Nano-Structured Lignin as Green Antioxidant and UV Shielding Ingredient for Sunscreen Applications

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Abstract: Green, biocompatible, and biodegradable antioxidants represent a milestone in cosmetic and cosmeceutical applications. Lignin is the most abundant polyphenol in nature, recovered as a low-cost waste from the pulp and paper industry and biorefinery. This polymer is characterized by beneficial physical and chemical properties which are improved at the nanoscale level due to the emergence of antioxidant and UV shielding activities. Here we review the use of lignin nanoparticles in cosmetic and cosmeceutical applications, focusing on sunscreen and antiaging formulations. Advances in the technology for the preparation of lignin nanoparticles are described highlighting structure activity relationships.

Keywords: lignin nanoparticles; cosmetic and cosmeceutical applications; antioxidant activity; UV shielding activity; sunscreen formulations

1. Introduction

1.1. Drawbacks of Current Antioxidant and UV Shielding Ingredients in Sunscreen Formulations

The harmful consequences of prolonged exposure of human skin to sunlight have long been explored [1]. UV radiation (190–400 nm) is the main cause of generation of radical reactive oxygen and nitrogen-centered species and related oxidative stress. Radicals are responsible for lipid peroxidation and degradation of elastin and collagen, promoting both loss of skin elasticity and aging [2]. In addition, they react with DNA promoting apoptosis, genetic mutation, and cancer [3]. In this latter case, the radical damage is related to melanoma, the most aggressive form of skin cancer, arising from melanocytes resistant to chemotherapy [4,5]. Sunscreen formulations are designed to protect the skin from solar radiation and possibly from melanoma. They contain active ingredients capable of absorbing (organic chemical filters, OCFs) or reflecting (physical mineral filters, PMFs) the UV radiation. PMFs are generally used as nanoparticles since the nanoscale improves the reflectance activity, as well as the consumer cosmetic acceptance [6]. In a typical high sun protection factor (SPF) sunscreen, the final concentration of PMFs and OCFs can reach 45% by weight [7]. In addition, UV boosters are used to further increase the SPF by physical effect, tuning the ratio between the UV shielding efficiency and the total UV filter concentration [8]. UV boosters are usually composed of plastic micro-sized spheres from petroleum origin, such as styrene/acrylate copolymers, that are well recognized as a waste in water pollution [9].

High amounts of PMFs, OCFs, and UV boosters, are detected in marine environments [6] as a consequence of their release from cosmetics, producing submicronic aggregates in freshwater, or alternatively, sediment settles in seawater [10]. Consequently, the growing consumption of sunscreens has gradually led to a significant increase in coastal pollution with a deleterious impact on marine organisms [11]. 3-Benzylidene-camphor
(3-BC) and 3-(4-methyl benzylidene)camphor (4-MBC), which belong in the OCFs family, induce severe and fast coral bleaching, altering the symbiosis between coral and zooxanthellae, and inhibiting the reproduction of both oligochaete *Lumbriculus variegatus* [9] and marine phytoplankton [12]. Moreover, they are concentrated in tissues of aquatic organisms (mussels, crustaceans, eels, fishes, marine mammals, and pelagic birds) due to the high lipophilicity [13]. In a similar way, PMFs are harmful to marine ecosystems. Zinc oxide nanoparticles contributed significantly to the whitening of the *Acropora* spp. [14], and titanium oxides negatively affect dinoflagellates, fish, algae, and marine invertebrates [15].

Risks for human health are also associated to UV filters [16] as a consequence of phototoxic and photoallergic responses and, in the long term, photoaging and cell damage [17]. The absorbance spectrum of OCFs changes during the UV exposure time as a consequence of structural transformation and degradation processes [18]. These processes can produce free radicals and interaction with other sunscreen ingredients and skin constituents (e.g., lipids, proteins, and nucleic acids), altering the absorbing property of the sunscreen and inducing oxidative damage [19]. Avobenzone (AVOB), that is a widely recognized OCF in commercial sunscreens, demonstrated photo instability after prolonged UV exposure to yield radical photoproducts (Figure 1A) [20], and octyl methoxycinnamate (OMC), the most used UV-B filter, is photo-unstable after exposure to sunlight, undergoing photodimerization and loss of shielding efficiency. In this latter case, the photoproducts 4-methoxy benzaldehyde (4-MBA) and 2-ethylhexanol (2-EH) are also produced (Figure 1B) [21,22]. Moreover, benzophenone-3 (BP-3), and octocrylene (OC) are able to penetrate in the epidermal nucleated layers generating in situ radical species after UV irradiation [23].

![Figure 1. Schematic representation of photodegradation processes operative in the case of avobenzone (AVOB) (A) and octyl methoxycinnamate (OMC) (B).](image-url)
Despite photodegradation and generation of radicals, OCFs cause other drawbacks for human health. For example, AVOB promotes obesogenic phenotypes in normal human epidermal keratinocytes (NHEKs), increasing the gene transcription of peroxisome proliferator-activated receptor γ (PPARγ) and fatty acid-binding protein [24], and affecting diabetes [25] with disruptive endocrine effects [26]. The toxic effect of some of the most representative OCFs are summarized in Table 1.

