

Journal Pre-proofs

Original Article

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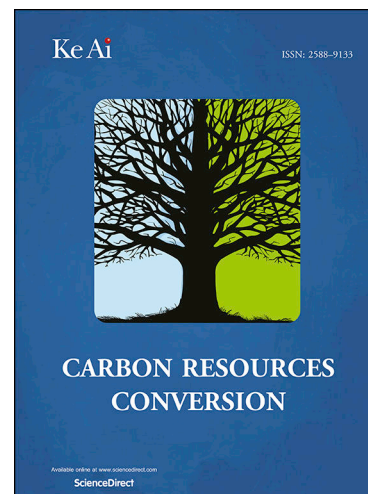
PII: S2588-9133(24)00016-4
DOI: <https://doi.org/10.1016/j.crcon.2024.100227>
Reference: CRCON 100227

To appear in: *Carbon Resources Conversion*

Received Date: 22 September 2023
Revised Date: 6 December 2023
Accepted Date: 17 January 2024

Please cite this article as: T. Liang, Y. Ma, Z. Jiang, J. Remón, Y. Zhou, B. Shi, New Insights into Greener Skin Healthcare Protection: Lignin nanoparticles as additives to develop natural-based sunscreens with high UV protection, *Carbon Resources Conversion* (2024), doi: <https://doi.org/10.1016/j.crcon.2024.100227>

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New Insights into Greener Skin Healthcare Protection: Lignin nanoparticles as additives to develop natural-based sunscreens with high UV protection

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Abstract

Despite lignin nanoparticles (LNPs) being extensively employed as assistant agents to improve the UV-blocking performance of sunscreens, there is a lack of information addressing how and to what extent the chemical and structural features of these particles relate to the improvements

observed in the Sun Protection Factors (SPF) of the sunscreens. In this study, lignin oligomers were prepared by a solvothermal extraction process of five typical biomasses in a water-acetone co-solvent without noticeable degradation of the cellulose fraction. Afterward, LNPs were produced from the self-assembly of these lignin oligomers via the solvent-shifting methodology. When incorporated into the sunscreen, these had different morphologies, and exerted different UV-blocking capacities. The effects of the chemical structure and size distribution of the LNPs were systematically studied and compared to those of the original lignin oligomers. LNPs exhibited better UV-blocking ability than soluble lignin oligomers due to the more exposed chromophore on the surface. Besides, compact LNPs with conjugating C=O and β -O-4 linkages, as well as the presence of the syringyl unit rich in the methoxyl group in the structures, were beneficial in boosting the UV resistance of the sunscreens. Even though smaller LNPs with higher surface area favored the UV shielding performance, LNPs with widely distributed sizes could further help decrease the UV transmittance. These findings provide an excellent basis for using lignin-derived materials as sunscreen additives and pave the way to developing new environmentally friendly materials for the cosmetic industry.

Keywords

Lignin nanoparticles; UV-blocking ability; Structural effect; Size effect

1. Introduction

Utilizing carbon-neutral lignocellulose to manufacture essential chemicals, materials [1], [2], and fuels contributes to the sustainable development of different established industries currently using petroleum-based chemicals as feedstock [3], [4]. Lignocellulose mainly contains cellulose, hemicellulose, and lignin [5]. In contrast to polysaccharides that consist of different sugar units, lignin contains a high concentration of aromatic rings [6], [7]. Lignin primarily consists of guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units linked by C-O and C-C bonds [8]. As a polymer, the molecular weight of lignin in lignocellulosic biomass is typically above 10,000 g/mol [9]. Lignin can be depolymerized to produce fractions with different molecular sizes via solvothermal degradation, such as lignin oligomers and benzene-derived monomers [10].

Retaining the structural features of lignin and producing and using lignin oligomer mixtures with similar, well-established, and controlled particle sizes on the different fields could help reduce the energy input for further degradation and eliminate the separation procedure of the products [11], [12], [13]. Due to benzene ring units and abundant hydrophilic groups in their structure, lignin oligomers can be self-assembled into lignin nanoparticles (LNPs) with a benzene ring core and a hydrophilic shell by several mechanisms, including π - π stacking, hydrogen bonding, and hydrophobic interaction [14], [15].

LNPs have been widely adopted as green nanomaterials for different applications, such as drug delivery or Pickering emulsion stabilization [16]. Due to the abundant functional

chromophore groups, including conjugated phenols, ketones, quinones, and intramolecular hydrogen bonds, lignin oligomers and LNPs have attracted extensive attention as UV shielding materials, especially as additives in sunscreens to improve their UV-blocking performance [17], [18], [19]. Two facts account for this. On the one hand, the free and etherified phenolic hydroxyl groups can block UV at a wavelength of 280–290 nm. On the other, the double bonds, especially carbonyl groups conjugated with benzene rings are responsible for the absorption at a wavelength of 300–400 nm [20]. Given these features, modifying the functional groups to change the distribution or induce new chromophores into lignin structures can enhance the UV shielding properties. An example of this strategy is forming novel quinone units by exposition to radiation [21], [22].

