

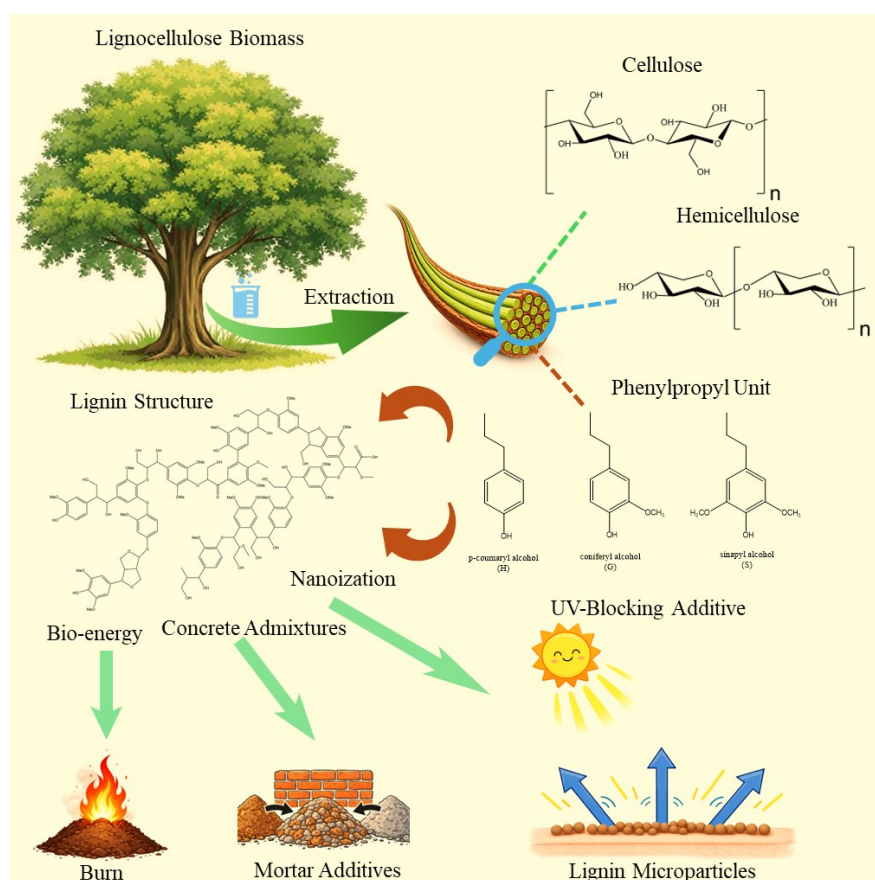
Progress on Lignin Separation and Its Application in Sunscreen

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GRAPHICAL ABSTRACT



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Lignin, a prospective bioresource from plants, has been undervalued for several dozen years because of the unpredictable structures and their changeability during extraction. Recently, lignin has become a star for certain researchers who are aiming to develop sunscreen products offering protection against UV radiation. The preparation of lignin into sunscreens as a natural alternative to chemical products may offer new perspectives. This review discusses how lignin isolation methods and the resulting structural characteristics affect UV absorption, thereby determining the potential of lignin as a UV-absorbing and blocking agent in sunscreen formulations. The application of lignin in cosmetics may present great benefit to humans and their skin care needs.

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INTRODUCTION

Lignocellulose, the most abundant renewable biomass on Earth, is regarded as a substitute to fossil resources (Chen *et al.* 2019). It has been widely used in traditional industries such as papermaking, energy generation, construction, food, and healthcare. Recently, research relative to its potential applications is springing up in cutting-edge fields, including novel batteries, biomedical materials, and ultraviolet (UV) protection (Xie *et al.* 2026; Abdelmula *et al.* 2025; Xu *et al.* 2025a; Zhang and Hu *et al.* 2025). Lignocellulosic biomass is mainly comprised of cellulose, hemicellulose, and lignin (Jin *et al.* 2017). These biopolymers constitute the skeletal framework of plant fiber cell walls, providing structural support and protection for plant growth (Cosgrove 2024; Chen 2014). Among them, lignin accounts for approximately 10% to 30% of the total plant mass, which is second to cellulose (Chen *et al.* 2019). However, the utilization of lignin for commercial products is far less than that of cellulose because of its complex and variable structure, which has long presented challenges. In particular, lignin is regarded as being difficult to separate and having low-value utilization. As a consequence, it is often treated as a “waste” or a low-valued by-product in the papermaking or biorefinery industries. The vast majority of industrial lignin is just utilized in low-value products, such as burnable fuel or concrete water-reducing additives (Kasana *et al.* 2025). In recent years, lignin has become a hot-point for research due to its UV resistance, antioxidant activity, and excellent mechanical rigidity (Feng *et al.* 2024). The high-value utilization of lignin is closely related to its isolation methods. Therefore, developing efficient lignin extraction and structural

modification techniques is crucial for manufacturing lignin-based functional materials and high-value products.

Lignin is an amorphous aromatic biomacromolecule that is primarily composed of structural units including syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H). These units are interconnected through disordered cross-links *via* ether bonds (*e.g.*, β -O-4, α -O-4) and carbon–carbon bonds (*e.g.*, β - β , β -5, 5-5'), forming a three-dimensional network structure (del Río *et al.* 2020). It is predominantly located in the middle lamella and secondary cell walls of plant fiber cells. Within the plant cell wall, lignin is linked to hemicellulose through lignin–carbohydrate complexes (LCCs), and encases cellulose microfibrils (Nishimura *et al.* 2018; Khodayari *et al.* 2021). The hydrophobic aromatic rings and phenolic hydroxyl groups in lignin confer hydrophobicity to plants, and it provides defense against microbial degradation (Kang *et al.* 2019; Yoo *et al.* 2020). Lignins derived from softwood, hardwood, and grasses differ in the relative abundance of guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units, which in turn influences their UV absorption behavior. Softwood lignins are predominantly composed of G units, which means that they may provide relatively strong UV absorption intensity, particularly in the UVB region. Hardwood lignins contain both G and S units, and their higher syringyl content generally introduces more methoxy groups, which favor red-shifted absorption and improved contribution in the UVA region. Grass lignins usually contain G, S, and H units, and their UV absorption performance is more variable because it depends on the relative proportions of these units as well as the degree of structural preservation during isolation and modification. Therefore, lignin source affects both absorption intensity and spectral distribution: G-rich lignins may be advantageous for UVB-dominant absorption, whereas S-rich lignins may be more favorable for UVA and broad-spectrum protection. However, no lignin source is absolutely superior, because the final sunscreen performance also depends strongly on the balance between methoxy and phenolic hydroxyl groups, quinone formation, molecular weight, aggregation state, and extraction-induced structural changes.

The unique conjugated chemical structure includes aromatic rings and attached phenolic hydroxyl groups, delocalized π -electrons, and lone-pair n-electrons in these systems of lignin. The outer electrons in the molecular orbitals can be excited by ultraviolet (UV) light, thereby undergoing $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. This confers a broad-spectrum UV absorption by lignin, covering the UV-B (280 to 320 nm) and part of the UV-A (320 to 400 nm) spectral regions (Liu *et al.* 2025; Jeon *et al.* 2025). In nature, this characteristic serves as a “natural sunscreen” for plants, protecting internal biological tissues and chemical components from photo-oxidative degradation. In the field of materials science, this property makes lignin an ideal candidate for the preparation of anti-UV aging materials.

Although lignin possesses the aforementioned superior properties, it is extremely challenging to isolate lignin from biomass while fully preserving its native structure (Zhao *et al.* 2020). In industry, the kraft process and the sulfite process involve the removal of lignin at high temperatures in the presence of strong alkali or acidic sulfite. However, the isolated lignin undergoes severe structural alterations during these processes. It is typically incinerated as waste (*e.g.*, black liquor from alkaline pulping) or recovered as a by-product (*e.g.*, red liquor from sulfite pulping: liginosulfonates). The black liquor is routinely used as an energy source during the recovery of pulping chemicals. The lignin products resulting from pulping processes are difficult to utilize for manufacturing high-value-added materials (Yang *et al.* 2023a). Organic solvent methods, in which the biomass is treated with ethanol or formic acid assisted by catalyst, can yield lignin with lower condensation

levels and higher purity. Nonetheless, their application is limited by the harsh reaction conditions and the high cost of solvent recovery (Yang *et al.* 2023b). In recent years, deep eutectic solvents (DESs) have emerged as green solvents with excellent dissolution capacity and mild reaction conditions. They can effectively disrupt the barriers of plant cell walls, cleave LCCs, and achieve efficient lignin extraction, while maximally preserving the active functional groups and molecular structure of lignin. Thereby, this method may provide a good way to isolate lignin for high-value utilization (Yue *et al.* 2025).

In the field of cosmetics, lignin with UV light absorption capabilities has the potential to be used as a natural sunscreen agent in sunscreens (da Mata *et al.* 2022). However, the conventional industrial lignin is often limited by its dark color, non-uniform particle size, and poor dispersibility within cosmetic emulsions. Recently, several strategies such as solvent exchange, self-assembly, or ultrasound-assisted methods have been employed to reconstitute lignin into spherical nanoparticles with well-defined morphology and controllable particle size (Lignin nanoparticles, LNPs) (Yue *et al.* 2025). Such an approach not only enhances the physical stability of lignin within cosmetic formulations but also improves the capture and dissipation efficiency of UV light energy through particle scattering effects and π - π stacking interactions (Srinivasan and Venkatachalam 2024; Sarengan *et al.* 2025).

For the reasons mentioned above, a careful comparison of lignin isolation methods is necessary for the later discussion of UV absorption and sunscreen application. The isolation history of lignin directly influences chromophore retention, functional-group distribution, molecular weight, condensation degree, color, and dispersibility, all of which affect its sunscreen-related performance. Therefore, this review first examines the steps, advantages, and disadvantages of industrial lignins (kraft, sulfite), organosolv lignins, MWL/CEL, and DES-derived lignins, and then discusses how these structural consequences govern UV shielding behavior and formulation potential in sunscreen systems.

ISOLATION METHODS OF LIGNIN

This section is organized from the perspective that the best lignin source for sunscreen is not determined by a single metric. Instead, the practical value of each isolation route must be evaluated by how it balances structural preservation, purity, color, yield, scalability, and downstream formulation suitability. The following discussion compares the major routes so that readers can understand why multiple isolation strategies remain relevant when evaluating lignin for sunscreen protection.

Industrial Lignin

Industrial lignin primarily refers to lignin dissolved during the pulping process in the paper industry, serving as a by-product of pulp and paper production. The typical industrial lignins include alkali lignin and lignosulfonate. Alkali lignin is derived from alkaline pulping processes, including kraft pulping and soda pulping. The former one yields kraft lignin, while the latter produces soda lignin. Lignosulfonate originates from sulfite pulping. Both alkali lignin and lignosulfonate are widely available and low-cost. However, their chemical structures and physicochemical properties have undergone significant alterations relative to native lignins, thereby presenting numerous challenges for high-value utilization (Sethupathy *et al.* 2022).

Kraft lignin

The kraft process is currently the dominant pulping method. This method involves digesting lignocellulosic biomass raw materials by immersing them in a strongly alkaline liquor composed of NaOH and Na₂S under high temperature and pressure conditions (Holladay *et al.* 2007). Under these reaction conditions, lignin is stripped from the lignocellulosic biomass and dissolved into the alkaline liquor. In the paper industry, this spent alkaline liquor is referred to as “black liquor” and burned for energy. By lowering the pH of the waste liquor, the kraft lignin can be obtained by its precipitation (Hubbe *et al.* 2019; Sewsynker-Sukai *et al.* 2020).

In this extreme chemical environment, the ether bonds within lignin undergo cleavage. Concurrently, the active sites on the lignin’s aromatic rings (the ortho and para positions relative to phenolic hydroxyl groups), particularly the C₅ position (which has high electron density), are highly susceptible to irreversible nucleophilic addition reactions with the side-chain structures of other lignin fragments. This leads to the formation of C-C condensation products (Cheng and Brewer 2017; Chakar and Ragauskas 2004). As a consequence, kraft lignin exhibits a highly complex structure, an extremely heterogeneous molecular weight distribution, and lower reactivity. These tough structures present a challenge for subsequent chemical modification and refined processing with lignin. As a compromise scheme, the vast majority of kraft lignin is merely burned as fuel in recovery systems within the pulp mills (Gosselink *et al.* 2004; Azadi *et al.* 2013).

Consequently, kraft lignin exhibits a highly condensed molecular structure, characterized by a significant increase in C–C bond content and substantial loss of native β–O–4 ether linkages. This structural transformation is accompanied by the formation of new chromophores, such as conjugated carbonyls and quinoid structures. While this can broaden the UV absorption spectrum to some extent, such enhancement comes at the cost of sacrificing the lignin's native structural integrity and chemical reactivity (Shin *et al.* 2022). The highly condensed structure not only results in heterogeneous molecular weight distribution and a darker color, but it also reduces the availability of reactive sites for subsequent modifications (*e.g.*, grafting or esterification), limiting further targeted optimization of its UV absorption properties (Jiang *et al.* 2022). Therefore, although kraft lignin is abundantly available and cost-effective as an industrial by-product, its inherent structural drawbacks pose challenges for its application in high-value-added fields such as sunscreens.

Sulfite lignin

The sulfite process is a method for treating lignocellulosic biomass that utilizes a cooking liquor consisting of sulfites (*e.g.*, calcium, magnesium, sodium, or ammonium salts) and an aqueous sulfur dioxide solution. Under the acidic condition, the C_α position on the lignin side chain is protonated to form a positively charged OH₂⁺ group. The HSO₃[−] ion, acting as a strong nucleophile, preferentially attacks this C_α site. Ultimately, the OH₂⁺ group leaves as a water molecule, and a hydrophilic sulfonic acid group becomes attached to the C_α position (Azadi *et al.* 2013). As ether bonds cleave, the resulting lignin sulfonate, bearing the sulfonic acid group, dissolves into the cooking liquor.

