

Synergy of Modified Lignin and *p*-Coumaric Acid for Improving the Function of Sun-protection in Sunscreen

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Lignin is a potential natural sunlight protector because its benzene derivative structure can absorb UV rays. Pure lignin is not good enough for sunblock because lignin is not fully dispersed in cream, and the range of absorbed UV rays is not broad. In this work, lignin was modified with polybutyl acrylate (PBA) and self-assembled into microspheres (L-PBA-NPs) to enhance its compatibility in cream, and it was blended with *p*-coumaric acid (CA) to extend its light absorbance. The hydrophobicity of grafted PBA on lignin and the microsphere of the modified lignin provided an ability to disperse in oily pure cream. To improve the sun protection factor (SPF) of the blended lignin-based sunscreen, CA with different UV absorbing ability was mixed inside the modified lignin to form CA@L-PBA-NPs. When CA and L-PBA-NPs (1:1) were added in cream with 5%, the SPF of the blended lignin sunscreen reached 18.8. After irradiation of the CA@L-PBA-NPs sunscreen under UV for 3 h, the SPF of the blended lignin-based sunscreen increased slightly because of more conjugated structures produced in lignin. The CA@L-PBA-NPs in sunscreens have great potential as a green ingredient to substitute for the small-molecule sunscreen active ingredients in commercial sunscreen products.

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INTRODUCTION

Lignin, a natural aromatic polymer in plants, accounts for about 20% to 30% of constituents in fiber cell walls, and it defends against the attack of microbials and sunlight (Björn 1997; Doherty *et al.* 2011; Tortora *et al.* 2014; Morena *et al.* 2022). The molecular structure of lignin contains abundant phenolic groups and multiple conjugated double bonds structures, including a benzene ring or its derivatives. Lignin is an underutilized by-product of the paper industry or biorefinery process (Tadesse and Luque 2011; Zhang *et al.* 2011; Ragauskas *et al.* 2014). Lignin can be upgraded for use in fuels, chemicals, and materials. Lignin can be used as a polymer electrolyte in rechargeable batteries (Ohnishi *et al.* 1989; Gnedenkov *et al.* 2013; Mukhopadhyay *et al.* 2018). After catalytic hydrogenolysis, lignin can be converted to liquid fuel products (Li *et al.* 2012; Ren *et al.* 2020). As a polymer it can be applied as phenolic resin adhesive in paneling (Kalami *et al.* 2018; Yang *et al.* 2018).

The defense against sunlight by lignin is contributed to its aromatic structure, along with various functional groups such as aryl, phenolic hydroxyl, ketone, and carboxyl

groups. The benzene ring combined with intramolecular conjugation bonds endows lignin with good ability to absorb UV light, which hints that lignin is a natural UV protectant (Hideyuki *et al.* 1989; Ugartondo *et al.* 2008). The low environmental impact of lignin extraction implies that lignin can be expected to be favorable for this application. Industrial lignin produced by paper mills is present as tiny particles, which provides the possibility for producing lignin-based sunscreen. Lignin-based sunscreens are prepared by blending lignin with pure cream. Compared with chemical sunscreens on the market, lignin-based sunscreens have the advantages of good photostability, simple preparation, low cost, and good cell compatibility (Pan *et al.* 2006; Li *et al.* 2019; Piccinino *et al.* 2022). Moreover, as a sun protection factor (SPF)-booster, lignin can replace or reduce the use of original petroleum-derived compounds in sunscreen, such as acrylates/C10-30 alkyl acrylate cross-polymer. If lignin-based sunscreens with good performance can be prepared, it will be of great benefit to broaden the application of lignin.

When lignin is blended directly with pure cream, of the type conventionally used in this class of products, the performance of lignin-based sunscreens against UV light is poor due to the insufficiently conjugated structure in lignin. It is well known that most of the lignin from paper mills consists of either alkali lignin or lignosulfonate. The successful application of lignosulfonate in sunscreen has been reported (Zhang *et al.* 2022). It is worth mentioning that though alkali lignin is an amphiphilic natural macromolecular compound, the dispersibility and compatibility of lignin from paper mills are disappointing in pure cream. To improve the performance of lignin-based sunscreens, it is necessary to improve the UV absorption ability (sunscreen effect) of lignin-based sunscreens and the compatibility and dispersibility of lignin in pure cream.