Compared to lignin oligomers, LNPs exhibit much better UV-blocking capacity according to the literature [23]. It is widely accepted that the higher surface area of LNPs allows for more chromophores in the structure. Consequently, a lower weight of lignin nanoparticles is required for the same number of chromophores [24]. Lee et al. applied rice husk lignin nanoparticles to moisturizing cream and commercial sunscreen. With 5 wt% lignin nanoparticles, the sun protection factor (SPF) of the cream was about twice that of pure cream, and the overall UV protection factor increased 5-fold, from SPF 5.4 to 30.0 in the commercial sunscreen [25]. Given these appealing and promising results, many works in the literature have addressed using lignin as an additive to improve the SPF of sunscreens. However, the effects of the chemical structures of constituting lignin oligomers in LNPs and the particle size distribution of LNPs were rarely investigated. Besides, the raw materials used in these works were mainly technical

lignin, whose structures significantly changed during the extraction process, making them unsuitable for studying the structural effect of UV-blocking. In this study, four kinds of lignin oligomers with different monomeric units and distinguishing side chain linkages were obtained from four biomasses via solvothermal extraction in a water-acetone co-solvent. Subsequently, LNPs were prepared via solvent shifting method and used as an additive in commercial sunscreen. Therefore, this work offers novel insights into this field, addressing the influence degree of the chemical structure and particle size distribution of LNPs affect their ability to block UV radiation.

2. Experimental

2.1 Materials

Four typical biomass powders, derived from birch wood, pine wood, corncob, and corncob residue, were collected from different local commercial companies. all the chemicals were purchased from Chengdu Kelong Chemical Co., Ltd. (China). Sunscreen lotion (Dabao, China) was purchased without further treatment.

2.2 Preparation of LNPs

The extraction of the lignin oligomers from biomass was operated in a 100 mL Parr autoclave reactor. 3 g of the raw material and 50 mL of H₂O-acetone co-solvent (3:7, vol.:vol.) were added in the reactor. Besides, 1 mL of 30% H₂O₂ was added into the reaction system for the solvothermal oxidation. With the reactor being sealed, it was heated to 200 °C for a duration of

1h with a mechanical stirring. After the reaction, the reactor was rapidly cooled by flowing air. The reaction mixture was filtered to isolate the solid residue and the liquid products for further characterizations. The cellulose, hemicellulose, and lignin in the starting materials and in the solid residues were quantitatively measured by the classical chemical titration methods [26].

The ultrasound-assisted solvent shifting method was used to prepare LNPs. 100 mL of the liquid precursor containing lignin oligomers was placed in a beaker. About 600 mL of distilled water was dropped into the liquid precursor consecutively. Then, the emulsion was centrifuged, washed with distilled water, and freeze-dried. For the preparation of the smaller LNPs, 600 mL of the deionized H₂O was placed in a beaker settled on a magnetic agitator, and 100 mL lignin oligomer solution (5 mg/mL) was poured into the beaker.

2.3 SPF Determination

LNP-incorporated sunscreens were prepared to determine the sun protection factor (SPF) following a previously reported methodology [22]. In detail, a 10 wt% lignin sunscreen was produced by continuously stirring 0.05 g of lignin oligomers or LNPs with 0.45 g of sunscreen cream in a dark brown bottle for 24 h. Then, lignin sunscreen with a certain weight was dispersed on the 3 M transpore tape stickering on quartz slides. The surface of the lignin sunscreen slide was slowly rubbed with nitrile gloves on the fingers. The slide was dried in a dark environment for 0.5 h before test. The Shimadzu UV-2700 apparatus with an integrating sphere (Shimadzu, Japan) was used to measure the UV transmittances of the lignin sunscreens. The SPF value was then calculated according to the following equation:

$$SPF = \sum_{290}^{400} E_{\lambda} S_{\lambda} / \sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda}$$

where E_{λ} = CIE erythral spectral effectiveness [27], S_{λ} = solar spectral irradiance [28], and T_{λ} = spectral transmittance of the sample.

2.4 Characterizations of LNPs

Scanning electron microscopy (SEM, JSM-7500F, JEOL, Japan) was employed to examine the morphology of the LNPs. Each particle's maximum (D_{\max}) and minimum (D_{\min}) diameters were measured manually, and the average diameter (D_{avg}) was calculated as the mean of both. The degree of sphericity for each particle was assessed according to the literature [14].

