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Review Article

Review of sunscreen and the emergence of non-conventional absorbers and their applications in ultraviolet protection

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Synopsis

Protection against ultraviolet (UV) radiation is the major function of sunscreen lotions and UV-protective coatings for vehicles, homes, equipment and clothing. Sunscreen formulations have been optimized to become protective over a broader spectrum of UV radiation and maintain greater photostability. They are comprised of organic and inorganic components that act as chemical and physical UV protectors, respectively. Some of the organic components are limited by their spectrum of protection and photostability. Studies using solid lipid nanoparticles, recently explored organic molecules, inorganic components and antioxidants attempt to further optimize UV protection. In this review, we examine traditional and emerging nanoparticle components and highlight novel ideas in UV protection which may provide pathways for future studies.

Résumé

La protection contre les rayons ultraviolets (UV) est la principale fonction des crèmes solaires et des revêtements de protection UV pour les véhicules, les logements, les équipements et les vêtements. Les formulations solaires ont été optimisées pour devenir des protections de large spectre UV et pour maintenir une plus grande photo stabilité. Ils sont composés de matières organiques et inorganiques qui agissent comme des produits de protection respectivement chimique et physique contre les UV. Certains des composants organiques sont limités par leur spectre de protection et leur photo stabilité. Les études récentes de nanoparticules lipidiques solides (SLN) des molécules organiques, inorganiques et antioxydants, ont exploré des voies d'optimisation de protection UV. Dans cette revue, nous examinons les composants traditionnels et les nanoparticules émergentes ainsi que les idées de protection UV pour proposer de futures études.

Introduction

Frequent exposure to solar ultraviolet (UV) radiation is well known to cause damage to exposed surfaces. Fading and ageing of paints, fabrics and plastic coatings as well as sun-related skin cancer are major industrial, environmental and health concerns. Advancing the field of UV protection is achieved by protecting against the broadest possible spectrum of UV radiation, such as the ultraviolet-A (UVA), 400–320 nm, and ultraviolet-B (UVB), 320–290 nm, wavelengths of sunlight, optimizing photostability of protective molecules and trapping reactive species before photochemical damage occurs. Hence, improved UV protection can potentially make a major impact in a wide range of applications, including paints and coatings, cosmetics, textiles, pharmaceuticals and environmental remediation. This review presents some of the recent innovations in UV-protective technology involving nanoparticles, nanoencapsulation, and nanocomplexation, recent novel applications, and potential future directions incorporating antioxidants and natural products.

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Conventional sunscreen ingredients

A familiar example of UV-protective technology is sunscreen lotion. Most sunscreen products are composed of organic and inorganic components. The organic, such as oxybenzone, usually acts as a chemical sunscreen by absorbing UV radiation. The inorganic component, such as titanium dioxide, usually acts as a physical sunscreen by absorbing, reflecting and scattering UV radiation. Sunscreen is applied to the skin topically, covering the stratum corneum and shielding the multiple layers of the skin. Although the direct cause of most skin cancers (melanoma and non-melanoma) is still under debate [1–3], the function of the sunscreen components is clearly to shield the skin from UV radiation as effectively as possible. An optimal sunscreen contains multiple elements which reflect and scatter UV radiation, absorb UV wavelengths, contain stabilizing mechanisms such as encapsulation or complexation for sustained efficacy, and trap free radicals, for example with antioxidants, to limit photochemical damage.

Organic sunscreen components

The commonly used organic sunscreen components are described in Table I.