The lignin sulfonate obtained *via* this method is a water-soluble industrial lignin. However, due to the introduction of sulfonic acid groups, it contains a high sulfur content. The inherent functional groups of lignin combined with the introduced sulfonic acid groups confer good water solubility and surface activity to lignin sulfonate. Consequently, it is used as concrete water reducers and fuel dispersants. Simultaneously, the sulfonic acid

groups interfere with subsequent fine modification processes, significantly limiting its potential for conversion into high-value-added chemical products (Anukam *et al.* 2021; Singh *et al.* 2021).

In terms of UV absorption, lignosulfonate still possesses the aromatic framework responsible for the intrinsic UV-shielding ability of lignin (Li *et al.* 2025). However, the sulfite process changes the chemical structure of lignin through ether bond cleavage, side-chain reactions, and sulfonation, which can modify the abundance and distribution of chromophore groups associated with light absorption (Deshpande *et al.* 2022). The introduced sulfonic acid groups greatly enhance water solubility and surface activity, but they also increase structural polarity and sulfur content, resulting in a lignin product with markedly altered chemical properties. Therefore, although lignosulfonate retains UV absorption to some extent, its strongly hydrophilic and chemically transformed nature may limit its structural controllability and practical compatibility in downstream sunscreen applications.

In summary, although traditional industrial separation methods yield substantial lignin resources, they compromise the natural structure and quality of lignin. This “destructive separation” results in products with fragmented structures, numerous impurities, and low reactivity, making them unsuitable for application in novel and high-end fields.

Organosolv Lignin

The organosolv lignin process, which is based on solvent extraction, is primarily aimed at obtaining high-quality lignin. The solvent system can dissolve some lignin fractions, allowing for their selective extraction. Based on the chemical nature of the solvents, the organosolv methods can be subdivided into alcohol-based, ketone-based, acid-based, and other solvent systems. Different solvents, with their unique polarity, acidity/basicity, and solubility parameters, exhibit distinct product characteristics.

Alcohols

Alcohol-based solvent methods, the most extensively studied, were thought commercially promising organosolv pulping technologies with ethanol (Alcell® process) and methanol (Azadi *et al.* 2013; Yong and Wu 2023). The process is typically conducted in the presence of an acid catalyst, where alcohol molecules act as nucleophiles attacking the α -carbon cations formed on lignin side chains. They further occupy reactive sites, preventing subsequent condensation and C-C bond formation (Hassanpour *et al.* 2020; Luo and Abu-Omar 2018; Zijlstra *et al.* 2020). The process not only cleaves the linkages between lignin and hemicellulose (LCC) and internal ether bonds, but it also grafts alcohol molecules onto the lignin side chains. This grafted groups effectively block highly reactive carbon cations, thereby significantly inhibiting the re-condensation of lignin fragments. For instance, Hua *et al.* (2025) utilized a mixture of 1,4-dioxane and methanol with hydrochloric acid catalysis to fractionate lignin by introducing methoxy groups onto the C α position of lignin to inhibit condensation and yield a light color lignin.

Lignin extraction with alcohols generally obtains high purity with relatively narrow molecular weight distribution and low condensation, retaining a significant number of active sites. However, the lignin extraction in alcohol system typically requires high temperatures and pressures (Rabelo *et al.* 2023). Such conditions necessitate stringent safety, explosion-proof, and alcohol vapor handling equipment, which may reduce its desirability from the perspective of commercial inventors.

In terms of UV absorption, alcohol-derived lignin generally shows favorable characteristics because the organosolv process suppresses lignin re-condensation and better preserves its aromatic structure (Zhang and Naebe 2021). As a result, the obtained lignin usually retains more phenolic hydroxyl groups and conjugated chromophoric structures, which are important for UV absorption (Chotirotukon *et al.* 2023). Its relatively low condensation degree, high purity, and narrow molecular weight distribution also contribute to more uniform and effective UV-shielding performance.

Organic acids

The process of separating lignin using organic acids is commonly referred to as “acid pulping,” with representative solvents including formic acid and acetic acid (Ying *et al.* 2022; Lin *et al.* 2023). In the reaction system, organic acids serve as both solvent and acid catalyst. Under high-temperature conditions, acidic protons can activate aryl ether bonds in lignin (e.g., β -O-4 linkages), promoting their cleavage to form phenolic products (Yu *et al.* 2013). Simultaneously, aliphatic hydroxyl groups within lignin molecules (e.g., γ -CH₂OH) can undergo *in situ* esterification reactions with the organic acid, thereby modifying the lignin structure (Liu *et al.* 2021; Hua *et al.* 2023). The *in-situ* esterification effectively blocks hydroxyl groups in the lignin molecules, significantly enhancing the hydrophobicity of the product and facilitating its separation from the aqueous phase. The organic acid method demonstrates strong adaptability to feedstocks, achieving high separation efficiency even for structurally complex and difficult-to-process herbaceous biomass. However, the main drawbacks of this method are: 1) organic acids exhibit strong corrosivity towards metal equipment under high-temperature conditions, requiring the use of more expensive corrosion-resistant alloys; 2) the esterification reaction reduces the content of reactive phenolic and aliphatic hydroxyl groups, which may adversely affect subsequent chemical modifications.

Organic acid lignin may show good UV-shielding potential because acid-catalyzed cleavage of aryl ether bonds can generate more phenolic structures associated with UV absorption. Meanwhile, the retained aromatic framework helps preserve conjugated chromophores. However, esterification of hydroxyl groups may partially reduce the number of active sites contributing to UV absorption.

Others

Besides alcohols and acids, some special polar aprotic solvents, cyclic ethers, and ketones also show strong capability for lignin dissolution. These include 1,4-dioxane, γ -valerolactone (GVL), and acetone (Cheng *et al.* 2023; Wu and Thoresen *et al.* 2024; Borah *et al.* 2023). They primarily rely on the high compatibility of solvent polarity and intermolecular interactions with lignin. For example, dioxane is often used in combination with water and trace amounts of hydrochloric acid to extract lignin under relatively mild conditions (Saha *et al.* 2019). Such extraction takes advantage of a synergistic effect of physical dissolution by the solvent and acid-catalyzed hydrolysis with less involvement in chemical modification such as grafting or esterification.

The lignin extracted with dioxane combined with mechanical method is widely recognized as the most structurally intact and least degraded form of lignin. However, dioxane is a high boiling point solvent so that it is hard to remove completely from lignin products. The difficulties of the method may limit its potential to be applied in large scale industry. In contrast, GVL is considered a green, renewable solvent, but its high cost currently restricts its widespread industrial adoption (Alonso *et al.* 2013). In summary,

various organosolv methods still face engineering challenges such as high energy consumption for solvent recovery, severe equipment corrosion, or flammability/explosion risks.

Milled Wood Lignin / Cellulolytic Enzyme Lignin

In stark contrast to industrial pulping processes that prioritize high throughput and economic efficiency, the field of fundamental lignin chemistry has developed a series of extremely mild isolation methods to accurately elucidate the native chemical structure of lignin within plant tissues. Among these, Milled Wood Lignin (MWL) and Cellulolytic Enzyme Lignin (CEL) are widely recognized as the two types of “standard lignins” whose structures most closely resemble the native state (Balakshin *et al.* 2020; Huang *et al.* 2022). Despite their time-consuming, costly, and low-yield preparation, these samples are regarded as “standards” for elucidating the molecular structure of lignin, calibrating analytical methods, and evaluating novel isolation processes due to their maximal preservation of lignin’s natural structure.

Milled wood lignin

MWL completely eschews high-temperature acid or base chemical reactions, relying instead on physical-mechanical forces and mild solvent extraction. The sample is broken into fine powder-sized particles through intense physical action during ball milling, which also induces some chemical reactions (Ali *et al.* 2025). The ball milling of the lignocellulosic biomass is carried out after pre-extraction to remove extractives. The ball milling process disrupts the supramolecular structure of the plant cell wall, cleaves some lignin-carbohydrate complex (LCC) linkages, and liberates lignin from the dense cell wall matrix (Balakshin *et al.* 2020). Subsequently, the ball-milled wood powder is extracted at room temperature using a dioxane/water solution as the solvent. MWL is then obtained from the extract mixture through steps such as centrifugation, concentration, and drying.

By avoiding severe chemical degradation throughout the extraction process, MWL preserves maximally the naturally occurring β -O-4 ether linkages, side chains, and various functional groups in lignin. The C-C bond condensation is very low so that the isolate is considered the best represents of original lignin in plants to date (El Hage *et al.* 2009). However, the low extraction efficiency and the high toxicity of the solvents used render this method unsuitable for scale-up, restricting its application to laboratory-scale.

Cellulolytic enzyme lignin

CEL represents a further refinement based on MWL, aimed at improving yield and obtaining fractions containing LCC structures. The initial part of its preparation is similar to that of MWL, involving ball milling to disrupt the cell wall structure. The core difference lies in the subsequent introduction of cellulolytic and hemicellulolytic enzymes (Madhavan and Uppuluri 2025). These specific enzymes hydrolyze the majority of carbohydrates (cellulose and hemicellulose), and enrich the residual solid fraction in lignin, which is then subjected to mild organic solvent extraction and purification (Zhang *et al.* 2010). The resulting product has high purity and excellent chemical structural integrity (Hu *et al.* 2006). The CEL is more often regarded as a model compound for studying LCC structural interfaces rather than a raw material for synthesis (Qin *et al.* 2018).

MWL and CEL, as the most representative “standard materials” in lignin chemistry research, provide high fidelity to β -O-4 linkages and native functional groups for assessing the degree of structural alteration in lignin during biomass refining processes (Balakshin *et*

al. 2011). It is noteworthy that with the rapid development of the “Lignin-First” concept, achieving significantly higher lignin yields while maintaining structural integrity close to that of MWL have become important in the current field of biomass refining.

Regarding UV-shielding performance, both MWL and CEL exhibit favorable characteristics because their isolation processes largely preserve the native aromatic framework, β -O-4 linkages, and functional groups of lignin. Their relatively low degree of C-C condensation helps retain natural chromophore structures and phenolic groups associated with UV absorption. Therefore, MWL and CEL are often regarded as representative lignin fractions for reflecting the intrinsic UV-absorbing properties of near-native lignin (Jahan and Mun 2010).

Deep Eutectic Solvent Lignin

Deep Eutectic Solvent (DES) lignin, a novel separation product driven by the concept of green chemistry, has garnered significant attention in recent years. DESs are typically formed through the self-assembly of a hydrogen bond acceptor (HBA, *e.g.*, choline chloride) and a hydrogen bond donor (HBD, *e.g.*, organic acids, polyols, amides) in a specific molar ratio *via* a hydrogen bond network (Busato *et al.* 2021). They exhibit notable advantages such as low vapor pressure, biodegradability, low toxicity, and high tunability. Based on the chemical nature of the HBD, DESs used for lignin extraction can be primarily categorized into acidic DESs (*e.g.*, lactic acid, oxalic acid, *p*-toluene sulfonic acid systems), neutral DESs (*e.g.*, glycerol, ethylene glycol, and other polyol systems), and alkaline DESs (*e.g.*, urea, potassium carbonate, alkanolamine systems) (Xiao *et al.* 2024). Acidic DESs function dually as both solvents and acid catalysts, effectively cleaving the internal β -O-4 ether linkages within lignin and key covalent bonds in lignin-carbohydrate complexes (LCCs), thereby achieving efficient delignification (da Costa Lopes *et al.* 2020). Neutral or polyol-based DESs primarily rely on solubilization and hydrogen bond competition under relatively milder condition so as to better preserve the natural structure and chemical reactivity of lignin, albeit with lower efficiency (Makoś-Chelstowska *et al.* 2021; Moradi and Farzi 2021). Alkaline DESs create a more lignin-affinitive environment within the system, allowing lignin to dissolve directly in the alkaline solution. Through selective solubilization and the establishment of a mild separation environment, alkaline systems avoid excessive degradation and condensation of lignin, thereby better preserving its structural integrity and functional groups (Yang *et al.* 2021a).

DES lignin achieves significantly higher isolation yields while maintaining high purity, and its extraction conditions are far milder than industrial pulping processes. Furthermore, DESs possess “tunability”; by adjusting DES components and ratios, the molecular weight distribution, hydroxyl content, and thermal stability of lignin can be influenced, enabling structural control and performance optimization tailored for different downstream applications (Cheng *et al.* 2024). However, the large-scale utilization of DES lignin is still constrained by several factors, including mass transfer resistance due to high viscosity, high energy consumption during solvent recovery, and potential side reactions (*e.g.*, esterification and etherification of lignin side chains) (Li *et al.* 2023; Zhou *et al.* 2024; Yiin *et al.* 2024; Hafezisefat *et al.* 2023; Margarita *et al.* 2023). Nonetheless, DES lignin is widely regarded as a crucial bridge connecting fundamental research with high-value applications. Therefore, such research can provide key technical support for constructing a future biorefinery system based on the “synergistic utilization of all components.”

Acidic deep eutectic solvents

Acidic DESs (Acid DESs) currently represent the most active fractionation system in research on efficient lignin separation. These solvents are typically constructed of organic acids (*e.g.*, formic acid, lactic acid, oxalic acid, or *p*-toluene sulfonic acid) as HBDs and HBAs such as choline chloride. In Acid DES systems, in addition to the stable microenvironment formed by strong hydrogen bonding, the high proton activity within the system constitutes the core driving force for chemical deconstruction (Zhang *et al.* 2023).