It is important to consider modifying alkali lignin to enhance its compatibility and dispersibility in pure oily cream. Pure oily cream is hydrophobic, and this implies that lignin should undergo hydrophobic modification to improve its compatibility with the cream. The hydrophobization modification of lignin generally includes acetylation (Buono *et al.* 2016; de Oliveira *et al.* 2020), atom transfer radical polymerization (ATRP) (Chung *et al.* 2013), graft copolymerization (Liu and Chung 2017), and esterification (Orebom *et al.* 2021). ATRP grafting is an effective method to modify lignin with special functions. ATRP controls the reaction to increase the hydrophobic groups on the lignin in a controlled manner. Wu *et al.* (2017) synthesized 4-benzoyl-3-hydroxyphenyl acrylate (BHA) by organic synthesis and then grafted it onto lignin macromolecules by ATRP polymerization to form AL-g-BHA. In the case of adding 10%, the SPF of AL-g-BHA sunscreen reached 59. However, the initial synthesis process of monomer is complicated, which is difficult in practical application. To improve the UV absorption performance of lignin-based sunscreens, lignin is used as an enhancer in sunscreens on the market (Qian *et al.* 2017). Lignin in microspheres added into commercial sunscreens increases the SPF of the sunscreen from 15 to 91 with 10% lignin (Qian *et al.* 2016). The active ingredients of commercial sunscreens are small chemical molecules, and they decompose into toxic substances under UV radiation. These toxic substances enter the skin through the pores, causing skin allergies (Lodén *et al.* 2011; Saewan and Jimtaisong 2015). Therefore, it would be beneficial if natural lignin-based sunscreen could be manufactured without small-molecule chemical active ingredients.

p-Coumaric acid (CA) is a natural phenolic compound that is a small molecule with an excellent UV-absorbing ability (Boz 2015). Compared to other UV-absorbing phenolic compounds, such as sinapic acid, CA can be easily extracted from natural vegetables and fruits. It also can serve as an antioxidative antibacterial and can delay the aging of skin.

Thus, the authors hypothesized that CA could be an effective UV-absorbing component when added to lignin-based sunscreen to improve the overall effectiveness of the sunscreen against UV.

In this work, BA was used as the monomer to hydrophobically modify lignin by ATRP to form L-PBA, which was self-assembled into L-PBA-NPs by adding antisolvent dropwise to the solution. The L-PBA-NPs complexed with CA was added to the pure cream to prepare a lignin-based sunscreen. The prepared lignin-sunscreen absorbed UV light, which demonstrated its potential application in sun protection.

EXPERIMENTAL

Materials

Alkali lignin was extracted from eucalyptus. 1,4-Dioxane, 1-(4-methoxyphenyl)-3-(4-tert-butylphenyl)-1,3-propanedione, butyl acrylate and p-coumaric acid (CA) were purchased from Macklin Biochemical Technology Co LTD. N,N,N',N'',N''-pentamethylene diethylenetriamine (PMDETA, purity>99%), triethylamine (TEA, purity > 99.5% (GC)), N,N-dimethylformamide (DMF, purity>99%), cuprous bromide (CuBr, purity >99%), 2-bromoisobutyryl bromide (BIBB, purity>98%), and dimethyl sulfoxide (DMSO, AR>99% (GC)) were purchased from Sigma-Aldrich. Pure cream was purchased as Johnson and Johnson's baby lotion.

Methods

Purification of lignin

The 10 g alkali lignin was dissolved in 1000 mL 0.01mol/L NaOH solution and then filtered. 0.01 mol/L HCl solution was added to the filtrate drop by drop until precipitation was generated. After standing, filtering, washing, and drying, purified lignin can be obtained.

Preparation of lignin macroinitiators (L-Br)

The procedure for synthesizing lignin macromolecular agents was adopted from previous work. (Kim and Kadla 2010). Dry alkali lignin (1 g), TEA (2.02 g), and BiBB (4.74 g) were dissolved in DMF with rapid stirring. Under the nitrogen atmosphere, BIBB was added dropwise to the reaction system at low temperature. After the dropwise addition of BIBB, the entire reaction continued for 24 h at room temperature. The reaction was terminated by adding deionized water. After washing, centrifuging, and drying the resulting solution, pure L-Br (1.6 g) was obtained.

Synthesis of L-PBA

L-Br (0.6 g), CuBr (0.05 g), PMDETA (0.30 mL), and BA (1.28 g) were sequentially added to the reaction flask, and the mixture was stirred at room temperature until the solid was completely dissolved. After that, the reaction mixture was made to be anhydrous and oxygen-free by the method of "freezing-evacuating-introducing nitrogen". The reaction mixture was stirred at 60 °C for 12 h. The reaction mixture was exposed to air and then precipitated by dripping into deionized water slowly. Finally, the precipitate was filtered, washed, and dried to obtain 0.7 g of L-PBA product.

Preparation of L-PBA nanospheres (L-PBA NPs)

L-PBA NPs were prepared by a self-assembly method. First, L-PBA (0.5 g) was completely dissolved in 100 mL of DMSO with rapid stirring. Deionized water slowly was added dropwise into the DMSO solution. Subsequently, the resulting solution was put into a dialysis bag (3500 Da) and dialyzed in deionized water for 3 days to remove the DMSO. The L-PBA NPs were obtained after freeze-drying.

Preparation of lignin-based sunscreen

Lignin-based sunscreens were prepared by simple blending and stirring. For example, a 10 wt.% L-PBA sunscreen was prepared by mixing 0.4 g of L-PBA NPs with 3.6 g of pure cream. The prepared sunscreen was stirred at room temperature for 2 h and left to stand for 12 h (in the dark condition).

