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Surface modification of polyelectrolyte multilayers by high radio frequency air plasma treatment

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ABSTRACT

Low-temperature plasma treatments are used to perform surface modification on polymers, aiming to improve the surface properties according to the desired application. In this work, polyelectrolyte multilayers (PEMs), built by layer-by-layer deposition technique, were treated using high frequency low-temperature air plasma. We evaluated the effect of the exposure time (20 and 300 s) and its effects on PEMs with two different top layers: alginate and carboxymethylcellulose. Chitosan was used as the cationic polymer to build the LbL films with the oppositely charged anionic polymers, alginate and carboxymethylcellulose. Our results showed that the surface topology, wettability and free charges within layers are highly correlated to the polymer pair used. PEMs of the chitosan/alginate system are thinner and hydrophilic, and present a surface with wider peaks. We found that plasma treatment promotes substantial changes on the PEMs and that 20 s of exposure time is enough to perform these changes. In all cases, after plasma treatment, PEMs' thickness and free charge distribution were reduced and wettability was enhanced.

1. Introduction

Polyelectrolyte multilayers (PEMs) are thin films that are generally assembled using oppositely charged polyelectrolytes. Different ways to build these multilayered thin films have been proposed since the 1930s [1–5]. However, it was only after the early 1990s, when Decher and colleagues presented the layer-by-layer (LbL) technique [1,2], that the production of PEMs became more efficient, attractive and viable for many applications.

In the LbL technique, PEMs are built by the alternate deposition of oppositely charged polyelectrolytes on a solid substrate in a self-assembling fashion [1]. The main advantages of this process are [1,3] i) no need of sophisticated equipment and rigorous control on stoichiometry, ii) no complex chemical reactions involved and iii) no restrictions for choosing solvents, polyelectrolytes and also the shape, nature and size of the substrates.

Among the different methods for polymer surface modifications [4], low-temperature plasma modification is one of the most promising techniques, since it affects a very thin layer near the surface. Several studies have showed that plasma modification can improve surface properties of polymeric coatings, which are important for several industrial fields [5–15]. However, no studies about how plasma treatments influence the surface properties of PEMs were found on literature.

The objective of this work is to evaluate the effect of low-temperature plasma treatment on LbL PEMs. Film thickness, contact angle and AFM measurements were performed to characterize surface structures, and dye uptake capacity was measured to evaluate the amount of free carboxylate and ammonium functional groups inside both untreated and plasma treated PEMs.

2. Experimental

2.1. Materials

Chitosan (CHI, low molecular weight $\approx 5 \times 10^4\,\mathrm{g\,mol^{-1}}$, 75–85% deacetylated, pKa ≈6.0 [16]), alginate (ALG, sodium alginate, low molecular weight $\approx 12–19 \times 10^4\,\mathrm{g\,mol^{-1}}$, pKa ≈3.3

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[17]), carboxymethylcellulose (CMC, low molecular weight $\approx 9 \times 10^4\,\text{g mol}^{-1}$, pKa ≈ 5.0 [18]), polyethyleneimine (PEI, $7.5 \times 10^5\,\text{g mol}^{-1}$), methylene blue (MB, $373.90\,\text{g mol}^{-1}$) and rose bengal (RB, $1017.64\,\text{g mol}^{-1}$) were all purchased from Sigma-Aldrich, USA. Sodium hydroxide (NaOH, molecular weight $40.00\,\text{g mol}^{-1}$), sodium chloride (NaCl, molecular weight $58.44\,\text{g mol}^{-1}$), and hydrochloric acid (HCl, molecular weight $36.46\,\text{g mol}^{-1}$) were purchased from Synth Brazil. All chemicals were used without further purification. All solutions were prepared using Milli-Q water with resistivity of $18.2\,\text{M}\Omega\,\text{cm}$ (pH ~7.6, otherwise mentioned). The substrates, a $75 \times 25\,\text{mm}^2$ glass slide (length × width), were purchased from Thermo Scientific, USA.

2.2. Solutions

PEI was dissolved in $0.5\,\text{mol L}^{-1}$ NaCl solution to $1\,\text{g L}^{-1}$. CHI was dispersed in Milli-Q water, followed by addition of $0.1\,\text{mol L}^{-1}$ acetic acid solution, to reach $1\,\text{g L}^{-1}$ of polymer concentration. ALG and CMC were dissolved to $1\,\text{g L}^{-1}$ in Milli-Q water. All solutions were prepared using a magnetic stirrer for 12 h. RB and MB solutions were prepared mixing $1.0\,\text{mmol L}^{-1}$ of the dye in a $25\,\text{mmol L}^{-1}$ HEPES solution and adjusted to pH 7. All solution pHs were adjusted using $1\,\text{mol L}^{-1}$ NaOH or HCl solution whenever needed.

