AFM studies of poly (5-amino-1-naphthol) ultrathin films obtained by associating Langmuir–Schaefer and Langmuir–Blodgett methods

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Abstract

Atomic force microscopy (AFM) was used to investigate ultrathin films of poly (5-amino-1-naphthol) (PAN) deposited by Langmuir–Schaefer (LS) and Langmuir–Blodgett (LB) on silicon substrates. The AFM probe was also used to perform nano-indentation and nano-delamination of the polymeric film. By measuring the applied vertical force at the beginning of the delamination process and by using an appropriate model for micro-indentation of elastic continuous systems, we estimate the critical interfacial shear strength for the PAN/Si interface as being approximately 160 MPa, which indicates that the polymer adheres well to the substrate. The conditions to obtain multiple depositions of the polymeric film on Si substrates are also described. The multilayer PAN films obtained by associating the LS and LB methods were very smooth and uniform, with approximately 5 nm/monolayer.

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1. Introduction

Poly (5-amino-1-naphthol) (PAN) is a conjugated polymer with good electrical conductivity and chemical anti-corrosive properties [1–3]. This material is usually obtained by electrochemical polymerization of 5-amino-1-naphthol (C10 H6 NH2 OH) on metallic electrodes [1–4]. The structure of PAN, showed in Fig. 1, is very similar to the emeraldine form of polyaniline, which is well known for its good passivating property with respect to iron [5,6]. Moreover, the presence of the free reactive –OH groups in the polymeric chain permits further surface reactions, allowing the use of PAN films as a primer coating, with good compatibility with other polymeric materials [2,4]. On the other hand, PAN films have proved to be useful for molecular electronic applications, owing to their semiconductive response and high chemical stability [7]. In view of any of these applications, well-adhered smooth films of controlled thickness and high substrate coverage are desirable.

The presence of the hydroxyl groups in the PAN molecule provides it with a hydrophilic moiety, which is a good departure condition for using the Langmuir–Blodgett (LB) technique. This method is usually applied to produce ultrathin films of different non-amphiphilic molecules of interest in molecular electronics, such as conjugated polymers and fullerenes [8,10–13]. In general, these materials need either to be mixed with classical surfactants (fatty acids) or to be chemically modified. Nevertheless, we showed recently that Langmuir films of PAN can be obtained in the air/water interface, without addition of surfactant molecules or chemical aids. We have also established the conditions of transferring relatively uniform Langmuir–Schaefer (LS) monolayers of this polymer on silicon substrates [14].

In the present work, we report on our investigations about the formation of PAN multilayer films either by using the LS method alone or by associating the LS and LB methods. The latter procedure allowed us to obtain a better control of the film thickness and roughness. Atomic force microscopy
Fig. 1. Schematic drawing of poly (5-amino-1-naphthol) molecule.

(AFM) was employed to analyze the morphology of the solid films, as well as to estimate the adhesion forces between the polymeric film and the substrate, by performing nano-delamination experiments.

2. Experimental details

PAN was obtained electrochemically on platinum electrodes in acidic aqueous solutions (1 M of HClO₄, Merck) containing $10^{-3}$ M of the monomer (Aldrich). The polymerization was performed electrochemically under potential cycling, at sweep rates of $\pm 50$ mV s⁻¹, for 15 min, between 0 and $+0.75$ V. For more details on the polymer synthesis see Ref. [4].

LB and LS PAN films were obtained in a KSV Mini-trough instrument (Teflon® trough), using Millipore purified water (resistivity $= 18.2$ MΩ cm⁻¹ and pH 5.6, at 20°C) as subphase and 400 ml of a sonicated (15 min) spreading solution of PAN/dimethylacetamide (polymer concentration equal to 0.20 mg/ml). After total evaporation of the solvent (15 min), PAN molecular films in the air/water interface were symmetrically compressed by two hydrophilic barriers (Delrin®), to a final pressure of 18 mN/m (measured by a Wilhelmy-based scale). The optimal conditions for the deposition of Langmuir single-layer films on hydrophilic silicon substrates ($10 \times 10$ mm²) were: subphase temperature of 22°C; compression rates of 10 mm/min (equivalent to 0.49 Å²/min) and stabilization time at the compressed state before deposition of 30 min. The Langmuir films exhibited a rather small mean molecular area, indicating the formation of aggregates instead of a monomolecular layer [14]. Z-type LB films (henceforth LB/Z) were transferred vertically onto the Si substrate, with dipping speed of 0.5 mm/min (up/down), while LS films were obtained by touching the surface of the Langmuir film with the substrate positioned horizontally and lifting upwards at that same slow speed.