The UV transmittance of the lignin sunscreen was measured by a Shimadzu UV-2700 (Japan). The transmittance (T) within the wavelength range of 290 to 400 nm was collected with the resolution of 1 nm.

The molecular weight distributions of the lignin oligomers in LNPs were examined using gel permeation chromatography (GPC) with a column size of 4.6×150 mm and a RI detector (Waters). The mobile phase used for the analyses was HPLC-grade THF with a flow rate of 0.5 mL min^{-1} . Prior to GPC analysis, approximately 5 mg of LNPs was fully dissolved in 1 mL of THF.

The Fourier-transform infrared (FT-IR) spectra of the LNPs were acquired on a Nicolet IS10 FT-IR spectrometer (Thermo Scientific, USA). The spectra were recorded within the range of 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} .

Analysis of the 2D HSQC NMR spectra of the LNPs was conducted on a Bruker Avance 400 MHz spectrometer. The LNP were redissolved in deuterated dimethyl sulfoxide (DMSO-d_6) for analysis.

3. Results and discussion

3.1 Extraction of the lignin oligomers from the biomasses

Soluble lignin oligomers were firstly extracted in a H_2O -acetone co-solvent system due to the high selectivity for lignin conversion of such a methodology [29], [30], [31]. Fig. 1 shows the variations of cellulose, hemicellulose, and lignin components in the biomasses, the solid reaction residues, and in the obtained liquid products. The contents of these three components in birch wood and pine wood were similar, with cellulose accounting for ca. half of the structural composition and lignin representing ca. 28 wt% of the woody biomasses. In contrast, the hemicellulose content in corncob was 30.7 wt%, much higher than that in the two woody biomasses, while the lignin content in corncob (14 wt%) was much lower, comparatively being only half than the amounts found in the two woody biomasses. Very differently, the corncob residue contains high proportions of cellulose and lignin, with the amount of hemicellulose being meager. This is accounted for by such a feedstock being previously subjected to an industrial process to produce xylose and xylitol.

The comparison between the structural composition of the original feedstocks and the solid residues resulting from the solvothermal process provides a good insight into the effectiveness of the H₂O-acetone co-solvent system. Such a comparison reveals that lignin is the most reactive structural component in the biomasses, with conversions in the range of 54.3% to 88.2%. This high reactivity is accounted for by H₂O and acetone exerting different and complementary functions in the co-solvent system. Specifically, H₂O can break the intermolecular linkages among the components, as well as the intramolecular chemical bonds in lignin. Acetone, which has a similar polarity to that of lignin, is responsible for dissolving the lignin oligomer fragments released and avoiding their repolymerization [14].

The conversions of hemicellulose were 62.2% to 81.5%, as a temperature of 200 °C is sufficient for the hydrolysis of this hetero-glycan with a relatively loose and disordered structure containing branched chains. Distinctly, cellulose could not be degraded significantly under these reaction conditions, and most of the cellulose was remained. The recalcitrance of cellulose is attributed to the robust structure of cellulose with a massive hydrogen bond network and crystalline region [32]. After solvothermal degradation, the concentrations of lignin-derived liquid products from the four biomasses were beyond 7.4 g/L, and the reaction liquids mainly containing lignin oligomers (confirmed by GC-MS) could be considered as a promising source for the preparation of LNPs. In addition, the concentration of (hemi) cellulose-derived products in the reaction fluids was found to be comparable to that of lignin. The soluble oligosaccharides generated from the degradation of (hemi) cellulose can form hydrogen

bonding networks with the lignin oligomers, which has been reported hindering the self-assembly of lignin oligomers into uniform LNPs [33].

H₂O₂ effect was tested for the depolymerization of the corncob residue. The experimental results revealed that using this oxidizing agent significantly influenced the cellulose and lignin degradation behaviors of this feedstock [34]. Using H₂O₂, the lignin conversion declined from 87.9% to 57.6%, while the cellulose conversion increased from 10.7% to 28%. H₂O₂ oxidation would introduce more free radical reactions, in which the generated lignin oligomers underwent further condensation into the solid state. Contrarily, oxidation of the cellulose could disrupt the inherent hydrogen bonding network and promote the cleavage of glycosidic bonds for the degradation of the glucose chains [35], [36], [37]. Consequently, the liquid products derived from cellulose reached a high concentration of 12.1 g/L.

