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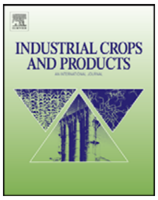

Layer-by-layer assembly of lignosulfonates for hydrophilic surface modification

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ABSTRACT

Lignosulfonates (LS) were used to modify the surface of a mica substrate using Cu^{2+} as the binding agent through layer-by-layer (LbL) self-assembly. The average thickness and roughness of the self-assembled multilayer of LS–Cu^{2+} complexes increased with the number of layers as revealed by atomic force microscopy. The hydrophilicity of the modified surface decreased with the increase in the number of layers. The contact angle was increased from 6.5° to 86° after the mica surface was coated with 18 layers of LS–Cu^{2+} complexes. This suggests that surface hydrophilicity can be modified in a controllable manner via LbL assembly of lignosulfonates.

1. Introduction

Lignosulfonates (LS), the most available commercial lignin, are produced as by-products of sulfite pulping (Nägele et al., 2002). LS macromolecule contains a hydrophobic backbone (C6–C3 structure monomers linked together by ether and carbon bonds) and hydrophilic branches (sulfonic, carboxyl, and phenolic hydroxyl groups), and thus possesses a certain degree of surface activity (Myrvold, 2008; Johansson and Svensson, 2001; Telysheva et al., 2001). It has negative charges and exhibits polyelectrolyte behavior in aqueous solution due to the ionization of functional groups (Telysheva et al., 2001; Fredheim and Christensen, 2003). Because of the amphiphilic and anionic properties, LS have been increasingly used to modify the surface wetting properties of solids, such as plastics, coal, sphalerite concentrate particles, etc. (Telysheva et al., 2008; Yang et al., 2007; Peng et al., 2009). It has been demonstrated that the hydrophobicity of a solid surface can be improved by adsorbing LS in an aqueous solution (Telysheva et al., 2008). This conventional adsorption method is not very efficient due to the limited amount of LS can be adsorbed at any one time. Furthermore, it negatively affects some other surface properties of the raw material when a large amount of LS is applied. For example, the addition of LS to bleached pulp may change the color and decrease the brightness of the final paper products.

Layer-by-layer (LbL) self-assembly of polyelectrolyte is a promising approach for selective surface modification (Hammond, 2000). By building up a multilayer ultrathin-film coating of macromolecules, the desired wetting properties of the modified surface can be achieved in a controlled manner (Chen and McCarthy, 1997). Recently, self-assembled multilayer films of LS and poly-(o-ethoxyaniline) (POEA) have been successfully produced using the LbL technique (Paterno and Mattoso, 2001, 2002; Paterno et al., 2002). The strategy was the alternate adsorption of oppositely charged polyelectrolytes onto a substrate via electrostatic interactions (Paterno et al., 2002). Unfortunately, polycations, such as POEA, are relatively expensive, which limits the applications of electrostatic LbL assembly to high-end products. It has been reported that the metal–ligand interactions can also be used for LbL assembly (Hatzor et al., 2000; Doron-Mor et al., 2004). LS are capable of binding transition metal ions, such as Co^{2+}, Cu^{2+}, and Fe^{2+}, etc., resulting in the formation of LS–metal complexes (Khvan and Abduazimov, 1990; Dalimova et al., 1998). Therefore, it is possible to construct LbL multilayers of LS using metal–ligand interactions. Because LS are inexpensive industrial by-products and available in large quantities (Nägele et al., 2002), LbL self-assembly of LS for surface modification has technical as well as economical significance.

The objective of this study was to demonstrate the feasibility of LbL assembly of LS for surface modification of mica using Cu^{2+} as the binding agent. Atomic force microscopy (AFM) was used to examine the morphology of LS–Cu^{2+} multilayers. The water contact angle was measured to describe the effect of LbL coating on the hydrophobicity of the modified surface. This may provide a new approach

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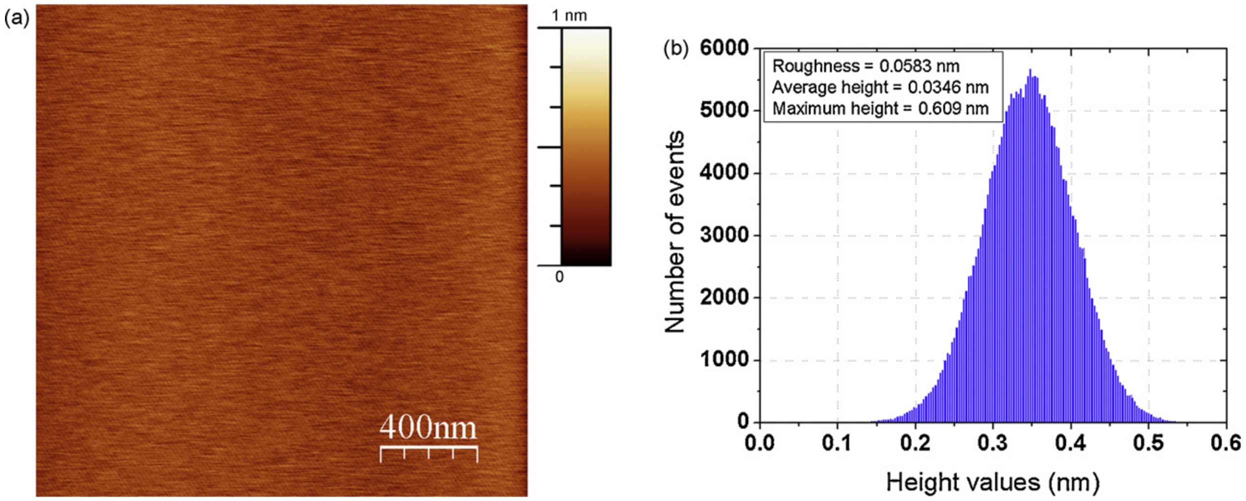