In order to perform multiple depositions, Langmuir films were first prepared within the same parameters described above. It is important to note that all attempts of preparing multiple vertical depositions produced LB/Z-type films with a single transferred layer and low surface coverage (below 40%), irrespective of the fact that the apparent transfer ratios (TR) were close to one, both in downstrokes as well as in upstrokes. Therefore, multiple depositions were only possible by subsequent LS depositions of Langmuir films (with a 12 h waiting time between depositions) or by associating LS and LB methods, i.e., by performing subsequent LB depositions on Si substrates that were previously covered by one PAN LS monolayer (surface coverage ~ 98%; 12 h waiting time between LB and LS deposition; drying time between two LB depositions of 30 min).

The association of the LS and LB methods has the advantages of simplicity and the use of only two virgin Langmuir films, while multiple LS depositions require virgin Langmuir films for each new deposition or the use of dividers [15], increasing the time of preparation or the complexity of the experimental set-up. Since we were interested in the development of the method rather than in having relatively thick samples, we have prepared LS and LS & LB PAN films from one to five nominal layers.

AFM images were acquired at room temperature in the tapping mode® (silicon cantilevers), using a Digital Instruments Multimode microscope with a Nanoscope IV controller. The images were obtained in various scales to determine different sample features like surface coverage, uniformity, thickness and roughness. The polymer/substrate adhesion forces were evaluated by indenting and delaminating the polymer from the substrate with the AFM probe operating in the indentation/scratching mode, with controlled vertical forces. In these cases, the sample surface was imaged in the tapping mode immediately before and after the indentation/delamination experiments.

3. Results and discussion

Single-layer PAN films with near 98% covered surface were obtained by the LS method, as exemplified in the AFM image of Fig. 2 (the scale of the figure is $3 \times 3 \mu$m²). The dark gray stripes correspond to regions where the polymeric film was intentionally withdrawn by the AFM probe, and the Si substrate can be seen. The gray and light gray
regions indicate the PAN covered regions. In general, AFM images at different magnifications show a flat and relatively smooth film, with a mean height of about 5 nm over more than 80% of the sample surface. We also observe that 15% of the surface has a height of approximately 7.5 nm. Another interesting feature is that we did not discern any in-plane preferential orientation of the PAN LB film, i.e., if the Langmuir film had some chain orientation relative to the barriers it was lost during the transfer. The film’s roughness around the average value (5 nm) was approximately 2 nm.

It is interesting to observe that the predicted thickness for a PAN monomolecular film is only 1.0 nm. The difference between predicted and observed values has been explained by the formation of polymer aggregates instead of monomolecular films, both in the Langmuir film as well as in the transferred monolayer films [14]. A similar behavior is presented by polyaniline, which is the archetype of the PAN family, where the formation of aggregates and bundles is also observed [16–20]. Nevertheless, compared to this polymer, our PAN films showed higher surface coverage and smoothness.

In order to use PAN films as anti-corrosive coatings, one needs to insure that they are well adhered to the substrate. So, we used the AFM probe to indent and delaminate the LS-PAN layer film with different vertical forces. The results are also presented in Fig. 2, where several stripes produced by pressing and gliding the AFM probe tip over the polymer are seen. The (i) and (ii) stripes were produced under an applied vertical force of 0.6 μN, while in (iii) the force was 1.0 μN. For the lowest force value we observe partial and discontinuous delaminating stripes with 45 nm width, indicating that the applied radial pressure (σr) was very close to the critical interfacial shear strength (σc), which is the pressure needed to delaminate the polymeric film, and thus, a measurement of the polymer/substrate adhesion strength.

On the other hand, the radial stress in (iii) was much larger than σc, so that the cracked interface (delamination) propagates well beyond the region beneath the indenter (the probe tip). Hence, the stripe formed in (iii) is very broad (125 nm width).

Neglecting the discontinuous nature of the PAN film in the scale of the experiment, i.e., by considering the polymeric film as a continuous elastic medium covering a relatively harder substrate, we apply the Matthews model developed for studying micro-indentation and micro-delamination of polymers to describe our nano-delamination results [21–23]. According to this model, different regimes should be considered, depending on the elastic and plastic behaviors of the polymer and substrate. In the present case, the applied pressures were very low compared to the Si microhardness (11 GPa, according to Ref. [24]). So, we assume that the probe tip did not indent the substrate. Also, hard polymers usually show indentation before interface delamination. In our (i) case, the topographic image permits the measurement of a small plastic height lowering (0.5–1 nm), with 35–40 nm width, between the discontinuous stripes seen in Fig. 2. Although we do not know the critical stiffness modulus of PAN, this result is a signature of the occurrence of polymer indentation and allows a direct evaluation of the contact area between the probe tip and the polymer, which can be used to estimate the pressures involved in the experiment. Considering a very simple model for the cases (i) and (ii) we will assume, within the continuous medium approximation, that the indented polymeric film allows the probe tip to touch the substrate and that the strain of the film is plastic below the tip and elastic far away. Thus, for a circular probe with a contact radius of 20 nm, the average normal stress (H = 0.6 μN/μm2) under the tip for the cases (i) and (ii) of Fig. 2 would be around 480 MPa. It is known that the delamination under the tip begins in the boundary between the plastic and elastic regions, a circle with a radius r ≈ 1.1 μm [21]. Outside and over this limiting line it is still possible to use the Poisson’s ratio (ν) to estimate the radial stress at the interface. In our case, this gives σr = 160 MPa, where, we assumed ν = 0.33, a common value for polymeric materials [21–22,25]. As we explained before, this should also be the value of σc. This value for the critical interfacial shear strength is relatively high compared to those obtained for other polymer/Si and polymer/glass systems, measured on the microscopic scale, such as, 50–60 MPa for polystyrene or polymethylmethacrylate over Si or glass, [23] 80 MPa for epoxy and 110 MPa for polyester, both over glass [21,22]. On the other hand, the system polyimide/glass, considered very hard and well adhered, showed σc = 600 MPa [22].

