

Full length article

Dissolution of lignin in green urea aqueous solution

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ABSTRACT

The dissolution problem is the main obstacle for the value-added modification and depolymerization of industrial lignin. Here, a green urea aqueous solution for complete dissolution of various lignin is presented and the dissolution mechanism is analyzed by AFM, DLS and NMR. The results show that the molecular interaction of lignin decreases from 32.3 mN/m in pure water to 11.3 mN/m in urea aqueous solution. The immobility of ¹H NMR spectra and the shift of ¹⁷O NMR spectra of urea in different lignin/urea solutions indicate that the oxygen of carbonyl in urea and the hydrogen of hydroxyl in lignin form new hydrogen bonds and break the original hydrogen bonds among lignin molecules. The shift of ¹H NMR spectra of lignin and the decrease of interactions in model compound polystyrene indicate that urea also breaks the π - π interactions between aromatic rings of lignin. Lignin dissolved in urea aqueous has good antioxidant activity and it can scavenge at least 63% free radicals in 16 min.

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1. Introduction

Lignin, the second most abundant component after cellulose in the plants, is also the dominant aromatic polymer in the nature [1–4]. As one of the essential biomasses, lignin has been modified into macromolecular surfactants [5], depolymerized into platform phenols [6], developed into natural sunscreens or antioxidants [7,8], and is being used in areas such as energy, materials and pharmaceuticals [9–13]. However, the solubility is one of the main obstacles. Most of industrial lignin, e.g. alkali lignin, enzyme hydrolysis lignin or organosolv lignin, can only be dissolved in volatile organic solvents, corrosive basic solutions and hazardous ionic liquids [14–18]. Organic solvents such as dimethylsulfoxide (DMSO), tetrahydrofuran (THF) are volatile and inflammable. The NaOH aqueous solutions cannot dissolve lignin completely until their pH values are beyond 12, which is corrosive. Various ionic liquids have been proved to dissolve lignin effectively [19–21], but Luo et al. found that ionic liquids facilitated the proliferation of antibiotic resistance genes in environmental bacteria and could increase risks to public health [22]. Recently, Xu et al. developed polysorbate/H₂O (Tween-80/H₂O) mixtures and their lignin solubility could reach

40 wt%. Equally worry is that the Tween-80 content was as high as 60% [23].

The dissolution of a polymer into solvents involves two processes, namely solvent diffusion and chain disentanglement [24]. These two processes are closely related to the interactions between solvent-solvent, solvent-solute and solute-solute. As an amphiphilic polymer, lignin molecules are easy to aggregate due to the strong interactions such as hydrogen bonds, π - π stacking, Van der Waals forces that derived from the hydrophobic phenyl-propane skeletons and different functional groups [25–27]. The intramolecular and intermolecular aggregations of lignin hinder the interaction between lignin and water. Therefore, industrial lignin cannot be dissolved in water until it is disaggregated.

Although the dominant role of hydrogen bonds and π - π stackings is still under debate during the aggregation of lignin [26], it should be better for the dissolution of lignin if these interactions are both weakened. Recently, we screened the hydrogen bonds between lignin and inorganic oxides by acetylating the hydroxyl groups of lignin and the adhesion forces determined by atomic force microscopy (AFM) decreased 35–70% [28]. However, phenolic hydroxyl groups are critical for the application of lignin. They are not only excellent modification sites, but also responsible for the antioxidant and sunscreen performances of lignin [29,30]. Urea is a good hydrogen bonding breaker. The oxygen of urea is able to combine with the aromatic rings and thus break the π - π stackings [31–33]. In addition, urea is the main active component in the urea creams and is widely used for keeping skin moisturizing and treat-