Advantages and disadvantages of organics

Organic components used in sunscreen formulations are fairly abundant and diverse in comparison to inorganic components. This gives manufactures flexibility with characteristics of the formula-

Table I Commonly used organic sunscreen components

Organic component	Description
Avobenzone	Oil-soluble and used to absorb the full spectrum of UVA rays. as avobenzone is highly degradable in the presence of sunlight it is often paired with a photo stabilizer in sunscreen formulations [4, 5]
Oxybenzone	Absorbs UVA radiation. Potentially harmful and a likely photocarcinogen. Derivative of benzophenone, a known photo-carcinogen [1].
Ensulizole	Protects against UVB and minimally against UVA. Water-soluble and is used in formulations for a light, non-greasy feeling [6].
Octinoxate	Absorbs UVB radiation. Reduces the appearance of scars. Water-insoluble, making it useful in waterproof formulations [7].
Octisalate	Formed by condensation of salicylic acid with 2-ethylhexanol. The salicylate portion of the molecule absorbs UV radiation, whereas the ethylhexanol adds water resistant properties [8]

tion such as the sun protection factor (SPF), water resistance and product feel. Organic components could be considered less effective because they absorb UV radiation rather than reflecting or causing it to scatter. This makes them vulnerable to photo-degradation and prone to generating free radicals. However, the main concern with organic sunscreens is the potential for photo-irritant or photo-sensitizing reactions in susceptible individuals. The use of *p*-aminobenzoic acid, one of the earliest active ingredients used in sunscreens, has come under heavy scrutiny because of skin sensitivity issues and has been removed from a majority of sunscreen products.

Organic UVA ingredients

A problem associated with current on-the-shelf sunscreens is that, in many cases, the only indicator of product efficacy is the SPF. This is an incomplete measure, because SPF is primarily dependent on UVB protection and does not adequately reflect the degree of UVA protection offered by the product [9]. However, protection against both ranges of UV radiation is critical because both are now implicated in skin cancer [1].

For some time, avobenzone was the predominant UVA protector in most sunscreen formulations. However, several new organic sunscreen ingredients have been developed in recent years. Most of these new ingredients, such as ecamsule, bemotrizinol and bisoctrizole protect against UVA and act as a photostabilizer when paired with avobenzone creating a synergistic effect for superior UVA protection. With the rise of new organic UVA sunscreen ingredients the FDA has proposed test methods and labelling of UVA protection to be used in addition to the current SPF rating system [9].

Nanoparticles

Inorganic pigments with a high refractive index, such as titanium dioxide and zinc oxide (ZnO), also block UV light. Nanoparticle grades of these materials are often incorporated into sunscreen formulations because, by virtue of their small particle size, they are more effective than the bulk pigments in absorbing and scattering UV light. Figure 1 illustrates this effect.

Inorganic nanoparticle components

Titanium dioxide and Zinc oxide

Titanium dioxide is a mineral which is prepared as ultra-fine nanoparticles. Sunscreen grades of TiO_2 have primary particle sizes ranging from about 10 to 60 nm [11]. These particles form aggregates which reflect UV radiation most efficiently with aggregates typically sized from 30 to 150 nm. In sunscreens, TiO_2 is usually treated with coating materials such as silicon oils, SiO_2 or Al_2O_3 to make it more passive with the organic components and improve its dispersion and UV absorption in the overall formulation [11, 12].

Zinc oxide is a mineral and prepared in particles that have a typical size ranging from 20 to 80 nm [13]. ZnO is usually coated with silicon oils, SiO_2 or Al_2O_3 in sunscreen formulations. It can be considered a better sunscreen ingredient than TiO_2 depending on the formulation requirements, because ZnO is more transparent and covers a broader UVA spectrum [14]. Alternatively, TiO_2 can be considered superior because it delivers a much greater SPF than ZnO.

Advantages and disadvantages of inorganic components

Inorganic components used in sunscreen are beneficial because they have been shown to absorb, reflect and scatter UV radiation, which is generally considered more effective than absorption of UV radiation. They cover a broad spectrum, so their addition can simplify the sunscreen formulation by minimizing the necessary number of organic components. This can be beneficial for those with sensitivity or skin irritation issues. Inorganic UV sunscreens have relatively high consumer acceptance because of their transparency, which increases the usage of sunscreen [3]. A drawback of using inorganic components is their dispersion issues, which often require an additional material for coating the inorganic material [12]. Coatings are also used to reduce the photoreactive nature of inorganic components protecting in part against the dominant drawback which is the potential risk caused by the generation of free radicals through oxidation when exposing inorganic molecules to UV radiation [1–3, 15].