Characterizations of L-PBA NPs and blending lignin-based sunscreen

To observe the appearance of L-PBA NPs, the samples were imaged by scanning electron microscopy (SEM, Merlin, Zeiss) under a vacuum with an accelerating voltage of 5 kV. Before the measurement, the lignin microspheres were dispersed in water to make the content of lignin microspheres in water below 0.02 wt.%. Subsequently, SEM samples were prepared by dropping the diluted lignin microsphere suspension onto aluminum foil and drying at 40 °C. The reason for selecting this relatively low temperature was to avoid condensation of the microspheres. The measurement of the SPF of blended lignin-based sunscreen samples was adopted from Qian *et al.* (2015). The wavelength interval was set to 2 nm to record the UV transmittance of the sunscreen sample. The wavelength range was from 290 to 400 nm. To obtain the sun protection factor (SPF) of the sunscreen sample, the UV transmittance data was added into Eq. 1,

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

where E_{λ} represents the human erythema-causing efficacy of sunlight at λ wavelength, S_{λ} represents the energy intensity of sunlight irradiated on the ground at λ wavelength, and T_{λ} represents the UV transmittance of the sample in the spectrophotometer test at λ wavelength. A higher SPF value means better UV protection (Sohn *et al.* 2016).

Dispersibility and rheological studies of lignin in blended lignin-based sunscreens

Lignin can fluoresce under UV light to evaluate the dispersion of lignin in sunscreen, so lignin dispersion in sunscreen can be observed by confocal laser microscopy (Leica TCS-SP5). The viscosity of lignin sunscreens was evaluated at room temperature in a rheometer (HAAKE MARS60) equipped with a 1 mm parallel plate geometry. The conditions for the kinetic viscosity test were set up to linearly increase the shear rate from 1 to 1000 s⁻¹.

RESULTS AND DISCUSSION

Characterization of L-Br and L-PBA Copolymers

The modification of lignin in this work involved the grafting of initiating groups onto lignin *via* hydroxyl groups, followed by controlled polymerization from the initiator

via ATRP. As shown in Fig. 1A, the hydroxyl groups in lignin underwent an esterification reaction with BiBB to form a lignin macroinitiator (L-Br). In the presence of CuBr/PMDETA, L-Br exhibits high initiation rate and polymerization efficiency for butyl acrylate monomers to obtain L-PBA polymers. The alkaline lignin, L-Br, and L-PBA were dissolved in deuterated dimethyl sulfoxide (DMSO-d₆) for ¹H NMR analysis (VANCE III HD 600, Bruker). The ¹H NMR spectra of alkaline lignin, L-Br and L-PBA are shown in Fig. 1B, C, D. In Fig. 1C, the new peak at $\delta=1.82$ ppm is derived from the 2-methylproton (-C(CH₃)₂Br) of bromo-isobutyryl bromide, indicating that BiBB was successfully grafted onto lignin macromolecules to form L-Br. In the L-PBA copolymer spectrum in Fig. 1D, the methyl proton of the brominated ester (-C(CH₃)₂Br) disappeared at 1.82 ppm, while the new peaks at 0.6 to 0.8, 1.2 to 1.4, and 1.6 to 1.8 ppm appeared, which can be attributed to -CH₃- (c) -CH₂- (b) and -CH- (a) group of PBA, respectively. This data confirmed that PBA was grafted onto the lignin to form L-PBA.

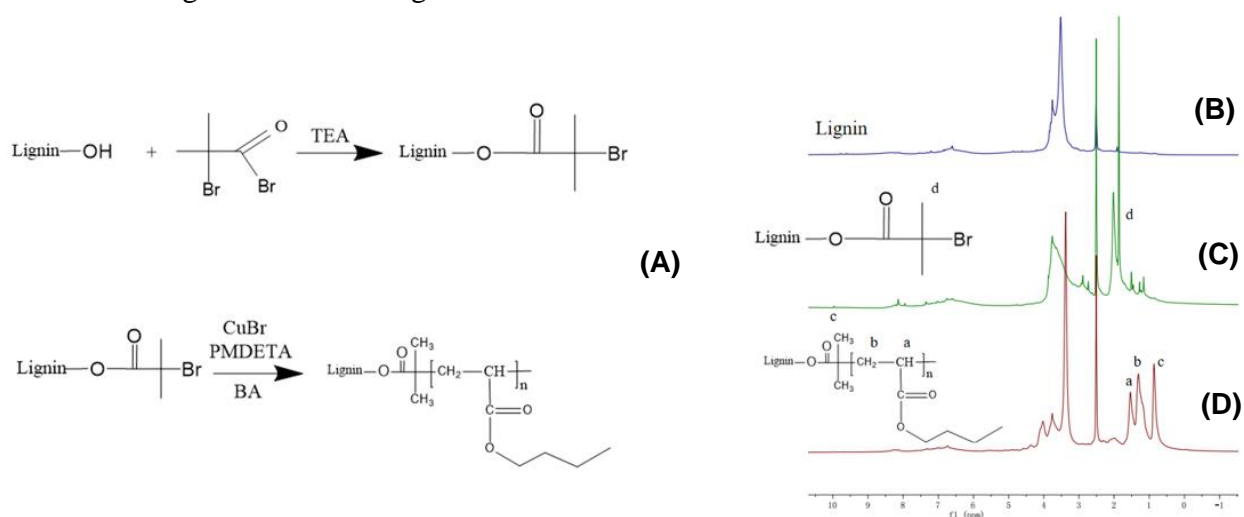


Fig. 1. Route to synthesize copolymers by ATRP of L-PBA copolymer. (A) ¹H NMR spectra of alkali lignin (B), L-Br (C), and L-PBA (D)