Table 1. Toxic effects of some of the most representative OCFs applied in sunscreen formulations.

| OCFs | UV Range | Photodegradation | Toxic Effects |
|------|----------|------------------|---------------|
| AVOB | 357      | yes              | Suppression of human trophoblast cells and apoptosis mediated by mitochondrial disruption [27], induction of obesogenic phenotypes [28], and hormone-like activity [29]. |
| HS   | 295–315  | no               | Skin penetration [30], disrupts estrogen [31]. |
| OMC  | 280–355  | yes              | Skin penetration, hormone like-activity; reproductive system, thyroid, and behavioral alterations in animal studies [17]. |
| OB   | 270–350  | yes              | Estrogenic activity, alteration of sperm production in the animal associated with endometriosis in women [32]. |

AVOB: avobenzone. HS: homosalate. OMC: octyl methoxycinnamate. OB: oxybenzone.

1.2. Alternative UV Shielding and Antioxidant Ingredients in Sunscreen Formulations

The use of PMFs and OCFs is regulated by directives from different agencies, such as the Food and Drug Administration (FDA) and the European Chemicals Agency, in order to adequate the UV protection to minimal side effects for health [33]. The use of alternative eco-friendly and natural ingredients, deprived of toxic effects, is strongly recommended and foreseen in future formulations.

The toxicity and pollution effects of actual commercial UV filters increased the interest for eco-friendly and natural alternatives [34]. Their use is considered an advantage not only for the ability to improve the SPF value in safer formulations, but also in improving the photostability of traditional UV filters [35]. Secondary metabolites of the cell, such as terpenoids and products of the shikimic acid and polyketide pathways, can play a relevant role bearing conjugated double bonds and aromatic pharmacophores with high UV absorbing and antioxidant properties [36]. They have been selected during molecular evolution by plants and microorganisms in developing defense strategies to minimize the damage of UV radiation and chemical oxidative stresses [37–39]. Sunscreen formulations containing mixtures of secondary metabolites from plants, algae, and fungi, as well as from cyanobacteria [40], showed a higher shielding effect with respect to commercial filters. In addition, mycosporins and mycosporin-like amino acids (MAAs) [41] produced by marine phototrophs (dinoflagellates, cyanobacteria, and macro algae) [42] are able to convert radiative energy in thermal energy without generation of radical species [43]. Sunscreen formulations containing MAAs from Porphyra umbilicalis showed a high protective effect on fibroblasts and keratinocytes exposed to UV-A [44]. Mixtures of secondary metabolites from the spent fraction of coffee grounds and green coffee oil (GCO) have a synergistic effect with traditional OCFs and increase the SPF value of sunscreen formulations (+20%) [45]. The protective effect from UV-B exposure by grapes wine extract of Jacquez (namely JW-E), containing high level of proanthocyanidins, anthocyanins, and hydroxycinnamic acids, has been evaluated by three-dimensional tissue cell model of the human epidermis [46]. Finally, the water resistance of OCFs is improved by natural waxes that stabilize the SPF value of sunscreen formulations after immersion in water [47]. Waxes also increase the SPF value and improved the photostability of OCFs and PMFs after UV irradiation [35]. Despite exhibiting strong sun protection effect, most crude plant extracts are insoluble in water, thus hindering their practical applications.
2. Lignin as a Novel Eco-Friendly Sunscreen Ingredient

The development of sunscreen formulations based on renewable and recyclable resources received a great interest, mainly due to circular economy and green chemistry concerns. In this context, lignin, the most abundant polyphenol in nature, is increasingly becoming one of the main protagonists since it is recovered in large amounts as a low-cost waste from pulp and paper industry and biorefinery [48]. The low environmental impact of lignin extraction and purification technologies has been reported and discussed, focusing on the expected benefits of lignin as a high added value material [49–51]. Current and potential application of lignin has been reviewed [52–56], focusing on power fuel and syngas production (Fischer–Tropsch synthetic fuels), material science and fine-chemicals, specialties, and commodities preparation [57,58]. Lignin confers rigidity and microbiological and mechanical resistance to lignocellulosic materials [59]. In addition, it shows low-medium UV-shielding [60], antioxidant activities [61,62] and biocompatibility [63]. The lack of toxicity of lignin has been reported by in vivo toxicity assessment in embryonic zebrafish (Danio rerio) [64]. The efficacy of lignin as an alternative sunscreen ingredient depends on its origin and composition, as well as from the structural order and dimensional scale [65]. The main lignin functions in sunscreen cosmetics are summarized in Table 2. The next paragraphs will report about these specific aspects.