Acid DESs possess multiple deconstruction functions. Firstly, a high concentration of active protons can precisely attack the covalent cross-links between lignin and carbohydrates (LCCs) *via* acid catalysis and induce the hydrolytic cleavage of internal β -O-4 linkages within the lignin macromolecule (da Costa Lopes *et al.* 2020). This targeted scission fragments high-molecular-weight lignin into soluble oligomers or monomers. Secondly, the dense hydrogen bond network within DESs generates strong penetration and swelling effects, effectively competing with and disrupting the original intermolecular/intramolecular hydrogen bonds within lignin. This reduces the compactness of the cell wall and promotes the diffusion and dissolution of lignin fragments into the solvent phase (Rahman *et al.* 2022; Chen *et al.* 2020).

It is noteworthy that the scope of Acid DESs has expanded from traditional Brønsted acids (proton donors) to Lewis's acid (electron acceptor) systems. Researchers often introduce metal chlorides (*e.g.*, AlCl_3 , ZnCl_2 , FeCl_3) as HBDs or additives. Through the coordination effect between metal cations and oxygen atoms in the lignin structure, the bond energy of C–O bonds are further weakened, demonstrating greater catalytic deconstruction potential than single proton acids (Zhao *et al.* 2025; Tang *et al.* 2021).

However, increasing acidity can also induce irreversible condensation reactions in lignin. Protons induce the formation of electrophilic benzylic carbocations at the C α -OH positions on lignin side chains, which readily undergo electrophilic aromatic substitution reactions with electron-rich sites on lignin aromatic rings (Li *et al.* 2024) and may lead to acidic degradation of cellulose surfaces (Chang *et al.* 2021; Wang *et al.* 2025). Therefore, finding a balance between maintaining efficient separation and inhibiting lignin structural condensation is a core challenge in current Acid DES lignin research.

Alkaline deep eutectic solvents

Alkaline DESs (Alkali DESs), another class of highly competitive solvents for lignin separation, demonstrates unique advantages in pursuing high lignin yield with less structural condensation. These solvents are typically constructed with nitrogen-containing compounds or polyols as HBDs with HBAs such as choline chloride (Yang *et al.* 2021a). In recent years, NaOH or KOH have been introduced into DES (Zhang and Zhou *et al.* 2025) to form strong alkaline eutectic systems with extremely high deprotonation capacity. In Alkali DES systems, the significant nucleophilicity and alkalinity within the system constitute the core driving force for deconstructing the biomass complex (Khimich *et al.* 2003).

Alkali DESs cause the strong nucleophilic alkaline species that efficiently mediate the hydrolysis (saponification) of ester bonds (Mou *et al.* 2024) to facilitate rapid dissociation of lignin from hemicellulose encapsulation (Wang *et al.* 2022; Mao *et al.* 2024). The alkaline environments tend to induce the cleavage of phenolic β -O-4 structures *via* the quinone methide intermediate pathway (Imai *et al.* 2007; Luo *et al.* 2025), rather than the carbocation pathway prevalent under acidic conditions (Ye *et al.* 2024). The depolymerized lignin fragments are more soluble in the solvent (Wang *et al.* 2024b). The

Alkali DESs also induce swelling of cellulose to disrupt its tight connection with lignin. The strongly nucleophilic hydroxide ions induce the deprotonation of phenolic hydroxyl groups in lignin, thereby disrupting the internal hydrogen bond network of lignin (Ge *et al.* 2025).

However, while achieving efficient lignin extraction, alkaline environments have a potent degrading effect on hemicellulose (especially xylan). Unlike the severe condensation mediated by Ca carbocations easily triggered in acidic systems, Alkali DESs can effectively avoid this specific structural alteration. Nevertheless, excessively high alkalinity may induce retro-aldol condensation of lignin side chains and a certain degree of oxidative degradation (Hirano *et al.* 2022). High-concentration alkaline components in DES also challenge the subsequent solvent recovery and chemical regeneration. Therefore, achieving simultaneous high-quality recovery of hemicellulose while ensuring high-purity lignin extraction is a key bottleneck for the industrial application of Alkali DES technology.

Neutral deep eutectic solvents

Neutral DESs (Neutral DESs), which are typically constructed of neutral polyols, amino acids, or sugars as HBDs with HBAs such as choline chloride (Wang *et al.* 2022a; Bertolo *et al.* 2021; Thi and Lee 2019; Tan *et al.* 2021), offer significant advantages in preserving the native structure of lignin. In Neutral DESs, the “physical solubilization” and “hydrogen bond competition” generated by their dense hydrogen bond network constitute the core driving force for deconstructing the lignocellulosic complex (Al-Ghamdi *et al.* 2022). Unlike the aggressive scission of chemical bonds in acidic or alkaline systems, Neutral DESs tend to gradually release lignin fragments and stabilize them in suspension within the solvent through physical swelling, without disrupting β -O-4 ether linkages and side chains.

However, the neutral environment lacks the chemical driving force for efficiently cleaving covalent bonds in LCCs and internal ether linkages in lignin. The delignification efficiency of Neutral DESs is typically low, often requiring higher reaction temperatures or longer processing times. Neutral polyol systems commonly suffer from high viscosity, which largely limits the mass transfer rate of the solvent within the macromolecular matrix, posing a technical barrier to industrial scale-up. The key for Neutral DES technology is to enhance separation efficiency while maintaining structural integrity assisted with microwave, ultrasonic, or introducing small amounts of co-catalysts.

DES lignin exhibits certain structural advantages. Lignin obtained from acidic DES systems generally has a lower molecular weight and reduced steric hindrance, which may facilitate subsequent aromatic ring stacking and thereby enhance its UV absorption capacity. In contrast, alkaline DES environments can better protect lignin and suppress condensation, although their ability to cleave β -O-4 linkages is relatively limited, resulting in lignin with comparatively higher molecular weight. The advantage of alkaline DES lignin lies in the preservation of reactive sites, which is beneficial for subsequent processing and may provide opportunities for developing products with more optimized UV-shielding performance (Yue *et al.* 2020).

Ionic liquids (ILs), like deep eutectic solvents (DESs), are considered designer solvent systems because both rely on tunable component combinations and solvent environments to disrupt the intermolecular interactions within lignocellulosic biomass and promote lignin dissolution or fractionation (Pereira *et al.* 2024). In both cases, lignin separation is mainly achieved through strong solvation effects, hydrogen-bond interactions, and the weakening of lignin-carbohydrate and ether linkages, thereby enabling the release

of lignin from the biomass matrix. Owing to these similarities, ILs are also recognized as an important green-chemistry-related route for lignin extraction. However, compared with DESs, IL systems often show several practical disadvantages, including higher cost, more complicated synthesis or purification, higher viscosity in some systems and especially in lignin-rich solutions, greater solvent recovery burden, and potential toxicity concerns for certain ion combinations (Rahman *et al.* 2025). Therefore, although ILs and DESs share similar conceptual foundations in lignin fractionation, DESs are generally more consistent with the present review's focus on accessibility, practicality, and sunscreen-oriented application potential.

Aromatic Rings and Conjugated Systems for UV-protection

The UV-protection of lignin is not just determined by a single structural feature, but rather by a synergistic effect involving multiple factors, including core structure (aromatic rings + conjugation) for UV absorption, substituents (electronic + steric effects), and an aggregated state (nano-dispersion) to modulate the broad-spectrum of UV absorption so that structural modulation may improve the UV-protect of lignin in sunscreen (Tran *et al.* 2021; Wu and Lian *et al.* 2024).

The structural features of aromatic rings in lignin

The aromatic ring is the basis structure of lignin from the phenylpropane units. It is primarily comprised of three types of structural units: guaiacyl (G-type), syringyl (S-type), and p-hydroxyphenyl (H-type) (Wang *et al.* 2020) (Fig. 1). The main differences among these units lie in the number and position of methoxy (-OCH₃) groups on the aromatic ring. The guaiacyl units contain one methoxy group, syringyl units contain two methoxy groups, and p-hydroxyphenyl units have no methoxy substitution (Cai *et al.* 2021; Lv *et al.* 2023). These structural units are interconnected *via* ether linkages (primarily β -O-4 aryl ether linkages) and carbon-carbon bonds (such as β -5 and 5-5 types), forming a complex polymeric structure, the skeleton of lignin (Antoun *et al.* 2024; Wu *et al.* 2025).

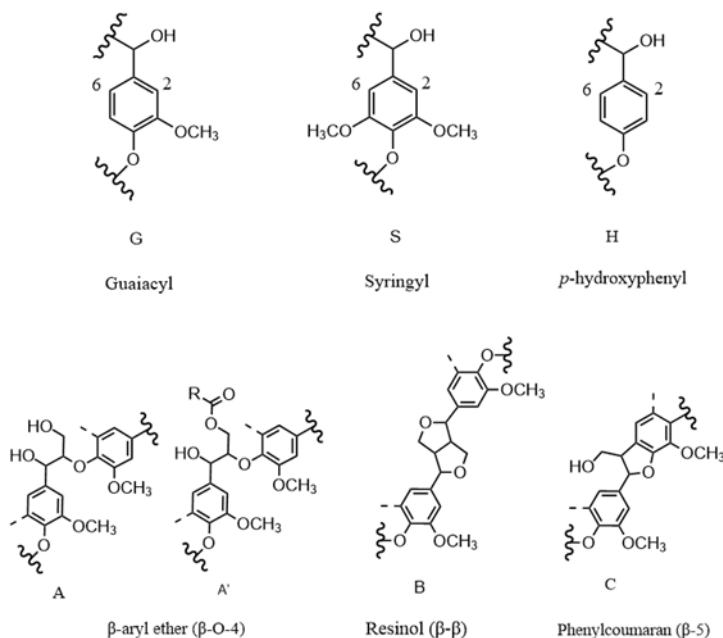


Fig. 1. Structural units and main connecting bonds of lignin

Lignins derived from different plant species exhibit significant differences in their phenylpropane unit composition. Softwood lignin is predominantly composed of guaiacyl units (G-type), hardwood lignin consists of both guaiacyl (G-type) and syringyl (S-type) structural units, while herbaceous plant lignin contains three types of structural units: guaiacyl (G-type), syringyl (S-type), and p-hydroxyphenyl (H-type) (Wu *et al.* 2025; Ait Benhamou *et al.* 2025; Zhang and Naebe 2021). Lignins with traditional isolation methods, such as kraft lignin and organosolv lignin, involve partial structural degradation during production, but they still retain the phenylpropane unit skeleton. The integrity of their aromatic ring structure is crucial for maintaining UV absorption capacity (Wu *et al.* 2023; Li and Zhao and Hu *et al.* 2022). Organosolv lignins, prepared under mild conditions using solvents such as ethanol or acetone, preserve the integrity of aromatic rings and their native linkages to the greatest extent, resulting in higher UV absorption intensity compared to kraft lignin (Wu *et al.* 2019). By contrast, kraft lignins, extracted under high-temperature and strongly alkaline conditions, has gone through some degradation and condensation, lessening their UV-absorption ability. Anyway, the polycyclic aromatic structures formed through condensation can partially compensate for the absorption capacity (Wu and Lian *et al.* 2024). Enzymatic hydrolysis lignin, due to minimal disruption of aromatic rings during cellulose enzymatic hydrolysis, exhibits an aromatic ring density and sun protection performance closer to those of native lignin (Fu *et al.* 2022).

Formation of conjugated systems to enhance UV absorption

The conjugated system in lignin is a dynamic structure constructed through synergistic multiple ways, primarily comprising three forms: the π - π conjugation network, p- π conjugation enhancement, and photo-induced conjugation extension. The aromatic rings in lignin are directly connected *via* ether or carbon-carbon bonds, forming a continuous π - π conjugation network. When S-type and G-type units are alternately linked, the electron-donating effect of the methoxy groups and phenyl OH or phenyl ether (Ph-O-R) can be transmitted through this conjugation network, thereby expanding the electron delocalization range and extending the absorption wavelength from the UVB region into the UVA region (Zhang and Naebe 2021; Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2024). Substituents on the aromatic rings, such as phenolic hydroxyl (-OH/R) and methoxy (-OCH₃) groups, provide lone pair electrons that form p- π conjugation with the π orbitals of the aromatic rings. This interaction increases the electron cloud density of the aromatic rings and reduces the energy gap for π - π^* transitions. Among these, the p- π conjugation effect of phenolic hydroxyl groups is the strongest; it is capable of enhancing UV absorption intensity by 20% to 40%, representing a crucial enhancement for lignin's UV absorption (Wu *et al.* 2025; Zhang and Naebe 2021). Furthermore, under UV irradiation, the phenolic hydroxyl groups in lignin are readily oxidized to form semiquinone radicals. These radicals, through electron delocalization, can induce conjugation linkages with adjacent aromatic rings, forming longer conjugated chains. Concurrently, partial aromatic ring opening occurs, forming quinone structures. The quinone groups, together with the original aromatic rings, constitute new conjugated systems, further broadening the absorption spectrum (Fu *et al.* 2022; Li and Zhao and Hu *et al.* 2022; Zhang *et al.* 2024). Studies have shown that after 2 h of UV irradiation, the average conjugated chain length in lignin increases by 1 to 2 aromatic ring units, and the absorption efficiency in the UVA region is enhanced by over 40% (Fu *et al.* 2022; Zhang *et al.* 2024).