Morphology and Dispersion of L-PBA NPs in Blended Sunscreen

In general, lignin did not have the ability to self-assemble into lignin microspheres until it was hydrophobically modified and completely dissolved in DMSO. When an anti-solvent such as water was added dropwise to DMSO, the lignin spontaneously formed an external hydrophilic microsphere structure. The morphology of L-PBA NPs was confirmed by SEM, as shown Fig. 2.

The microsphere structure of L-PBA NPs prepared by self-assembly method was clearly apparent. The tentacle-like adhesions between L-PBA NPs microspheres were attributed to the PBA grafted onto the lignin. After the measurement of particle size analysis in Fig. 2d, the average size of L-PBA NPs was confirmed as 448 nm. Compared with the previous work, the particle size of the lignin microspheres increased, and the particle size was evenly distributed in the range of 377 to 514 nm. To evaluate the dispersion of L-PBA NPs in blended lignin-based sunscreens, confocal laser microscopy was applied to observe the distribution of fluorescence of lignin in blended lignin-based sunscreens. As shown in Fig. 3a-f, alkali lignin fluoresces distinctly in the alkali lignin sunscreen under UV light irradiation.

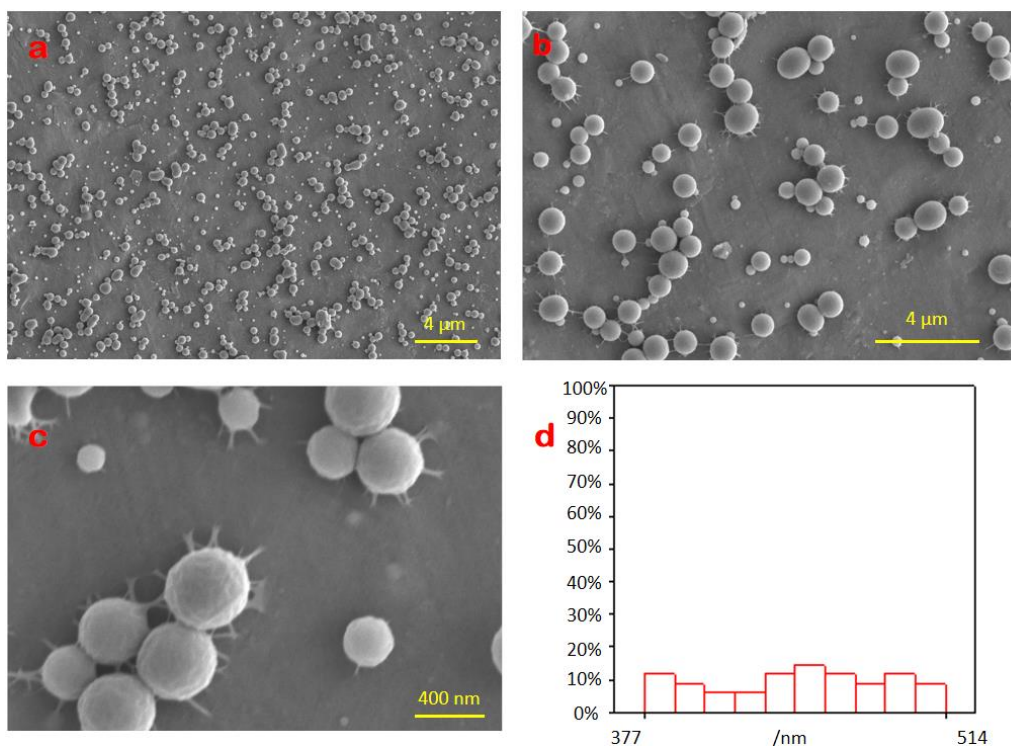


Fig. 2. The SEM micrographs of L-PBA NPs with different magnification (a-c) and the particle size measurement of L-PBA NPs (d)

