cosmetics

Review

Lignin-Based Sunscreens—State-of-the-Art, Prospects and Challenges

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Abstract: This review covers the latest developments and challenges in the field of broad-spectrum sunscreens and how sunscreens based on lignin address their requirements in terms of sunlight protection, antioxidants, and preservatives.

Keywords: antioxidant; biobased; lignin; nanoparticles; preservatives; skin; sunlight; sunscreen; UV light; visual light

1. Background

Sunlight is the portion of solar electromagnetic radiation that reaches the Earth's surface and includes ultraviolet (UVB, 290–320 nm and UVA, 320–400 nm), visual (VIS, 400–700 nm) and infrared (IR, 700–1000 nm) wavelengths, all of which induce photoaging and can cause skin cancer [1–3]. While limited exposure to sunlight is beneficial [4], clinical investigations support the application of broad-spectrum (UVB + UVA) sunscreens to mitigate the damage associated with prolonged or frequent sun exposure [3].

The effectiveness of sunscreens in preventing UVB-induced sunburn is denoted by their Sun Protection Factor (SPF). For example, an individual wearing the recommended dose of SPF 15 sunscreen is able to stay in the sun without suffering sunburn 15 times as long as they could if not wearing sunscreen [5]. The UVB absorbance of sunscreens increases non-linearly with an increase in their SPF and those with moderate-to-high SPFs of 15–50 block 93–98% of UVB radiation when applied as recommended [3]. Broad-spectrum sunscreens also block a significant portion of the skin-aging UVA radiation. In the US and EU, sunscreens claiming broad-spectrum UV protection must have a so-called critical wavelength of 370 nm or more, meaning that 10% of the protection that the sunscreen offers has to be for UVA wavelengths above 370 nm. This ability is represented by the UVA Protection Factor (UVA-PF). The EU also requires that the UVA-PF offered by a broad-spectrum sunscreen be at least one third of the labelled SPF.

SPF is determined in vivo based on the UV energy required to produce a minimal erythemal dose (MED) in sunscreen-protected skin (applied at 2 mg/cm^2) divided by the UV energy required to produce a MED on unprotected skin [3,6]. To determine sunscreen SPF in vitro, UVB transmittance is measured through a layer of sunscreen spread at a standard dose (2 mg/cm^2) on a UV-transparent slide. UVA-PF can be determined by similar in vivo and in vitro methods.

Broad-spectrum chemical sunscreens of SPF 15 or higher typically contain over 20% of various UVB- and UVA-absorbing synthetic organic compounds [5,7], while mineral-based (physical) sunscreens usually have somewhat lower levels of titanium dioxide (TiO_2) and/or zinc oxide (ZnO) nanoparticles that scatter, reflect and absorb UV rays. It should be noted that the so-called herbal or natural sunscreens [8,9], formulated without synthetic chemical UV absorbers, usually contain these metal oxides as the main UV active component while their plant-based components mainly act as antioxidants and emollients.

An estimated 14,000 tons of sunscreen originating from wastewater effluent discharges, water-based recreational activities and other sources [10] end up in the world's oceans every year. Chemical UV absorbers such as oxybenzone and octinoxate commonly used in chemical sunscreens have come under increased scrutiny because of their deleterious effects such as coral bleaching on marine ecosystems and their high environmental persistence [11–14]. In consequence, the sale of sunscreens containing these UV active components has already been banned in ocean-bordering countries such as Australia and island regions such as Hawaii [13,14]. The fact that chemical UV absorbers are small molecules that are poorly captured by wastewater treatment plants aggravates the problem. Regarding the environmental impact of physical sunscreens, ZnO (but not TiO_2) nanoparticles have been found to be detrimental to coral reefs [15].