Fig. 1. Morphological image and roughness histogram of a mica surface. (a) Morphological image and (b) roughness histogram.

for controlling the surface morphology and hydrophobicity of mica properly using the LbL technique.

2. Materials and methods

2.1. Materials

Commercial sodium lignosulfonates (Na-LS) were purchased from Jiangmen Sugarcane Chemical Factory Co. Ltd. (Guangdong, China). LS were previously purified in a Minitan Ultrafiltration system (Millipore Co., MA, USA). The fraction with relative molecular weight 10–50 kDa was collected. The weight-average molecular weight (M_w) of the fraction was 46 500 g/mol determined by gel permeation chromatography and the polydispersity was 1.78. No carbohydrate was detected (DNS method) in the LS solution after ultrafiltration.

Muscovite mica (Veeco Co., CA, USA) was used as the substrate for LbL assembly of LS. Other chemicals used were all ACS reagent grade. All aqueous solutions were prepared with Milli-Q ultrapure water (Millipore Iberica, Spain).

2.2. Zeta potential

The zeta potential of the LS solution (50 mg/L) was determined by a Delsa 440SX Zeta Potential Analyzer (Coulter-Beckman, Miami, USA) as a function of pH (range from 1 to 12). The desired pH was adjusted using concentrated HCl or NaOH solutions.

2.3. LbL self-assembly

The first layer (monolayer) was produced by immersing a piece of freshly cleaved mica in Na-LS solution (LS concentration of 0.5 g/L) at ambient temperature for 10 min. The mica was then washed by Milli-Q water and dried by a stream of nitrogen. The subsequent layers were obtained by alternately immersing the monolayer coated mica into $CuSO_4$ (10 mM) and LS solutions for 10 min. The modified mica was rinsed with water to remove excess LS or Cu^{2+} and was then dried using nitrogen gas after each immersing step. The layer number used in this article is referred to the number of LS coating steps in the LbL process. Several samples were made for AFM examinations and contact angle measurements.

2.4. Atomic force microscopy

The modified mica surface was examined by Tapping Mode (TM)-AFM (Nanoscope IIIa Multimode, Veeco Co., USA) in air at a temperature of 28 °C with a relative humidity of 65%. The AFM system was equipped with an E-type piezoelectric scanner and a silicon cantilever with a resonance frequency of about 290–320 kHz. All morphological images were captured at a scan rate of 1 Hz with a resolution of 512 × 512 pixels. Software *Version5.12 r3* (Veeco Co., USA) was used for online data recording. Software *WSxM* (Nanotec Electronica, Spain) was used for offline data analysis. No image processing except flattening (the first order) was made. At least 5 different spots on each sample were measured. Reported results were the average of at least 5 individual measurements. The diameters and heights of LS particles on mica surface were determined using the cross-sectional analysis tool of the offline software. The measured heights were used to calculate the root mean square height as the surface roughness of the LS coated surface. The average thickness of each layer was represented by the average of the height values measured for the layer.

2.5. Contact angle

The contact angle of water droplets on a multilayer of LS was measured with a JC2000A contact angle meter (Powereach, China) using the Pendant Drop technique. A water drop (1.5 μL) was gently placed on the multilayer coated surface at 28 °C. Digital images of the water droplets on the surface were captured and simultaneously analyzed using the *NewJC2000* analytical software (Powereach, China) provided with the apparatus.

3. Results and discussion

3.1. Monolayer formation on mica

Mica was selected as the model hydrophilic material in this study. The contact angle of freshly cleaved mica measured was approximately 6.5°, close to that reported by Zhang et al. (2003). AFM morphological analysis is shown in Fig. 1. The maximum height difference was 0.609 nm and roughness was 0.058 nm in a given area of 2 μm × 2 μm. The low contact angle of 6.5° suggests that the substrate surface is highly hydrophilic and the roughness of less than 1 nm indicates that the surface is atomically flat.

The adsorption of the first LS layer (monolayer) onto mica surface was conducted at pH 2, 7, and 12, respectively. When prepared at pH 2 and 7, the monolayer is in the form of patches of almost completely aggregated LS particles (Fig. 2a and b). At pH 12, LS particles in the monolayer are well attached and uniformly cover the mica surface. The individual particles stick to one another rather than