Table 2. Cosmetic and cosmeceutical application of lignin.

| Lignin Property       | Petroleum Derived Compounds Substituted by Lignin                          | Ref. |
|-----------------------|----------------------------------------------------------------------------|------|
| Antioxidant           | BHT, BHA                                                                   | [66] |
| UV booster            | acrylates/c10-30 alkyl acrylate cross-polymer                              | [67] |
| Antimicrobial agent    | phenoxyethanol, hydroxybenzoates and triclosan                            | [68] |
| Chelating agent       | EDTA, THPE                                                                 | [69] |
| Emulsifier and stabilizer | acrylamides salts                                                         | [70] |

BHT: butylated hydroxytoluene; BHA: butylated hydroxyanisole, EDTA: ethylenediaminetetraacetic acid; THPE: tetrahydroxypropyl ethylenediamine.

2.1. Structure, Availability, and Green Application of Lignin

Lignin is an important source of phenolic compounds [71]. It is one of the main components in the plant cell wall beside cellulose, hemicellulose, pectin, and extractives. This polymer is biosynthesized by a cascade of oxidative radical couplings, involving three phenylpropanoid monomers (monolignols), namely para-hydroxyphenyl (H), syringyl (S), and guaiacyl (G) alcohols (Figure 2A) [72]. These compounds differ in the degree of methoxylation of the aromatic ring and are present in the polymer in a different ratio depending on the plant species considered [59]. The biosynthesis of monolignols starts in the cytoplasm, from which they are successively transported to the apoplast and delivered in different zones of the secondary area (central lamella and secondary wall of the xylem) [73,74]. The physiological significance of this distribution is apparently simple: differential targeting allows for the construction of lignified cell walls with distinct biophysical properties [75].

The first step of the lignification process is the dehydrogenation of monolignols to corresponding phenoxy radicals plant cell-wall oxidases (lignin-peroxidase LiP, manganese-peroxidase MnP, hybrid LiP-MnP, versatile-peroxidase VP, and laccase) [72]. Monolignols form a network of inter-unit linkages to yield relatively low molecular weight oligomers involved in the formation of stable supramolecular π-π aggregates into a complex 3D molecular architecture [76]. The main types of inter-unit linkages are the alkyl-aryl ether β-O-4, phenylcoumaran (β-5), 1,2-diaryl-propane (β-1), diaryl (5-5), diaryl ether (4-O-5), pinoresinol (β-β), and dibenzodioxin structural residues (Figure 2B).

Lignin is classified into three basic types depending on the number and quality of sub-units: softwood, hardwood, and grass lignin (Table 3). In addition, some unconventional types of structural motif, such as caffeyl lignin units (C-lignin), were also found [77].
Table 4. Major technologies available for the production of LNPs.

| Lignin Tech. | Size (nm) | pH | Shape | Advantages | Application(s) | Limits | Ref. |
|--------------|-----------|----|-------|------------|----------------|--------|------|
| SL SEP       | 50–250    | 7  | S     | no aggregation | drug delivery and stabilizer | toxic chemicals [109,110] | |
| SL AP        | 50–250    | >7 | I     | drug delivery, bio- | | | |
| AL AFR       | 30–100    | <12| S     | high yield | bioplastic | aggregate | [94,113,114] | |
| AL AP        | 30–100    | <12| S     | high stability | sunscreen | high ionic strength [115] | |
| AL MR        | 30–100    | <12| S     | dispersibility | antioxidant, antimicrobial | toxic chemicals [116,117] | |
| AL SEP       | 30–100    | <12| S     | antioxidant, antimicrobial | toxic chemicals | [115,118] | |
| KL AFR       | 38–250    | 4–12| I     | stability | adhesives | | [113,119] | |
| KL PCA       | 38–250    | 4–12| S     | high solubility | commodities | high ionic strength [120,121] | |
| KL FP        | 38–250    | 4–12| S     | UV-shielding materials | | | [110,122] | |
| KL MP        | 38–250    | 4–12| S     | commodities | | | [110,122] | |
| OL AFR       | 30–250    | 3.5–8| S     | high yield | adhesives | aggregate | [110,113,116] | |
| OL FP        | 30–250    | 3.5–8| S     | stability | commodities | high ionic strength | [122] | |
| OL SEP       | 30–250    | 3.5–8| S     | stability | materials | toxic chemicals | [112] | |

S: spherical shape. I: irregular shape. SEP: solvent exchange precipitation. AP: acid precipitation. AFR: aerosol flow reactor. MR: microchannel reactor. PCA: compressed fluid antisolvent technique. FP: flash-precipitation. MP: mini-emulsion polymerization.

Figure 2. Chemical structure of the main components in lignin. (A) Monolignols; (B) representation of the main type of inter-units in lignin.

Table 3. Classification of different types of lignin depending on the amount of para-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) sub-units.

| Type | Grass Lignin | Softwood | Hardwood |
|------|--------------|----------|----------|
| H    | 5–35%        | <5%      | 0–8%     |
| G    | 35–80%       | >95%     | 25–50%   |
| S    | 20–55%       | 0%       | 45–75%   |

Proportion of different monolignols in lignin of different plants source. Adapted from [78–80].

