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Probing the interactions between lignin and inorganic oxides using atomic force microscopy

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ABSTRACT

Understanding the interactions between lignin and inorganic oxides has both fundamental and practical importance in industrial and energy fields. In this work, the specific interactions between alkali lignin (AL) and three inorganic oxide substrates in aqueous environment are quantitatively measured using atomic force microscopy (AFM). The results show that the average adhesion force between AL and metal oxide such as Al_2O_3 or MgO is nearly two times bigger than that between AL and nonmetal oxide such as SiO_2 due to the electrostatic difference and cation-π interaction. When 83% hydroxyl groups of AL is blocked by acetylation, the adhesion forces between AL and Al_2O_3, MgO and SiO_2 decrease 43, 35 and 75% respectively, which indicate hydrogen bonds play an important role between AL and inorganic oxides, especially in AL-silica system.

1. Introduction

Lignin, the second most abundant biomass in plant, accounts for 15–30% by weight, 40% by energy of lignocellulose [1]. Industrially, more than 50 million tons of lignin is produced as by-product from pulping black liquor and bioethanol fermentation every year [2–4]. Basic phenylpropane units and functional groups such as phenolic and aliphatic hydroxyl groups, carboxylic groups and aromatic rings endow industrial lignin a great potential for application [5–7]. For example, industrial alkali lignin (AL) is hydrophilically modified and used as high performance concrete water-reducer, coal-water-slurry and dye dispersants, pesticide adjuvant [8–11]; AL itself can be catalytically carbonized as carbon fiber or catalytically degraded as biofuel and chemicals [12–15]. Among these applications, the interactions between lignin and inorganic oxides play a key role since most of the dispersates contain inorganic oxides and catalysts are fixed on or mixed with inorganic oxides. Full understanding and accurate determination of the interactions between lignin and inorganic oxides can help improving the dispersion performance and catalytic efficiency.

Li et al. investigated the interactions between sodium lignosulfonate and alumina (Al_2O_3) and found that cation-π interaction and electrostatic interaction were dominant interactions between lignin and Al_2O_3, while hydrogen bond has almost no contribution [16]. Palmqvist et al. compared dispersibility of poly(acrylic acid), lignosulfonate and comb copolymer in highly concentrated aqueous Al_2O_3 suspensions [17]. The results indicated that the chain-like poly(acrylic acid) and comb copolymer provided steric repulsion to stabilize Al_2O_3 particles, whereas only electrostatic repulsion contributed by lignosulfonate. To stabilize silica (SiO_2), lignin/SiO_2 complex microspheres are usually prepared since hydroxyl groups in lignin are easy to form hydrogen bonds with silanol groups on the surface of SiO_2 [18]. Dominant interactions between lignin and inorganic oxide are deduced by indirect analysis and direct quantitative investigations are necessary.

Atomic force microscopy (AFM) or its chemical force microscopy (CFM) module is more and more widely used to investigate molecular interactions between protein and medicine, material and surface, and even enable researchers to combine (sub) molecular imaging with quantitative mapping of physical, chemical and biological interactions [19–25]. Due to its high lateral, spatial and normal resolutions and interaction measurement at Pico Newton level, AFM has been tried in biomass field [26–30]. Tan et al. studied adhesion forces between wood pulp fibers and demonstrated that interfiber bonding was mainly due to hydrogen bonding between fiber surfaces [26]. In order to explain what holds paper together, Robert Schennach et al. made a nanometre scale exploration of bonding between paper fibres by AFM, and found that fibrils or fibril bundles play a crucial role in fibre–fibre bonding by bridging interactions [27]. Lignin always comes with cellulose and hemicellulose, Notley et al. probed the molecular interactions between cellu-

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lose and lignin under the different pH conditions and concluded that the interaction between cellulose and lignin was dominated by electrostatic forces [28]. In order to investigate the specific effect of lignin on the enzymatic hydrolysis efficiency of cellulose, Clareke et al. and Abu-Lail et al. got the same conclusion that the hydrophobic–hydrophobic interaction was a major feature in the non-productive binding of cellulose to lignin [29,30].

In this work, we use AFM to investigate and quantitatively analyze the specific interactions between AL and inorganic oxides. The hydroxyl groups of AL are blocked by acetylation to demonstrate and compare the proportion of the contribution of hydrogen bond in different AL-inorganic oxide systems.

2. Experimental section

2.1. Materials

Alkali lignin (AL) separated from wheat pulping black liquor was supplied by the Quanlin Paper Mill (Shandong, China). The alkali lignin sample was purified carefully by acidification, filtration, and washing. Acetyl bromide was purchased from Sigma-Aldrich (StLouis, MO, USA). Deionized water (resistivity ≥ 18 MΩ/cm) was obtained from a Millipore water purification system and was used for the experiments conducted in this work. Other reagents and solvents were purchased commercially as analytical grade products and used as received without further purification. Inorganic oxide substrates (Al_2O_3, SiO_2 and MgO wafers) were purchased from Hefei Kejing Materials Technology Co. Ltd (Anhui, China). Prior to experiments, inorganic oxide wafers were ultrasonic cleaned in 95% anhydrous ethanol solution. Then, wafers were rinsed with deionized water and dried by high-purity nitrogen.

