



# Fabrication of uniform lignin colloidal spheres for developing natural broad-spectrum sunscreens with high sun protection factor



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## ABSTRACT

Lignin can protect plants from sunshine radiation, thus making its development as a natural macromolecular sunscreen for human skin protection against UV radiation attractive. In this work, lignin colloidal spheres with different sizes and structures are prepared by self-assembly and then blended with pure skin cream to develop lignin-based sunscreens. Results show that the creams with lignin colloidal spheres added to it as actives have better sunscreen performance than those blended with original lignin. The sun protection factor (SPF) value of the sunscreens decreases with the size of lignin colloidal spheres. Phenolic hydroxyl groups play an important role during the lignin's sun blocking process. When lignin is acetylated, SPF values of the sunscreens decrease dramatically, but will recover to a certain degree when acetylated lignin forms uniform colloidal spheres. Therefore, organosolv lignin (OL) with more phenolic hydroxyl groups is applied. The SPF value of the sunscreen containing 10 wt% OL colloidal spheres with the size of about 50 nm reaches 15.03. The SPF value of sunscreen containing 10 wt% middle size OL colloidal spheres can be boosted from 10.69 to 47.71 by adding 2 wt% UVA and 2 wt% UVB chemical sunscreens.

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## 1. Introduction

Ultraviolet (UV) rays from sunshine threatens the skin health of human beings. Usually, long time exposure to UVB (280–320 nm) radiation easily induces skin erythema on sunny days, while that from UVA spectra (320–400 nm) has accumulated effect, finally causing photo-aging on skin and/or skin cancer (Hanson et al., 2006; Rass and Reichrath, 2008; Deng et al., 2015). Due to discomfort associated with physical sunscreens, people prefer to use chemical sunscreens (Reisch, 2001; Laszlo et al., 2003). At least 20 wt% of chemical sunscreen actives is needed to meet the basic requirement of sun lotions or creams, which is a sun protection factor (SPF) of 15. However, most of the synthetic chemical sunscreen actives are small molecules and not stable under UV radiation, e.g., the widely used homosalate (UVB) and avobenzone (UVA), which can be photo-degraded into free radicals (Pattanaargson and Limphong, 2001; Scalia et al., 2004; MacManus-Spencer et al., 2011; Miura et al., 2012). Free radicals accelerate the photo-aging of skins and some coupling products damage the cells (Wakefield et al., 2004; Karlsson et al., 2009; Damiani et al., 2010).

Botanical extracts with UV-blocking property are ideal alternatives to synthetic chemical sunscreens (Saewan and Jimtaisong, 2015). Mishra et al. (2012) analyzed the sunscreen performance of the gel containing 1.42 wt% Rosa kordesii petal extract, which had SPF value of 3.25. Jarzycka et al. (2013) extracted sunscreen actives from *Helichrysum arenarium*, *Crataegus monogyna*, *Sambucus nigra* and formed sunscreen emulsions respectively. The SPF values of the emulsions containing 10 wt% extracts ranged from 6.00 to 9.88 (Jarzycka et al., 2013). Most botanical extracts, especially aromatic molecules, are good at blocking radiation from UVB, but extracts from aquatic cyanobacterium *Aphanizomenon flos-aquae* exhibit good UVA blocking performance (Torres et al., 2006). Lichen chromophores absorbing UVA and UVB might be good candidates for developing broad-spectrum sunscreens, although there is also a report that lichen extracts are good UVB blocker (Rancan et al., 2002; Boehm et al., 2009). Chiari et al. (2014) found that the sunscreen performance of green coffee oil was not satisfactory, but it had synergistic effect with chemical sunscreen due to the existence presence of phenolic hydroxyl groups and antioxidant protection. In fact, natural polyphenol extracts such as phenolic acids, flavonoids, anthocyanins, catechins, flavones, flavonols, proanthocyanidins, procyanidins, stilbenes and tannins are all potential natural skin protectors, since they not only filter UV radiation, but also have antioxidant abilities and be able to repair

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DNA (Nichols and Katiyar, 2010). However, most of the botanical sunscreen extracts are small molecules or oligomers and have poor photo-stability. The sunscreen performance would weaken after UV irradiation. Additionally, these extracts usually consist of more than one component, with some volatile components like olefins. Therefore, more stable macromolecular natural sunscreens are desired.

Lignin is the unique aromatic polymer, as well as the second most abundant component in plants (Rahimi et al., 2013). During the pulping and bioethanol producing processes, cellulose and hemicellulose in plants are extracted to make paper or produce bioethanol, while lignin is discharged as byproduct (Doherty et al., 2011; Xiong et al., 2015). Annually, more than 50 million tons of industrial lignin is produced and more and more efforts are devoting to the value-added use of lignin (Saito et al., 2012; Ragauskas et al., 2014). Natural three-dimensional network structure, high carbon content, good renewability and degradability endow lignin various application potentials and it has been widely investigated as macromolecular surfactants, carton fibers, green thermoplastics, and other functional materials (Lou et al., 2013; Schorr et al., 2014; Li et al., 2015; Imel et al., 2016; Tran et al., 2016). Due to its broad-spectrum UV-absorbing and excellent antioxidant properties (Pan et al., 2006; Ban et al., 2007; Sun et al., 2012), we developed lignin as natural macromolecular sun blocker in recent years (Qian et al., 2015). Lignins from different technical resources have different sunscreen performance, but all lignin exhibits dramatic synergistic effect with chemical sunscreens, especially after UV irradiation (Qian et al., 2016). It means lignin-based sunscreens can provide a lasting protection. Related works are highlighted by Chemistry World and reported as ACS news (Haynes, 2014). However, pure cream containing 10 wt% organosolv lignin has the highest SPF of only 8.66, which does not meet the basic requirement of daily sunscreen (SPF  $\geq$  15) (Qian et al., 2016). Too much addition of hydrophilic lignin e.g. lignosulfonate will demulsify the sunscreens (Qian et al., 2016). More efforts are needed to improve the performance of lignin-based sunscreens.