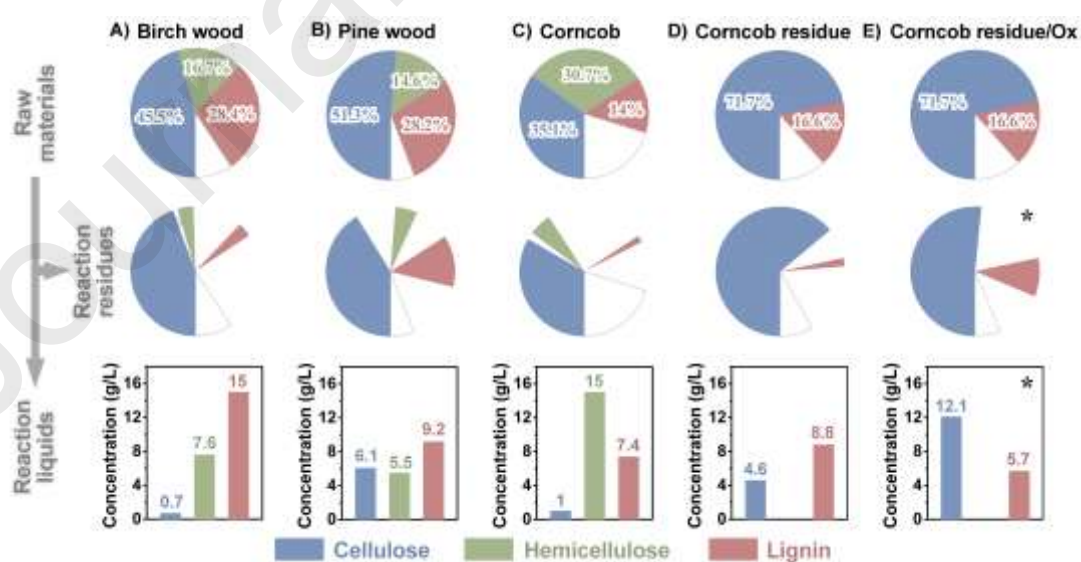


Fig. 1 The cellulose, hemicellulose, and lignin contents in the raw materials (A. Birch wood, B. Pine wood, C. Corncob, D. Corncob residue, E. Corncob residue/Ox) and the reaction

residues, as well as the liquid products' concentrations from the degradation of these components s. with the use of H_2O_2 in the solvothermal treatment.

3.2 Fabrication of spherical LNPs from the lignin oligomers

The lignin oligomers, containing different chemical structures, produced from the four biomasses were subsequently used to prepare LNPs via a solvent-shifting procedure. The morphology of the LNPs was examined using SEM analysis, with the particle size distribution and the sphericity degree (S) also being measured. Fig. 2 shows that even though the average size of the LNPs from the two woody biomasses (birch wood and pine wood) was quite different, the morphology of these LNPs was regularly and uniformly spherical with smooth particle surfaces. Notable, the average S value of the LNPs from birch wood was as low as 0.023, and 89.8% of these particles could be regarded as standard spherical with an S value below 0.05. In comparison, the LNPs from corncob were irregular and sphere wrapped with various nonspherical fragments, with a proportion of particles with $S_{<0.05}$ being only 36.8%. These differences might be attributed to a significant amount of lignin-carbohydrate complex (LCC) in corncob with high hemicellulose content and the concentrated polysaccharide-derived chemicals in the reaction liquid. Specifically, without being driven by π - π interaction, the carbohydrate end in LCC unfavored the self-assembly of the lignin end, while the widely existing polysaccharide-derived chemicals were demonstrated to restrain the self-assembly of lignin oligomers into the nanosphere by forming the undesirable hydrogen bonding with lignin oligomers [33]. When corncob residue, a hemicellulose-free feedstock, was used, the generated LNPs exhibited a regular sphere again, confirming the abovementioned deduction. Accompanying with H_2O_2 oxidation during solvothermal lignin extraction from corncob

residue, the S value of the prepared LNPs slightly increased, ascribing to that oxidation of aliphatic hydroxyl groups into carbonyl groups would stretch the conjugated chains from benzene rings and enhance the π - π interaction strength for self-assembly. Noticeably, the particle size distribution was highly correlated to the sphericity degree, i.e., the more concentrated the particle size distribution, the higher the average S value might be. When the structures of the lignin oligomers were similar, the interaction forces among the lignin oligomers were uniform, leading to the regular-shaped particle size.