2.3. Glass slides pre-treatment

Glass substrates (Thermo Scientific, USA) were cleaned using a commercial detergent and then sonicated in $1\,\text{mol L}^{-1}$ NaOH solution and in Milli-Q water for 16 min each. All samples were air-dried. To enhance polymer deposition and provide a less heterogeneous electrical charge distribution onto the glass surface [19,20], a single PEI ($1\,\text{g L}^{-1}$, adjusted to pH 4.0, containing $0.5\,\text{mol L}^{-1}$ NaCl) layer was deposited onto the substrates using an automatic dipping procedure (LbL Nanostructure Pro, ECSIA NanoScience, Brazil) with constant agitation under ambient conditions. Substrate immersion in the PEI solution was conducted during 15 min, followed by three rinse steps in $0.5\,\text{mol L}^{-1}$ NaCl solution, also adjusted to pH 4.0, for 2, 1 and 1 min, respectively.

2.4. Multilayer assembly

Fig. 1 shows the experimental steps described in Sections 2.4, 2.5 and 2.6. ALG/CHI PEMs were built by alternate immersion of substrates in ALG and CHI solutions (pH 3.0) for 15 min, respectively, followed by three consecutive immersions in Milli-Q water (pH 3.0) for 2, 1, and 1 min, respectively. CMC/CHI PEMs were built similarly using polyelectrolyte solutions and Milli-Q water at pH4.0. All experiments were performed using an automatic dipping procedure (LbL Nanostructure Pro, ECSIA NanoScience, Brazil) with constant agitation under ambient conditions. All PEMs contained 30.5 bilayers [one bilayer consists of a deposition of one ALG/CHI (or CMC/CHI) layer] and the polyanion was set as the top layer.

2.5. Plasma treatment

Air plasma treatments (Plasma Cleaner PDG32G, Harrick Plasma, USA) were conducted at 0.2 Pa and at high radio frequency (12 MHz). All samples were maintained at the specified pressure for 5 min, and then individually treated with air plasma during the desired time. To assess the effect of exposure time, the PEMs were treated during two different predetermined time intervals: 20 and 300 s. For each test, a newly assembled PEM was used. After the tests, all samples were kept in a desiccator, to avoid structure modifications due to humidity. All results were compared with PEMs without plasma treatment, used as controls.

2.6. PEMs characterization

PEM thickness was measured using a Dektak 150 (Veeco USA) profilometer with the following parameters: 1 mg of applied force, duration of 18 s, length of 500 μm and a mean range of 6.5 μm. All thickness measurements were performed at 15 predetermined locations per film, before and after plasma treatment. To evaluate the influence of plasma treatment on the thickness of the PEMs, the subsequent statistical analysis included: i) average thickness of each PEM before plasma treatment, ii) Dixon Q-test for detection of anomalous values and their exclusion and a Paired Student's t-test to evaluate reproducibility of PEM assembly and also iii) average thickness over each film after plasma treatment and Student's t-test. All statistical tests were performed at 95% confidence.

RMS roughness measurements and images of PEMs surface topography were obtained using AFM (Nanosurf Easyscan 2 AFM, Nanosurf, Switzerland). The tapping mode analysis was conducted with a 3.5 μm range for each sample. The images obtained were then treated using Gwyddion® software for subsequent statistical analysis.

Contact angle measurements between the PEMs' surface and a drop (5 μL) of Milli-Q water were performed using an Easy Drop DSA-150 goniometer Krüss (Germany) in sessile drop mode. Measures in five different predetermined locations were performed per sample and averaged over each film for subsequent statistical analysis.

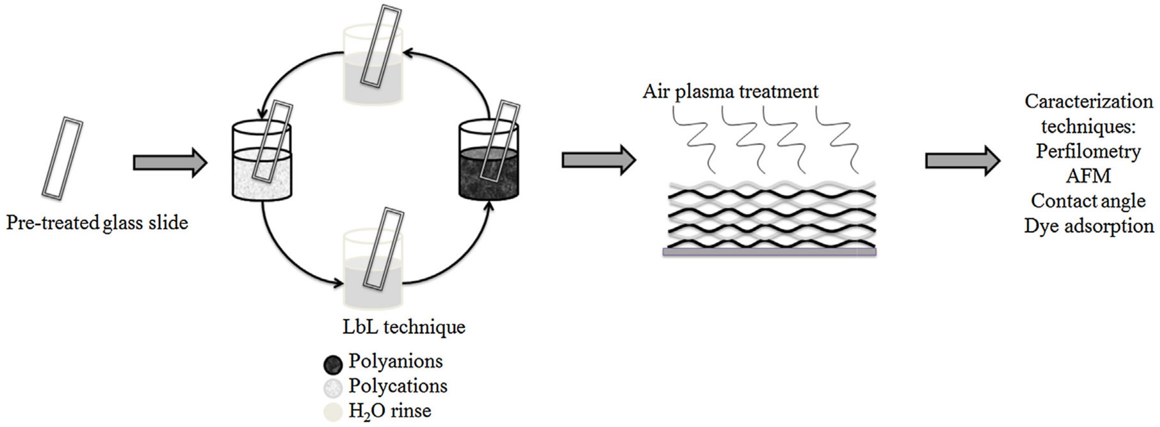

Fig. 1. Experimental setup.