Applied Surface Science 330 (2015) 104–110

Contents lists available at ScienceDirect

Applied Surface Science

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

Inscribing wettability gradients onto polymer substrates with different stiffness using corona discharge in point-to-plane geometry

Alexander Eifert[a,*,1], Julien Petit[a,b,1], Tobias Baier[a], Elmar Bonaccurso[a,2], Steffen Hardt[a]

[a] Center of Smart Interfaces, TU Darmstadt, Alarich-Weiss-Straße 10, 64287 Darmstadt, Germany
[b] Max Planck Institute for Dynamics & Self-Organization, 37077 Göttingen, Germany

ARTICLE INFO

Article history:
Received 23 September 2014
Received in revised form
24 December 2014
Accepted 24 December 2014
Available online 2 January 2015

Keywords:
Corona discharge
Wettability gradient
Material stiffness
Surface modification
Condensation
Electrostatic potential measurements

ABSTRACT

We use direct current (DC) corona discharge to create wettability gradients on polymer surfaces. The inhomogeneous current density distribution due to a point-to-plane arrangement induces local changes of the wettability of polymer surfaces, resulting in macroscopic wettability gradients. We found that condensation of water vapor on the surface allows a more precise characterization of the wettability gradient than macroscopic contact angle measurements. Condensation experiments allow characterizing different zones with different wettability. The wettability pattern depends on the stiffness of the substrate. We conjecture that Coulomb interactions influence the spatial distribution of wettability. Indirect measurements of the electrostatic surface potential after exposure support this assumption.

1. Introduction

In the past decades, the modification of the wettability of polymer surfaces was in the focus of extensive research efforts. Many surface modification techniques such as coating, chemical treatment, or exposure with X-rays/electron beams have been used for this purpose [1]. Among these techniques, one of the most frequently applied to reduce the hydrophobicity of polymer surfaces is based on plasma or UV-treatment [2–13]. Plasma treatment has become an important process and is widely used in industrial applications [14–16].

In recent years, a number of research efforts were also devoted creating wettability gradients on polymer surfaces in a controllable way. Wettability gradients offer a great potential for biological or microfluidic applications [17–22]. There are several ways to produce wettability gradients, which are often based on wet-chemical or topographical surface modifications [23]. Another possibility to generate a wettability gradient based on a contactless approach is to use plasma treatment. Lee et al. [24,25] showed that it is possible to inscribe wettability gradients on polymer substrates by applying a radio frequency (RF) plasma and changing the input power with the position where the treatment is applied. Recently, we demonstrated that radial wettability gradients on carbon nanotube surfaces can be formed by using direct current (DC) corona discharge [26]. DC corona discharge is a low-temperature plasma process, which is based on asymmetric electric fields around appropriate electrodes [27,28]. In the present study, we demonstrate that applying a DC corona discharge in a point-to-plane geometry, localized changes of the wettability of polymer surfaces are induced, resulting in wettability gradients. This new method is based on the spatially non-uniform current density distribution on the polymer surface during corona discharge. It allows producing radial wettability gradients and is easy to apply compared to other techniques.

We further investigated the influence of the mechanical stiffness of the substrates on corona-generated wettability gradients. We used silicone-based elastomers whose stiffness was easy to modify, leaving their chemical composition unchanged. As one way of characterization of the wettability we measured the contact angle (CA) of a sessile drop. While this technique is easy to perform, it is not fully suitable for characterizing wettability gradients induced by corona discharge due to the disparity of characteristic length scales of the wettability gradient (significant changes of the wetting characteristics on a scale of micrometers) and of the sessile drops (millimeter scale). In addition to CA measurements we carried out

* Corresponding author. Tel.: +49 6151 16 2553; fax: +49 6151 16 72021.
E-mail addresses: eifert@csi.tu-darmstadt.de (A. Eifert), hardt@csi.tu-darmstadt.de (S. Hardt).

1 Both the authors contributed equally to this work.

2 Current address: Airbus Group Innovations, Metallic Technologies & Surface Engineering, 81663 Munich, Germany.

http://dx.doi.org/10.1016/j.apsusc.2014.12.169
0169-4332/

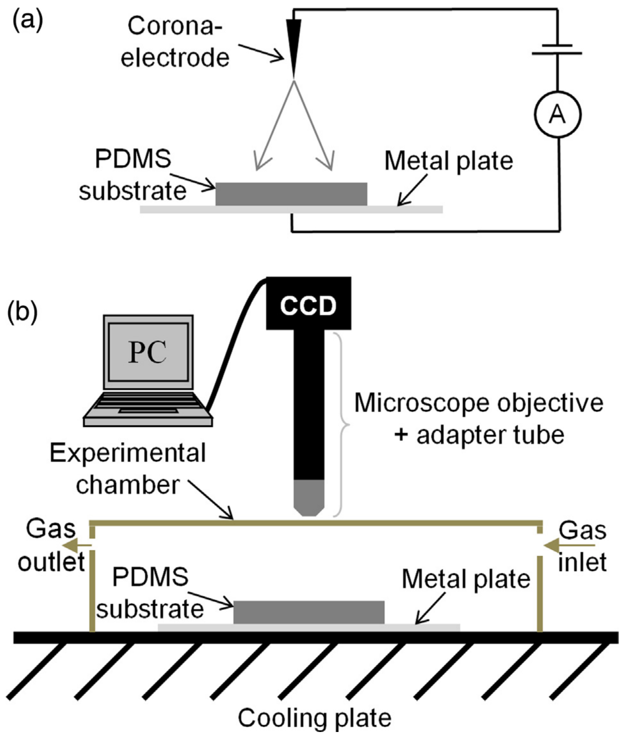

Fig. 1. (a) Sketch of the experimental setup for wettability gradient generation on polymer surfaces. (b) Schematic of the setup for studying the condensation process on corona-treated polymer substrates.