The UV protection by the lignin is provided by an efficient cyclic process of “photon capture-electron transition-energy dissipation”. The energy gap from occupied

molecular orbitals to unoccupied orbitals of the conjugated structural lignin closely matches the photon energy in the UVA (320 to 400 nm) and UVB (280 to 320 nm) regions, enabling efficient capture of ultraviolet photons and excitation of electrons from the ground state to excited states (Wu and Lian *et al.* 2024; Zhang *et al.* 2024; Sadeghifar *et al.* 2017; Kim *et al.* 2023). The excited-state electrons dissipate energy through two primary pathways: firstly, converting energy through intramolecular vibrations into heat release to prevent structural degradation; secondly, dissipating energy through a dynamic conversion cycle of “quinone-semiquinone-hydroquinone” while maintaining the stability of the conjugated system and enabling long-lasting UV shielding (Zhang *et al.* 2024; Hararak *et al.* 2023). Upon irradiating the material for 4 h with UV light, lignin can generate an additional 136% of semiquinone radicals, more than half of which remain stable after irradiation ceases, which endows lignin with persistent sun protection capability (Wu *et al.* 2023; Fu *et al.* 2022).

However, it is important to note that the same photon-absorption process that enables UV shielding can also promote electronic excitation from bonding or nonbonding orbitals to antibonding orbitals, thereby increasing the photochemical reactivity of lignin itself. Under prolonged or intense UV irradiation, these excited states may facilitate bond cleavage, radical formation, and photooxidative degradation of the lignin structure (Deng *et al.* 2024; Kaya *et al.* 2023). This potential self-decomposition is an important consideration for the long-term efficacy of lignin in sunscreen applications and highlights the need for strategies, such as nanoparticle formation or chemical modification, to improve photostability while preserving UV-absorbing functionality.

Moreover, when lignin is combined with commercial sunscreens (*e.g.*, ethylhexyl methoxycinnamate), π - π stacking interactions can occur between their aromatic rings. This further reduces the electron transition energy gap, synergistically enhancing UV absorption efficiency (Li and Zhao and Hu *et al.* 2022; Piccinino *et al.* 2021a).

Structure-activity relationship

The aromatic ring with conjugation parts in lignin are the core factors corresponding to UV-protection. A greater number of aromatic rings per unit mass of lignin signifies more UV absorption sites and a greater absorption capacity (Wu and Lian *et al.* 2024; Li and Zhao and Hu *et al.* 2022). For instance, organosolv lignin from hardwood possesses a higher aromatic ring content (3.2 to 3.8 mmol/g) compared to softwood lignin (2.5 to 3.0 mmol/g), showing a higher molar extinction coefficient in the UVB region ($\epsilon = 1.2 \times 10^4$ - 1.5×10^4 L·mol⁻¹·cm⁻¹). In contrast, excessively degraded lignin shows a significant decline in UV-absorption due to aromatic ring cleavage (Wu and Lian *et al.* 2024; Zhang *et al.* 2024). Conjugation chain length is the key factor governing the spectral width of UV-absorption because longer conjugation leads to a more pronounced red-shift in absorption. Short conjugation chains absorb photons in the UVB region (280 to 320 nm), lowering protection in the UVA region. Medium-length conjugation chains can absorb light in the range of 280 to 360 nm, covering full UVB and partial UVA. Long conjugation chains or conjugated systems containing quinone structures exhibit absorption peak red-shifts to 320 to 400 nm, enabling full-spectrum protection against both UVA and UVB radiation (Wu and Lian *et al.* 2024; Li and Zhao and Hu *et al.* 2022; Fu *et al.* 2022; Xiang *et al.* 2024). For example, lignin grafted with benzotriazole demonstrates enhanced absorption efficiency in the UVA region and a significant increase in Sun Protection Factor (SPF) (Wu and Lian *et al.* 2021, 2024).

Aromatic ring opening or conjugation chain breakage (*e.g.*, due to excessive degradation) during extraction or modification can lead to the UV absorption in a narrow range. An intact lignin conjugated system can provide efficient protection for 8 to 12 hours under UV irradiation (Wu and Lian *et al.* 2024; Hararak *et al.* 2023; Kong *et al.* 2016). Furthermore, lignin nanoparticles enhance the stability of the conjugated system through π - π stacking interactions. Their UV-protection durability is improved by 2 to 3 times compared to micron-sized lignin. They maintain a high level to anti-UV even after 12 hours of UV irradiation (Xiang *et al.* 2024). The synergistic effects exist between the conjugated system and other structural features: phenolic hydroxyl groups enhance the electron cloud density of aromatic rings *via* p- π conjugation, further increasing the intensity of π - π^* transitions; methoxy groups, acting as electron-donating substituents, can modulate the energy gap of the conjugated system, causing a red-shift of the absorption wavelength into the UVA region (Li and Zhao and Hu *et al.* 2022; Zhang *et al.* 2024).

Functional Groups: Tuning the Performance of UV-protection of lignin

Functional groups (*e.g.*, hydroxyl, methoxy, and quinone structures) on aromatic rings enable to tune the UV-range, absorption intensity, and long-term efficacy. The type, content, and relative proportions of these functional groups directly determine lignin's absorption efficiency and photostability in the UV region, serving as key regulatory factors in its transformation from a natural aromatic polymer into a high-performance sunscreen material.

Hydroxyl groups

Hydroxyl groups are the most abundant functional groups in lignin, categorized into phenolic hydroxyls and aliphatic hydroxyls. Phenolic hydroxyls play a dominant role in contributing to UV-absorption, while aliphatic hydroxyls primarily modulate properties indirectly by influencing the aggregation state (Zhang and Naebe 2021; Li and Zhao and Hu *et al.* 2022; Widsten *et al.* 2020).

Phenolic hydroxyl groups significantly increase the electron cloud density of the aromatic ring through p- π conjugation, lowering the π - π^* transition energy gap and enhancing UV absorption intensity. Simultaneously, they act as radical scavenging sites, maintaining photostability. Their content shows a strong positive correlation with the UV absorption coefficient. Within the range of 0.32 to 5.5 mmol/g, a higher phenolic hydroxyl content leads to greater UVB (280 to 320 nm) absorption efficiency. However, an excessive phenolic hydroxyl content (>5.5 mmol/g) can induce excessive intramolecular hydrogen bonding aggregation within lignin and facilitate the formation of unstable catechol structures, accelerating photodegradation. This results in a more than 30% decrease in the spin content of semiquinone radicals and a significant reduction in photostability (Wu *et al.* 2025; Fu *et al.* 2022; Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2024). The ratio of phenolic hydroxyl to methoxy groups (Ph-OH/OMe) is a critical parameter. When this ratio is between 0.44 and 0.64, lignin exhibits both efficient UV absorption and long-lasting photostability. Ratios that are too high (>1.09) or too low (<0.22) lead to narrowed absorption spectra or insufficient photo-induced radical generation (Zhang and Naebe 2021; Zhang *et al.* 2024). Under UV irradiation, phenolic hydroxyl groups are readily oxidized to form semiquinone radicals, which subsequently participate in the dynamic conversion cycle of “quinone–semiquinone–hydroquinone.” This cycle not only dissipates UV energy but also maintains structural stability through radical scavenging, thereby allowing lignin

to retain high sunscreen performance even after prolonged irradiation (Wu *et al.* 2023; Fu *et al.* 2022).

Aliphatic hydroxyl groups are primarily distributed on the side chains of lignin (*e.g.*, at the α and γ positions of β -O-4 linkages). Although present in high quantities and not directly involved in UV absorption, they modulate UV-protection through the following ways: First, hydrogen bonding between phenolic hydroxyl groups can cause lignin molecular aggregation, reducing the exposure efficiency of UV absorption sites. Second, the hydrogen bond network formed between aliphatic and phenolic hydroxyl groups can stabilize the p - π conjugated structure of phenolic hydroxyl groups, slowing the photo-oxidation rate and enhancing the photostability of lignin (Wu *et al.* 2025; Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2024).

Methoxy groups

Methoxy groups are characteristic functional groups on the aromatic rings of lignin. By exerting an electron-donating conjugation effect, they regulate the UV absorption range and intensity (Lv *et al.* 2023; Korányi *et al.* 2020). The lone pair electrons of the methoxy group are transferred to the aromatic ring *via* conjugation, lowering the π - π^* transition energy gap and causing a red shift of the UV absorption peak from the UVB region (280 to 320 nm) into the UVA region (320 to 400 nm). Additionally, the electron-donating effect of methoxy groups stabilizes the conjugated system of the aromatic ring, reducing ring-opening degradation under UV irradiation. Experimental evidence showed that organosolv lignin with a methoxy content ≥ 7.59 mmol/g exhibited only a 5% decrease in UV absorption intensity after 8 hours of UV irradiation, whereas lignin with a low methoxy content (2.24 mmol/g) showed a 25% decrease (Vega-Aguilar *et al.* 2021). The interaction between methoxy and phenolic hydroxyl groups determines the upper limit of sunscreen performance. When the Ph-OH/OMe ratio is between 0.44 and 0.64, their synergistic effect is strongest: methoxy groups broaden the absorption range, while phenolic hydroxyl groups enhance absorption intensity. This synergy enables lignin to achieve a UVA/UVB absorption ratio of 0.84, approaching the standard for an ideal broad-spectrum sunscreen agent. Converting phenolic hydroxyl groups to methoxy groups is suitable for UVB-dominant protection scenarios, increasing the molar extinction coefficient in the UVB region by 15% to 20%. Moderating demethylation (retaining some methoxy groups) increases the phenolic hydroxyl content, bringing the Ph-OH/OMe ratio into the optimal range, enhancing radical scavenging capacity and increasing the photostability of lignin by 1.5-fold (Zhang *et al.* 2024).

Quinone structure

The quinone structure is formed in lignin during its natural biosynthesis or photo-induced oxidation processes, including benzoquinones and semiquinones. The quinones broaden the UV absorption range and participate in dynamic transformation cycles to achieve long-lasting protection. Under UV irradiation, lignin generated fresh semiquinone radicals, with the SQ radical content increasing by 136% after 4 h; more than half of the newly generated radicals were retained after UV withdrawal, indicating an SQ-based hydroquinone/quinone dynamic transformation cycle (Fu *et al.* 2022). The conjugated system of quinone structures can shift UV absorption in the region of 350 to 400 nm, which complements the UVB absorption region of aromatic rings, enabling lignin to achieve full-spectrum protection. Oxidized lignin OL-UVO3 containing quinone structures was found to increase the absorption intensity in the UVA region. The modified lignin had an

absorbance 1.25 times higher than that of the original lignin. The critical wavelength (λ_c) reached 375 nm (Gordobil *et al.* 2020; Liu *et al.* 2022).

As noted, quinone structures achieve long-term UV shielding through a reversible “quinone-semiquinone-hydroquinone” cycle. Under UV irradiation, hydroquinone is oxidized to semiquinone radicals, which capture UV energy and convert it into heat for dissipation. The semiquinone radicals are further oxidized to quinone structures or reduced back to hydroquinone, establishing a dynamic equilibrium. This cycle not only prevents the degradation of lignin but also continuously scavenges reactive oxygen species (ROS) induced by UV radiation. The content of quinone structures can be directionally increased through mild oxidative modification (*e.g.*, enzymatic oxidation), thereby enhancing UVA absorption efficiency without disrupting the three-dimensional network structure of lignin (Zhang and Naebe 2021; Wu *et al.* 2023; Zhang *et al.* 2024).

Table 1 summarizes the correlations between lignin functional groups and UV-protection. The broad-spectrum, high-efficiency, and long-lasting UV-protection of lignin stem from the synergistic effects of its various functional groups. Methoxy groups primarily contribute to UVA absorption, while phenolic hydroxyl groups strengthen UVB absorption. Quinone structures fill the gap in the long-wave UVA region, achieving full-spectrum coverage from 280 to 400 nm. The redox cycle between phenolic hydroxyl groups and quinone structures maintains free radical scavenging capacity and photostability, addressing the common drawback of easy degradation in traditional sunscreen agents.

Table 1. Data Table of Correlation between Lignin Functional Groups and Sunscreen Performance

Functional Group Type	Core Mechanism of Action	Modification and Regulation Methods	Sunscreen Efficacy	Impact on Photostability
Phenolic Hydroxyl (Ph-OH)	1. p- π conjugation enhances the electron cloud density of the aromatic ring, reducing the π - π^* transition energy gap; 2. Scavenges UV-induced free radicals; 3. Participates in the "quinone - semiquinone - hydroquinone" redox cycle.	1. Demethylation (moderate): Increases content to an optimal range; 2. Methylation: Reduces content for UVB-dominant scenarios; 3. Acetylation: Moderately blocks groups to reduce excessive aggregation.	1. UV absorption coefficient shows a strong positive correlation with content ($r=0.95$); 2. Under optimal proportion, the SPF value increased by 83% after 8 h irradiation; 3. UVB absorption efficiency improved by 50% to 80%.	1. Content ≤ 5.5 mmol/g: Absorption intensity decreased by $\leq 5\%$ after 8 h irradiation; 2. Content > 5.5 mmol/g: Spin content decreased by $> 30\%$, with significantly reduced photostability.
Aliphatic Hydroxyl (-OH)	1. Forms hydrogen bond networks to stabilize conjugated structures; 2. Influences lignin aggregation state, regulating the	1. Acetylation / Esterification: Blocks hydroxyl groups to reduce aggregation; 2. Grafting Modification:	1. After blocking, UVA absorption intensity was increased by 20% to 30%; 2. After optimizing dispersion,	1. Moderate content: Extends photostable period by 4 to 6 hours; 2. Excessive content:

	exposure efficiency of UV absorption sites.	Introduces hydrophilic / hydrophobic chains to optimize dispersibility.	sunscreen uniformity improved, with SPF fluctuation reduced by 15%.	Leads to aggregation, reducing photostability by 20%.
Methoxy Group (-OCH ₃)	1. Electron-donating conjugation effect red-shifts the absorption spectrum; 2. Stabilizes the aromatic ring conjugated system, reducing photodegradation; 3. Synergizes with phenolic hydroxyl groups to broaden the absorption spectrum.	1. Methylation: Converts phenolic hydroxyl to methoxy groups; 2. Moderate demethylation: Adjusts the ratio to phenolic hydroxyl groups to an optimal range.	1. S-type (dimethoxy) UVA absorption is 30% higher than G-type (monomethoxy); 2. Absorbance peak red-shifted to 340 nm (UVA region); 3. UVA/UVB absorption ratio reached 0.84.	1. Content ≥ 7.59 mmol/g: Absorption intensity decreased by $\leq 5\%$ after 8 h irradiation; 2. Content < 2.74 mmol/g: Decrease reached 25%.
Quinone Structure (Benzoquinone / Semiquinone)	1. Extended conjugation covers the 350 to 400 nm long-wave UVA region; 2. Participates in a dynamic conversion cycle for long-lasting energy dissipation; 3. Forms spectral complementarity with aromatic rings.	1. Enzymatic Catalytic Oxidation: Directionally increases content; 2. Amination Modification: Stabilizes quinone structure to prevent excessive degradation; 3. UV Pretreatment: Induces generation of semiquinone radicals.	1. Absorption intensity in the UVA region increased by 1.25-fold; 2. Critical wavelength (λ_c) reached 375 nm, meeting broad-spectrum standards; 3. Full-spectrum (280 to 400 nm) coverage efficiency improved by 40%.	1. After amination, the photostable period extended from 8h to >12 h; 2. The dynamic cycle maintained $>90\%$ of the initial SPF value after 12 h irradiation.