In this work, acetylated enzymatic hydrolysis lignin (AcEHL) is first prepared to form uniform colloidal spheres with sizes from nano to micrometers. It is then added into pure cream to prepare lignin-based sunscreens. To investigate the effect of phenolic hydroxyl groups on the sunscreen performance, EHL without acetylation and OL with more phenolic hydroxyl groups are directly used to prepare colloidal spheres and their sunscreen performances are analyzed. To meet the higher sunscreen request, small amount of chemical sunscreen actives are added into lignin-based sunscreens and their synergistic effect are demonstrated.

## 2. Materials and methods

### 2.1. Materials and reagents

Enzymatic hydrolysis lignin (~80%, EHL) extracted from corn-cobs and organosolv lignin (86.7%, OL) extracted from pines were supplied by Shenquan Biotechnology Co. Ltd. (Shangdong, China) and Chemical Point UG (Deisenhofen, Germany), respectively. The

impurities in OL were 6.5% moisture, 0.2% residual sugar, 5.5% acid-soluble lignin and 1.1% ash, while those in EHL were ~5% cellulose and ~15% ash, residual sugar and cellulose enzyme. Lignin samples were carefully purified by alkaline dissolving, acidification, filtration, and washing at least three times. The physicochemistry parameters of EHL and OL can be found in Table 1. The acetyl bromide was purchased from Sigma-Aldrich (Shanghai, China). Analytic grade acetone, acetic acid, and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used as received. Deionized water with resistivity of more than 18 M $\Omega$ /cm was obtained from a Millipore water purification system. Chemical sunscreen active Avobenzone (BMDM) was purchased from Aladdin Industrial Corporation (Shanghai, China) and Octinoxate (OMC) was purchased from TCI Development Co. Ltd. (Shanghai, China). Pure cream used was NIVEA refreshingly soft moisturizing cream (75 mL) (Cream). Sunscreen lotions were LIFE SPF 15 and 50 sunscreen lotions (SPF15 and SPF50). The cream and lotions were purchased from Chinese and Canadian drug markets. The active and inactive ingredients can be found in Table S1.

### 2.2. Acetylation of EHL

Acetylated EHL (AcEHL) was prepared by dispersing EHL in acetyl bromide/acetic acid at 55 °C for 3–5 h according to the method described in reference 34 (Qian et al., 2014). After removing acetic acid and residual acetyl bromide by vacuum drying, AcEHL was obtained.

### 2.3. Preparation of large lignin colloidal spheres

Taking EHL as an example. 1 g EHL was first dissolved in 100 mL acetone/water (8:1, vol/vol) mixture to prepare 10 g/L EHL solution. 400 mL of 0.1 M NaCl aqueous solution was then gradually added into the lignin solution while stirring at room temperature. As the content of NaCl solution increased, the solution became emulsified and some particles began to precipitate, thus forming large EHL colloidal spheres (EHL-L). The suspension was then centrifuged at a speed of 10000 rpm to collect the crude EHL-L. Clean EHL-L were obtained after washing out NaCl by deionized water for five times and dried via freeze drying. The preparation of large AcEHL or OL colloidal spheres (AcEHL-L or OL-L) was similar to that of EHL-L, with AcEHL or OL being used in place of EHL.

### 2.4. Preparation of midsize lignin colloidal spheres

Taking EHL as an example. First, 10 g/L EHL acetone/water (8:1, vol/vol) solution was prepared. Then, 400 mL of deionized water was added into 100 mL EHL solution while stirring at room temperature. The suspension was then centrifuged at a speed of 10000 rpm to collect the insoluble colloids. Midsize EHL colloidal spheres (EHL-M) were obtained after washing with deionized water for three times and dried via freeze drying. The preparation of midsize AcEHL or OL colloidal spheres (AcEHL-M or OL-M) was similar to that of EHL-M, where instead of EHL, AcEHL or OL was used.

**Table 1**

The molecular weights and contents of functional groups of purified EHL and OL<sup>a</sup>.

Lignin	$M_w$ (g/mol)	–COOH (mmol/g)	–OH <sub>Ar</sub> (mmol/g) <sup>b</sup>	–OH <sub>Al</sub> (mmol/g) <sup>c</sup>	–OMe (mmol/g)
EHL	2300	1.42	1.14	0.63	2.24
OL	2600	1.98	1.69	0.71	5.19

<sup>a</sup> The purities of OL and EHL are 96% and 94%, respectively.

<sup>b</sup> OH<sub>Ar</sub>: aromatic phenolic hydroxyl.

<sup>c</sup> OH<sub>Al</sub>: aliphatic hydroxyl.

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