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Tailored adhesion behavior of polyelectrolyte thin films deposited on plasma-treated poly(dimethylsiloxane) for functionalized membranes

Joelle Bassil[a], Halima Alem[a,*], Gérard Henrion[a], Denis Roizard[b]

[a] Institut Jean Lamour (IJL), UMR CNRS 7198, Université de Lorraine, Parc de Saurupt CS50840, 54011 Nancy, France
[b] Laboratoire Réactions et Génie des Procédés (LRGP), UMR CNRS 7274, ENSIC, Université de Lorraine, 1 rue Grandville, 54011 Nancy, France

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ABSTRACT

Completely homogenous films formed via the layer-by-layer assembly of poly(diallyldimethylammonium chloride) (PDADMAC) and the poly(styrene sulfonate) were successfully obtained on plasma-treated poly(dimethylsiloxane) (PDMS) substrates. To modify the hydrophobicity of the PDMS surface, a cold plasma treatment was previously applied to the membrane, which led to the creation of hydrophilic groups on the surface of the membrane. PDMS wettability and surface morphology were successfully correlated with the plasma parameters. A combination of contact angle measurements, scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis was used to demonstrate that homogeneous and hydrophilic surfaces could be achieved on PDMS cold-plasma-treated membranes. The stability of the assembled PEL layer on the PDMS was evaluated using a combination of pull-off testing and X-ray photoelectron spectroscopy (XPS), which confirmed the relevance of a plasma pre-treatment as the adhesion of the polyelectrolyte multilayers was greatly enhanced when the deposition was completed on an activated PDMS surface at 80 W for 5 min.

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1. Introduction

Due to its bulk properties (e.g., good chemical resistance, high thermal stability and rubbery properties), poly(dimethylsiloxane) (PDMS) can be used in many applications, ranging from microfluidic devices [1,2] to nanofiltration membranes [3]. Nevertheless, the hydrophobicity of PDMS can limit its use when a hydrophilic surface is required. To optimize PDMS surface properties, plasma treatments have been shown to be very promising routes [4–6] as they can ensure rapid and efficient modifications of the membrane surface in a very short period of time (i.e., minutes) [7]. This work aims to investigate deeply the effect of plasma treatment parameters on membrane surface properties to enable a perfectly homogeneous deposition of polyelectrolyte (PEL) layers on the PDMS. The final motivation for this work was to enable the fabrication of a variety of membranes for molecular separation with transport properties that can be tuned by simple surface modifications, such as layer-by-layer assembly of polyelectrolytes.

Indeed, in the field of separation processes, some previous studies have already used plasma treatments to modify PDMS surface properties [4–6]. For example, researchers have shown that when plasma-modified membranes are subjected to gases such as Ar [5,6,8], N_2 [5,8], O_2 [5,8] or NH_3 [6], their permeability toward gas mixtures decreases drastically; this result is essentially related to the new polar groups created on the surface of the membrane as well as to chain cross-linking. However, at the same time, it was demonstrated that the modified surface was unstable since the hydrophobicity was recovered as soon as the plasma treatment was ended [9,10].

To ensure stable hydrophilicity of a PDMS membrane, a post-plasma modification can be applied. Post-plasma functionalization of a PDMS membrane surface using multilayers of polyelectrolytes [11] appears to be an appropriate solution for stabilizing the hydrophilicity of the membrane surface. Indeed, the process of layer-by-layer (LbL) polyelectrolyte assembly has been demonstrated to be a rapid, powerful and versatile method for modifying thin films with nano-scale control of structure and chemical composition in environmentally friendly conditions [11–13]. Moreover, the versatility of this method allows its application either on organic substrates or on various inorganic substrates [14]. Recently, different works have shown the efficient use of layer-by-layer polyelectrolyte assembly for the development of solvent-resistant membranes for organic media nanofiltration applications [15–17].

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* Corresponding author.
E-mail addresses: joelle.bassil@univ-lorraine.fr (J. Bassil), halima.alem@univ-lorraine.fr (H. Alem), gerard.henrion@univ-lorraine.fr (G. Henrion), denis.roizard@univ-lorraine.fr (D. Roizard).

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All relevant previous works agree that it is important to pay attention to the control of membrane surface properties, which play important roles in further applications of a material. In other words, it is essential to ensure that optimized adhesion occurs between a membrane and the first polyelectrolyte layer. Different techniques suitable for polymer surface modification include plasma treatment with reactive and inert gases, such as O_2 and Ar, respectively; these techniques result in an increase of PDMS wettability via the grafting of polar groups to the PDMS surface [4,9,10,18]. During this process, hydrogen atoms are first removed from the polymer chains to generate radicals at the surface. The latter can then combine with free radicals created in the plasma to form functional groups at the surface, up to a depth of a few hundred nanometers [19–21]. Moreover, oxidized species could be created on the surface [6,22,23] due to exposure to ambient air; this oxidation leads to the formation of strong intermolecular bonds.

The structure and interfacial properties of PEL multilayers have been studied with respect to their stability, polyelectrolyte structure [24], ionic strength and pH of the deposition solutions [25], adsorption time, influence of the NaCl concentration in the films obtained [26], and rinsing procedure used during formation of films [27]. However, to the best of our knowledge, a small number of groups have concentrated their efforts in the development of a plasma procedure able to provide a homogeneous multilayer deposition.

