ELSEVIER

Colloids and Surfaces A: Physicochem. Eng. Aspects 252 (2005) 193–200

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Lignin molecular arrangements in Langmuir and Langmuir–Blodgett films: the influence of extraction processes

D. Pasquini[a], D.T. Balogh[b,*], O.N. Oliveira Jr.[b], A.A.S. Curvelo[a]

[a] *Instituto de Química de São Carlos, USP, CP 780, CEP 13560-750 São Carlos, Brazil*
[b] *Instituto de Física de São Carlos, USP, CP 369, CEP 13560-250 São Carlos, Brazil*

Received 1 April 2004; accepted 8 October 2004

Abstract

The influence of the extraction process has been investigated in the formation of Langmuir and Langmuir–Blodgett films of lignins. In order to focus on the extraction process, lignins from a single source, sugar cane bagasse, were extracted via four methods, viz. acetone–oxygen (AO), soda (SO), ethanol–water (EW) and acetone/water/sulfuric acid (SAC). Langmuir films were spread onto ultra pure water by dissolving the lignin in a mixture of *N*,*N*-dimethylacetamide (DMA) and chloroform. The major effect arises from the presence of strong polar groups, which depends on the extraction process. Lignins with larger contents of carbonyl, such as AO and EW, yielded more expanded surface pressure–area isotherms and lower surface potentials (or dipole moments). Carbonyl groups therefore contribute negatively to the surface potential, i.e. the oxygen in the carbonyl linkage somehow points to the air when the film is in the compressed state. When the subphase conditions were altered by changing temperature, pH and ionic strength, the monolayers from EW lignin were the most affected, presumably because of the different degrees of difficulty in removing the COOH groups from the water/film interface. For example, EW displays one of the lowest dipole moments at $\mathrm{pH} = 6$ but one of the highest at $\mathrm{pH} = 1$, as the non-dissociated COOH may no longer be removed from the interface. Confirming previous studies, all monolayers are amenable to transfer as LB films only with special procedures, particularly a low dipping speed. The molecular arrangement in the LB films also depended on the contents of polar groups, which is reflected in the film roughness. AFM images of five-layer LB films deposited on mica indicated a much lower roughness for the lignins with higher contents of COOH groups, with the root mean square roughness being 0.24, 0.30, 1.25 and 3.80 nm for a scanned area of $5\,\mu\mathrm{m} \times 5\,\mu\mathrm{m}$ for EW, AO, SO and SAC lignins, respectively.

Keywords: Lignins; Langmuir–Blodgett; Ultra-thin films; Molecular arrangements

1. Introduction

The Langmuir–Blodgett (LB) technique nowadays is applied to a large number of different substances like proteins, lipids, polymers, organic dyes, etc. [1]. This film forming technique allows the fabrication of nanostructured films with controllable thickness, low number of defects and some degree of organization at the molecular scale, even for polymers and natural macromolecules such as lignin [2,3]. In the case of LB films of lignins, films with extremely low roughness could be obtained [3], which can be possibly applied, for example, as coatings for nanoscale smooth surfaces, and with properties such as oxygen scavenger [4]. Furthermore, the investigation of the properties of lignins in nanostructured films may help understanding how these macromolecules are arranged at interfaces in plants.

Several parameters may affect the Langmuir and LB films properties of lignins, including the source of the lignin, method of extraction, molecular weight and chemical composition, in addition to experimental LB conditions such as spreading solvent, temperature, pH and ionic concentration of the subphase [3,5–16]. With such a multitude of variables, studies on the formation of Langmuir and LB films

---

[*] Corresponding author. Tel.: +55 16 33739825; fax: +55 16 33715365.
E-mail address: balogh@if.sc.usp.br (D.T. Balogh).

0927-7757/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2004.10.091

had an exploratory character, primarily to probe the possibility of obtaining stable (or at least metastable films) that were amenable to LB transfer [8]. From these studies, an overall behaviour could be established for the lignins in nanostructured films in spite of the diversity of the results. Indeed, it was possible to show that the properties of Langmuir and LB films were not significantly affected by the molecular weight [8]. The molecules from higher MW lignins obviously occupied a larger area per molecule [8], but the surface pressure and surface potential isotherms preserved a similar shape. An important implication of this finding is that lignin fragments with low MW may be used as model systems for inferring the properties of larger fragments. It should nevertheless be noticed that this extrapolation can only be made if low-dispersity lignin samples are used as model systems, since isotherms are strongly affected by the dispersity of the lignins [9]. Investigations into the effects from the source and method of extraction pointed to a considerable influence from the presence of polar groups in the lignins [12]. More oxidizing extraction methods, such as the acetone/oxygen, lead to lignins with more expanded surface pressure isotherms and lower surface potentials, due to the availability of a large proportion of carboxyl groups [12]. Because the latter study was carried out with lignins extracted from distinct sources, one could not rule out the possible influence from the source.