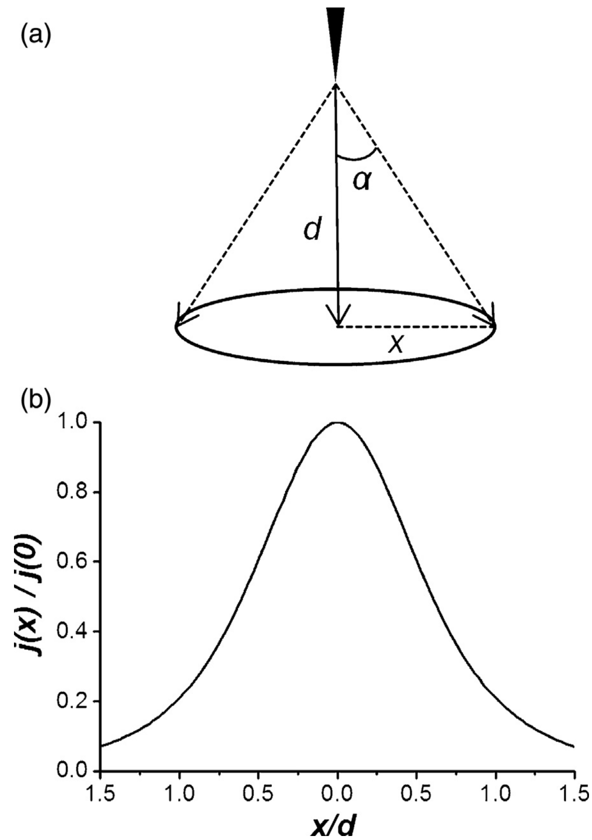

Fig. 2. (a) Geometrical parameters characterizing the corona discharge in point-to-plane geometry. (b) Typical distribution of the current density as a function of the radial distance x according to Warburg's law, Eq. (1), with $m = 4.5$.

water drop condensation experiments as a more accurate visualization method for corona-generated wettability gradients. During condensation, small droplets nucleate and grow on the surface in a pattern depending on the local wettability. The condensation pattern can be used to analyze the wettability gradient and the size of the exposed area. In addition to the wettability characterization, we performed measurements of the electric potential of charged PDMS surfaces after corona discharge for varying substrate stiffness.

2. Materials and methods

We used polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Germany) as a polymer substrate. In order to create substrates with similar surface chemistry but different stiffness we varied the ratio between the base (monomer) and the curing agent (cross-linker). The modification of the ratio PDMS:cross-linker determines the elasticity of the substrate. The PDMS:cross-linker ratios considered in the present study were 10:1, 20:1, and 40:1, exhibiting Young's moduli of 5.4, 1.8 and 0.7 MPa, respectively; for details see our earlier work [29]. Each substrate was cast with a thickness of about 1 mm.

In Fig. 1(a) a sketch of the experimental setup for the DC corona discharge treatment is shown. The needle electrode is connected to a high voltage supply (Heinzinger PNC-series 20 kV, Germany). The PDMS substrate is placed on a stainless steel plate (0.25 mm, Record Metall-Folien GmbH, Germany), which serves as the counter electrode. The spacing between the corona electrode and PDMS substrate was always set to 4 mm. In order to deposit a constant charge per unit time onto each PDMS substrate, the corona current was held constant at 2.4 μA by tuning the voltage between 3.1 and 3.9 kV, depending on the substrate's stiffness. A pico-amperemeter (Keithley 6485, USA) was used to measure the current. All substrates were treated for 10 min using a negative polarity at the electrode tip.

The water drop condensation experiments were performed using the same setup as in our earlier work [29], schematically presented in Fig. 1(b). The condensation process was observed in top view for about two hours, with the temperature of the cooling plate being $T_{plate} = 0\,^{\circ}$C, while the temperature of the vapor-laden air was 22 °C.

We used the point-to-plane geometry, the most common electrode geometry for corona discharge, where a sharp needle acts as the corona electrode and a metal plate is used as the counter electrode (see Fig. 1(a)). Above a critical magnitude of the electric field the neutral gas around the needle becomes ionized. The electric field accelerates ions toward the metal plate producing the characteristic corona current. For current measurements the plate is connected to a pico-amperemeter which is grounded.

In the case of the point-to-plane geometry (without PDMS substrate), the spatial distribution of the current density on the metallic plate electrode is non-uniform and obeys the so-called Warburg's law [30,31]. Warburg's law is an empirical approximation of the current density as a function of the radial distance from the normal projection of the electrode tip onto the surface, reading

$$j(x) = j(0)\cos^m \alpha, \quad (1)$$

with

$$\alpha = \arctan(x/d), \quad (2)$$

where $j(0)$ is the peak current at $x = 0$ (center of the corona spot), m is an empirical parameter (typically between 4 and 5) which has to be determined experimentally, α is the opening angle of the ionization cone, and d the distance between needle and plate. A typical Warburg function is shown in Fig. 2(b). Owing to the non-uniform distribution of the current density, the corona treatment of