Molecular Weight and Aggregation State improving UV-Protection

The UV-protection of lignin depends not only on the inherent structure of its aromatic rings and functional groups but also on its molecular weight and aggregation state characteristics, which synergistically regulate the exposure efficiency of UV-absorbing sites, the integrity of the conjugated system, and light-scattering capability.

Influence for UV-protection from molecular weight

The molecular weight of lignin directly affects its UV-protection by altering the length of the conjugated system, the density of UV-absorbing sites, and dispersibility (Zhang and Naebe 2021). Low-molecular-weight lignin (<1000 Da) typically has an incomplete conjugated system (mostly 2 to 3 connected aromatic rings), dispersed UV-absorbing sites, and phenolic hydroxyl groups prone to excessive aggregation, leading to

insufficient UVB absorption intensity and incomplete UVA coverage (Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2022). The sunscreen blended lignin with a molecular weight of 844 Da exhibits a Sun Protection Factor (SPF) value of only 7.14 (at 10 wt% addition), and the UVA/UVB absorbance ratio is approximately 0.3. Medium-molecular-weight lignin (1000 to 5000 Da) with moderate conjugated length (4 to 6 connected aromatic rings) retains a complete π - π conjugated network while maintaining good dispersibility, thereby balancing the density and exposure efficiency of UV-absorbing sites (Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2022; Wu *et al.* 2022). Sunscreen with this lignin can achieve SPF values of 15 to 22.8 (at 10 wt% addition). Lignin with high-molecular-weight (>5000 Da) inclines to form aggregation into micron-sized particles, encapsulating UV-absorbing sites and poor dispersibility, limiting broad-spectrum protection capability (Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2022).

Organic solvent fractionation (*e.g.*, ethanol/water systems) can precisely regulate molecular weight distribution by controlling conditions. Lignin extracted with this system at 160 °C has a narrow molecular weight distribution (Polydispersity Index, PDI=2.7) with molecular weight 3800 Da, improving UV absorption uniformity by 30%. When carried out at 180 °C, lignin was degraded to 2300 Da, decreasing UVA absorption efficiency by 40% (Zhang and Naebe 2021; Jasiukaitytė-Grojzdek *et al.* 2025). Low-molecular-weight lignin has an extremely low β -O-4 content (only 2 per 100 C9 units), whereas medium-molecular-weight lignin can contain up to 44 per 100 C9 units. The continuity of the conjugated system directly influences the red-shift effect in UV absorption (Li and Zhao and Li *et al.* 2022). When synergizing with chemical UV filters, low-molecular-weight lignin, due to its small size, more readily forms π - π stacking interactions, enhancing synergistic effects with the filters.

Enhancement of UV-absorption from aggregation state

The aggregation state of lignin (specific surface area, aggregation morphology, dispersibility) significantly amplifies sun protection performance by altering the exposure number of UV-absorbing sites and light-scattering efficiency, with the nano-scale aggregation state being the optimal choice.

The specific surface area of lignin increases substantially upon conversion from its original micron-scale powder form (approximately 11.3 m²/g) to nanoparticles (Lignin Nanoparticles, LNPs) obtained through dissolution and self-assembly (approximately 143 m²/g). This 12-fold increase in specific surface area greatly enhances the exposure of UV-absorbing sites, such as phenolic hydroxyl groups and aromatic rings. LNPs with a particle size of 40 to 80 nm exhibit a 1.25-fold increase in UVA region absorption intensity compared to non-nanoscale lignin, with the critical wavelength (λ_c) red-shifted to 375 nm. Excessive nanonization (particle size <20 nm) leads to an overly large specific surface area, making phenolic hydroxyl groups susceptible to oxidation and reducing photostability (Zhang and Naebe 2021; Li and Zhao and Li *et al.* 2022; Zhang *et al.* 2022).

Lignin with different aggregation morphologies also exhibits varying UV-protection performance. Spherical LNPs possess the lowest surface energy and optimal dispersibility; it can prolong the UV light path through multiple light scattering (Zhang and Naebe 2021). Lignin reverse colloidal spheres (LRCS) 130 nm exhibit 50% higher light-scattering efficiency than irregular aggregates, achieving an SPF value of 56.1 (at 10 wt% addition) in sunscreen maintaining visible light transmittance above 70% (Wu *et al.* 2019). Rod-shaped LNPs concentrate light scattering more directionally, showing 20% higher UVA region shielding efficiency than spherical particles (Zhang *et al.* 2022).

Hollow-structured LNPs further enhance UV capture capability through multiple reflections within the internal cavity, reducing UVB region transmittance to 0.06% (Zhang *et al.* 2022; Wu *et al.* 2022).

Besides increasing the exposure of UV-absorbing sites, lignin particles can also contribute to UV protection through light scattering. When the particle size and morphology are properly controlled, a portion of incident UV radiation can be diffusely reflected away from the surface, while the remaining radiation is absorbed by lignin chromophores (Dghoughi *et al.* 2025). Thus, UV absorption and scattering act synergistically in lignin-based sunscreen systems (Li *et al.* 2025). In addition, stronger scattering is generally associated with a lighter visual appearance, which is relevant to the formulation design of sunscreen products.

Directed regulation of the lignin aggregation state is a core technical pathway for enhancing its UV-protection. Self-assembly for morphology construction through anti-solvent method, dialysis, or pH adjustment utilize differences in intermolecular π - π stacking, hydrogen bonding, and hydrophilic/hydrophobic interactions of lignin to directionally prepare spherical, rod-shaped, or hollow nanoparticles (40 to 150 nm), significantly increasing specific surface area and maximizing the exposure efficiency of UV-absorbing sites (Zhang *et al.* 2022). Surface modification involves chemical modifications such as acetylation, amination, or grafting of UV-absorbing groups. This process seals excessive hydroxyl groups to inhibit intermolecular aggregation, adjusts surface charge and hydrophilicity/hydrophobicity, optimizes the zeta potential of lignin to below -37.5 mV, maintains dispersion stability for over 22 hours, and simultaneously reinforces the integrity of the conjugated system (Jasiukaitytė-Grojzdek *et al.* 2025). Composite formation involves blending lignin with polymers such as polyvinyl alcohol (PVA) or cellulose, or with inorganic particles such as titanium dioxide (TiO₂) or zinc oxide (ZnO). Leveraging interfacial hydrogen bonding, electrostatic interactions, or π - π synergistic effects, this approach further suppresses lignin aggregation and achieves synergistic enhancement of UV absorption and light scattering. For example, LNP/PVA composite films achieve a UV shielding rate of 99.6%, and LNP/TiO₂ composite systems exhibit SPF values twice as high as those of single components (Li and Zhao and Li *et al.* 2022). The synergistic action of these three strategies enables precise regulation of the particle size, dispersibility, and interfacial properties of the lignin aggregation state, providing a structural foundation and technical support for its efficient application in the field of sun protection.

Synergistic regulation of molecular weight and aggregation state

A significant synergistic effect exists between the molecular weight and the aggregation state of lignin. Low-molecular-weight lignin (<1000 Da) tends to self-assemble into small-sized nanoparticles (40 to 80 nm). However, its insufficient conjugation requires compensation through grafting modifications, such as with benzotriazole (Wu *et al.* 2019; Zhang *et al.* 2022). Medium-molecular-weight lignin (1000 to 5000 Da) can directly self-assemble into an optimal spherical aggregation state without complex modifications, thereby achieving a Sun Protection Factor (SPF) value of 20 to 30 (Zhang *et al.* 2022; Wu *et al.* 2022). High-molecular-weight lignin (>5000 Da) requires either fractionation to reduce its molecular weight to the medium range or nano-processing (*e.g.*, physical grinding) to break up agglomerates, thereby enabling the utilization of its long conjugated chain advantage (Li and Zhao and Li *et al.* 2022; Jasiukaitytė-Grojzdek *et al.* 2025).

A summary of the effects of lignin molecular weight and aggregation state on its sunscreen performance is provided in Table 2. The aggregation state of lignin can amplify the effects of its molecular weight. For low-molecular-weight lignin, nano-aggregation facilitates π - π stacking, extending the conjugated system and increasing UVA absorption efficiency by 40%, thereby compensating for its inherent conjugation deficiency (Wu *et al.* 2019). For medium-molecular-weight lignin, self-assembly into lignin nanoparticles (LNPs) increases the specific surface area and fully exposes UV absorption sites, thereby elevating the SPF value from 8.48 to 22.81 (at a 10 wt% addition) (Wu *et al.* 2022). For high-molecular-weight lignin, nano-processing improves dispersibility while preserving its advantage of long-term photostability, allowing it to maintain a high SPF value even after 12 hours of UV irradiation (Li and Zhao and Li *et al.* 2022; Jasiukaitytė-Grozddek *et al.* 2025).

Table 2. Correlation Data Table of Lignin Molecular Weight, Aggregation State, and Sunscreen Performance

Molecular Weight Range (Da)	Aggregation Morphology	SPF Value (Loading)	UV Absorption Range	Photostability (8 h UV Irradiation)	Regulation Methods
<1000 (Low Molecular Weight)	Small-sized nanoparticles (40-80 nm), good dispersibility	7.14 (10 wt%, Fraction F5); 55.56 (10 wt% F5 + EHMC synergy)	Primarily UVB (280-320 nm), insufficient UVA coverage (320 to 340 nm)	AUC R=0.75-0.85; UVA absorption decreased by 40%.	1. Organic solvent fractionation (acetone/methanol system); 2. Grafting benzotriazole to extend conjugated chain; 3. Formulation with EHMC
1000 to 5000 (Medium Molecular Weight)	Spherical nanoparticles (80 to 130 nm), uniform dispersion	22.81 (10 wt%, AL-UVO ₃); 56.14 (10 wt%, LRCS)	Full spectrum (280 to 400 nm); λ_c =373 to 375 nm	AUC R>0.95; Absorption intensity decrease $\leq$ 5%	1. Ethanol/water system fractionation (160°C); 2. Reverse self-assembly; 3. Acetylation modification to prevent agglomeration
>5000 (High Molecular Weight)	Micron-scale aggregates (1 to 5 μ m); Spherical particles (200 to 500 nm) after nano-sizing	1.58 (5 wt%, Fraction F1); 15-20 (10 wt% after nano-sizing)	Primarily UVB before nano-sizing; Broad-spectrum (280 to 380 nm) after nano-sizing	AUC R=0.80 to 0.90; Localized degradation due to agglomeration	1. Physical grinding for nano-sizing; 2. Amination modification to reduce hydrogen bonding; 3. Composite with PVA to restrict aggregation

Substituents and Chemical Modification for UV-protection

The regulation of the electronic and steric effects of substituents along with chemical modification may overcome the structural limitation of natural lignin, which may

extend the sunscreen performance (broad-spectrum coverage, efficiency), stability, and compatibility of lignin in viable sunscreen functional material. The substituents in lignin structure (*e.g.*, methoxy, hydroxyl, quinone groups) influence its UV absorption ability. Chemical modification, on the other hand, involves to optimize lignin polarity, dispersibility, conjugation length, and stability, thereby achieving a synergistic enhancement in UV-protect efficiency and application suitability.

Acetylation modification

Acetylation modification is a method to introduce acetyl groups into the lignin molecular structure *via* an esterification reaction, resulting in the formation of acetyl ester bonds (Heo *et al.* 2023) (Fig. 2). The essence of this modification lies in replacing the hydrophilic hydroxyl groups with hydrophobic acetyl groups, thereby regulating the hydrophilic-lipophilic balance of lignin while preserving the core UV-absorbing structures of aromatic rings.