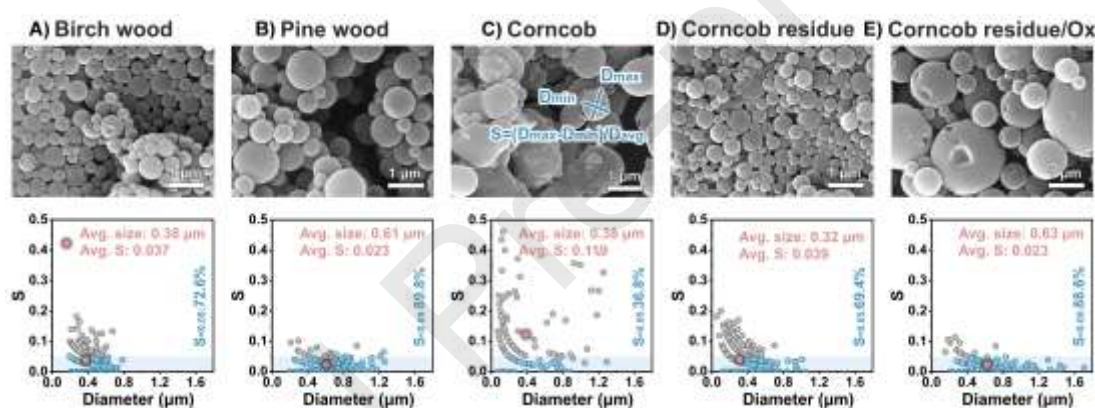


Fig. 2 SEM micrographs, statistic diameter distributions, and sphericity of the LNPs produced from the different biomasses (A. Birch wood, B. Pine wood, C. Corncob, D. Corncob residue, E. Corncob residue/Ox).

3.3 LNPs-enhanced UV-blocking performance

The Sun emits electromagnetic radiation across three ultraviolet (UV) wavelength regions. The rays with the shortest wavelengths, including vacuum-UV and UVC (100-290 nm), are absorbed by the Earth's atmosphere. However, both medium-wavelength (UVB, 290-320 nm)

and long-wavelength (UVA, 320-400 nm) radiation are able to reach the surface of the Earth [38].

To reveal the UV-blocking ability of the LNPs with a different structure obtained from the four biomasses, the LNPs were applied as the promoter to blend into a commercial sunscreen to prepare the advanced sunscreens (Fig. 3). The SPF value of the commercial sunscreen was tested as 21.1, similar to 20 reported in its commodity leaflet. After blending with different LNPs, the incorporation of LNPs resulted in a significant increase in the SPF values, as well as a varying degree of reduction in UV transmittance. Among the LNPs from different biomasses, pine wood-derived LNPs produced the smallest increase (to 24.6) in the SPF value of the sunscreen. In contrast, the sunscreens blended with LNPs from birch wood, corncob, and corncob residue had SPF values ranging from 27.0 to 31.9. The UV-blocking ability was mainly caused by the aryl, phenolic hydroxyl, keto, and other functional groups in lignin, as well as the intramolecular hydrogen bond and conjugation [17], [18], [39]. The H₂O₂ oxidation treatment during solvothermal extraction of lignin of the corncob residue endowed the as-prepared LNPs with higher UV-blocking performance, where the SPF value of the LNPs participated sunscreen reached 34.1, and a more significant reduction in the UV transmittance was achieved, especially in the UVA region. These results indicate that the presence of H₂O₂ in the solvothermal treatment might increase the content of carbonyl groups of the lignin oligomers, which not only benefited their self-assembly into spherical particles but also improved the UV absorbance of the final LNPs. Additionally, it should be noticed that previous studies have reported an increase in the SPF value of sunscreens with a decrease in the size of LNPs. This is because a smaller

particle size led to a higher concentration of chromophores and auxochromes on the surface, which enhanced the UV-blocking performance [24] , [40].

The UV-blocking properties of the soluble lignin oligomers from the oxidation-assisted extraction process and their self-assembled LNPs were compared in the sunscreen lotion with 2.5% concentration (Figs. 3C and 3D). The addition of LNPs to the sunscreen resulted in lower UV transmittance compared to the sunscreen containing soluble lignin oligomers, particularly in the UVB region. This outcome is consistent with previous studies, where higher surface area of LNPs enables more chromophores to contribute to UV absorption. Thus outstanding compatibility and dispersion brought about excellent UV protectant ability [16], [41], [42]. Meanwhile, the spherical shape of the particle can wrap the chromophores inside the particle and thus reduce the color. Besides, the π - π stacking interactions between the aromatic rings in their chemical structure also improved the UV-blocking ability of LNPs, which lowers the energy gap of the electron transition [25], [39]. In the case of the LNP-incorporated sunscreen, the SPF value increased with the increasing concentrations of LNPs. Specifically, the SPF value of the sunscreen with 2.5% LNPs was 29.5, while it could reach 35.6 with the increased LNPs concentration to 15%.