Nanoencapsulation

Solid lipid nanoparticles

In the mid-1980s, Dior introduced the liposome in their product, *Capture*. This product opened the door for the research and production of micro and nanoparticles in the pharmaceutical and cosmetic industries [16].

Solid lipid nanoparticles (SLNs) were developed in the early 1990s and are advantageous in comparison with liposomes because of their protection against chemical degradation and controlled drug release properties [16]. Figure 2 depicts the structural differences between liposomes and SLNs.

Pharmaceutical and cosmetic uses

Solid lipid nanoparticles are established in the field of pharmaceuticals and drug delivery [16, 17]. Many drugs have been incorpo-

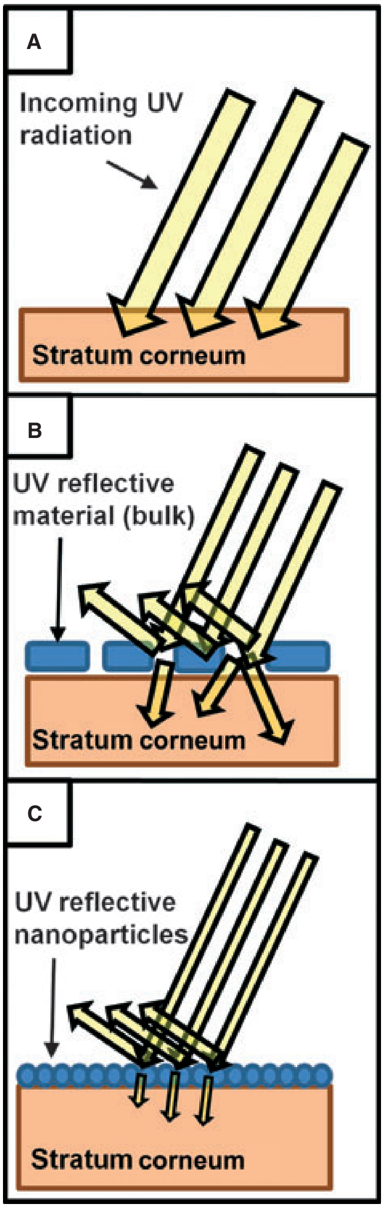

Figure 1 (A) Incoming UV radiation penetrates the stratum corneum. (B) UV reflective material in bulk form (e.g. ZnO) is applied to the surface of the stratum corneum. Some incoming UV radiation is blocked by reflection/scattering and some UV radiation is unblocked/deflected to the stratum corneum. (C) UV reflective nanoparticles (e.g. ZnO) are applied to the surface of the stratum corneum. Most of the incoming UV radiation is reflected by the nanoparticles, leaving less UV radiation to penetrate to stratum corneum.

rated into SLNs and are effective within the body because of their structural stability, drug release profile, high loading capacity and biocompatibility [17]. SLNs are used in cosmetic applications because of favourable characteristics including skin hydration, lubrication, skin whitening effect, chemical stability and UV protection [16, 18, 19].

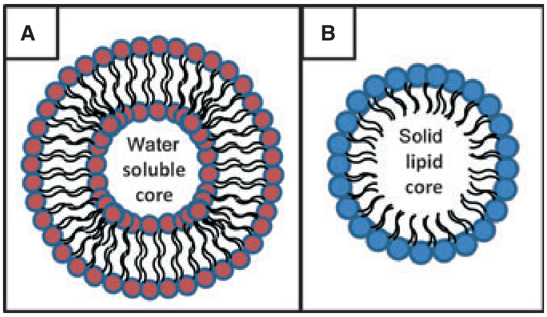

Figure 2 (A) The liposome is a spherical lipid bi-layer (bi-layer of polar hydrophilic head groups attached to non-polar hydrophobic fatty acid tails) which encapsulates a water soluble core. (B) The SLN is a spherical lipid monolayer (polar hydrophilic head groups attached to non-polar hydrophobic fatty acid tails) which encapsulates a solid lipid core.