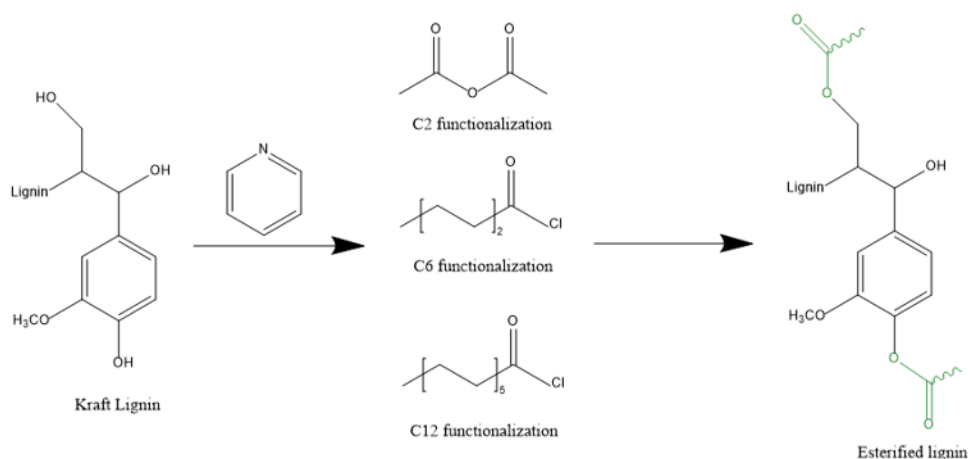


Fig. 2. Lignin acetylation and esterification modification

The mainstream acetylation approaches are categorized into traditional and green types. The traditional process employs acetic anhydride as the reagent and pyridine as the catalyst, reacting at 100 to 110 °C for 2 to 4 hours. However, this method suffers from high energy consumption, and pyridine is toxic (da Mata *et al.* 2022). In contrast, green processes utilize acetic acid or acetic acid/acetic anhydride mixtures as reagents. They replace pyridine with a MgCl₂-HCl composite catalytic system or employ microwave-assisted techniques for lignin acetylation. These methods not only enhance lignin yield but also preferentially substitute aliphatic hydroxyl groups while preserving phenolic hydroxyl groups, thereby maintaining the conjugated UV-screening function (da Mata *et al.* 2022; Qian *et al.* 2014; Khalil and Kamel 2025). Acetylation modification reduces the hydroxyl content of lignin, weakens intermolecular hydrogen bonding and π - π stacking interactions, and transforms lignin from irregular aggregates into uniform nanoparticles, thereby increasing the specific surface area. The integrity of the lignin aromatic rings and conjugated systems remains intact, ensuring the preservation of the core UV-absorbing structure (Heo *et al.* 2023).

Acetylation improves lignin's dispersibility in various matrices, such as water, PLA, and cosmetic emulsions. Here, "dispersibility" refers to matrix-dependent dispersion rather than simple molecular dissolution: water, PLA, and cosmetic emulsions correspond to aqueous nanoparticle dispersion, polymer-lignin compatibility, and emulsion formulation

stability, respectively, as reported in studies on hydrodispersible acetylated lignin nanoparticles, acetylated-lignin/PLA nanocomposites, and lignin nanoparticle sunscreen emulsions (Marchand *et al.* 2020; Cavallo *et al.* 2021; Piccinino *et al.* 2021b). This enables it to form nanoscale particles, increasing the exposure rate of UV-absorbing sites. Nanoscale dispersion allows lignin to distribute uniformly within matrices (*e.g.*, cosmetic emulsions), avoiding the shielding of absorption sites covered by agglomeration, and thereby enhancing UVB absorption efficiency (Khalil and Kamel 2025; Cavallo *et al.* 2021). The acetylation optimizes lignin hydrophobicity, reducing surface moisture adsorption and preventing swelling in humid environments (Heo *et al.* 2023). The color of lignin after acetylation changes from dark brown to light yellow, with visible light transmittance reaching 70% to 80%, thereby addressing the limitation of natural lignin's color for applications in cosmetics (Khalil and Kamel 2025).

Esterification modification

Long-chain esterification modification is an extension of acetylation modification, referring to a modification method in which hydroxyl groups on lignin are substituted by long-chain acyl groups with a carbon chain length ≥ 6 (*e.g.*, hexanoyl, dodecanoyl) (Xu *et al.* 2025b). The distinction lies in the steric hindrance and strong hydrophobicity of the long-chain acyl groups, which not only optimize dispersibility but also significantly enhance the stability and UV scattering efficiency of lignin.

Due to the steric hindrance, the reaction of long-chain acyl groups is preferentially carried out on surface hydroxyl groups, forming a “lignin core–long-chain shell” core–shell structure. Long-chain acyl chlorides exhibit high reactivity and readily combine with hydroxyl groups, whereas long-chain fatty acids are environmentally friendly and low in toxicity but require catalytic assistance (*e.g.*, pyridine, triethylamine) (Gordobil *et al.* 2017). A typical esterification procedure uses DMF as the solvent, with lignin and long-chain acyl chloride mixed at a molar ratio of 1:1.1, followed by stirring at 80 to 110 °C for 4 to 6 h to ensure uniform reaction (Xu *et al.* 2025). It should be noted that the acyl chain length should be controlled within C6 to C12. Excessively long chains may disrupt the conjugated system of lignin due to steric hindrance, leading to reduced UV absorption efficiency. The core structural change in long-chain esterification is “surface hydrophobic modification + densification of the aggregated state,” which differs from short-chain acetylation.

Long-chain esterification enhances hydrophobicity with more durable effects. The steric repulsion of long-chain acyl groups promotes the self-assembly of lignin into dense nanoparticles. The Mie scattering effect of these dense nanoparticles synergizes with the UV absorption of aromatic rings, improving the shielding efficiency of lignin against UVA and UVB. Although the specific surface area is lower than that of acetylated lignin, the particulate structure is more stable, with stronger resistance to moisture and agglomeration. Moreover, long-chain acyl groups only substitute surface hydroxyl groups without penetrating the conjugated core region of lignin, thereby preserving the intact UV-absorbing structure of aromatic rings and quinone groups. Additionally, the hydrophobic interaction between long-chain acyl groups and polymer matrices (*e.g.*, epoxy resins, polyurethanes) is enhanced, facilitating uniform dispersion in outdoor coatings without compromising the mechanical properties of the material (Gordobil *et al.* 2017; Tran *et al.* 2021; Xu *et al.* 2025b).

Esterified lignin exhibits strong hydrophobicity, making it suitable for open outdoor environments. The synergistic effect of UV scattering and absorption results in superior protection against long-wave UVA compared to acetylated lignin. However, the

esterification process is more complex than acetylation, and long-chain reagents are more costly. The modified lignin tends to have a darker color (light brown), which limits its application in transparent or light-colored cosmetics. Furthermore, excessively long chains can disrupt the conjugated system, necessitating precise control over chain length and degree of substitution.

Amination modification

Amination modification refers to a chemical modification method that introduces amine groups ($-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$) into the molecular structure of lignin. The core reaction is the Mannich reaction, which utilizes formaldehyde as a bridging agent. In this reaction, amine compounds undergo electrophilic substitution with the active hydrogens at the ortho/para positions of lignin's phenolic hydroxyl groups, forming a lignin-methylene-amine conjugate structure (Du *et al.* 2014) (Fig. 3). Its unique advantage lies in the simultaneous introduction of both UV protection and antioxidant functionalities, achieving a synergistic effect where “1+1>2”.

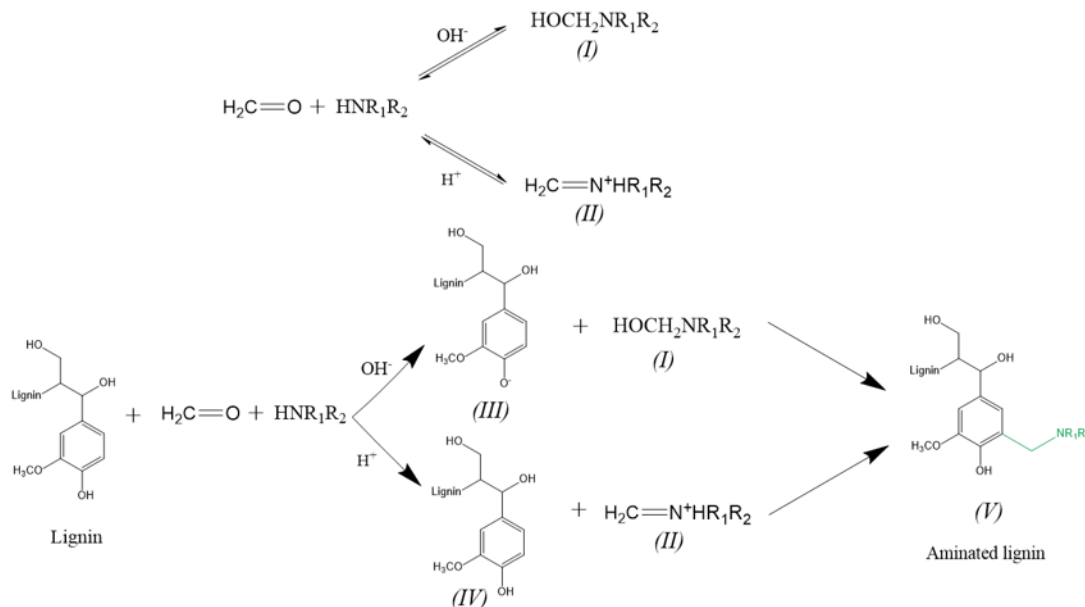


Fig. 3. Lignin amination modification

In the amination modification of lignin *via* the Mannich reaction, the major safety concerns are generally associated with the starting reagents and residual organic solvents rather than with the intended grafting pathway itself. Formaldehyde, a key reactant, is well known for its strong irritancy and carcinogenicity. Amine reagents such as ethylenediamine and dimethylamine can also be irritating or corrosive, and dimethylamine may serve as a precursor for nitrosamine formation under certain conditions. In addition, solvents sometimes used in these reactions, such as 1,4-dioxane or DMF, raise toxicological concerns, while DMSO may enhance the dermal penetration of co-existing chemicals. By contrast, the desired Mannich reaction pathway is commonly described as mainly generating water as a benign by-product, while reactive intermediates such as hydroxymethylamine species and iminium ions are generally transient. Therefore, the principal health risks in practice are more likely to arise from unreacted reagents and solvent residues if purification is incomplete. Nevertheless, the biosafety of the final

aminated lignin product should still be evaluated on a case-by-case basis, since it depends on the degree of modification, residual impurities, and the intended application scenario.

The choice of reagents and process conditions for amination modification directly affect the degree of amination and the conjugation effect. Currently, common approaches include the classic Mannich process and optimized processes. In the classic Mannich process, ethylenediamine and methanol are added to an aqueous lignin solution (1.0 wt%), the pH is adjusted to 11.4, and the reaction is carried out at 90 °C under a N₂ atmosphere for 4 hours, followed by dialysis for 3 days to remove impurities, thus achieving an amination degree of 6.6% (Yang *et al.* 2021b). An optimized process involves a formaldehyde-free Mannich reaction, using glyoxylic acid as the bridging agent to reduce toxicity, combined with microwave-assisted amination to enhance reaction efficiency, resulting in a 20% increase in the degree of amination (Tran *et al.* 2021).

Amination modification enhances UV-protection performance primarily through a dual mechanism of radical scavenging capacity and improved dispersion, while simultaneously imparting antioxidant functionality. In Mannich-type aminated lignin, the introduced amine groups are connected to the aromatic units through a methylene (–CH₂–) bridge, which precludes direct p- π conjugation between the nitrogen lone pair and the aromatic π -system. Therefore, the improved UV performance should not be directly attributed to classical conjugation extension. Instead, aminomethyl substitution may alter the local chemical environment of lignin and improve the accessibility of UV-active aromatic structures, while the major enhancement is more reasonably associated with the synergistic radical-scavenging effect of amine groups and phenolic hydroxyl groups, which suppresses the photo-oxidative degradation of lignin by quenching UV-induced free radicals. In addition, the polarity of the amine groups improves the dispersibility of lignin in aqueous systems, reduces aggregation, and promotes the formation of more uniform nanoparticles. Furthermore, because the Mannich reaction occurs mainly at the ortho/para positions of phenolic hydroxyl groups, the core lignin framework, including the aromatic rings and ether linkages, remains largely preserved, thereby maintaining the intrinsic chromophoric structure responsible for UV absorption (Tran *et al.* 2021; Du *et al.* 2014; Yang *et al.* 2021b).

Aminated lignin exhibits synergistic dual functionalities of UV protection and antioxidation. It demonstrates broader-spectrum efficacy compared to acetylated or esterified lignin, along with good biocompatibility and outstanding photostability. However, the inherent dark color of lignin (light brown) limits its application in transparent scenarios. Additionally, the degree of amination requires precise control; excessively high degrees can lead to aggregation, while excessively low degrees result in insufficient synergistic effects. Moreover, some processes utilize formaldehyde, posing toxicity risks.

Graft modification

Grafting modification refers to a modification method in which functional side chains (UV-absorbing groups or polymer chains) are covalently grafted onto the lignin backbone *via* controlled polymerization or nucleophilic substitution reactions. Its core lies in constructing a composite structure of “lignin backbone (UV-absorbing core) + functional side chain (performance regulator)”. Based on the type of side chain, it can be categorized into two classes: first, grafting of UV-absorbing groups (*e.g.*, benzophenone, spiropyran), which directionally enhances broad-spectrum sun protection performance; second, grafting of polymer chains (*e.g.*, PLA, PBA), which optimizes matrix compatibility and mechanical properties (Boarino *et al.* 2022; Wang *et al.* 2021) (Fig. 4).