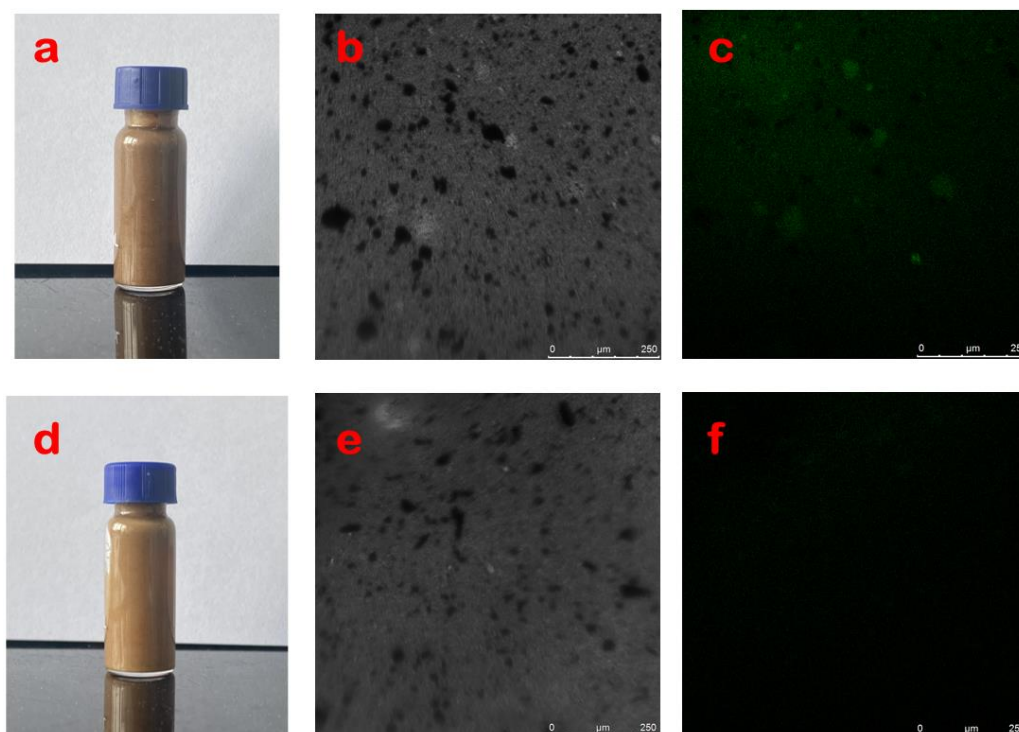


Fig. 3. Digital photographs of alkali lignin sunscreen (a) and L-PBA sunscreen (d); photographs of alkali lignin sunscreen (b) and L-PBA sunscreen (e) under optical microscopy; fluorescence photographs of alkali lignin sunscreen (c) and L-PBA (f) sunscreen under confocal laser microscopy.

The distribution of fluorescence in sunscreen was not uniform, and the particles of alkali lignin were observed under the microscope, indicating the bad dispersion of alkali lignin in pure cream. At the same time, L-PBA NPs emitted weak fluorescence in the blended sunscreen under the same UV irradiation, which may be related to the substitution of hydroxyl groups in lignin after grafting PBA, resulting in the decrease of fluorescence intensity. The fluorescence emitted by L-PBA NPs was well dispersed in the blended sunscreen, and the L-PBA NPs in the blended sunscreen did not produce obvious particles. Therefore, the dispersion of L-PBA NPs in the blended sunscreen was better than that of alkali lignin.

Evaluation of Sunscreen Effect of Blended Lignin-Based Sunscreen

CA is a small molecule that is very friendly to the skin. It can inhibit the formation of melanin and delay skin aging and has a certain inhibitory effect on bacteria. Lignin-based sunscreens were prepared by adding different concentrations of L-PBA NPs, CA, and CA@L-PBA NPs mixtures (ratio: 1:1) to pure cream with simply blending. As shown in Fig. 4a, b, the original pure cream had a very high UV transmittance and did not have a satisfying sun protection effect. With the addition of L-PBA NPs and CA, the UV transmittance of the sunscreen after blending decreased gradually. When the additional amount of L-PBA NPs was 5%, the sunscreen transmittance was reduced to below 20%.