The use of chemical sunscreens results in systemic exposure to their small UV absorbers that are readily absorbed through human skin and remain in the body for extended periods [16]. Many of them are known to cause skin rashes in sensitive individuals and have been shown to act as hormone disruptors in animal trials. However, evidence is lacking on the severity of any hormone-disruptive effects in humans. Nanoparticulate UV filters of physical sunscreens are considered safer to humans than chemical sunscreens despite conflicting evidence regarding their ability to penetrate human skin [12]. In addition, systemic exposure to harmful sunscreen ingredients can occur by inhalation of sprayable sunscreens.

Besides the UV active components of sunscreens, concerns have been raised for the safety of their synthetic antioxidants and preservatives [17–19]. There is clearly scope to improve not only the sunlight protection provided by commercial sunscreens but also their environmental and user safety. The benefits and challenges of potentially safer lignin-based sunscreens are addressed below.

2. Technical Lignins and Their Effectiveness as Sunscreen UV Absorbers

In recent years, attention has focused on lignin [7,20–23] as a safer and biodegradable substitute for synthetic UV absorbers in sunscreens [24–38]. Found in trees and other lignocellulosic plants, native lignin is a polyphenolic polymer that acts as the glue between cellulosic woody cells. During kraft (sulfate), soda, organosolv and other chemical pulping processes of lignocellulosic raw materials, lignin undergoes partial depolymerization and other structural changes and is dissolved in the black liquor or organic solvent [21]. Unless burnt at the pulp mill for energy, this mostly water-insoluble by-product (technical lignin) can be recovered for various value-added applications [7,20,21,39]. Lignocellulosic biorefineries and agricultural by-products are becoming another important source of technical lignins [28].

Technical lignins [23] contain more chromophoric and auxochromic structures than native and milled wood lignin (MWL) [22,37] per unit of mass, making them more absorbent in the UVB–UVA wavelength area targeted by broad-range sunscreens. The main chromophoric moiety of a lignin structural unit is its aromatic ring but the UV absorbance of simple aromatic compounds such as benzene and phenol falls in the UVC area that is not relevant for sunscreens (UVC radiation is blocked by the Earth's atmosphere). However, the 2–3 auxochromic phenolic hydroxyl and/or methoxyl substituents of guaiacyl, syringyl and catechol-type rings of technical lignins [23] cause a redshift in the lignin's UV absorbance, imparting them with absorbance in the UVB area [24–38]. Ring-conjugated -C=C- and -C=O bonds in the lignin side chain as well as any quinonoid structures formed by oxidation of e.g., catechol units can contribute to UVB and UVA absorbance [30,31]. In addition, electron-accepting *ortho*-quinones and electron-donating phenolic groups may interact via charge-transfer complexes, causing a strong increase in absorbance and a further redshift to VIS [40].

The sunscreen applications of different types of technical lignins are discussed in many recent publications [24–38]. In many of these studies, lignin sunscreens were formulated by including up to 15% lignin in a base of low-SPF (~1) cream and the sunscreen SPFs were determined in vitro at the international standard in vivo application thickness of 2 mg/cm^2. In most cases, the level of UVA protection provided was also reported. In light of these studies, it is apparent [31] that the

UV absorbance of the usual types of technical lignins, in their standard microparticulate size, is not high enough for high-SPF broad-spectrum sunscreens. However, the SPF of lignin sunscreens can often be significantly increased if the lignin is comminuted to nano-sized particles [24,31]. This can be accomplished, e.g., by a solvent/antisolvent method [31] in which lignin is first dissolved in a mixture of a low-boiling organic solvent such as acetone (solvent) and water (antisolvent). When the solvent is then gradually removed by evaporation (and recycled in the process), the lignin molecules arrange themselves into nanoparticles that can be recovered from the antisolvent. A variant of this method that generates smaller nanoparticles entails adding dissolved lignin in small portions into a large excess of vigorously stirred antisolvent [31]. A larger particle surface area-to-mass ratio of lignin usually enhances its sunscreen performance so smaller nanoparticles tend to outperform larger ones [24,31]. Modification of the chemical structure of lignin is another way to enhance its UV absorbance. The patented CatLignin process [41]—thermal post-treatment of kraft black liquor to produce partially demethylated and demethoxylated CatLignin ("CatecholLignin")—provides an example of this strategy. Lignin has also been demethylated/demethoxylated by iodocyclohexane under reflux in DMF to increase its UV absorbance, but this method is unlikely to be commercially viable [38]. By combining the two strategies, i.e., thermal modification and conversion to nanoparticles, SPFs of >20 and low UVA transmittance were achieved for sunscreens formulated with 10% CatLignin nanoparticles [31]. Although higher SPFs have been reported for lignin-containing sunscreens, this has only been in cases where lignin was combined with synthetic UV absorbers or added to a commercial sunscreen [25,26,29,38].