Different technologies are available to separate wood components, and they can be classified depending on the scale of the treatment [81]. At the analytical scale (from mg to gram), milled wood lignin (MWL) is considered the most reliable model of native lignin. MWL is produced from wood chips by extraction with 1,4-dioxane and successive precipitation in water [82]. At the industrial scale (ton scale), two main types of lignin are prevailing: sulfur-containing lignin and sulfur-free lignin. Sulfur-containing lignin include lignosulfonate (LS) and kraft lignin (KL), which are produced in a strong alkaline and oxidative medium. The second category includes soda lignin (SL), organosolv lignin (OL) ionic liquid lignin (ILL), and steam-exploded lignin (SEL) [83].

Sulfur-free lignins have been applied in the production of probiotics for animals due to their capacity to improve the growth of beneficial bacteria [84,85], influencing the absorption of bile acids in the lipid metabolism [86,87]. In addition, LS is used as a binder, dispersing agent, emulsifier, and heavy metal sequestant in the design of advanced materials and wastewater treatment, as in the case of absorption of toxic chromium, copper, cadmium, lead, zinc, nickel, cobalt, and mercury ions [88]. From the biological point of view, KL and SEL showed antioxidant activity in preserving human red blood cells [89]. This activity was associated to non-etherified phenolic hydroxyl groups, ortho-methoxy groups, and aliphatic hydroxyl groups in the side chain. In particular, ortho substituents, such as methoxy groups, stabilize phenoxy radicals by resonance and hinder their propagation. Conjugated double bonds can also improve the antiaging activity by extensive electronic delocalization. In some cases, the antioxidant activity was associated to antiviral [90], antimicrobial, and anticancer properties [91].
2.2. The Technology for the Self-Assembling of Lignin Nanoparticles

The low solubility of lignin represents a limit for its application in the cosmetic and cosmeceutical formulations [92]. This bias can be solved by the self-assembly of the native polymer into highly ordered lignin nanoparticles (LNPs) [93]. LNPs are characterized by improved chemical and physical properties compared to the native state [94]. Their size tunability and spherical shape allowed to broaden the fields of application, encompassing drug delivery systems [95], flame retardant [96] and reinforcing materials [97], and waste treatment [98]. Remarkably, LNPs show improved UV shielding [94] and antioxidant properties [99] (see next paragraph). Table 4 reports the major technologies available for the production of LNPs, the relative experimental conditions, and some of their specific applications. Briefly, the following technologies have been reported for the preparation of LNPs: (i) solvent exchange precipitation method where the starting solvent was slowly replaced by an anti-solvent by dialysis; (ii) treatment of lignin solution by adding strong acid; (iii) aerosol flow reactor equipped with collision-type jet atomizer; (iv) microchannel reactor in which the lignin solution is continuously mixed with the antisolvent; (v) CO\(_2\) compressed fluid as antisolvent; (vi) flash-precipitation by fast adding of anti-solvent in lignin solution; and (vii) mini-emulsion between oil-phase and aqueous lignin solution under ultrasound treatment followed by polymerization with cross-linker agent. The formation of LNPs is influenced by different experimental parameters, including the physical properties of the medium (solvent, pH, temperature, stirring speed), and the chemical structure of the starting substrate (composition, molecular weight, polarity, and impurities). Among them, the pH value controls the ionization of the phenolic moieties, which in turn affect inter- and intra-molecular electrostatic interactions in the polymer. Recent studies based on light scattering analysis and pulse field gradient NMR, showed that the KL self-association process occurs below pH 9.0–11.5, the process being more efficient in water than in organic solvents [100]. In addition, a low value of temperature favors the aggregation [101], and a combined effect of temperature and pH can finely control the particle dimension [102]. As a general trend, softwood lignins show a higher degree of aggregation with respect to the hardwood counterpart, suggesting the greater presence of efficient intermolecular HOMO-LUMO interactions [103].

The structuration process of LNPs is driven mainly by noncovalent interactions, including H-bonding, van der Waals forces, and π-π stacking aggregation between the aromatic rings of different molecules [104]. Although no studies have been carried out on the specific role played by H-bonding in the self-assembly of lignin, this is commonly cited as a relevant contributing interaction due to its directional nature [105,106]. In accordance with this hypothesis, the formation of H-bonding network affects the mechanical properties of KL gels [107]. The specific role of the Van der Waals forces in tuning the macro-syneresis of KL gel has been also reported [108].