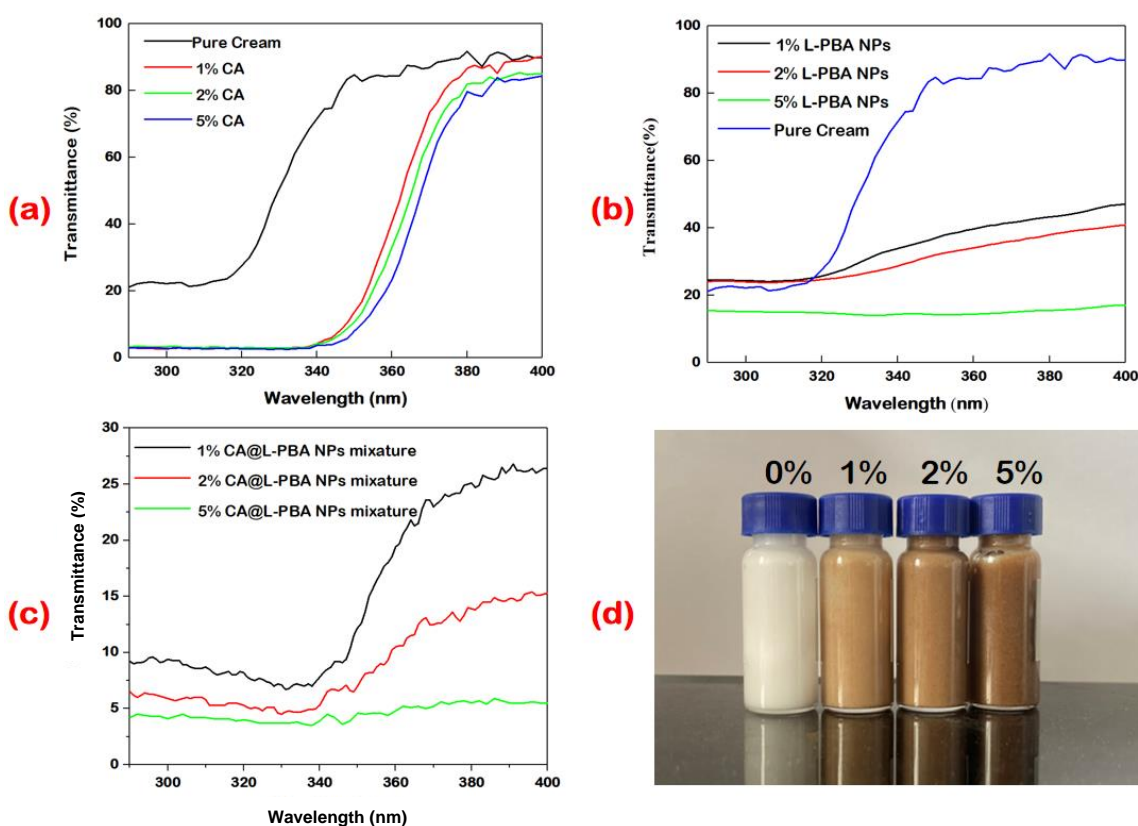


Fig. 4. The UV transmittance of CA (a), L-PBA NPs (b), CA@L-PBA NPs (c) with different addition and the performance of CA@L-PBA NPs sunscreen with different addition (d)

The SPF values of the blended baby cream with different L-PBA NPs and CA additions are shown in Table 1. The SPF of pure cream was only 1.60, which meant

applying baby cream to the skin could not provide UV protection. When the L-PBA NPs content reached 5%, the SPF value of the blended baby cream was 6.64, which means that sunscreen applied to the skin can reduce the transmission of UV by an average of 85% and had a certain UV protection effect. When CA was added at 5%, the SPF of sunscreen was 3.57. The SPF of the blended sunscreen prepared by adding CA and L-PBA NPs separately to pure cream, respectively, did not meet the requirements of sunscreens on the market (SPF>15). Furthermore, the SPF value of sunscreen cannot be improved because lignin and CA lack strong enough conjugated structure on the natural structure. Therefore, the CA@L-PBA NPs mixture was added to the pure cream, and the lignin-based sunscreen was prepared after being fully blended. The UV transmittance and the performance of CA@L-PBA NPs sunscreen was investigated.

Figure 4d shows the color performance of lignin-based sunscreens with the addition of different CA@L-PBA NPs mixtures. The color of the lignin-based sunscreen deepened with the increase of the addition amount of the CA@L-PBA NPs mixture. As shown in Fig. 4c, the UV protection performance of lignin-based sunscreen also kept pace with its color performance, and its UV transmittance gradually decreased with the deepening of the color. The SPF of CA@L-PBA NPs lignin-based sunscreen is shown in Table 1. Under the same amount of adding condition, CA@L-PBA NPs sunscreen had higher SPF than that of L-PBA NPs sunscreen and CA sunscreen. When the addition amount of CA@L-PBA NPs was 5%, SPF of the sunscreen reached 18.79, indicating that the SPF value had been increased by nearly three times while reducing the color impact of lignin. It not only met the standard of commercial daily sunscreen, but also had better performance in appearance.

Table 1. SPF of CA, L-PBA NPs, and CA@L-PBA NPs at Different Amounts

Type of Sample	SPF
Pure Cream	1.60±0.03
1% CA	3.03±0.17
2% CA	3.28±0.20
5% CA	3.57±0.21
1% L-PBA NPs	2.89±0.03
2% L-PBA NPs	3.24±0.03
5% L-PBA NPs	6.64±0.17
1% CA@L-PBA NPs mixture	6.63±0.07
2% CA@L-PBA NPs mixture	11.02±0.6
5% CA@L-PBA NPs mixture	18.79±2.61