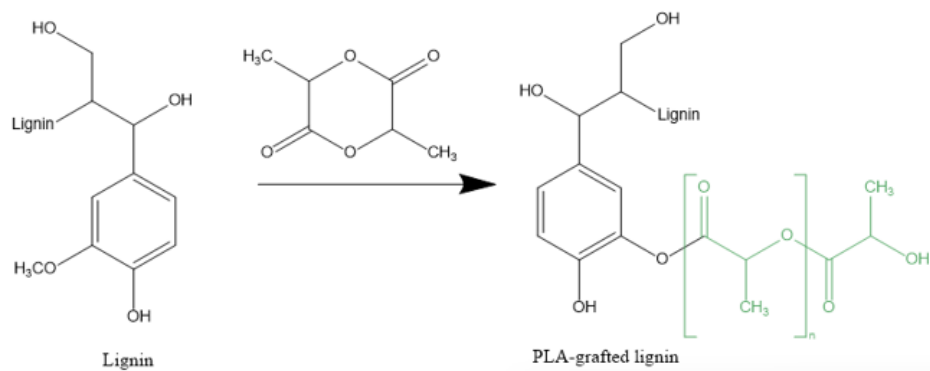


Fig. 4. Mechanism diagram of lignin graft modification (taking PLA as an example)

The reagents and processes for grafting modification vary depending on the side chain type, with an overall trend towards precision and controllability. For UV-absorbing group grafting, benzophenone derivatives (*e.g.*, 2,4-dihydroxybenzophenone), spiropyran derivatives (*e.g.*, SP-Br), and cinnamate esters are commonly used. For polymer chain grafting, monomers (lactic acid, butyl acrylate, methyl methacrylate) and catalysts (DBU for ring-opening polymerization of PLA, AIBN for RAFT polymerization) are typically employed.

Grafting modification induces fundamental changes in the lignin structure through the introduction of side chains, thereby enabling precise performance regulation. The conjugated structure of UV-absorbing groups forms a “dual conjugation” system with the aromatic rings of lignin, further reducing the π - π^* transition energy gap (Wu *et al.* 2019). Polymer side chains, being structurally similar to the matrix, can form strong interfacial bonds with the matrix, thereby enhancing matrix compatibility (Wu *et al.* 2023; Boarino *et al.* 2022). Concurrently, the introduction of side chains incorporates numerous functional groups (*e.g.*, carbonyl groups from UV-absorbing moieties, ester groups from polymer chains), which further strengthens UV absorption and intermolecular interactions (Wu *et al.* 2019; Boarino *et al.* 2022; Wang *et al.* 2021).

Lignin modified *via* grafting exhibits relatively superior sun protection performance, stronger broad-spectrum capability, and can achieve intelligent responsiveness. Furthermore, polymer-grafted lignin has demonstrated excellent matrix compatibility. However, the grafting modification process is the most complex and costly among the methods. Some UV-absorbing groups (*e.g.*, spiropyran) are expensive, and polymer grafting requires controlled polymerization techniques, imposing high demands on equipment and presenting significant challenges for large-scale production.

A brief comparison of the four modification methods is presented in Table 3. Substituents regulate the UV absorption characteristics of lignin’s conjugated system through electronic effects. Chemical modification addresses the core deficiencies of natural lignin—poor dispersibility, narrow absorption spectrum, and insufficient stability—by directionally introducing or modifying substituents. Methods such as acetylation, amination, and grafting modification target hydrophobicity, antioxidant activity, and broad-spectrum performance, respectively, synergistically enhancing sun protection efficiency, photostability, and application suitability. Future efforts should focus on “precise substituent design, greening of modification processes, and synergistic optimization of multiple functions” to advance the industrial application of lignin-based sun protection materials.

Table 3. Core Differences and Selection Guidelines for Four Major Lignin Modification Methods

Modification Type	Core Advantages	Key Performance Highlights	Applicable Scenarios	Cost Level
Acetylation	Environmentally friendly, light color, good dispersibility	Visible light transmittance 70% to 80%, SPF 35	Cosmetics, transparent packaging	Low-Medium
Esterification (Long-chain)	Strong hydrophobicity, outstanding weather resistance	Outdoor stability $\geq 80\%$ after 3 months, contact angle 93°	Outdoor coatings, textiles	Medium
Amination	Synergistic UV protection and antioxidant activity, biocompatibility	DPPH scavenging rate 97.9%, cell viability $\geq 72\%$	Skincare products, biomedical applications	Medium
Grafting	Broad-spectrum efficacy, smart/compatibility adaptability	SPF dynamically increased to 89, dispersed particle size < 200 nm	High-end sunscreens, smart materials, packaging	Medium-High

The UV-shielding performance of lignin is synergistically governed by its core aromatic structures, substituent effects (electronic and steric), and aggregation states. While the conjugated aromatic framework provides the fundamental absorption capacity, substituents modulate the spectral range and photostability, and the aggregation behavior dictates the exposure efficiency of active sites. Targeted chemical modification of these three structural dimensions enables the overcoming of natural lignin limitations, achieving a synergy between high sun protection efficiency and application compatibility.

Application and Performance of Lignin in Sunscreen Products

Studies have shown that long-term exposure to UV radiation can lead to skin inflammation and premature aging in humans. More severely, prolonged UV exposure can accelerate the onset and progression of melanoma and non-melanoma skin cancers (Hong *et al.* 2023). Methods for UV protection include wearing sun-protective clothing, with the simplest and most effective method being the application of sunscreen. Currently available sunscreens on the market are categorized into physical (mineral) and chemical sunscreens. Physical sunscreens primarily utilize minerals such as TiO_2 and ZnO as common active ingredients (Choi *et al.* 2024; Cavalcanti *et al.* 2025). They offer excellent photostability, exhibit minimal skin penetration, and are less irritating to sensitive skin. However, traditional formulations are often associated with a heavy texture and a whitish cast upon application. While nano-sizing these components improves transparency and dispersibility, a drawback is the enhanced ecotoxicity to marine organisms such as algae and echinoderms in high-salinity environments. Chemical sunscreens typically contain small-molecule organic compounds with aromatic structures (*e.g.*, methoxycinnamates, benzophenones). These compounds absorb UV energy through their aromatic rings and release it as heat. They are characterized by a lightweight texture, transparency without whitening, and

superior user experience. Nevertheless, the energy conversion process can generate free radicals, and long-term use may cause skin irritation or allergies. Some components are prone to penetrate into deeper skin layers and possess inherent ecotoxicity to aquatic organisms such as algae (He *et al.* 2021; Limsakul *et al.* 2023). Lignin has emerged as a significant focus in recent sunscreen research due to its aromatic structures (*e.g.*, benzene rings), abundance of phenolic and ketone groups, intramolecular hydrogen bonds, and the safety profile of its nano-sized forms. As a natural polymer with excellent UV absorption properties and abundant reserves in nature, lignin holds substantial potential for replacing traditional active sunscreen ingredients. This application aligns with goals for the high-value utilization of lignin and environmental sustainability.

Despite its outstanding UV protection capabilities, the application of lignin in sunscreens remains relatively nascent, with limited reports available. As illustrated in Fig. 5, compared to research on lignin nanoparticles and polymeric applications of lignin, publications focusing on lignin's UV resistance and its use in sunscreens are still in the early stages of investigation. Although research interest in lignin utilization has steadily increased over the past five years, studies specifically dedicated to lignin-based sunscreens remain scarce. Therefore, research on lignin's sunscreen applications needs to be comprehensively aligned with market demands and addressed with targeted investigations to facilitate the emergence of lignin-based sunscreens in the market. Consequently, this section will introduce the modifications and current research status of lignin as an active ingredient in sunscreen formulations. Furthermore, existing challenges and future perspectives in the development of lignin-based sunscreens are discussed to propose potential avenues for further research.

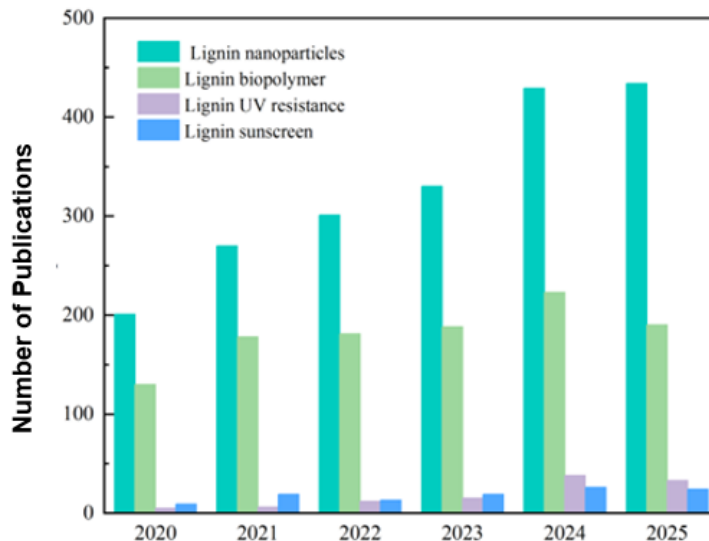


Fig. 5. Annual publication quantity of lignin related to different keywords in the past five years (Drawn from Scopus database)

Lignin-Based Sunscreen Products

Lignin, as a natural UV absorber, is incorporated into a base cream to formulate lignin-based sunscreen. To evaluate the UV protection capability of lignin sunscreen, the UV-blocking efficacy is represented as Sun Protection Factor (SPF). The calculation method for SPF is as follows:

$$SPF = \sum_{290}^{400} E_{\lambda} S_{\lambda} / \sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} \quad (1)$$

Here, E_{λ} is the CIE erythral spectral effectiveness, S_{λ} is the solar spectral irradiance, and T_{λ} is the spectral transmittance of the sample (Sadeghifar and Ragauskas 2020). The earliest preparation of lignin into a chemical sunscreen was reported in 2014 by Qian *et al.* (2015). Using alkali lignin purified *via* an alkali-acid method (with particle sizes ranging from nano- to micro-scale) as the core material, samples were prepared by mixing at different mass fractions (1 to 10 wt%) with a commercial pure facial cream and SPF15/30/50 sunscreens *via* magnetic stirring at room temperature in a dark room. The results showed that a 2 wt% addition could elevate the protective effect of an SPF15 sunscreen close to that of SPF30, while a 10 wt% addition enabled some SPF15 sunscreens to outperform SPF50 products. Furthermore, the protective efficacy of lignin-containing sunscreens was further enhanced after UV irradiation, confirming that lignin can serve as a green alternative ingredient for developing high-performance sunscreens (Qian *et al.* 2015). Although research on lignin-based sunscreens is progressing, it is undeniable that obstacles remain. Despite natural lignin in wood being nearly colorless, the presence of chromophoric groups in its structure and limitations in production and purification processes typically result in lignin forming yellow to dark brown particles after isolation. This severely restricts the market applicability and feasibility of lignin-based sunscreens. Another key challenge is the poor dispersibility of lignin within sunscreen matrices, which is attributed to its solubility characteristics (Widsten *et al.* 2020; Wen *et al.* 2023).

Reducing the color of lignin in the production process

Lignin, as the sole renewable natural aromatic compound, holds significant importance for achieving carbon neutrality goals through its high-value utilization. However, the unavoidable condensation reactions during its isolation process lead to darkening and reduced reactivity, thereby severely limiting its application in cosmetic fields such as sunscreens. To address the deep coloration issue caused by lignin during production processes, the typical solution involves modifying the formulation of the DES used for lignin extraction, aiming to obtain lignin with a lighter color.

In recent years, green extraction strategies based on DES have become a core direction for overcoming this bottleneck. Related studies, through precise design of solvent systems and regulation of solvent composition, synergistic effects, and reaction conditions, have achieved a significant transformation of lignin from dark brown/black to light-colored or nearly colorless. This color improvement is closely related to structural preservation and chromophore removal, enabling the simultaneous protection of lignin structure and preparation of light-colored lignin. Although traditional DES (*e.g.*, ChCl/lactic acid, ChCl/oxalic acid) can separate lignin, their strong acidity or high temperature can easily induce lignin C-C condensation and aryl ether bond cleavage, generating chromophores such as quinones and conjugated carbonyl groups. This results in extracted lignin appearing dark brown or even black (L^* value only 34.3 to 69.3), with a concurrent decrease in purity and activity (Zhang and Xu *et al.* 2025; Xu *et al.* 2023).

To address this problem, researchers have achieved gradient optimization of lignin color through DES system modifications, focusing on three core directions. The first involves constructing polyol-based ternary DES systems. By introducing polyols such as 1,2-propanediol, glycerol, ethylene glycol, and 1,4-butanediol as HBDs and combining them with Lewis's acids (*e.g.*, AlCl_3) to regulate Kamlet-Taft parameters (α , β , π^*), the hydrogen bond donor/acceptor capacity and polarity of the solvent are significantly enhanced. This system can graft polyols onto the α -position of the benzylic carbocation in

lignin, blocking condensation reactions. Consequently, lignin color shifts from the dark brown obtained with traditional DES to a light cream color (at 80°C) or light brown (at 90 to 100°C), with L^* values approaching those of CEL (Cheng *et al.* 2024). Specifically, lignin extracted using the 1,2-propanediol-based DES retained 52.82 β -O-4 linkages per 100 aromatic units, exhibited suppressed chromophore formation, and displayed uniform, light coloration. Furthermore, the glycerol-based DES further increased lignin brightness to 29.8% ISO, far exceeding that of natural CEL (22.4% ISO). The extracted lignin presented a light-colored, regularly microspherical morphology, and its $L^*a^*b^*$ values were highly similar to those of natural lignin, completely overcoming the deep coloration defect associated with traditional DES extraction (Zhao *et al.* 2025). Additionally, synergistic effects between organic substances and DES can be utilized to inhibit condensation reactions, thereby achieving lignin lightening. For instance, the modified DES-isopropanol (IPA) synergistic system leverages the synergy between an acidic DES (BTEAC/formic acid) and IPA. This approach utilizes the DES to cleave LCC bonds, while IPA competitively binds to the C α carbocation of lignin, inhibiting condensation reactions and removing chromophore precursors such as methoxy groups (36.5% removal) and p-coumaric acid (PCE) units (80.9% removal). This modification significantly lightened the lignin color from the dark brown ($L^*=22.4$) obtained with DES alone, increasing the L^* value to 54.1. The morphology changed from irregular blocks to uniform spherical nanoparticles. Macroscopically, the reduced packing density (0.24 to 0.28 g/cm³) further diluted the chromophore concentration, resulting in a light yellow to nearly white appearance (Zhang and Xu *et al.* 2025). In a recent study conducted by Zhou *et al.* (2025), tea stem waste was innovatively used as raw material. A modified one-step system constructed with PEG200-oxalic acid DES and H₂O₂ was employed for lignin extraction. Results showed that with 50 wt% H₂O₂ dosage, the color difference of the extracted lignin decreased by 48.5% compared to milled wood lignin (MWL). Furthermore, a cream base incorporated with 2.0 wt% of this light-colored lignin achieved a SPF exceeding 50, confirming that DES modification strategies can efficiently achieve lignin decolorization while preserving its UV protection functionality. Another approach involves adding water to the DES, which reduces system viscosity while also protecting the lignin structure. Research indicates that adjusting aqueous DES systems by introducing 30% to 50% water into DES (BTEAC/formic acid) can balance delignification efficiency with structural protection, avoiding excessive condensation and chromophore generation. The addition of water gradually lightened the lignin color with increasing water content. Lignin extracted with 30% aqueous DES (L-H30) appeared light brown. It retained 87.4% of its β -O-4 linkages, exhibited reduced phenolic hydroxyl content (diminishing p- π conjugated chromophore structures), and showed an approximately 30% increase in L^* value compared to products from pure DES extraction. It also maintained good UV absorption performance, achieving a balance between color and functionality (Xu *et al.* 2023). All the aforementioned studies confirm that modified DES systems, through structural protection (e.g., polyol grafting, water content adjustment), active site blocking (e.g., IPA competitive binding to carbocations), and synergy with other chemical reagents, can yield high-purity, low-condensation, light-colored lignin under mild conditions. This enhances its application potential in fields such as sunscreens and bio-based chemicals.