The main objectives of this work were the investigation of the influence of plasma parameters (e.g., process time and plasma power) on PDMS surface properties to establish correlations between the plasma conditions and the characteristics of the modified PDMS films (e.g., morphology and wettability). We have evaluated the wettability and thickness of deposited PEL layers and have shown how to enhance the adhesion of polyelectrolyte layers on PDMS using a pre-plasma treatment with two widely used polyelectrolytes, i.e., PDADMAC/PSS.

2. Experimental

In this paper, the development and optimization of a plasma-based process to achieve a homogeneous and stable multilayer deposition of polyelectrolytes are reported. PDMS membranes were first treated by adjusting the plasma power and the treatment time. The microstructure and hydrophilicity of the plasma-treated membranes were studied using a combination of different techniques. Polyelectrolyte multilayer assemblies were constructed with two, five, seven or 10 deposited bilayers in solutions of different ionic strengths (0 M, 0.5 M). The relations between the parameters of the modification plasma processes and the morphology, wettability and adhesion of the polyelectrolyte layer-based PDMS membranes were investigated in detail using SEM, X-ray reflectometry (XRR), water contact angle and pull-off testing with atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The influence of plasma treatment on the successful coating of PDMS is shown.

2.1. Materials

A series of PEL nanofilms was deposited on commercial PDMS membranes (Pervap 4060 Sulzer) and Si wafers using two strong polyelectrolytes (Sigma–Aldrich). PDADMAC (poly-diallyldimethylammonium chloride; Mw = 100,000–200,000) and PPS (poly(sodium 4-styrenesulfonate); Mw = 70,000) were used as the cationic and anionic polyelectrolyte, respectively. For all of the experiments, deionized water (MilliQ® water) (18 MΩ cm) was used for the polyelectrolyte solutions and cleaning steps. Prior to PEL deposition, the silicon wafers (boron-doped, p-type Si (100)) were cleaned with piranha solution (30% hydrogen peroxide and sulfuric acid in a 1:1 ratio) for 20 min; this cleaning was followed by three MilliQ® rinsing steps.

2.2. Plasma treatment

Plasma surface modifications were conducted using a microwave post-discharge reactor consisting of a 3-cm diameter cylindrical glass chamber that was pumped by a primary pump; the residual vacuum was 10^{-2} mbar. A 2.45-GHz microwave generator was used to generate the plasma. The plasma atmosphere consisted of an Ar and O_2 gas mixture with flow rates of 400 sccm and 40 sccm, respectively. The plasma gases were fed into the system via gas flow meters. A PDMS sample with dimensions of 2 cm × 2 cm was placed downstream in the plasma at 30 cm from the plasma outlet (Fig. 1). After plasma treatment, the system was vented up to atmospheric pressure, and then the sample was removed from the reactor. The maximal exposure time of the sample with air was approximately 45 min before starting the LbL polyelectrolyte deposition. For the present study, plasma power and processing time were varied, ranging from 80 W to 120 W and 5–15 min, respectively.

2.3. LbL deposition technique

The polyelectrolyte solutions included PDADMAC (10^{-2} mol L^{-1} without and with 0.5 mol L^{-1} NaCl as the supporting electrolyte) and PSS (10^{-2} mol L^{-1} without and with 0.5 mol L^{-1} NaCl as the supporting electrolyte). The pH of the solutions was not adjusted because these polyelectrolytes are fully ionized for pH values between 1 and 14.

Multilayers of PEL were deposited using an ND-3D 3-axis controlled dip-coater (Nadetech). This dip-coater allows a wide range of immersion speeds (from 1 mm min^{-1} to 2000 mm min^{-1}) and ensures good reproducibility of the thin films.

The PDMS membrane was positioned by clamps and immersed in PDADMAC solution for 10 min. The polycation solution was deposited first because the PDMS became negatively charged by the Ar/O_2 plasma treatment, leading to the presence of Si-OH (silanol) groups at the surface of the PDMS [18]. Next, the membrane was removed and rinsed thoroughly with MilliQ® water for 1 s/15 times, 5 s/3 times and 15 s/1 time, successively. Subsequently, the membrane was immersed in PSS solution for 10 min. The membrane was removed and rinsed with MilliQ® water for 3 min [31]. Thus, one bilayer, or one cycle of forming a self-assembled membrane, was completed. Additional bilayers were deposited similarly until the required number of bilayers was achieved.

2.4. Membrane characterization

The surface morphology of the plasma-modified PDMS and the PDMS modified with polyelectrolyte coatings as well as the cross section of the prepared self-assembled polyelectrolyte multilayers on Si wafers were investigated using a Quanta 600 FEG (FEI) scanning electron microscope (SEM). The low vacuum mode was used (pressure = 100 Pa, under hydrated conditions) for all of the samples (regardless of the support), which were attached with double-sided tape onto a microscope support.

The hydrophilic character of the modified membranes was analyzed by measuring the membrane surface contact angle using a Digidrop contact angle meter (GBX Scientific Instruments).

Before modification with polyelectrolyte multilayers, the plasma-modified PDMS membranes were examined to determine the optimal plasma discharge power and duration parameters.

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