Lignin@CA Enhanced Sunscreen Effectiveness

As shown in Fig. 5a-c, lignin, CA, BMDM and CA@lignin exhibited different UV absorbance. In the range of 290 to 400 nm, the higher the degree of conjugation of the molecule, the higher the UV absorbance it exhibits. BMDM has a stronger conjugated structure than CA, so it has better UV absorption properties at specific wavelengths. Compared with such UV absorbent with high purity and regular molecular structure, lignin is composed of three structural units connected by covalent bonds, and it has a relatively high relative molecular mass and a certain conjugated structure. Therefore, lignin can also exhibit a certain UV absorption effect. The relatively weak conjugated structure of lignin and CA can explain that the blended sunscreen showed poor sunscreen effective when L-PBA NPs and CA were blended respectively with pure cream without any sunscreen effect. However, when CA@L-PBA NPs mixture was blended with sunscreen, the SPF of blended sunscreen was increased highly. The enhanced effect of sunscreen is attributed to the

synergistic effect between lignin and CA. The synergistic effect between lignin and CA in pure cream becomes interesting and puzzling. To explore the improvement from synergistic effect between lignin and CA in sunscreens, avobenzone (BMDM), a commonly used active chemical in the sunscreen market were used as reference. The same mass of lignin, CA, CA@Lignin mixture (m/m 1:1), and BMDM were added to the mixed solution of dioxane/water (v/v 4:1). The absorbance of the mixed solution was measured by the UV spectrophotometer. BMDM has a high absorbance at 320 to 410 nm and a relatively low absorbance at 290-320 nm. While CA has high absorbance at 290 to 340 nm, it had almost no absorbance at 350 to 410 nm. If there is no synergy between lignin and CA, the UV absorbance of CA@Lignin should be located at the average position of the two absorbances, that is, the position of the I line. However, the results showed that the absorbance of the CA@Lignin mixed solution was far beyond the position of the I line, which indicated a clear synergistic effect between lignin and CA. It is proposed that the synergistic effect can be attributed to π - π stacking between CA and lignin. Furthermore, since CA is a small molecule, it is easier than other macromolecules to generate π - π stacking with lignin, which has a three-dimensional structure

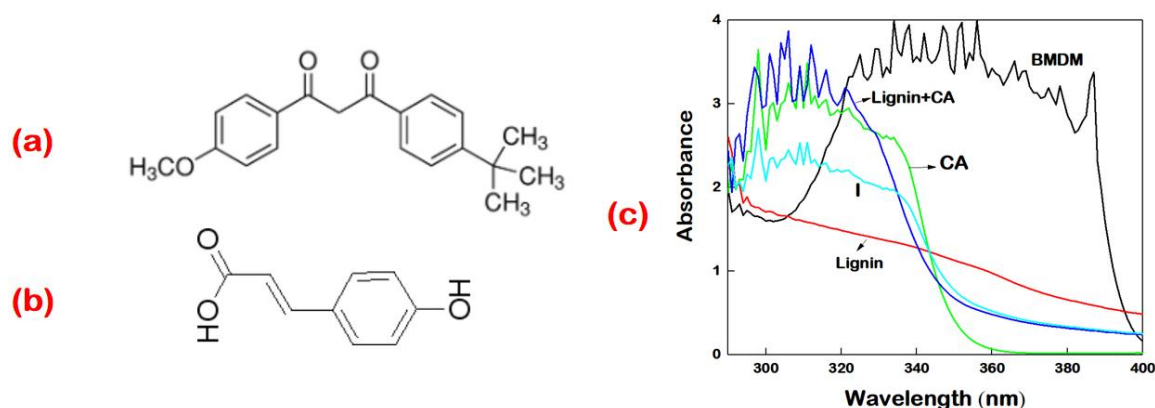


Fig. 5. The chemical structure of BMDM (a) and CA (b). The UV absorption spectrum of lignin, CA, BMDM, and CA@lignin (c)

Light Stability of Blended Lignin-Based Sunscreen Cream

In practical production applications, most products, including sunscreens, will deteriorate under ultraviolet radiation. Therefore, it is necessary to prepare a blended lignin-based sunscreen with good photostability. The sunscreens containing the mixture of CA@L-PBA NPs with different added amounts were irradiated by UV light with a wavelength of 365 nm for 3 h. Subsequently, the UV transmittance of the blended lignin-based sunscreen after irradiation was tested, and the results are shown in Fig. 6a. The UV transmittance of the sunscreen after UV radiation decreased slightly, which meant that the sunscreen after radiation had better UV absorption ability. The SPF results of sunscreens were shown in Table 2. The SPF of sunscreen was slightly higher than it was before UV radiation, indicating that the CA@L-PBA NPs blended lignin-based sunscreen had good photostability. The good stability of CA@L-PBA mixture under 365nm UV light was attributed to the good photostability of lignin. Of course, CA also possesses UV-stability, which was demonstrated by Arruda *et al.* (2019).