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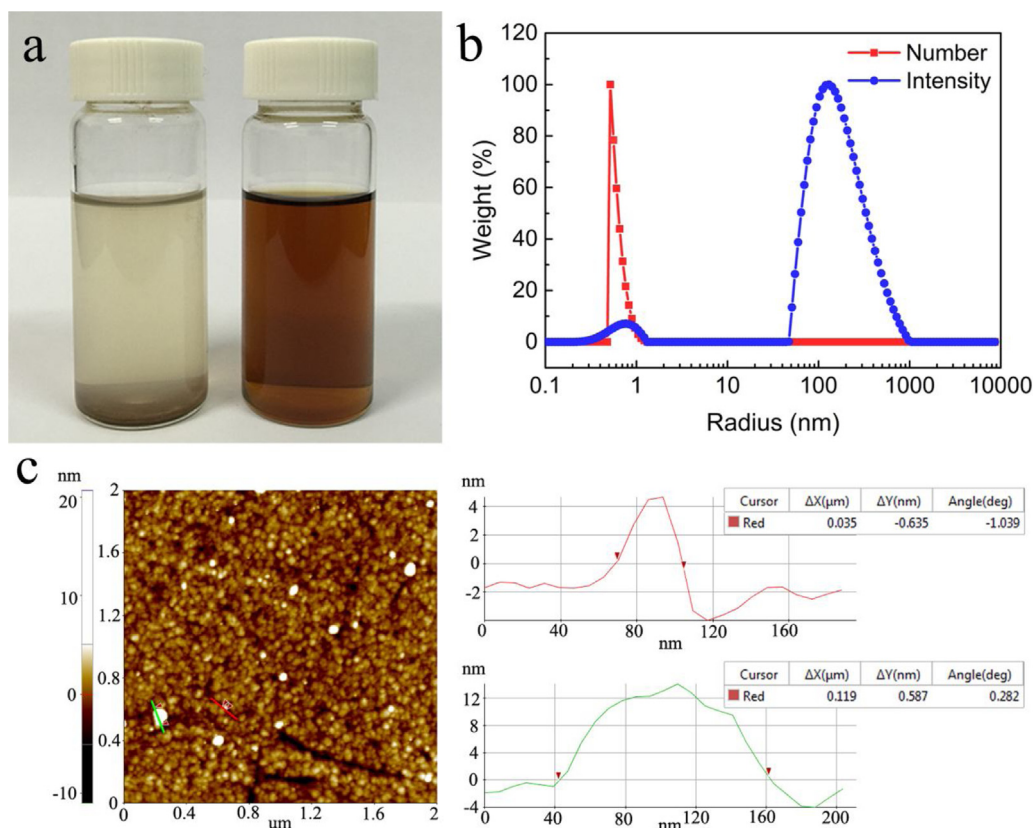


Fig. 1. (a) Photos of AL in water (left) and in 5 M Urea (right). (b) Radius distribution of AL in 5 M urea. In DLS measurement, the concentration of lignin in urea aqueous is 0.3 g/L and the measurement was performed at 60°. (c) AFM image of AL in 5 M urea.

ing inflammatory skin. After a clinical study to 30 normal subjects and 40 patients, Pigatto et al. concluded that the cream containing 10% urea was safe for human skin and was effective for atopic dermatitis [34]. Ademola et al. clinically evaluated the efficiency of 40% urea and 12% ammonium lactate in the treatment of xerosis and the results showed that 40% urea cream was superior to 12% ammonium lactate for most of the instrumental and clinical assessments at day 14 of treatment [35]. Urea creams also used to treat hand dermatitis, moccasin tinea pedis and ichthyosis skin problems [36–38]. Comparing with strong basic solutions, organic solvents and ionic liquids, urea is green and safe for human beings. Unfortunately, urea is never tried to solubilize lignin, although it is widely used to promote the dissolution of cellulose [39,40].

In this study, a green urea aqueous solution was developed to dissolve different industrial lignins completely. The solubilization mechanism was investigated and the antioxidant of the dissolved lignin was also measured. The new lignin/urea aqueous solution not only can be used to develop multi-functional skin care products, but also a good media for the value-added modification of lignin or its efficiently depolymerization.

2. Materials and methods

2.1. Materials

Alkali lignin (AL) separated from wheat pulping black liquor was supplied by the Quanlin Paper Mill (Shandong, China). The AL sample was purified carefully by acidification, filtration, and washing. Another AL was purchased from Simga-Alderich (Shanghai, China). Organosolv lignin (OL) was purchased from Chemical Point UG (Deisenhofen, Germany). Enzymatic-hydrolyzed lignin (EHL) was donated by Longlive Bio-Technology Co. Ltd. (Shandong,

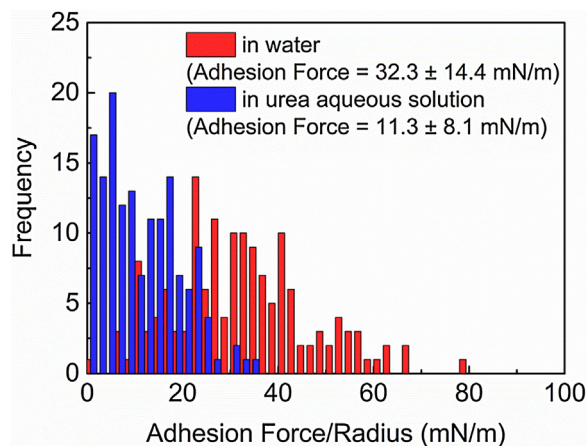


Fig. 2. Histogram of AFM measured adhesion forces between AL-coated tip and AL-coated substrate in pure water (red) and in urea aqueous solution (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

China). Acetylated lignin (ACL) was obtained by acetylating AL in acetyl bromide/acetic acid solution under 55 °C. The contents of the hydrophilic groups of these lignin types were measured and shown in Table S1. Deionized water (resistivity ≥ 18 M Ω /cm) was obtained from a Millipore water purification system and was used for preparation of samples and solutions as needed. Other reagents including urea and solvents were purchased commercially as analytical grade products and were used for the experiments conducted in this work as received without further purification.

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