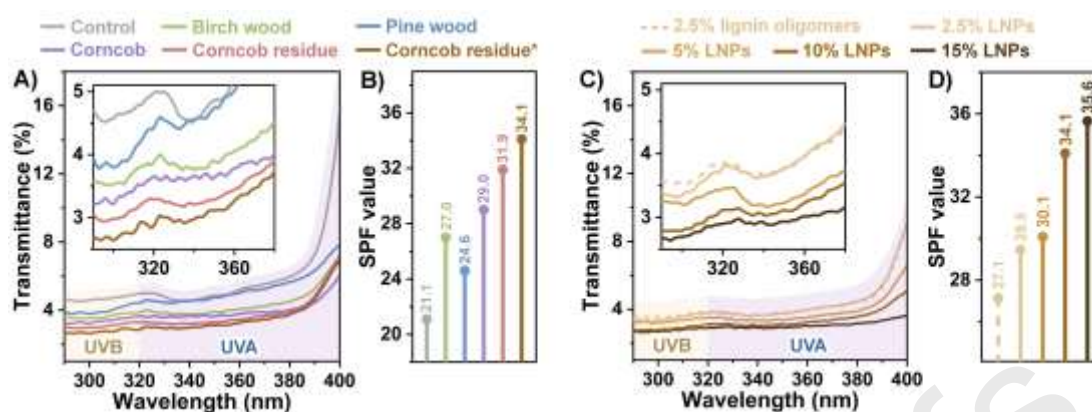


Fig. 3 UV transmittances and SPF values of the sunscreen blended with the lignin oligomers and LNPs. A) and B) UV-blocking performance of LNPs from different biomasses. C) and D) Comparison of UV-blocking properties between soluble lignin oligomers and self-assembled LNPs (Corncobresidue/Ox).

3.4 Chemical structural effects of the LNPs on UV-blocking performance

The constituted lignin oligomers in LNPs were redissolved into THF solvent for GPC analysis (Fig. 4A), to reveal the molecular weight distribution of the lignin oligomers in LNPs obtained from the different biomasses. The lignin oligomers present in LNPs, which were extracted from polar protic solvent systems, exhibited relatively lower weight-average molecular weights. The similar molecular weight distributions of the lignin oligomers from different biomasses would not affect their self-assembly behavior significantly, but primarily influence the particle size. [14], [33].

Then, FTIR was used to investigate the correlation between the UV shielding properties and the chemical structure of the LNPs. The FTIR spectra of the five LNPs were collected and shown in Fig. 4 The C-O tensile vibration signal of the G unit at 1267 cm^{-1} existed in the five

LNPs, indicating that the G unit is abundant in all lignin structures [43]. In comparison, the C-O stretching vibration signal of the S unit at 1328 cm^{-1} was significantly more robust in the birch wood-derived LNPs than in the other four LNPs. Such differences indicate that the higher content of the S unit led to better UV shielding performance, explaining the higher blocking capability of the birch wood-derived LNPs than that of the pine wood-derived LNPs. Additionally, the stretching vibration signal of lignin carbonyl conjugated aryl ketone C=O (1631 cm^{-1}) was observed in all LNPs except pine wood-derived LNPs, demonstrating that the conjugated aryl structure would improve UV blocking performance, these phenomena being beneficial for UV absorption at $300 \sim 400\text{ nm}$ [20]. In addition, the absorption peaks of unconjugated carbonyl are mainly in 1705 and 1694 cm^{-1} [44].

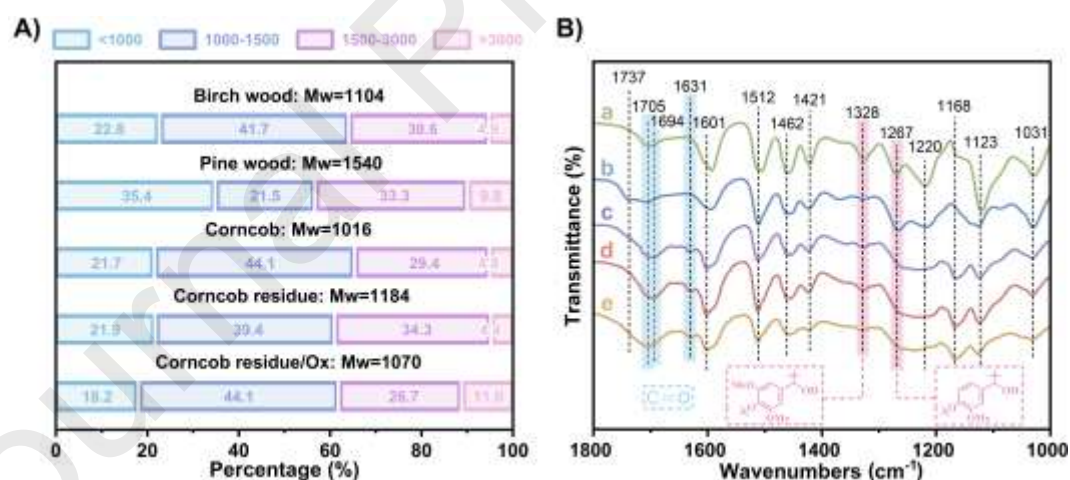


Fig. 4 Structural features of the lignin oligomers in LNPs. (A) Molecular weight distribution; (B) FTIR spectra ((a) Birch wood, (b) Pine wood, (c) Corncob, (d) Corncob residue, (e) Corncob residue/Ox).