In this work, we devised experiments to establish the importance of the functional groups with lignins from a single source. Therefore, lignin samples were chosen which were all extracted from sugar cane bagasse, but employing four distinct extraction procedures that lead to different chemical compositions. By employing a fractionation process, we processed the lignins extracted to obtain low-polydisperse samples that were used in the fabrication and characterization of Langmuir films, using surface pressure and surface potential isotherms. Analogously to the case of lignins used in previous works [8–10,12,13], the Langmuir films to be reported here are metastable, but can be transferred onto solid substrates under special conditions to form LB films. We show that the molecular arrangement of the LB multilayer is also dependent upon the functional groups of the lignin samples, which may be studied by analyzing the film morphology using atomic force microscopy (AFM).

2. Experimental

2.1. Lignin extractions

Prior to the lignin extraction, the bagasse was wet screened to remove the pith and pre-extracted with hot water to remove low molecular weight polysaccharides and inorganic compounds, and with hot cyclohexane/ethanol to remove mainly polyphenols. The acetone–oxygen process (AO) [17] was carried out in a pressurized autoclave at 160 °C using an acetone–water mixture (6:4, v/v) and a liquor to bagasse ratio of 20:1; the oxygen pressure was fixed at 120 psi at room temperature, with reaction time of 180 min. The soda process (SO) [18] was carried out in pressurized autoclave at 160 °C, for 60 min, using an aqueous NaOH 1% solution in the presence of 0.15% anthraquinone with respect to the dry bagasse, and a liquor to bagasse ratio of 20:1. The ethanol–water process (EW) [19] was carried out in pressurized autoclave at 180 °C, for 60 min, using an ethanol–water mixture (1:1, v/v) and liquor to bagasse ratio of 20:1. The liquors obtained in the delignification processes were acidified with concentrated H_2SO_4 until pH = 2 and the lignins were precipitated, filtrated and dried. The lignin obtained from acetone–water saccharification process (SAC) was supplied by Dedini S.A. In order to reduce the polydispersity of the lignins, solvent fractionation [20] was performed using dichloromethane and acetone in succession. The lignins were suspended first in dichloromethane, stirred for 30 min, and filtered. This procedure was performed twice. The dichloromethane insoluble, vacuum dried solids were then suspended in acetone, stirred for 30 min and filtered. The filtrate, containing the lignin fraction soluble in acetone, was evaporated to dryness and used in the experiments.

2.2. Lignin analysis

FT-IR spectra were recorded from KBr pellets in a Bomem MB102 spectrophotometer. Molecular weight distributions were determined by size exclusion chromatography (SEC) using three Plgel columns (500, 10^3 and 10^4 Å), THF as solvent at 1 mL/min and polystyrene standards. C_9-formula was calculated based on C, H, O elemental analysis, methoxyl and hydroxyl contents determined by ^{13}C NMR spectroscopy [21] of acetylated samples in a Bruker AC200 at 50 °C using dimethyl sulfoxide (DMSO) as solvent. ^{13}C NMR spectra of non-acetylated samples were used only to analyze the samples qualitatively. The acetylation reaction was carried out in acetic anhydride/pyridine (1:1) for 48 h at room temperature, followed by addition of a large excess of ethanol and evaporation of the samples to dryness under reduced pressure. The relative carbonyl contents were estimated from the FT-IR spectra by dividing the integrated areas for absorption of carbonyl groups to the integrated area of absorption from aromatic rings at 1500 cm^{-1}. The carboxyl contents were determined with the chemisorption method, by treating the lignin samples with calcium acetate 0.4 M at 85 °C for 30 min and, after filtration, titrating the acetic acid formed with lithium hydroxide [22].

2.3. Langmuir and Langmuir–Blodgett experiments

The formation of Langmuir and LB films was carried out with a KSV-5000 LB system placed on an anti-vibration table in a class 10,000 clean room. The mean molecular area axes (*X*-axis) of the isotherms are based on the number average molecular weight (M_n) (or based on the molecular weight of C_9 units where stated). In the isotherm studies, the monolayer was compressed at a barrier speed of 10 mm/min with