Table 4. Major technologies available for the production of LNPs.

| Lignin | Tech. | Size (nm) | pH | Shape | Advantages | Application(s) | Limits | Ref. |
|--------|-------|-----------|----|-------|------------|---------------|--------|------|
| SL     | SEP   | 50–250    | 7  | S     | no aggregation | drug delivery and stabilizer | toxic chemicals | [109,110] |
| SL     | AP    | 50–250    | >7 | I     | high yield   | bioplastic  | aggregate    | [94,113,114] |
| AL     | AFR   | 30–100    | <12| S     | high stability | sunscreen | high ionic strength | [115] |
| AL     | AP    | 30–100    | <12| S     | dispersability | antioxidant, antimicrobial | toxic chemicals | [116,117] |
| AL     | SEP   | 30–100    | <12| S     | high stability | antioxidant, antimicrobial | toxic chemicals | [115,118] |
| KL     | AFR   | 38–250    | 4–12| I     | stability     | adhesives | - | [113,119] |
| KL     | PCA   | 38–250    | 4–12| S     | high solubility | commodities | high ionic strength | [120,121] |
| KL     | FP    | 38–250    | 4–12| S     | UV-shielding  | materials | - | [110,122] |
| KL     | MP    | 38–250    | 4–12| S     | -            | commodities | - | [110,122] |
| OL     | AFR   | 30–250    | 3.5–8| S     | high yield   | adhesives | aggregate  | [110,113,116] |
| OL     | FP    | 30–250    | 3.5–8| S     | stability    | commodities | high ionic strength | [122] |
| OL     | SEP   | 30–250    | 3.5–8| S     | stability    | materials | toxic chemicals | [112] |

S: spherical shape. I: irregular shape. SEP: solvent exchange precipitation. AP: acid precipitation. AFR: aerosol flow reactor. MR: microchannel reactor. PCA: compressed fluid antisolvent technique. FP: flash-precipitation. MP: mini-emulsion polymerization.
2.3. Antioxidant Activity

Radical species take part in various degenerative processes, including aging and inflammatory response triggered by UV exposure [123]. For this reason, antioxidants are common ingredients in sunscreen formulations [124]. Lignin shows antioxidant activity due to the presence of the phenolic pharmacophore able to scavenge reactive radical species with formation of highly stabilized mesomeric forms. Figure 3 describes the main phenolic sub-units responsible for the radical scavenger activity. Phenolic hydroxyl groups, ortho-methoxy groups, and aliphatic hydroxyl groups play a crucial role in this activity. In particular, ortho substituents, such as the methoxy groups, stabilize phenoxy radicals by both resonance and steric hindrance effects.

![Figure 3. Classification and structural representation of lignin sub-units with antioxidant activity and chromophoric groups.](image)

The demethylation process of these groups, as well as the presence of conjugated double bonds, further increase the antioxidant activity by increasing the total amount of OH and favoring extensive electronic delocalization. Table 5 reports the antioxidant activity of a panel of low molecular weight compounds commonly considered as simplified models of lignin, as evaluated by the DPPH assay [103]. As a general trend, the antiradical power (ARP; defined as the reverse of the dose inhibiting the 50% of the DPPH radical) and the number of reduced DPPH units (NRD; which represents the moles of DPPH reduced per mole of compound) show that syringyl-like derivatives have higher antioxidant activity than guaiacyl and para-hydroxy phenyl counterparts (Table 5, entry I versus entry II). In addition, lower values of ARP and NRD were observed when a carbonyl moiety was present in the phenylpropanoid side-chain (Table 5, entry III, IV), while the presence of a conjugated double bond system increased the antioxidant activity (Table 5, entry VII, VIII, IX, and X) [125].

In addition to the capacity of sequestering radical species, lignin is promising to inhibit lipid peroxidation and, from a general point of view, the oxidative degradation of other cosmetic ingredients. For example, the ability of KL to inhibit the undesired radical production by PMFs (e.g., TiO$_2$) in sunscreen formulations has been demonstrated [126]. Interestingly, the antioxidant activity of LNPs was different order of magnitude higher than that of native lignin [94,127]. This behavior can be explained by the higher density of phenolic and carboxylic groups on the surface of LNPs with respect to the native polymer [128], as well as by the occurrence of favorable electron transfer processes between the ordered $\pi-\pi$ stacked aromatic moieties [117]. In order to further increase the antioxidant activity,
LNPs with mixed adsorbed polyphenols were prepared, highlighting the synergistic effects among the components [129]. The application of LNPs as UV filter or, alternatively, UV booster in broad-spectrum sunscreen formulations has been explored [130–132], confirming the beneficial role of lignin when used in the nanoscale form.