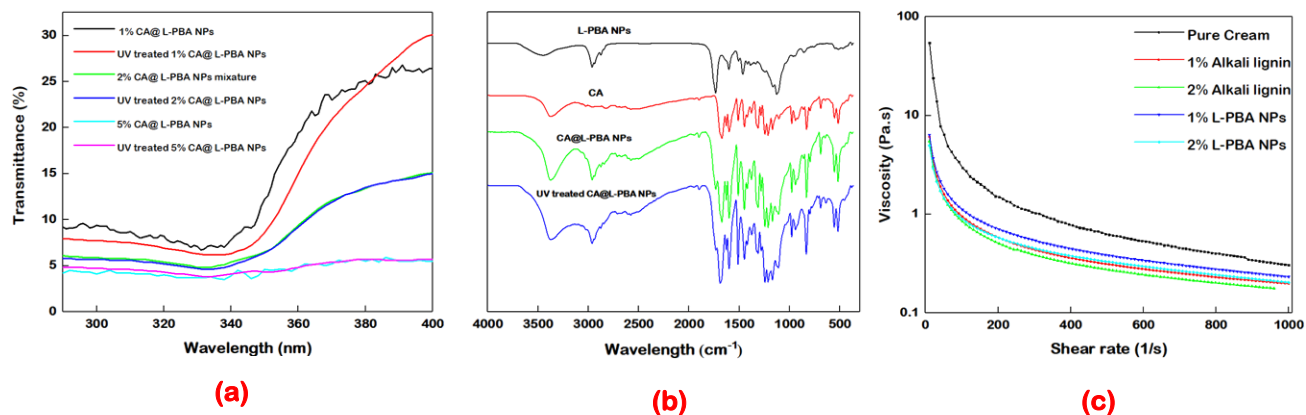


Fig. 6. The UV transmittance of the CA@L-PBA NPs sunscreen Before and after UV radiation(a). The FTIR spectrum of L-PBA NPs, CA, CA@L-PBA NPs and CA@L-PBA NPs treated by UV light (b). Viscosity versus shear rate curves of pure cream blended with 1%, 2% alkali lignin and 1%, 2% L-PBA NPs polymers (c)

To explore the reason for the increased SPF of CA@L-PBA NPs blended sunscreens, the CA, L-PBA NPs, and CA@L-PBA NPs were analyzed by FT-IR. As Fig. 6b shows, there were significant absorption bands at 3000 to 3500 cm⁻¹ and 1687 cm⁻¹. The signal at 3000 to 3500 cm⁻¹ was attributed to the carbon-carbon double bond in the -C=C- structure, while the signal at 1687 cm⁻¹ was attributed to the C-H bond in the -C=CH-. Under UV radiation, the transfer of electrons within the lignin molecule produced a quinoid structure. The generation of these signals indicated that the CA@L-PBA NPs irradiated by UV lamps produced more conjugated structures, resulting in the increasing of SPF of CA@L-PBA NPs blended sunscreen.

Table 2. The SPF of CA@L-PBA NPs at Different Amounts

Type	SPF
1%CA@L-PBA NPs	6.63±0.07
UV treated 1%CA@L-PBA NPs	7.31±0.55
2%CA@L-PBA NPs	11.02±0.6
UV treated 2%CA@L-PBA NPs	11.76±0.22
5%CA@L-PBA NPs	18.79±2.61
UV treated 5%CA@L-PBA NPs	21.56±0.35

Rheological Property

In the preparation process of lignin-based sunscreen, a facile blending method of lignin and pure cream was carried out. Therefore, the compatibility between lignin and pure cream was a key issue worth considering. A large amount of lignin in sunscreens might lead to lignin-based sunscreen having poor performance due to poor dispersion of lignin. If there was good compatibility between lignin and pure cream, then it would be easy to form a uniform and protective film on the skin surface to fight against UV radiation. Therefore, the rheology of blended lignin-based sunscreens was investigated. Figure 6c showed the variation in the viscosity (versus shear rate) of the blended lignin sunscreen. When alkali lignin was blended with pure cream, the viscosity of the sunscreen was significantly reduced. Moreover, with the increase of the addition amount of alkali lignin, the viscosity further decreased. This may be because there is the poor compatibility of

alkali lignin in pure cream, resulting in phase separation of lignin and pure cream. However, compared with the sunscreen blended with alkali lignin, the viscosity of the L-PBA NPs blended sunscreen increased significantly, attributed to the long PBA chains grafted onto lignin. In this work, grafting of PBA onto lignin not only enhanced the hydrophobicity of such lignin copolymers, but it also improved their compatibility and miscibility in sunscreens.

While it is surprising that lignin-based sunscreen was able to break away from the chemical sunscreens commonly used in the market, much of the mechanism behind it is not well understood. The compatibility of lignin with pure cream and the synergistic effect of CA@lignin needs to be further studied. Notably, this work further developed lignin-based sunscreen products. The high-quality applications of lignin in natural spherical sunscreens can provide an alternative to daily skin care products.

CONCLUSIONS

1. Alkaline lignin was successfully modified by atom transfer radical polymerization (ATRP) with butyl acrylate monomer, which self-assembled into lignin polybutylacetate nanoparticles (L-PBA NPs) having strong hydrophobicity.
2. L-PBA NPs combined with p-coumaric acid (CA) to prepare a blended lignin-based sunscreen exhibited an excellent effect against UV light. The SPF of the sunscreen reached 18.8 under the condition of adding 5% CA@L-PBA NPs.
3. The sun protection factor (SPF) value of the sunscreen rose slightly after 3 h of UV light radiation, indicating that the lignin-based sunscreen had well established photostability
4. This chemically modified lignin microsphere is an environmentally friendly and excellently natural sunscreen agent and has a good application potential in the field of sunscreen.

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