UV protection

Solid lipid nanoparticles have been emerging as a carrier system for sunscreens. SLNs are advantageous in comparison with conventional o/w emulsions because they have been shown to exhibit a zero-order release profile of organic components. Thus, SLNs release less of the sunscreen formulation over a given period of time resulting in a longer-lasting sunscreen [20].

Although the use of SLNs solely as UV filters is neither recognized nor commercially available, they have been shown to have a synergistic effect when paired with UV filters with regards to overall UV protection and photostability. This results in a reduced need for high concentrations of potentially photo-carcinogenic sunscreen formulations without sacrificing the SPF [21]. This advantage of the SLNs is based upon their ability to reflect and scatter incoming UV radiation. It has been shown that the scattering properties of SLNs depend on their degree of crystallinity. More crystalline SLNs have a greater ability to reflect and scatter radiation [22].

Polymeric nanoencapsulation

Similar to SLNs, poly(D,L-lactide) (PLA), is an established polymer in the drug delivery industry. Nanoencapsulation of octinoxate using PLA results in increased photostability [23]. Similarly, a study by the same research group show that encapsulating octinoxate with poly-D,L-lactide-co-glycolide (PLGA) also has greater photostability than octinoxate alone [24]. Lee *et al.* show avobenzone encapsulated by poly(methyl methacrylate) (PMMA) to have improved photostability, thermal stability and UV protection. PMMA/avobenzone nanoparticles can be applied to develop very stable sunscreens [25]. All three of these nanoencapsulations are promising because of their polymer biocompatibility. Polymeric encapsulation holds great promise as an emerging sunscreen technology because of the great variety and versatility of polymers and detailed understanding of the polymer properties.

Cyclodextrin complexation

Cyclodextrins are cyclic oligiosaccharides composed of five or more α-D-glucopyranoside units. They exist in three natural forms, α, β and γ. They can entrap appropriately sized molecules into the

Table II Australian/New Zealand UV protection factor (UPF) standard

UPF rating	UV radiation transmission (%)	UPF description
15–24	6.7–4.2	Good
25–39	4.1–2.6	Very good
40–50, >50	<2.6	Excellent

hydrophobic lumen of their ringed structure [26]. Cyclodextrins are complexed with compounds to increase aqueous solubility and dissolution rate of poorly soluble drugs. They are also used to protect against oxidation and improve photostability [26, 27].

Cyclodextrins complexed with ibuprofen have been shown to be effective in reducing the damage caused by UV radiation after sun exposure. Godwin *et al.* show that topically applying ibuprofen immediately following UV exposure is crucial in reducing epidermal lipid damage. Complexing ibuprofen with hydroxypropyl-β-cyclodextrin provided enhanced protection [28].

Future directions in UV protection

This section summarizes a few of the recent studies which present novel ideas in UV protection applications, as well as the incorporation of antioxidants and natural products in UV protection. Areas for future study are highlighted.

Application to textiles as UV absorbers

A new idea in UV protection is to incorporate UV-protective nanoparticles into fabric used for clothing to reduce the fading of colours. ZnO nanoparticles have been incorporated into the surface of cotton and wool fabrics. The addition of ZnO increases the mechanical strength of both fabrics and results in an UV-absorbing fabrics [10, 29]. Another study by Sun *et al.* incorporated ZnO nanoparticles into polyester fabrics. This study had mixed results; although a polymer/ZnO coating not in direct contact with the fabric decreased the fading rate of the dyed fabric, the polymer/ZnO coating increased the fading rate of one dye used when in direct contact with the fabric. Sun *et al.* attributes this increased fading rate to the generation of free radicals when ZnO is exposed to UV radiation [30].