Table 5. Antioxidant activity comparison of main lignin subunit.

| # | Name                  | Structure             | ARP a | NRD b | # | Name                  | Structure             | ARP  | NRD  |
|---|-----------------------|-----------------------|-------|-------|---|-----------------------|-----------------------|------|------|
| I | Guaiacol              | ![Structure](image1)  | 2.6   | 1.3   | VI| Guaiacyl propanol-1   | ![Structure](image2)  | 3.0  | 1.5  |
| II| Syringol              | ![Structure](image3)  | 3.6   | 1.8   | VII| Coniferyl alcohol     | ![Structure](image4)  | 4.2  | 2.1  |
| III | Guacyl propanone-1   | ![Structure](image5)  | 0.2   | <0.1  | VIII| Coniferyl aldehyde    | ![Structure](image6)  | 1.9  | 0.97 |
| IV| propiosyringone       | ![Structure](image7)  | 0.5   | 0.2   | IX | Isoeugenol            | ![Structure](image8)  | 2.2  | 1    |
| V | Propyl guaiacol       | ![Structure](image9)  | 3.5   | 1.75  | X  | Eugenol               | ![Structure](image10) | 4    | 2    |

a ARP: antiradical power, reverse of the dose inhibiting the 50% of the DPPH radical. b NRD: number of reduced DPPH units, moles of DPPH reduced per mole of compound.

2.4. UV Shielding Activity

The Sun emits electromagnetic radiation in three ultraviolet (UV) wavelength areas. Rays with the shortest wavelength (UV-C, 100–290 nm) are captured by atmosphere, UV-A radiation at medium wavelength (UVA, 290–320 nm) and longer wavelength (UV-B, 320–400 nm) reach the surface of Earth. Excessive exposure to UV-B causes sunburn, while UV-A penetrates deeper into the skin. Both UV-A and UV-B are causing agents for DNA damage and cancer [133]. Lignin shows a broad absorption range in the UV region due to the presence of different chromophores and auxochromic groups (Figure 3), the maximum of absorbance being located at 283 nm [134,135]. Auxochromic groups (from ancient Greek ἀυξανό “increase” and χρῶμα “color”) are groups of atoms bearing non-bonding electrons (OH, OCH3, NH2, CO, SH, and SCH3) able to increase the chromophore effect. The contribution of auxochromic groups in lignin to generate a bathochromic effect (redshift phenomena) is reported [136] (Figure 4). LNPs are characterized by improved UV-shielding properties in relation to the native counterpart. For example, KL nanoparticles showed a higher absorption efficacy (up to 30%) than native KL, associated to the presence of a larger absorption band in the region of the longest wavelengths [94,137]. This effect is mainly due to the occurrence of π-π stacking interactions between the aromatic moieties, that can form two main types of aggregates, namely sandwich-type (H-orientation) and head-to-tail (J-orientation) aggregates. The J-orientation (water media) is the most efficient...
to decrease the energy gap for the $\pi-\pi^*$ electronic transition, thus enhancing the absorption efficacy of UV photons [138]. In addition, charge transfer complexes between electron-donating phenolic groups and electron acceptor ortho-quinones moieties can further increase the UV photo-absorbing capacity of LNPs [139].

![Figure 4. UV-VIS assay to evidence of bathochromic effect of organosolv lignin nanoparticles (OLNPs; green line) after the nanostructuration of starting technical organosolv lignin (OL; red line).](image)

Notably, experimental data highlighted that the UV-absorbing capacity of lignin increases during the exposition to radiation as a consequence of the formation of novel chromophores, such as quinonoid units [140]. The negative charged surface of LNPs can be further functionalized by consecutive deposition of natural macromolecules or polyelectrolytes with opposite charge by the layer-by-layer technique (LbL) [141,142]. In this way, mixed LNPs containing layers of other natural polyphenols, such as tannic acid, showed enhanced UV shielding properties, by occurrence of a synergistic effect between the aggregate polymers [116]. Finally, the cavity of LNPs can be exploited for the physical encapsulation of both OCFs and PCFs to yield functionalized LNPs with UV shielding properties higher than the parent compounds. One example of this strategy is represented by the encapsulation of TiO$_2$ inside lignin-based colloidal nanoparticles to afford a stable UV filter deprived of undesired side-chain catalytic effect in the generation of radical species [143].

2.5. Other Physical and Chemical Properties of LNPs Useful in Sunscreen Formulation

LNPs are characterized by a large panel of physical and chemical properties useful for the design of sunscreen formulations, encompassing emulsion stabilizer, antimicrobial, and chelating properties. These properties will be explored in the following paragraphs.

2.5.1. Emulsion Stabilizer Properties

The emulsions are unstable systems due to the high surface energy exerted between the two immiscible phases. For this reason, the presence of a surfactant able to reduce the surface energy is required [144]. Most surfactants derive from non-renewable precursors and are generally not biodegradable [145]. Lignin is considered an amphipathic polymer due to the presence of both hydrophilic and hydrophobic components. In addition, the presence of ionizable groups make it an efficient stabilizer by the occurrence of electrical repulsion effects [146]. A case of study for the application of LNPs as a stabilizer is
represented by the production of Pickering emulsions, which were characterized by a higher deformation resistance compared to that stabilized with conventional surfactants. This effect was associated to the barrierless adsorption of the LNPs at the interfaces of two immiscible liquids, thanks to their partial wetting properties [147]. LNPs were also efficient Pickering emulsifiers to stabilize oil emulsions in water (O/W) in the formulation of sunscreen containing low soluble organic substances [148].