2D HSQC NMR analysis was further employed to reveal the chemical structure of the LNPs (Fig. 5). For the LNPs synthesized from the oxidized corncob residue, with the highest UV shielding performance, the signal strength of the side chain structure was weak, revealing a more severe degradation. As a result, these developments indicate that more exposed active groups would enhance UV shielding. Besides, the abundant *p*-coumaric acid (PCA) side chain with conjugate benzene ring structure also provided these LNPs with a high UV shielding capability. On the contrary, lacking methoxy-rich S unit and containing conjugated benzene ring structures were the structural factors responsible for the poor UV shielding ability. This was evident from the minimum content of the S unit in the pine wood-derived LNPs, indicating their limited UV shielding capacity. In addition, the UV blocking efficiency of the LNPs exhibited a positive correlation with the content of A linkage, ranging from 81.5% to 100%. This correlation can be attributed to the better rotation flexibility of A linkage than B or C linkages, which facilitated the self-assembly of π - π stacking in the nanoparticles [14], and consequently improved the UV shielding of the sunscreens [25].

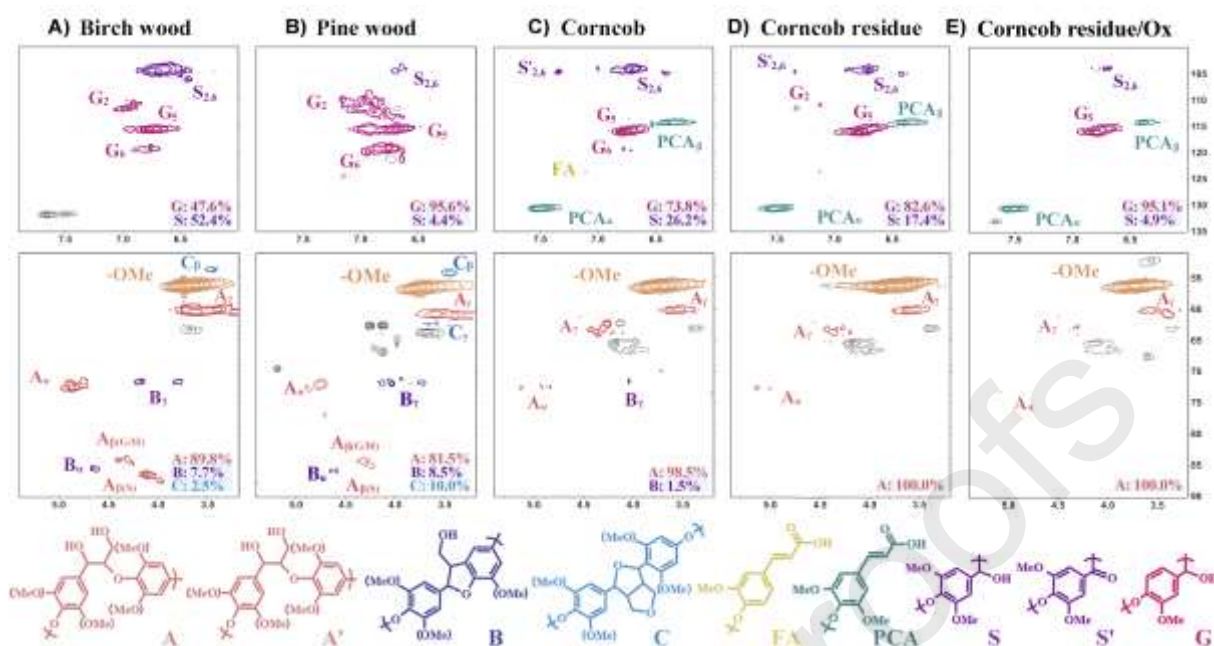


Fig. 5 2D HSQC NMR spectra of the lignin oligomers in different LNPs (A. Birch wood, B. Pine wood, C. Corncob, D. Corncob residue, E. Corncob residue/Ox).

