl groups on the side chains, and the hydrophobic groups on the main chain form a dense film layer. When the molecular weight is between 50,000 and 200,000 Da, the tensile strength can reach 8-12 mpa, and the elongation at break is 250% [1]. Polyurethane film-forming agents (such as Carfil®9221) form a three-dimensional network structure through cross-linking of isocyanate groups. The film layer is flexible and wear-resistant. Experiments have shown that it can extend the retention time of sunscreens on the skin to 8 hours [2]. Vinyl polymers (such as VP/ hexadecene copolymer) regulate the hardness and permeability of the film layer through the length of alkyl chains. When the alkyl chains are C16-C20, the contact Angle can reach 110°, and the water vapor transmission rate (WVTR) is 800-1200g/(m^2·24h), approaching the natural sweating rate of human skin [3].

Silicone resin film-forming agents (such as trimethylsilanoxy silicate) have a silicon-oxygen bond as the main chain, forming a nanoscale pore structure with a permeability coefficient of less than 1×10^{-13} cm^2/s, which can effectively prevent water molecule penetration [4]. Organosilicon elastomers (such as DOWSIL™ FA 4004ID) form a soft and uniform film layer on the skin surface through a mixed system of polytrimethylsiloxane methacrylate copolymer and isododecane. Experiments have shown that it can increase the dispersibility of sunscreens by 40% [5].

2.2 Film Formation Process and Film Layer Characteristics

The film-forming process is divided into three stages: solvent evaporation, molecular rearrangement and cross-linking curing. Take waterborne polyurethane as an example.

After application, the evaporation of water causes the polymer chain segments to move freely. The hydrophobic groups aggregate through van der Waals forces to form an ordered structure, and finally crosslink and cure through isocyanate groups [6]. The contact Angle experiment shows that the contact Angle of the film layer containing silane-modified film-forming agent can reach 110°, which is 25% higher than that of the unmodified product. The WVTR of the polyvinyl alcohol/polyacrylic acid composite film is 800-1200g/(m^2·24h), approaching the natural sweating rate of human skin. The elongation at break of nanoparticle enhanced film-forming agents (such as SiO_2/ polymer complexes) can reach 300%, which is twice that of pure polymers [7].

2.3 Synergistic Effects of Film-forming Agents and Sunscreens

The film-forming agent forms a "core-shell" structure by encapsulating the sunscreen agent, reducing the loss of active ingredients caused by solvent penetration. Experiments have confirmed that acrylate film-forming agents can increase the light stability of avobenzone by 40%. The mechanism lies in the difference in the refractive index of the film layer (1.5-1.6) and that of the sunscreen agent (1.3-1.4), which causes total light reflection and increases the optical path. In addition, film-forming agents can regulate the release rate of sunscreens. For instance, the layered gel structure film-forming agent extends the release period of titanium dioxide to 8 hours, which is three times longer than that of traditional formulas.

3. The Influence of the Compatibility of Sunscreens on Their Impermeability

3.1 Interaction between Physical Sunscreens and Chemical Sunscreens

Physical sunscreens (such as TiO_2, ZnO) provide protection by reflecting and scattering ultraviolet rays, while chemical sunscreens (such as OMC, BMDM) absorb ultraviolet energy and convert it into heat energy for release. The combination of the two can cover the entire UVA and UVB bands, but improper compatibility will lead to a significant decrease in light stability. For instance, BMDM is prone to cis-trans isomerization under light exposure. After binding with the hydroxyl groups on the surface of TiO_2, the isomerization rate accelerates, leading to the destruction of its molecular structure. Experiments show that untreated TiO_2 can increase the photodegradation rate of BMDM by 60%, directly weakening the UVA protection capability. In addition, EHMC and BMDM may undergo a [2+2] cycloaddition reaction under ultraviolet irradiation, generating products with no protective activity, which reduces the SPF value by 35% after compounding and significantly lowers the protective efficacy.

To solve this problem, surface modification technology becomes the key. By coating TiO_2 with polymethylsiloxane, a hydrophobic layer can be formed, reducing its direct contact with BMDM and lowering the photodegradation rate of BMDM to 15%. Similarly, silane treatment of ZnO can optimize its surface charge distribution. After compounding with BMDM, the SPF value retention rate reaches 90%, significantly enhancing the stability of the formula.

3.2 Compatibility of Sunscreen Agents with Solvents

The choice of solvent directly affects the solubility, film-forming property and light stability of sunscreen agents. The ideal solvent should simultaneously meet the requirements of dissolving sunscreens and stabilizing film-forming agents. For instance, phenethyl benzoate (X-tend226) has a solubility of up to 25% for BMDM and can queng the excited state of BMDM under light, inhibiting its photodegradation through energy transfer. Experiments have shown that it doubles the photostability of BMDM. In contrast, the remaining amount of BMDM in traditional solvents (such as isododecane) after one hour of exposure to light is less than 40%, and the protective efficacy is significantly reduced.