3. Effect of Lignin Color on Its Suitability to Sunscreens

The colors of lignin sunscreens typically range from brown to black, which precludes lignin from the most commonly used white daily-use sunscreen lotions. Chemical modification by acetylation [27,35] or UV irradiation [34] can make the lignins brighter but these modifications target structural moieties such as the auxochromic phenolic hydroxyl groups that play an important role in lignin UV absorption. Hence, the SPF values of sunscreens formulated with whitened lignins [24,26,27,34,35] tend to be significantly lower than those prepared using their original counterparts.

High-SPF sunscreens offer good protection against UVB rays that can cause skin burns while also blocking most of the UVA rays. However, because of the perceived need for most sunscreen lotions to be white for the majority of consumers, the UV active organic compounds (chemical sunscreens) and minerals (physical sunscreens) in these products tend to have high VIS transmittance. In fact, the UV absorbance of commonly used chemical UVA absorbers such as avobenzone and chemical sunscreens decreases precipitously in the wavelength area of ca. 380–400 nm [31,33]. As a result, chemical sunscreens often give a low degree of protection in this near-VIS UVA area. Furthermore, it has been shown that not only UV but also VIS and IR light, accounting for most of the sunlight wavelengths, can produce free radicals (reactive oxygen species, or ROS) and damage the skin [1,2], particularly when exposure to all these radiation wavelengths occurs simultaneously as in the case of sunlight [1]. VIS light alone has the ability to increase skin pigmentation and cause dyschromia. As white chemical or physical sunscreens offer no VIS protection, tinted sunscreens that absorb VIS rays have started to receive increased attention [2]. While tinted physical sunscreens featuring enhanced VIS protection can be fabricated by including, e.g., yellow iron oxide or other pigmentary metal oxides in their formulations, technical lignins offer themselves as potential UV-VIS absorbers for tinted chemical sunscreens. Native lignin is very lightly-colored but many technical lignins such as regular kraft lignin and CatLignin contain quinonoid and other chromophoric and auxochromic structures that provide them with a much greater degree UVB, UVA and VIS absorbance and a darker shade of brown or black color [32,34]. Although people with light skin tones may be more inclined to use lightly-colored sunscreens that do not show on their skin, lignin-based sunscreens may be an attractive proposition for individuals with darker skin tones. Many daily-use sunscreens and tinted cosmetics on the market already come in a range of colors, from light to very dark, to accommodate for the different skin tones.