3.5 Particle size effects of the LNPs on UV blocking performance

As observed from the above results, the UV-blocking performance of the LNPs may be influenced not only by the structure of the lignin oligomers, but also by their particle size distribution. With an intensively dispersed particle size, birch wood-derived LNPs were chosen to study the effect of particle size distribution. As shown in Fig. 6A, two series of LNPs were prepared via different water addition methods during solvent-shifting: i.) small, with particle size below 0.2 μm , and ii.) big with particle sizes between 0.2 and 0.8 μm . Besides, a third category (mixed) was obtained by mixing big and small LNPs. Then, the UV blocking performance of the sunscreens containing the three samples was compared (Fig. 6B). The experimental results revealed that the UV blocking performance depended on the size distribution of LNPs. Blending with bigger LNPs, the SPF value of the sunscreen was 27, while

smaller LNPs increased the SPF value to 28.6. This is in agreement with the literature, as higher phenolic hydroxyl groups and a larger surface area have been reported to benefit the UV-blocking performance of the LNPs [45]. In this study, using the same lignin oligomers, the aforementioned latter factor was mainly responsible for the higher SPF value. Noticeably, the theoretical SPF value of the sunscreen blending with a mixed big and small LNPs was 27.8, while the experimental value was as high as 30.8. These results suggest a synergistic effect between small and big particles. Notably, the LNPs with a wide range of particle sizes favored UV blocking, where the arrangement of non-uniform LNPs filled the gap between the adjacent particles, and a more compact LNPs shield improved the UV blocking ability.

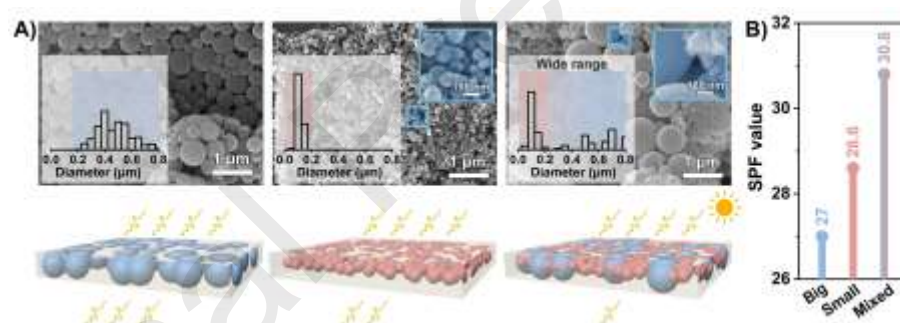


Fig. 6 SPF values of the LNP-sunscreens produced from birch wood with different particle size distributions.

4. Conclusions

Lignin oligomers were extracted from several typical lignocellulosic biomasses in a H₂O-acetone co-solvent. Then, LNPs with distinguished morphology and size distributions were prepared by continuously adding H₂O into the reaction liquids and tested as additives to improve the SPF value of sunscreens. The addition of the LNPs could increase the SPF value

from ~20 to 34.1, with the blocking capability depending on the lignin structure, being much higher for the LNPs than for the lignin oligomers. β -O-4 linkage with better rotation flexibility, as well as the H₂O₂ oxidation-induced conjugated C=O group, improved the self-assembly of the lignin oligomers and further increased the SPF value of the sunscreens. In addition, the SPF value of the sunscreens containing a mixture of big and small LNPs was much higher than those containing LNPs with a concentratedly distributed size. The arrangement of non-uniform LNPs accounted for the improved values of the former type of particles. This disorder allowed some particles to fill the gap between them and the adjacent particles, leading to a more compact LNPs shield which improved the UV-blocking ability of the mixture. The findings of this study offer new perspectives for the design and development of natural-based UV-blocking materials. Besides, the detailed correlation established in this work between the structural characteristics of the lignin-derived materials (LNPs and oligomers) paves the way not only for using them in sunscreen formulations but also for developing alternative and environmentally friendly materials in the cosmetic industry.

CRedit authorship contribution statement

Tianyu Liang: Investigation, Data curation, Visualization, Formal analysis, Writing - original draft. **Ya Ma:** Investigation, Data curation, Visualization, Formal analysis. **Zhicheng Jiang:** Conceptualization, Methodology, Writing - review & editing, Funding acquisition, Supervision. **Javier Remón:** Validation, Formal analysis, Writing - review & editing, Funding acquisition. **Yingdong Zhou:** Investigation, Formal analysis. **Bi Shi:** Resources, Supervision.

Declaration of competing interest

There are no conflicts to declare.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (22078211). We appreciate Hui Wang from the Analytical & Testing Center of Sichuan University for helping with the SEM characterization. We also thank Dr. Xiu He and Dr. Ying Song at the College of Biomass Science and Engineering, Sichuan University, for the experimental assistance. Javier Remón thanks MCIN/AEI/10.13039/501100011033 and the European Union «NextGenerationEU»/PRTR» for the Ramón y Cajal Fellowship (RYC2021-033368-I) awarded, and the Aragón Government (Research Group Reference T22_23R) for providing frame support.

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Journal Pre-proofs

Highlights

Lignin oligomers were extracted from different biomasses via solvothermal method

LNPs were used as additives to significantly increase the SPF value of sunscreens

LNPs with conjugating C=O, β -O-4 linkages and S unit showed better UV resistance

A mixture of big and small LNPs resulted in a more compact LNP shield

Graphical abstract