In addition, the ratio of the oil phase to the water phase also has a significant impact on the impermeability performance. In high oil phase formulations (with an oil phase proportion >60%), the migration rate of the film-forming agent decreases, the density of the film layer increases, and it can effectively reduce the penetration of ultraviolet rays. However, excessive increase in the oil phase may cause the product to become sticky, affecting the user experience. Therefore, emulsification technology is needed to balance the protective power and skin feel.

3.3 The Synergistic Effect of Biological Sunscreens

Biological sunscreens (such as vitamin C and SOD) reduce light damage by eliminating free radicals and form a three-level protection system with physical/chemical sunscreens. Experiments show that compounding 0.5% vitamin C can increase the SPF value by 15%. The mechanism lies in that vitamin C can regenerate oxidized chemical sunscreens (such as avobenzone), extending their effective protection time. In addition, biological sunscreens can reduce the risk of sunscreen penetration. For instance, Ectoine can enhance the barrier function of the stratum corneum of the skin, accelerate its recovery rate by 40%, reduce the entry of active ingredients into the dermis, and thereby lower the risk of irritation.

4. The Influence of Environmental Factors on the Impermeability of Water-resistant Sunscreens

4.1 The Role of Humidity and Temperature

A high humidity environment (RH>80%) will significantly affect the water resistance of the film layer. Take polyacrylate film-forming agents as an example. Under a 90%RH environment, their water absorption rate can reach 15% within 24 hours. The contact Angle on the film surface drops from 120° to 80°, and the hydrophilicity increases, resulting in a significant reduction in water resistance. This is because when water molecules penetrate the membrane layer, they break the hydrogen bonds between the polymer chains, making the membrane layer structure loose. At the same time, high humidity may promote the dissolution of water-soluble components in sunscreens, further weakening their protective efficacy.

An increase in temperature (above 35°C) will accelerate the evaporation of the solvent, but excessive evaporation will cause the film layer to become brittle. Experiments show that after drying at high temperatures, the elongation at break of traditional sunscreen films decreases by 50%, the film layer is prone to cracking, and the anti-

permeability is significantly weakened. In dynamic thermal and humid composite environments (such as sauna tests), the SPF value of traditional formulas can decrease by up to 60%. Products that use temperature-sensitive film-forming agents (such as polyN-isopropylacrylamide) can adjust the film layer structure through temperature response, forming a denser protective layer at high temperatures and increasing the SPF value retention rate to 85%.

4.2 Friction and Mechanical Stress

Friction during daily activities is one of the main factors that cause damage to the sun protection film layer. Experiments show that wiping with cotton cloth can reduce the thickness of the film layer by 40% and lower the SPF value by 55%. This is because the shear force generated by friction will directly peel off the surface of the film layer, especially when the adhesion between the film layer and the skin is insufficient. Nanoparticle reinforcement technology can significantly enhance the wear resistance of film layers. For instance, after 50 frictions, the contact Angle retention rate of SiO_2/ polymer composite films reaches 90%, which is 30% higher than that of pure polymers. The principle lies in that nanoparticles can fill the gaps between polymer chains, forming a denser cross-linked network and enhancing the anti-peeling ability of the film layer.

In addition, elastomer film-forming agents (such as polyurethane) can absorb stress through deformation, reducing the risk of film cracking. Experiments show that the polyurethane film layer can remain intact when stretched by 30%, while the traditional film layer cracks when stretched by 15%. This elastic deformation ability enables the sun protection film layer to maintain effective protection even when the skin is active, such as during exercise or changes in expression.

4.3 Water Quality and Chemical Erosion

The effects of different water qualities on water-resistant sunscreens vary significantly. Salt ions (Na^+, Cl^-) in seawater can disrupt the charge balance of the membrane layer. Experiments show that after being immersed in seawater for one hour, the Zeta potential of the membrane layer drops from -30mV to -10mV, causing the dissolution rate of the membrane layer to increase by two times. This is because salt ions compress the double electric layer on the surface of the film layer, weakening the electrostatic adsorption force between the film layer and the skin.

Hypochlorous acid in chlorine water (swimming pools) will oxidize the polymer chains of the film layer, reducing the molecular weight of acrylate film-forming agents by 40% and causing them to lose their water resistance. Hypochlorous acid attacks the unsaturated bonds in the polymer chain, causing chain breakage and a decrease in crosslinking degree, which leads to the disintegration of the membrane structure. For such environments, the development of amphoteric ionic film-forming agents (such as phosphatidylcholine polymers) can significantly enhance chemical resistance. Experiments show that the mass loss rate of the membrane layer containing phosphatidylcholine polymer in seawater is 70% lower than that of traditional products. The principle lies in that the amphoteric ion structure can form a hydrated layer, which can block the erosion of salt ions and chlorine.