Although, the model used above is a rough approximation to estimate σc, we believe that it gives a reasonable value for the bonding forces between PAN and Si, showing good adhesion of the polymer to the substrate, justifying its use in anti-corrosive coatings for different metals, as previously proposed [2,4,6].

Once having obtained good quality and well-adhered single-layered LS-PAN films, we prepared multilayer films by using this method alone or its association with the LB one. Fig. 3a presents the AFM topographic image (3 x 3 μm2) of a LS-PAN double-layer deposited on a hydrophilic Si substrate. We observe a very flat and uniform film with a mean height of 12.5 nm, over approximately 90% of the substrate. The average surface roughness was 2.8 nm and about 10% of the covered surface showed 17 nm height. This result shows that this method for obtaining a second deposition was successful, despite the fact that the film thickness was more than twice as large as that showed by a single-layer film.

The success in transferring a second layer of the Langmuir PAN film by the LS method (near 100% of surface coverage) shows that multilayer films can be obtained by this method. Nevertheless, as explained in Section 2, the association of LS and LB methods can have some advantages when compared to the individual methods. So, we have prepared double-layer PAN films by transferring one LS layer followed by one LB/Z layer; both coming from independent virgin Langmuir films. In order to perform the vertical deposition, Si substrates covered by the LS-PAN films were immersed in the
Fig. 3. AFM topographic image of a double-layer PAN film on Si substrate obtained by: (a) two individual depositions with the LS method; (b) the association of the LS and LB (Z-type) techniques.

Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Number of intended layers</th>
<th>Height (nm, %)</th>
<th>Roughness (nm)</th>
<th>Number of transferred layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS</td>
<td>1</td>
<td>5 (80) + 7.5 (15)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>LB-Z</td>
<td>1</td>
<td>5 (40) + 0 (60)</td>
<td>2.5</td>
<td>1*</td>
</tr>
<tr>
<td>LS</td>
<td>2</td>
<td>12.5 (90) + 17 (10)</td>
<td>2.8</td>
<td>2</td>
</tr>
<tr>
<td>LS&amp;LB/Z</td>
<td>2</td>
<td>11.5 (85) + 17 (15)</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>LS&amp;LB/Y</td>
<td>5</td>
<td>12 (90) + 15 (10)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>LS&amp;LB/Z</td>
<td>4</td>
<td>15 (50) + 22 (50)</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

The number of intended layers is also indicated.

* Over 40% of the sample.
Fig. 4. Height profiles of single- and multilayer PAN films, obtained from their topographic AFM images. The curves a, b, c(153,113),(412,212) and d correspond respectively to LS mono-layer, LS-double-layer, LS + LBZ double-layer and LS + LBZ multilayer (four layers).

demonstrating that the forces needed to delaminate multilayer films are the same as for the monolayer ones (0.6 N), demonstrating that the polymer/substrate adhesion is completely determined by the first deposited layer. The results of Fig. 4 agree well with those presented in Table 1, obtained by averaging over larger areas (3 × 3 mm²), and confirm the presence of tailored supra-molecular PAN structures, with desired thickness and roughness specifications, i.e., the thicknesses of the samples were proportional to the number of deposited layers and their roughness lower than the thickness of one single-layer.

4. Conclusions

In the present work we used AFM to show that very uniform PAN films can be transferred onto Si substrates by using the LS (single-layer films) technique or by combining this technique with the LB (multilayer films). The films were relatively smooth, with approximately 5 nm per monolayer. The AFM probe was also used to perform nano-indentation and nano-delamination of the polymeric film. By treating the polymer as an elastic continuous medium, we could estimate the critical interfacial shear strength for the PAN/Si interface. The results indicate that the PAN film is well adhered to the substrate.

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