2.5.2. Antimicrobial Properties

Lignin is characterized by antimicrobial activity as a consequence of the capacity to interact with the bacterial cell causing lysis with consequent release of the cell content. KL is effective against Erwinia carotovora and Xanthomonas campestris pv. vesicatoria (but not against Pseudomonas syringae), while AL showed antimicrobial activity against Escherichia coli, Staphylococcus aureus, and Pseudomonas [149]. In particular, the C=C double bond and γ-methyl groups in the side chain confer to lignin a higher antimicrobial activity than phenolic and aliphatic groups [150]. Again, LNPs showed higher antimicrobial activity than the native counterpart, as a consequence of the highest contact surface area available for the interaction with the microorganisms [134], associated to the possibility to penetrate into the bacterial cell. In addition, LNPs favored the damage of the bacterial cell by electron transfer processes able to generate local radical species [115]. Examples of the synergy activity between silver nanoparticles [150] and lignin against Gram-positive and Gram-negative bacteria have been reported, focusing on the role of lignin as a recognizer and delivery system for the controlled release of the silver ion [151]. In this latter case, the amount of silver ions used in the treatment was 10 times lower than conventional materials, reducing the known negative impact of silver wastes on the environment. Examples of the use of lignin as a green antimicrobial ingredient in the formulation of cosmetics are reported, as in the case of the reduction or substitution of high environmental impact antimicrobial agents, such as phenoxyethanol, hydroxybenzoates, and triclosan [68].

2.5.3. Chelating Properties

Chelating agents are ingredients able to complex metal ions in a stable way. These compounds play a crucial role in the stability and efficacy of cosmetics since the chelation mechanism stabilizes metal ions by preventing them from reacting with other substances and skin. The adsorbing capacity of lignin has been studied against different metal species, including chromium, copper, cadmium, lead, zinc, nickel, cobalt, and mercury [152,153]. The chelating process occurs by coordination of the metals with Lewis basic sites in lignin, such as carbonyl, carboxylic, and phenolic groups [154]. The adsorption was found to be pH dependent, being favored by deprotonation of the active groups in lignin [155]. In this context, the use of lignin to replace commercial chelating agent characterized by a well-known environmental pollution impact (e.g., EDTA) has been reported [156].

3. Color Agreeableness of Lignin

The dark color of lignin, that is mainly due to the harsh conditions of physical and chemical treatments (e.g., high temperature and oxidative transformations), hinders the promotion of lignin-based cosmetics on the market [157]. The principal methods to assess the lignin color are the Munsell and CIELAB procedures [158]. The Munsell color system determines the classification of the color by measuring the human perceptual response, and consists in the evaluation of three independent variables, represented by the color hue (measured in degrees on a horizontal circle), saturation (measured radially from the neutral gray axis outwards), and brightness (measured vertically on the gray axis from 0 for black and to 10 for white) parameters. This method is accurate and quantitative, but it is limited by a laborious visual matching. The CIELAB method is based on a spectrophotometer analysis in two different modes: (i) specular component included (SCI); and (ii) specular component excluded (SCE) modes. SCI is used to evaluate the actual color using both specular and diffuse reflected light, while SCE determines the color by excluding any
specular reflected light. In the International Commission on Illumination L*a*b* (CIELAB) color space, the L* value represents a bright behavior of a sample as follows: white when L* = 100 and black when L* = 0; +a* is a red shade and −a* is a green shade; +b* is a yellow shade and −b* is a blue shade. A total color difference value (ΔE) is defined as following Equation (1):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where ΔL*, Δa*, and Δb* are the differences in L*a*b* values between a reference and a sample. In order to enhance the color agreeableness of lignin, the chromophore and auxochrome groups should be blocked or cleared. This is of particular relevance in the case of sunscreen formulation. The main techniques applied to lighten lignin are described in the following paragraphs.

3.1. Drying of Lignin

Drying of lignin involves the control of the organization of the polymer structure at the morphological level by removal of the water molecules included in the sample [159]. An appropriate drying procedure can significantly reduce the dark color of lignin without extensive structural modification of chromophores and auxochrome moieties. This procedure has been applied in the preparation of light-colored sun creams, the control of the color intensity depending on the specific drying method (i.e., oven, vacuum, freeze, and spray drying) [160]. Oven and vacuum drying procedures favored the formation of large particles with a glossy surface and a dark color, while spray and freeze drying make the lignin as a lighter colored fine powder. In addition, a correlation between the particle size and the lignin color was observed, small-sized particles being less colored.