5. The Correlation between Skin Physiological State and the Penetration of Sunscreen Agents

5.1 The Influence of Skin Barrier Function

The integrity of the stratum corneum determines the penetration rate of sunscreens. Experiments show that in damaged skin with a transdermal water loss (TEWL) value greater than 20g/(m²·h), the penetration amount of chemical sunscreens is three times that of normal skin. Film-forming agents can reduce penetration through physical barrier effects. For instance, film-forming agents with layered gel structures can lower TEWL to below 10g/(m²·h) while retaining sunscreen agents in the stratum corneum. In addition, ceramide complexes can repair the skin barrier. Experiments have shown that they can reduce the penetration rate of sunscreens in the dermis from 15% to 5%.

5.2 Regulation of pH Value and Enzyme Activity

The pH value of the skin surface (4.5-6.0) affects the charge state of the film-forming agent. An acidic environment (pH<5) protonates carboxyl groups, reducing the adhesion between the film layer and the skin. Experiments show that when pH=4.5, the peel strength of the film layer decreases by 30%, while the use of PH-responsive film-forming agents (such as polyacrylic acid/polyvinyl alcohol interpenetrating network) can automatically adjust the charge density within the skin pH range, achieving a peel strength retention rate of 95%. Skin esterase can degrade certain film-forming agents (such as polyesters). Experiments show that the mass loss rate of the film layer in the presence of esterase can reach 20% per day, while the degradation rate of polyurethane film-forming agents linked by ether bonds is less than 5%.

5.3 Individual Differences and Applicability

Age, gender and racial differences lead to different skin characteristics, which affect the impermeability of sunscreens. For instance, the stratum corneum of the skin of the elderly becomes thinner, and the penetration of chemical sunscreens increases by 50% compared to young people. Men have a higher sebum secretion rate on their skin, and the use of oil-based film-forming agents can easily lead to clogged pores, increasing the risk of acne by 30% compared to women. In response to such differences, developing zoned applicable products (such as T-zone oil control and U-zone moisture retention) can enhance usage compliance. Experiments show that the user satisfaction rate of zoned design products reaches 85%, which is 20% higher than that of traditional products.

6. Optimization Strategies for the Efficacy of Water-resistant and Sun-protective Agents

6.1 Regulation of Molecular Weight and Crosslinking Degree of Film-forming Agent

By controlling the polymerization reaction conditions to adjust the molecular weight distribution, experiments show that the polyurethane film-forming agent with a molecular weight ranging from 80,000 to 150,000 Da has a tensile strength of 10MPa and an elongation at break of 250%, achieving the best comprehensive performance.

The degree of crosslinking affects the compactness of the film layer. When the dosage of diisocyanate crosslinking agent increases from 3% to 8%, the water absorption rate of the film layer drops from 18% to 5%, but excessive crosslinking (>10%) leads to an increase in the brittleness of the film layer.

6.2 Optimization of the Blending Ratio of Sunscreen Agents

Based on the principle of spectral overlap, a compounding scheme is designed. For instance, by compounding OMC with an absorption peak at 310nm and BEMT at 340nm in a 2:1 ratio, full-band protection from 290 to 400nm can be achieved. Experiments show that the SPF value of the optimized formula reaches over 50, which is three times higher than that of a single sunscreen agent. Meanwhile, controlling the particle size of physical sunscreens (<50nm) can reduce uneven light scattering. Experiments show that TiO_2 with a particle size of 30nm increases the transparency of the film layer by 40% and significantly reduces the whitening phenomenon.

6.3 Formula HLB Value and Rheological Design

The HLB value affects the stability of the emulsion and the uniformity of the film layer. Experiments show that emulsifiers with an HLB of 8-10 can concentrate the oil droplet size distribution within 1-5μm and increase the smoothness of the film layer by 30%. Rheological design achieves the characteristic of "low viscosity during application and high viscosity after film formation" by controlling the thixotropic index (TI=0.3-0.5). Experiments show that the formula with TI=0.4 reduces the application resistance by 50%, while the hardness retention rate of the film layer reaches 90%.

7. Conclusion

The impermeability of water-resistant and sun-protective agents is jointly determined by the molecular design of the film-forming agent, the compatibility of the sun-protective agent, and environmental adaptability. Future research should focus on developing intelligent responsive film-forming agents such as temperature-sensitive/ph-sensitive to achieve adaptive protection in dynamic environments. A multi-functional composite system of "sun-protective agent - film-forming agent - bioactive substances" should be constructed using nanotechnology to enhance the comprehensive performance of the product. And in combination with the skin biomechanical model, optimize the formula to adapt to the skin characteristics of different groups of people, and promote the development of water-resistant and sun-protective agents towards more efficient, broad-spectrum and personalized protection through multi-disciplinary cross-innovation.

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