Sensors and Actuators A 197 (2013) 25–29

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Singularities in hydrophobic recovery of plasma treated polydimethylsiloxane surfaces under non-contaminant atmosphere

Jalal Bacharouche, Hamidou Haidara, Philippe Kunemann, Marie-France Vallat, Vincent Roucoules*

Institut de Sciences des Materiaux de Mulhouse, IS2M – C.N.R.S. – UMR 7361 – UHA, 15, Rue Jean Starcky, 68057 Mulhouse Cedex, France

ARTICLE INFO

Article history:
Received 7 December 2012
Received in revised form 19 March 2013
Accepted 2 April 2013
Available online 13 April 2013

Keywords:
Argon plasma
Polydimethylsiloxane
Hydrophobic recovery
Contact angles
Surface dynamics

ABSTRACT

Herein, the hydrophobic recovery of argon plasma treated polydimethylsiloxane surfaces is explored. In contrast to previous works, environmental contamination is here taken into account. We find that diffusion and reorientation strongly dominate the hydrophobic recovery under high thermal activation (60 °C), no matter the surrounding environment during storage. However, at lower temperature (24 °C and below), we find that contamination plays a major role in lab atmosphere environment. By working at low temperature and under inert nitrogen atmosphere to slow down the diffusion and reorientation dynamics and to avoid contamination, we identify two different temperature-dependent regimes in the kinetics of the hydrophobic recovery. One is fast and involves exclusively relaxation processes occurring in the surface region. The second, much slower, concerns diffusion phenomena in the sub-surface region. Thereby, the specific impact of bulk diffusion and surface reorientation processes can be distinguished during aging by slowing down the surface dynamics and by eliminating all possible sources of contamination.

1. Introduction

Polydimethylsiloxane (PDMS) substrates possess many advantages like biocompatibility [1,2], thermal stability [3,4], low toxicity [5,6] and high optical transparency [7], which make it an attractive material. This substrate is used for adhesives, lubricants, as well as in defoaming agents, damping fluids, implants, cosmetics and other applications [8]. The inherently low surface energy and chemical inertness have generally required elaborate surface modification schemes to optimize favorable bonding interactions. PDMS surfaces can be directly and easily activated by plasma, resulting in the introduction of polar functional groups on the surface [9–15]. The ease of bonding of oxidized PDMS to other substrates has simplified the fabrication of biomedical or microfluidic devices. But among the interesting phenomena with plasma treatments are the aging and the relaxation processes of the induced surface modifications and still not well known [16]. Probably the most extensively studied aspect in this field is the hydrophobic recovery of plasma treated PDMS surfaces evaluated by water contact angle (CA) measurements [17,18]. During plasma treatment, the surface is driven away from its thermodynamic equilibrium by developing concentration gradients of polar groups in the surface region or in the sub-surface region. After treatment, the modified surface reconstructs in order to minimize its surface energy and to return to an equilibrium state [18]. This entails migration of non-modified low molecular weight species from the bulk to the near surface region, the migration of oxidized low molecular weight from the top most layer inside the bulk, the migration of unmodified low molecular weight macromolecules towards the surface, the reorientation of the bulk polar chemical groups especially that near the surface and even the relaxation of the surface roughness [18,19]. The kinetic of this surface dynamics is affected by many factors including plasma parameters (pressure, gas, time and power), molecular structure (mobility, glass transition, degrees of crystallinity and crosslinking) and storage conditions [17] (temperature, humidity and dielectric constant of environment). Surprisingly, the role of environment contamination during aging is rarely discussed whereas this can dominate the hydrophobic kinetics, especially when the plasma treatment results in the formation of highly reactive surfaces. In this case, surface deactivation (decrease of hydrophilicity) proceeds through the combined effect of the relaxation processes and organic contamination. Besides, although temperature-dependent relaxation processes (mainly reorientation and diffusion) have been generally proposed to account for the hydrophobic recovery of plasma treated surfaces, the characteristic time scales associated to these processes and their assessment through standard CA measurements still remain poorly studied and understood.

In this report, the impact of bulk diffusion and surface reorientation is investigated and both impacts decoupled using experimental conditions that significantly reduce all possible sources of environment contamination. PDMS specimens were exposed to radio-frequency (r.f.) argon plasma at 100 Pa pressure

* Corresponding author. Tel.: +33 0389608782.
E-mail address: Vincent.Roucoules@uha.fr (V. Roucoules).

