

Surface thermodynamic properties of polyelectrolyte multilayers

Stefan Köstler^{a,*}, Angel V. Delgado^b, Volker Ribitsch^a

^a *Institut für Chemie, Physikalische Chemie, Universität Graz, Heinrichstraße 28, 8010 Graz, Austria*

^b *Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, 18701 Granada, Spain*

Received 4 October 2004; accepted 19 January 2005

Available online 10 March 2005

Abstract

Multilayer architectures of polyelectrolytes fabricated by the layer-by-layer technique (LbL) on pretreated polymeric and inorganic substrates were studied by contact angle measurements. Poly(diallyldimethylammonium chloride), PDADMAC, and poly(sodium 4-styrene-sulfonate), PSS, were used as polyelectrolytes. Contact angle data were used to calculate the van der Waals and Lewis acid–base components of the surface tension of the investigated surfaces. Knowledge of these quantities provides valuable information on surface composition, coating density, and possible interactions of the surface with other substances. Unusual wetting behavior of PDADMAC layers upon prewetting of the multilayer surfaces was found and described in terms of surface tension changes. A model of polymer chain rearrangement upon wetting was proposed to explain this behavior.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Surface tension components; PDADMAC; PSS; Polyelectrolyte; Layer-by-layer deposition; Polymer substrates; Contact angle; Wetting

1. Introduction

Building-up of self-assembled multilayers of polyelectrolytes is an interesting and very promising technique of surface modification. It has gained increasing interest in the last years, as it makes it possible to tailor a great variety of well-defined surface properties and can be applied to a very broad range of substrates. It was first described by Decher [1,2] that polyelectrolytes of either charge sign can be used to construct multilayer architectures.

A polyelectrolyte layer can be deposited onto an oppositely charged substrate by a simple adsorption step. A monolayer will be adsorbed when the substrate is dipped into the polyelectrolyte solution. This procedure can be referred to as a self-assembled monolayer deposition. The crucial step in the adsorption of polyelectrolyte layers is the so-called charge-overcompensation and charge-reversal of the surface. This charge reversal has two important consequences. The first one is self-regulation of the adsorption

process: because of electrostatic repulsion, only a monolayer is likely to adsorb on the substrate. The second is that a subsequent layer of an oppositely charged polyelectrolyte can be adsorbed on top of the first one. Cyclic repetition of this process of alternating adsorption of oppositely charged polyelectrolytes leads to the formation of different ultrathin multilayer architectures. Other studies have shown that many optical, electrical, and surface properties of these layers can be adjusted to definite values [3,4].

One possible and very promising field of biomedical application for these multilayers involves the manufacture of implants or vascular grafts. Therefore, interactions of these systems with proteins have been extensively studied [5,6]. Another possible field of application is that of electronic devices such as polymer light-emitting diodes (PLED) and liquid crystal displays [7]. Incorporation of other charged and uncharged molecules and nonpolar polymers [8] is currently under investigation.

Up to now most studies on polyelectrolyte multilayers have been accomplished on silicon, glass or quartz substrates. But with a focus on possible future biomedical or organic electronic device applications, studying polyelectrolyte mul-

* Corresponding author. Fax: +43-316-380-9850.

E-mail address: stefan.koestler@uni-graz.at (S. Köstler).

tilayer deposition on polymeric substrates appears increasingly important. It is known especially that the properties of the first few deposited layers depend on the nature of the underlying substrate, while the properties of the “bulk zone” of thicker assemblies are almost independent [9]. So to evaluate the applicability of different substrate materials for LbL deposition, investigation of the first few layers is especially interesting. Moreover, because for many applications LbL coating is used as a kind of surface modification of the substrate, in order to deposit other substances or objects on top of the assembly, it is important to know how many layers are necessary to get the desired surface properties.

For all the applications mentioned before, a crucial step is the interaction of the multilayer assembly surfaces with the solution components, and a profound knowledge of the surface thermodynamic properties of the solid surface is required. This is so because technologically relevant properties such as colloidal stability, adsorption behavior, wettability, adhesion, and catalytic activity are mainly determined by surface properties. Especially for such fields as sensors, biomedical applications, and surface patterning techniques it is indispensable to control the surface properties of the used materials.