3.2. Fractionation of Lignin with Solvents

Light-colored lignin nanoparticles (CEL-NP) have been obtained from rice husks through initial extraction of cellulolytic enzyme lignin (CEL) followed by the solvent shifting procedure [161]. The color of CEL-NP and CEL was evaluated using the L* a* b* (CIELAB) color space method and compared with lignin from rice husks without cellulase treatment (RH) and organosolv lignin (OL), as references. The brightness (L*) and redness (a*) values of CEL were similar to those of RH as a consequence of the low effect of cellulase activity on phenolic and quinoid chromophore groups. The L* value of CEL was higher than that of OL and the a* value of CEL was lesser than OL. This is because CEL was prepared under much milder conditions than OL. As expected, the nanostructuration process further increased the lightness of the sample (CEL-NP). The effect of mixture of organic solvents in the lightness of lignin has been also reported [162].

3.3. Heat Treatment

The thermal processing of lignin involves the cleavage of β-O-4 linkages and demethoxylation. Usually, this process produces condensed structures and increases the amount of chromophores groups [163,164]. As an alternative, the steam and heat treatment of wood (steam explosion procedure) for the extraction of lignin, consists in heating the starting material at temperatures between 180 °C and 220 °C and high pressure. This procedure affords an effective discoloration of lignin [165]. In this latter case, the degree of color change (as evaluated by the DE* value) was highly dependent from the temperature and pressure parameters.

3.4. Chemical and UV Whitening of Lignin

Traditional chemical bleaching procedures are not suitable for lignin color reduction as their aim is to profoundly degrade the lignin structure. Softener procedures are therefore required to whiten lignin without reducing the antioxidant and UV shielding capability. Among them, sulfonation, sulphonmethylation, and butane sulfonation treatments at high temperature and pressure have been shown to be effective in whitening
eucalyptus lignin [166]. The reaction occurred preferentially at the C-α position of the phenylpropanoid side chain, while, when performed in the presence of formaldehyde and Na$_2$SO$_3$, the aromatic C-5 position was also modified [167]. UV irradiation combined with a long-time (20 h) H$_2$O$_2$ treatment effectively decolorizes sulfonated alkali lignin (SAL) by reducing the amounts of aromatic moieties and methoxyl and phenolic hydroxyl groups. Thanks to this treatment, SAL was successfully used as a dye dispersant [168]. Pre-treatments of the starting material can facilitate the bleaching procedure. They include autohydrolysis, steam explosion, and treatment with dilute acids. In particular, the autohydrolysis process improved the whitening of KL and decreased the excessive consumption of the sample during the overall whitening processes [169]. Selective functionalization procedures can also be applied in the whitening of lignin. For example, the acetylation of solvent-fractionated KL with acetic anhydride reduced the color intensity of the sample without interfering with its UV absorption capability (313.5% and 145.6% in brightness and L* value, respectively). In this latter case, the acetylation process was responsible for the inhibition of the auxochrome effect of the phenolic moieties, as a consequence of its electron withdrawing effect. Acetylation prevented demulsification processes due to the fine control of the polarity of lignin [158]. As a general trend the lightening process slightly interferes with the antioxidant and UV shielding properties.

4. Conclusions

The future trend in the application of lignin in solar screen formulations appears to be dependent on two main variables: (a) the availability of adequate technologies for lignin transformation and enhancement; and (b) the availability of an economically sustainable and stable market over time. In the first case, different nanotechnologies are presently available for the transformation of technical lignin into nanoparticles with a controlled dimension and superficial charge, which are useful for the formulation of solar screens. The undoubted advantage of these new active ingredients lies in their proven biocompatibility, complete biodegradability, and antimicrobial activity, associated with improved antioxidant and UV shielding properties, emerging from the reduction of the molecular scale as a consequence of specific no covalent interactions. The great variety of lignin wastes from pulp and paper, agro-industrial, and biorefinery transformations also allows for a large panel of starting materials that differ in the solubility and other chemical and physical properties favoring compatibility with the ingredients of the formulation. In addition, lignin has peculiar UV absorbing properties which cover both the UV-A and UV-B range, thus reducing the actual requirements of complex mixtures of synthetic organic and inorganic filters. Being empty, the beneficial properties of lignin nanoparticle may be further increased by drug delivery processes involving the time-dependent release of selected natural substances [170]. Finally, a careful choice of the starting material, combined with enzymatic or chemical pre-treatments, also allows the control of the color of the nanoparticles, better meeting the consumer’s tastes. With regard to the sustainability of the economic market, the lignin industry demand is expected to register around 6% of compound annual growth rate (CAGR) between 2020 and 2026, and as a case of study, the demand for lignin-sulphonate wastes from pulp and paper is expected to grow at a CAGR of 1.6% over the forecast period, mainly for application in paint and coating products, laundry and cleaning detergents, biomaterials, and cosmetic and cosmeceutical formulations [171]. Processes for the extraction and recovery of technical lignin are available at the industrial scale as a result of collaboration between universities and private groups [172], and high quality grade lignin is available at approximately 600 $/t, a cost that is significantly lower than that of current sunscreens, also considering the benefit for human health and the environment [55]. Taken together, these data highlight lignin as one of the main alternatives for petroleum-based compounds in cosmeceutical and sunscreen formulations.

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