0924-4247/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sna.2013.04.003

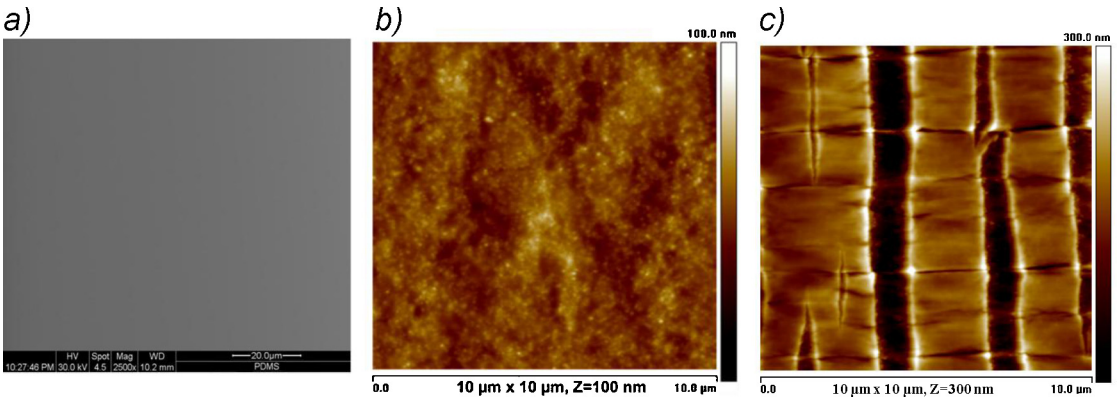

Fig. 1. (a) SEM image and (b) AFM image of the plasma treated PDMS surface at rest. A large fraction of the surface was composed of silica fillers or more likely of silica aggregates. In the AFM image the bright areas correspond to the aggregates-rich regions while the dark areas are related to the aggregates-poor regions. (c) AFM image of the plasma treated under elongation.

for 60 s. Then, we examine the competition between relaxation processes and surrounding contamination at three different temperatures (i.e. 4 °C, 25 °C and 60 °C) by comparing the hydrophobic recovery in air and under inert nitrogen atmosphere. By working at low temperature and under nitrogen, two distinct temperature-dependent regimes in the kinetics of hydrophobic recovery were identified. The first and fast regime involves essentially processes which are confined to the near surface region. The second and more slower regime concerns the sub-surface region and involves the diffusion process that brings low molecular weight species at the surface.

2. Experimental

2.1. Materials

Substrates of silicone (PDMS) were molded by Statice Santé SAS (France) using MED-4750 from NuSil Silicone Technology LCC (Carpinteria, CA 93013, USA).

2.2. Plasma treatment

Plasma surface modifications were conducted using a radio-frequency (r.f.) inductive coupling plasma reactor (Plassys MDS 130) consisting in a cylindrical glass chamber (14.5 cm diameter and 5.5 L volume) enclosed in a Faraday cage. In the Ar plasma reactions the PDMS (with approximate dimensions of 15 mm × 45 mm × 0.3 mm) was placed into the plasma chamber at 27 cm from the gas inlet. The reactor was evacuated to 0.1 Pa, following by purging with Ar gas to the desired experimental pressure, typically 100 Pa. At this point, r.f. radiations were turned on (60 W) to induce plasma reactions during 1 min. Upon completion, the r.f. generator was switched off. Then, the system was vented up to atmospheric pressure and the sample was immediately removed from the reactor (the exposure time with air was less than 15 s) and stored under air or under nitrogen at three different temperatures (4 °C, 24 °C and 60 °C).

2.3. Contact angle measurements

Static contact angle measurements were carried out using a video capture apparatus (DSA100, Germany) with 2-μl high-purity liquid drops (water). Measurements were made on both sides of the drop and were averaged. Each result is the average of five experiments.

2.4. Electronic microscopy

The Scanning Electron Microscopy (SEM) observations were performed by using a FEI environmental microscope (Quanta 400 model, The Netherlands) working at 30 keV. The films were observed using low vacuum mode without metallization.

2.5. Atomic force microscopy

AFM images were realized with a Dimension 3000 scanning probe microscope (Digital Instrument, United States). Silicon cantilevers (ARROW-NC from Nanoworld) were used for all measurements. The spring constant was 48 N/m. Typically the surface morphology of 10 μm × 10 μm areas near the center of each sample were observed in the tapping mode of the scanning probe microscope.

3. Results and discussion

PDMS samples are exposed to a low pressure argon plasma leading mainly to chain scissions and formation of *silyl free* radicals [18,20]. All experimental details are presented in supporting information. In a previous study, we have shown the silyl radicals react mainly with oxygen of the atmosphere (after removal of the samples from the plasma chamber) to form an oxidized and hydrophilic layer whose structure is somewhere between $Si(O,CH_3)O$ and SiO_2 species [21]. SEM image (Fig. 1a) and AFM image (Fig. 1b) did not show any defects (i.e. buckling or cracks) at the plasma treated surface when the PDMS substrate was kept at rest. However, because of the brittleness of the plasma treated layer, mechanical deformations readily underwent fragmentations at the PDMS surface (Fig. 1c). This point has been largely described in the literature.

The aging of the plasma treated surface is followed here by contact angle measurements ONLY on the samples kept at rest meaning free of cracks. No change has been observed during aging by SEM and AFM analysis. Fig. 2 shows the contact angle values of water drops on plasma treated PDMS surfaces which were stored in air (Fig. 2a) or under inert nitrogen atmosphere (Fig. 2b) at three different temperatures, 4 °C, 24 °C and 60 °C respectively. The initial contact angle value is measured between 1 and 3 min after plasma treatment and this time is considered as the time t_0 for the aging on the graph. The contact angle values of the water drop which initially wets completely the surface ($\theta_0 \sim 5°$) increase during aging to a plateau value which depends on the storage temperature. This hydrophobic recovery is usually attributed to diffusion and molecular reorientation as depicted in Scheme 1a [22,23].