Another approach to protecting fabric is to incorporate multiwall carbon nanotubes (MWNT). Mondal *et al.* developed a polyurethane coating containing UV-protective MWNT. Several weight percentages of the coating were applied to cotton fabric and the transmission of UV radiation through the fabric was measured. An UV protection factor (UPF) of the fabric was calculated based upon the transmission of UV radiation. UPF ratings are listed according to the Australian/New Zealand standard (Table II).

This coating applied to cotton fabric achieved a UV protection factor of 174 for only 1 wt% of MWNT used in the cotton fabrics [31]. Because of the UV-protective benefits and nil effect on clothing comfort, the addition of trace amounts of UV-protective material into textiles is a likely trend to continue to be studied.

Antioxidants

Antioxidants and other natural products such as carotenoids are currently being explored as UV-protective additives to limit photochemical damage. The new molecules, applied in conjunction with nanoencapsulation and nanocomplexation have the potential for powerful new sunscreen ingredients.

Antioxidants are found naturally in plant species. Excessive exposure to UV radiation triggers production of non-photosynthetic pigments, cinnamic acid derivatives and flavanoids which are responsible for blocking UV radiation in addition to their antioxidant activity [32]. Incorporation of antioxidants into sunscreen formulations is a logical approach to combat potentially hazardous photogenerated free radicals. Antioxidants contain many free electrons which are donated to unpaired electrons present in free radicals. Antioxidants are used in the cosmetic industry to prevent the formation of new wrinkles and reduce skin ageing caused by UV radiation. These antioxidants, such as vitamin C, vitamin E and pycnogenol, have been shown to have a synergistic effect when combined for UV protection [33]. Photostabilizers have also been shown to exhibit antioxidant properties. Chaudhuri *et al.* showed that diethylhexyl syringylidene malonate can be used as a photostabilizer for avobenzone as well as an effective antioxidant [5]. Synthetic antioxidants are also a possibility. Otani *et al.* developed a new UVB radiation absorbent molecule with efficient antioxidant activity by modification of the glycoside. This new molecule is expected to be available for sunscreen formulations [34].

Carotenoids

Carotenoids are produced in plants and other photosynthetic organisms. The yellow, orange and red colour of many fruits is caused by the caroteniod content. Green plants also contain carotenoids, but their colour is masked by their chlorophyll content. Humans cannot self-produce carotenoids and depend on a dietary supplement [35–38]. Carotenoids are important because they play a role in protecting plants from UV damage. They are effective natural antioxidants because of their singlet oxygen quenching ability and scavenging of peroxyl radicals [39–41].

When incorporated into daily dietary intake, carotenoids have been shown to have a variety of positive health effects. A decreased risk for prostate cancer has been associated with the consumption of lycopene found in tomatoes [42].

Carotenoids have potential in skin protection applications. Heinrich *et al.* showed that a dietary mixture of the β-carotene, lutein and lycopene protects against UV-induced erythema [43].

In homogenous solution, carotenoids are efficient blue light (near UVA) filters [44]. When complexed with β-glycyrrhizic acid, a cyclodextrin, their antioxidant activity increases (increased scavenging rate of peroxyl radicals by carotenoids) [45]. Because of their antioxidant function and blue light filtering, carotenoids are plausible components to use in a sunscreen formulation.

Mycosporine-like amino acids

Marine algae are able to synthesize mycosporine-like amino acids (MMAs) which effectively absorb UV radiation between 310 and 360 nm [46, 47]. MMAs have been shown to be photostable and require light, oxygen and a strong photosensitizing agent such as riboflavin and/or sea water for photo-degradation to occur [48–50]. Additionally, MMAs will photo-degrade slower under high irradiance conditions without the presence of a photosensitizer [48]. MMAs are a likely natural sunscreen additive because of their ability to absorb UV radiation and strong photostability.

Conclusions

We have reviewed the traditional components, the use of nanoparticles and the emerging technologies of UV protection. New techniques offer improved UV protection, safety and enhanced photostability. Particularly promising is the polymeric encapsulation of UV absorbers, and the divergence from chemical absorbers towards the use of antioxidants and other natural product additives.

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