Modification of lignin morphology

The morphology and particle size of lignin significantly influence the SPF of lignin-based sunscreens. Processing lignin into nanoparticles can effectively reduce the color intensity of lignin-based sunscreens and enhance the dispersion of lignin within the cream matrix, thereby further improving the application performance of lignin-based sunscreens. The morphological regulation of lignin serves as a green and mild modification strategy. By altering the particle size, packing state, and aggregation structure of lignin, significant color optimization is achieved. The core mechanisms are closely related to the dilution of macroscopic chromophore concentration and the adjustment of microscopic light reflection properties.

1) *Reduction of lignin particle size: From macroscopic blocks to micron/nano-scale particles.* Reducing the particle size of lignin is a key morphological factor for lightening its color. Conventionally extracted lignin (e.g., organic solvent lignin, OL) typically exists as macroscopic blocks actually constituted of large aggregated particles. The tight packing leads to a high local concentration of chromophores, resulting in a dark brown color (L^* value of 55.1). After particle size reduction *via* methods such as mechanical grinding/sieving, the color gradually lightens with decreasing particle size. When ground and sieved to over 500 mesh, the average diameter of lignin particles decreases to 13.3 μm , with the L^* value increasing by 47% and brightness improving by 30% compared to the 60 to 80 mesh sample. Further processing, such as obtaining light-colored CEL from rice husk via cellulase treatment, yields more uniformly sized particles with an L^* value of 66.8, presenting a light brown color, which is significantly superior to the dark brown hue of traditional OL. Color optimization is even more pronounced after nano-sizing. For instance, CEL nanoparticles (CEL-NPs) prepared *via* the solvent shifting method have an average diameter of 225 nm and a substantially increased specific surface area. At this scale, the nanoparticles exhibit a significantly lighter perceived color, which can be primarily attributed to enhanced light scattering. According to Mie theory, particles with diameters comparable to the wavelength of visible light (typically in the range of 200 to 300 nm) maximize light scattering per unit mass. This intensified scattering returns a greater portion of incident light back to the observer before it can be deeply absorbed by the lignin chromophores, thereby ‘brightening’ the macroscopic appearance and reducing the perceived dark brown intensity of the lignin (Wrigglesworth and Johnston 2021). The color of creams formulated with CEL-NPs is further lightened compared to those with CEL, without obvious dark-colored defects, meeting the requirements for cosmetic applications (Lee *et al.* 2020).

2) *Regulation of Lignin Packing State: From Dense Aggregates to Loose Porous Structures.* The packing density and aggregation state of lignin directly affect its color appearance. Oven drying or vacuum drying tends to cause dense aggregation of lignin particles, forming large, smooth-surfaced blocks with a packing density as high as 0.69 g/cm^3 . The overlapping of chromophores in such structures results in a dark color. In contrast, spray drying or freeze-drying can yield fine particles with loose, porous structures. Among these, spray-dried samples exhibit the lowest packing density and the lightest color (appearing light brown). Further construction of loose particle aggregates can be achieved through solvent precipitation (using systems such as pyridine/ether) or acetylation-precipitation composite treatments. These methods create aggregates with dense interstitial spaces between particles, increasing the specific surface area from 1.58 m^2/g for ground samples to 9.86 m^2/g and reducing the packing density below 0.34 g/cm^3 . Macroscopically, this weakens the visual superposition effect of chromophores, rendering the lignin nearly

white with an L^* value of 51.0, representing a 318% increase in brightness compared to oven-dried samples (Zhang *et al.* 2018). This loose structure optimizes color performance by reducing the light absorption superposition between particles while simultaneously enhancing visible light reflection.

3) *Reconstruction of Lignin Aggregation Structure: From Random Aggregation to Ordered Nano-assembly.* The reconstruction of lignin's aggregation mode also significantly impacts its color. Native lignin molecules undergo random aggregation *via* π - π stacking and hydrogen bonding, forming structures where chromophore conjugation is superimposed, thereby deepening the color. However, color is noticeably lightened after reconstructing the aggregation structure through methods such as self-assembly or solvent induction. For example, LNPs formed *via* solvent exchange precipitation or anti-solvent self-assembly techniques adopt spherical, ordered aggregates. The intermolecular π - π stacking in these structures is predominantly of the J-aggregate type, which not only enhances UV absorption performance but also avoids excessive conjugation and superposition of chromophores. Lignin subjected to acetylation modification followed by reprecipitation not only has its phenolic hydroxyl groups blocked by acetylation (reducing the auxochrome effect) but also forms ordered, loose aggregates. This results in a significant increase in visible light diffuse reflectance, particularly in the long-wavelength region, yielding a color closer to neutral white. Furthermore, sunscreens containing 5 wt% of this modified lignin show no obvious skin staining and achieve an SPF value of 50.7 (Piccinino *et al.* 2021b). In summary, morphological changes in lignin drive color optimization through three main pathways: 1) reducing particle size from macroscopic blocks to micron/nano-scale to lower the local concentration of chromophores; 2) transitioning the packing state from dense aggregation to loose porosity to reduce the visual superposition of chromophores; and 3) transforming the aggregation structure from random conjugation to ordered assembly to weaken the auxochrome effect and light absorption superposition. These morphological regulation methods enable a gradient color transition from dark brown ($L^* = 24.1$ to 55.1) to light brown, light yellow, and even near-white ($L^* = 51.01$ to 83.4) without damaging the core structure of lignin. Simultaneously, its UV absorption and antioxidant functionalities are preserved. This lays the foundation for the application of lignin in high-end fields such as sunscreens and represents a green and efficient pathway for the high-value utilization of lignin.

Lignin as an Antioxidant/Anti-Aging Component

The core advantage of lignin as a green antioxidant in sunscreen formulations lies in the efficient free radical scavenging capability of the phenolic hydroxyl groups within its molecular structure. This enables lignin to exert anti-aging effects by interrupting the oxidative chain reactions associated with skin photoaging, while simultaneously providing synergistic UV shielding. Studies have shown that the reaction rate constant between lignin phenolic hydroxyl groups and free radicals can reach 10^4 to 10^6 $M^{-1}s^{-1}$ (Piccinino *et al.* 2021a). Its antioxidant activity is comparable to that of the commercial antioxidant butylated hydroxytoluene (BHT), and it exhibits stable free radical scavenging capacity across the entire UVA (long-wave ultraviolet) and UVB (medium-wave ultraviolet) spectrum, thereby providing synchronous protection against UV-induced skin photo-oxidative damage. To further enhance its application efficacy in sunscreen formulations, the performance of lignin can be significantly optimized through nano-sizing or chemical modification. Lignin nanoparticles not only enhance its intrinsic antioxidant activity but also improve skin compatibility, thereby improving the anti-aging efficacy and storage

stability of sunscreen products. Chemical modification can further strengthen its antioxidant performance. For instance, spiropyran-modified lignin (DAL-SP) functions in sunscreen systems through a dual mechanism: scavenging free radicals *via* the hydrogen-donating action of phenolic hydroxyl groups and dissipating UV radiation energy through its conjugated structure, while the “encapsulation effect” protects the structural integrity of the spiropyran moiety to enhance the photostability of the system (Wu *et al.* 2023). In summary, relying on the core mechanism of phenolic hydroxyl-mediated free radical scavenging, lignin delivers multiple synergistic values in sunscreen formulations, including antioxidant, anti-aging, and UV shielding effects. Nano-sizing and chemical modification can further strengthen its performance advantages, providing a feasible pathway for developing highly efficient, green, and long-lasting sunscreen products, thereby highlighting its core application potential as a natural sunscreen additive.

Current Challenges

Lignin with environmental-friendliness and UV-protection is supposed to apply in sunscreen cosmetics. Anyway, it still faces a series challenge to convert the production technology of lignin from laboratory to large-scale industry. There are significant differences of lignin in the composition of phenylpropane units, linkage patterns, and functional group distribution from various raw material sources (*e.g.*, wood, crop straw, agricultural and forestry residues), and even from different parts of the same plant (Rosado *et al.* 2021; Zou *et al.* 2022). Methods for lignin extraction also led to considerable fluctuations related to molecular weight, active functional groups, stability and industrial scalability of sunscreen formulations (Gao *et al.* 2025; Sapouna *et al.* 2023).

For application, the inherent brownish color and natural plant-derived odor of lignin can easily lead to customer resistance. Lignin usage can contribute to issues such as uneven coloration and a dull appearance in sunscreen products, significantly affecting their sensory quality and consumer acceptance (Li and Zhao and Li *et al.* 2022; Lok *et al.* 2022). Beyond the influence of lignin structure, cost considerations are unavoidable in all steps prior to the preparation of lignin-based sunscreens. Newly developed technologies for lignin extraction are hard to scale up to production lines, so that it is difficult to meet the economic demands of the cosmetics industry. Another major obstacle to the production and application of lignin-based sunscreens in the market is the regulatory discrepancies concerning natural additives in cosmetics across different countries and regions. Key indicators for lignin as a sunscreen additive, such as safety thresholds and permissible usage ranges, have not yet been fully aligned with mainstream international cosmetics regulations, further constraining its marketization process.

CONCLUSIONS

1. Lignin, a renewable aromatic polymer that is available in large quantities from nature, possesses a unique three-dimensional aromatic network structure. This structure is formed by the cross-linking of syringyl, guaiacyl, and *p*-hydroxyphenyl units *via* ether and carbon-carbon bonds, which endows lignin with inherent broad-spectrum ultraviolet (UV) absorption (covering the 280 to 400 nm band) and antioxidant activity for applying in green sunscreens.

2. Regarding lignin manufacturing, no existing isolation route is unambiguously superior for sunscreen-oriented lignin sourcing because each one reflects a different compromise among structural preservation, color, purity, yield, scalability, and process cost. Traditional industrial lignins (from kraft, soda, and sulfite processes) are abundant but suffer from structural damage, condensation, or sulfur-containing groups. Organosolv lignins can provide higher-quality fractions but remain constrained by solvent recovery and equipment corrosion. MWL and CEL retain structures closest to native lignin but are unsuitable for large-scale production because of their low yield and high cost. DES methods are especially promising because they can combine relatively high yield with better retention of active functional groups, although current systems still face challenges related to viscosity, solvent recovery, and side reactions.
3. The UV-absorption of lignin originates from the synergy of the aromatic ring-based conjugated systems and aggregation state, which provide a potential application for UV-protection in sunscreen. Functional groups such as phenolic hydroxyl, methoxy, and quinone structures in lignin precisely regulate absorption intensity, spectral width, and photostability through electronic effects and dynamic transformations. The ratio of phenolic hydroxyl to methoxy groups (0.44 to 0.64) is a key parameter balancing absorption efficiency and stability. Quinone structures achieve long-lasting protection through a dynamic “quinone-semiquinone-hydroquinone” cycle. A low molecular weight ranging from 1000 to 5000 Da and a nano-scale aggregation state (80 to 130 nm spherical particles) can significantly enhance the UV absorption. Structural modification (*e.g.*, acetylation, esterification, amination, grafting) can address the inherent drawbacks of natural lignin, such as poor dispersibility, narrow spectrum, and dark color. Acetylation improves the dispersibility and lightens color of lignin, esterification enhances hydrophobicity and outdoor applicability, amination concurrently imparts sun protection and antioxidant functions, and grafting can directionally improve broad-spectrum of UV-absorption and matrix compatibility.
4. Lignin can be applied as UV-absorption agent in sunscreen. The greatest benefit is that the lignin adding can augment the UV-proof performance of sunscreen. Only 2 wt% lignin addition in product can elevate the SPF of sunscreen from 15 to nearly 30. With an addition of 10 wt% lignin, the SPF value of sunscreens can outperform 50. The protective efficacy further increases after UV irradiation when lignin is added in sunscreen. The antioxidant activity of lignin is comparable to that of the commercial antioxidant BHT. This allows lignin act a multi-synergistic effect of UV shielding, antioxidation, and anti-aging in sunscreen formulations.

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