2.2. Preparation of acetylated lignin (ACL)

ACL with average molecular weight ($M_{w,m}$) 4200 was obtained by acetylating AL in acetyl bromide/acetic acid solution under 55 °C. The details of acetylation process can be found in the previous work [31].

2.3. Modification of AFM probes

Silicon nitride (Si_3N_4) probes (DNP-S10, Bruker Inc., Germany) with nominal cantilever spring constant of 0.12 N/m were purchased from Bruker. 0.1 g AL was dissolved in 0.1 L acetone/water (9:1 vol/vol) solvent. Then, these probes were soaked in AL solution for coating. As 0.2 L deionized water was added to the solution, AL could aggregate on tips. After 24 h, AL coated probes were dipped in deionized water to remove unstable AL and residual solvents and dried for use. ACL was coated by the same procedures, but the initial solvent was replaced by tetrahydrofuran.

2.4. Tip radius of curvature characterization

Tip size is one of the most important factors in AFM measurement [32–34]. High resolution scanning electron microscope (Merlin, Zeiss, Germany) was used to obtain accurate, direct and non-destructive topography of AFM tips. As shown in Fig. 1, tip radius of curvature was measured according to the method described in Skulason and Frisbie [35], which is drawing a circle on the images such that an arc of the circle coincided with the tip end.

2.5. AFM force measurements

Commercial atomic force microscope (XE-100, Park Systems, Korea) was utilized for all AFM force measurements. Force measurements were performed in deionized water under room temperature. Prior to force measurements, the spring constant and deflection sensitivity of each cantilever were determined. Although the nominal spring constant is given by manufacturer, it is difficult to ensure every cantilever has the same spring constant. Thermal method was also used to calibrate spring constant of each cantilever [36]. Deflection sensitivity of every cantilever was determined on a hard surface of Al_2O_3 wafer. A limited force of 20.0 nN, a set point of 5.0 nN and a force distance of 1.0 um were used within all AFM force measurements. To avoid the inflence of the interaction/dwell time on the force measurement [37,38], a fixed interaction time of 500 ms was set for all the measurement in this work. Every measurement was repeated 150 times from three different tips to ensure credibility of data.

2.6. Quantitative ^{31}P NMR

5.0 mg/mL chromium acetylacetonate and 10.85 mg/mL cyclohexanol was prepared in pyridine/deuterated chloroform (1.6:1 vol/vol) mixed solvent to serve as relaxation reagent and internal standard, respectively. 30 mg of dry AL or ACL was then dissolved in 0.5 mL mixed solvent and 100 μL internal standard solution, 100 μL relaxation reagent solution, 50 μL tetramethylphospholane were added successively for ^{31}P NMR analysis.

The ^{31}P NMR spectra of AL and ACL were recorded on a nuclear magnetic resonance spectrometer (Bruker, AVANCE HD III 600, Germany) by using methods identical to the method described by Granata and Argyropoulos [39,40]. 25 s relaxation delay was used and a total of 1024 scans was collected

3. Results and discussion

3.1. Coating AFM probes with lignin

To study the interaction between lignin and substrates, lignin should be coated on the AFM probe uniformly. Since lignin can self-assemble into colloidal spheres in selective solvents, lignin thus can aggregate on the surface of the Si_3N_4 probe by the same method. As shown in Fig. 1, uniform AL distributes on the surface of the Si_3N_4 probe after dipping the Si_3N_4 probe in AL acetone/water solution and adding water. The radius of curvature of the tip increased from 36 to 84 nm. ACL was coated with the same procedure with the tip radius of curvature of 85 nm. No obvious random aggregates are observed by SEM on the tip, which is suitable for the interaction determination.

3.2. Typical AFM force-distance curve and interactions between lignin and inorganic oxides

Usually, the AFM force-distance curve contains trace curve and retrace curve. Fig. 2a shows a typical force-distance curve between AL-coated Si_3N_4 probe and Al_2O_3 substrate. From A to B, the probe tip is approaching the Al_2O_3 substrate surface. From B to C, the distance between tip and substrate tends shorter. Once the distance is short enough, the tip jumps onto the substrate surface because the change of spring elastic force with the distance cannot counterbalance the corresponding change of attractive force, which is called jump-to-contact. From C to D, the repulsive force increases immediately when the tip keeps being pushed to the substrate after they contact. From D to E, the tip is pulled away gradually from substrate surface and the repulsive force reduces to zero. From E to F, adhesion force produces and prevents the tip leaving away from the substrate surface (attractive force). From F to G, the power from outside is beyond the maximum adhesion force and the tip jumps off from the substrate. The maximum adhesion force can be obtained