Measurements of the contact angle of water on the tailored surfaces can give us qualitative clues to detect polyelectrolyte adsorption on certain surfaces, but in this work we propose a more quantitative approach, that to our knowledge has never been tried before for polyelectrolyte multilayers. In this study we will determine the surface tension components of the bare substrates and of substrates covered by one to five layers of polyelectrolytes by contact angle measurements with different liquids. We will investigate how the surface properties of the different underlying substrates influence polyelectrolyte multilayer build-up.

In the present work we will use two polymeric substrates, namely, poly(ethylene terephthalate) (PET), and poly(tetrafluoroethylene) (PTFE). Si wafers and glass were used as inorganic substrates, for the sake of comparison. Since conventional polymers are usually uncharged, surface pretreatment is necessary to generate charged groups. For the PET surface, pretreatment consisted of hydrolysis with sodium hydroxide. PTFE was irradiated with UV light in the presence of hydrazine as reactive gas according to a recently described procedure [10–12].

In this work, we will focus on the changes of surface thermodynamic properties and wetting behavior of these substrates upon polyelectrolyte deposition. We will show, that the extension of contact angle information by the concept of surface tension components and surface thermodynamics can yield valuable additional information about the structure and build-up of polyelectrolyte layers, beyond solely the degree of wettability. These information would not be accessible by the usual qualitative interpretation of contact angle data.

2. Materials and methods

2.1. Substrates and surface pretreatment

Commercial poly(ethylene terephthalate) (PET), films from DuPont (Mylar: thickness 175 μm) were used. The composition and purity of the PET films were confirmed by ATR-FTIR spectra, and their surface roughness was determined to be ~ 6 nm using a Nanoscope III AFM in tapping mode. For cleaning purposes these substrates were first immersed in ethanol (98% v/v) for 10 min and then rinsed with water (Milli-Q quality, Millipore). To generate free carboxylic acid groups the PET films were hydrolyzed with aqueous sodium hydroxide solution. This surface hydrolysis has been used by several authors for PET surface modification and promotion of polyelectrolyte adsorption [13,14]. Samples were treated with sodium hydroxide solution (1 mol/l) at 60 °C for 1 h. They were then immersed in hydrochloric acid (0.1 mol/l) for 10 min at room temperature to stop the hydrolysis reaction. Finally, the hydrolyzed PET substrates were immersed in Milli-Q water for 10 min and air-dried at room temperature. This treatment caused the water contact angle of the PET surface to drop from about 80° to about 60°.

PTFE foils of thickness 0.3 mm were purchased from Hostra, Graz, Austria. The purity of the PTFE foil was also confirmed by ATR-FTIR measurements. A surface roughness of ~ 180 nm was determined using the AFM technique as described. PTFE samples were cleaned with ethanol (98% v/v) in an ultrasonic bath for 5 min and subsequently immersed in distilled water for another 5 min and air-dried at room temperature. In order to introduce charged amino groups onto the PTFE surface, the cleaned PTFE samples were irradiated for 90 min with UV light (Hg high pressure lamp) in the presence of hydrazine acting as a reactive gas. This surface treatment was performed in an especially constructed irradiation/reaction chamber and is described elsewhere in more detail [11,12,15]. After irradiation, PTFE samples were stored overnight in a vacuum drier at 40–50 °C and characterized by ATR-FTIR, XPS, and zeta potential.

A so-called surface-group extraction effect in water after this kind of PTFE surface treatment has been described and proved by ATR-IR, XPS, zeta potential, and contact angle measurements in former studies [11,12,15]. To avoid interference due to this effect, the PTFE samples were immersed in water for 50 min before the first polyelectrolyte adsorption step.

Si wafers from Austriamicrosystems, Graz, Austria and commercial microscope glass slides (Superior, Germany) were used as inorganic reference substrate materials. The silicon wafers were covered by a natural silicon oxide layer of about 2–3 nm thickness (determined with a Woollam VASE ellipsometer). Due to this natural oxide layer, the Si surface is negatively charged in water at neutral pH, and no special chemical transformation was necessary to charge the surface. First, the Si wafers were cut into 1–2 cm broad slices

Download English Version:

<https://daneshyari.com/en/article/10377708>

Download Persian Version:

<https://daneshyari.com/article/10377708>

[Daneshyari.com](https://daneshyari.com)