4. Technical Lignins as Sunscreen Antioxidants

As mentioned earlier, UV, VIS and even IR wavelengths of sunlight accelerate skin aging by generating ROS that can cause oxidative damage to skin. However, besides protecting the skin by absorbing sunlight across its whole spectrum, lignin also offers a second level of protection from sunlight by neutralizing ROS. By the same token, lignin can help prevent rancidity of lipids and other sunscreen ingredients that are susceptible to oxidation. The antioxidant properties of lignin depend on the substituents of the aromatic ring and side chain structures. Resonance effects (-C=C- and -C=O conjugation with the aromatic ring) and electron-donating functional groups (phenolic hydroxyl and methoxyl) tend to increase antioxidant properties while electron-withdrawing functional groups (carbonyls) display an inductive effect that reduces antioxidant properties [42–48]. As with UV absorbance, the antioxidant activity of lignin per mass unit can be increased by demethylation of methoxyl groups [38,47] to increase the content of phenolic hydroxyls that may be oxidized to phenoxy radicals. This process is the main antioxidant mechanism of lignin and, depending on the lignin structure, phenoxy radicals may regenerate the phenolic hydroxyl, which can then be oxidized again [47]. Lignin whose phenolic hydroxyls have been etherified has no antioxidant activity [48]. Removal of moieties such as aliphatic hydroxyl that have little direct impact on antioxidant activity can also improve antioxidant activity per mass unit of lignin. In terms of electron-withdrawing structures (-C=C- and -C=O) of the lignin side chains, their deactivating inductive and activating resonance effects clash and the net result is hard to predict [31]. The parameters of alkaline pulp cooking can be optimized to maximize the antioxidant properties of the dissolved lignin [30]. The antioxidant activity of kraft lignin and many other technical lignins is higher or similar to that of the commercial antioxidants butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) [28,32,39,49–51]. While these compounds that are used in commercial sunscreens and cosmetics have been found to be non-carcinogenic [52], they have raised health concerns, warranting further investigations into their potential effects on menopause [17]. Because of this radical-scavenging antioxidant activity [32,39], the need for additional and potentially harmful synthetic antioxidants is reduced or eliminated for lignin-based sunscreens.

5. Technical Lignins as Sunscreen Preservatives

Sunscreen lotions are equipped with synthetic preservatives such as phenoxyethanol, hydroxybenzoates and triclosan to inhibit the growth of harmful bacteria that would otherwise spoil the sunscreen [19]. Similar to commercial chemical UV absorbers, some of them have been recognized as environmental pollutants that largely originate from rinse-off skin-care products such as sunscreen lotions and are difficult to remove at wastewater treatment plants [18,19]. However, technical lignins have demonstrated significant antibacterial and antifungal activities against common spoilage and pathogenic microorganisms [21,53,54]. The antibacterial properties are mostly attributed to phenolic hydroxyl groups that damage the bacterial cell walls, inducing lysis and leakage of the cell contents. The antimicrobial activity of technical lignins suggests a reduced requirement for additional synthetic and possibly deleterious preservatives for lignin-based sunscreen products. However, to confirm any preservation effect of lignins in sunscreen and cosmetic formulations, this topic should be directly addressed in a future investigation.

6. Safety of Technical Lignins

Unlike the UV-active, antioxidant and preservative ingredients of commercial sunscreens, most of which are small monomeric molecules passing easily through filtration and other purification stages of wastewater treatment plants [55], the polymeric technical lignins that are insoluble in water at pH levels below 9 would be far easier to remove from wastewater and would thus contribute little to marine pollution caused by effluent discharges of wastewater treatment plants.

Lignins show low cytotoxicity to normal mammalian cells but a certain degree of cytotoxicity to cancerous cells [28,39,50,51,54,56]. However, it was recently reported [28] that mammalian cell proliferation may be negatively impacted with prolonged exposure to high lignin doses.

On balance, lignin sunscreens offer themselves as a relatively safe option for both the environment and consumers of sunscreens and SPF cosmetics.

7. Conclusions

Dark-tinted sunscreens and cosmetic products formulated with technical lignins, ideally in the form of nanoparticles and/or enhanced by the CatLignin process, can provide broad-spectrum sunlight protection by absorbing its UV, VIS and IR rays and suppressing free radicals generated by this radiation. Technical lignins are also characterized by low cytotoxicity to normal mammalian cells and significant antioxidant and antimicrobial (preservative) properties. The substitution of lignin for synthetic sunlight-protective, antioxidant and preservative ingredients in skin care products and cosmetics may allow mitigation of their environmental and health impacts. The total additive loading of functional additives can potentially be decreased because of the multi-functional nature of lignin. The main drawback of lignin is its dark color that makes it unsuitable for whitish formulations. However, this could also be an advantage regarding dark-tinted sunscreens and SPF cosmetics.

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