

# Oxygen plasma treatments of polydimethylsiloxane surfaces: effect of the atomic oxygen on capillary flow in the microchannels

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Modification of polydimethylsiloxane/water interaction, to promote a spontaneous water flux through the microchannels, is a crucial task in microfluidic applications. For that reason, in this research, the authors study the hydrophilicity improvement induced by low-power oxygen plasma treatments (15 W) on the polydimethylsiloxane (PDMS) microchannel. The effects of the oxygen plasma treatments on wettability and water-work of adhesion on PDMS surfaces have been studied by sessile contact angle. The chemical composition of the plasma has been investigated by means of optical emission spectroscopy. The results indicate that the improvement of wettability on treated PDMS is led by the percentage of atomic oxygen in the plasma discharge. Super-hydrophilic surfaces (contact angle  $< 5^\circ$ ) have been obtained optimising the atomic oxygen percentage in the plasma discharge varying only the plasma working pressure. Super-hydrophilic PDMS microchannels show the highest spontaneous capillary flow in the channels while the hydrophilic microchannel shows only a small capillary flow.

**1. Introduction:** Polydimethylsiloxane (PDMS) has excellent chemical and physical properties such as optical transparency, chemical inertness, and good permeability to gases [1, 2]. Unfortunately, the native PDMS surface is hydrophobic [3–5]. The hydrophobic behaviour of PDMS implies that micro-fluidic systems, fabricated with PDMS, require active pumping mechanisms. To render PDMS hydrophilic and therefore to increase the capillary flow in the microchannels of the device, different chemical or physical processes can be used such as plasma treatment, amminosilane layer or coatings of zein protein [6–9]. Moreover, several papers report that hydrophilic surfaces can be successfully used in microfluidic applications avoiding external pumping system [10–13]. Some works report that the oxygen plasma treatments can improve the wettability of the surface and PDMS with the strong-hydrophilic surface can be achieved [6, 14–17]. In any case many aspects should be optimised to use systematically the plasma-activated surfaces in the field of microfluidics such as (i) plasma process control (ii) the managing of the plasma effect (iii) improvement of stability of the plasma treatment, (in particular loss of hydrophilicity). The loss of hydrophilicity in the plasma treated PDMS compromises the temporary stability, in term of wetting, of the surfaces. After 1 h of the treatment there is, usually, a sensible increase of the contact angle, as demonstrate, by Hillborg *et al* [18] and Gustavsson and Gubanski [19] this is due to a rearrangement of polymer chains on the surface. Similar behaviour has been observed also on other polymers as SU-8, and different strategies can be used to promote the stability of plasma treatments as the increase of plasma power, the increase on time of treatment or particular storage method [20, 21]. The loss of hydrophilicity is a critical issue and remains the main bottleneck in the use of plasma in microfluidic field. However also the link between plasma chemistry, wettability and final effect on the microdevice is strategic for the microfluidic field and are not entirely understood. In this work, we explored the latter two points using microfluidic devices typically used for the

polymerase chain reaction (PCR), as a realistic model of study. We investigate in particular the effect of low power plasma treatments (15 W) on the fluidics of water in the microchannels. In the first part of the Letter, we study the plasma conditions to obtain a super hydrophilic surface (contact angle  $< 10^\circ$ ) changing the working pressure of plasma. Then, we report the chemistry of plasma, using the optical emission spectroscopy (OES), and the correlation of the plasma species with the water adhesion with PDMS surface (work of adhesion). Finally, we study the consequences of plasma treatment on capillary water flow in PDMS microchannels.

**2. Materials and methods:** The PDMS pieces were cleaned with isopropanol in the ultrasound bath for 5 min and dried by nitrogen flux for 1 min. The polymers were treated by RF oxygen plasma. (Colibri Gambetti, Binasco Milano). The pressure was changed from 0.4 to 0.1 mbar keeping constant the power 15 W and the distance. After the plasma treatment, we used a home-made system to measure the contact angle. The system is equipped with a high-resolution dispenser. In this work, the drops of 2  $\mu$ l of distilled water were placed on treated surface. The images were acquired with Cmos camera and analysed by drop-analysis software [22]. For each sample, nine drops were placed in different zones. The reported results are the average value of the standard deviations. The interaction (work of adhesion) of water with surface has been estimated by Young–Dupre equation

$$Wa = \gamma_s(1 + \cos(\theta)) \quad (1)$$

$W_a$  is the work of adhesion,  $\gamma_s$  is the water surface tension (72.8 mJ/m<sup>2</sup>) and  $\theta$  is the contact angle [23]. The OES was acquired by optical fibre connected to monochromator and photomultiplier. We acquired the plasma signal in the region near the PDMS surface (spot diameter 4 cm). The signal was acquired from 400 to 850 nm. Chemical characterisation was performed

using a Kratos Axis Ultra DLD system. Each sample was characterised acquiring wide spectra 1250–0 eV.

The microchannels were realised in PDMS by replica moulding. A master of the device was obtained by spinning and patterning a thick layer of SU-8 on a silicon substrate. PDMS Sylgard 184, in a ratio of 10:1 (10 g of pre-polymer and 1 g of curing agent), was then poured on the master, let polymerise for 5 h at 65°C and peeled away. The microchannel had two small reservoirs areas in the extremities of the device and PCR reaction area in the centre. The reservoirs areas were connected by means of microchannels of 3 mm length, 200  $\mu\text{m}$  in depth and 200  $\mu\text{m}$  wide. The microchannel was mounted under a microscope equipped with photo-camera to monitor the effect of plasma treatment on water flow in the microsystem.

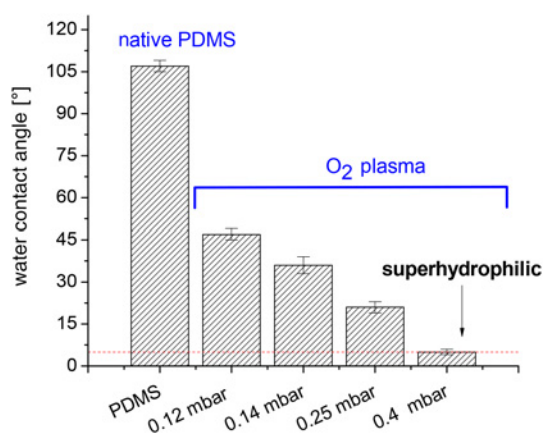
**3. Results and discussion:** Low-pressure plasmas have been widely studied to modify the liquid-solid interaction, in particular on polymer surfaces. Plasmas have many advantages such as low-power consumption, control of the surface modification and low temperature of the process [24]. Different kind of plasmas have been used to modify the surface of PDMS. Bartali *et al.* [25] used air plasma to render the surface more hydrophilic and Jokinen *et al.* [26] used oxygen and nitrogen plasma to reduce in efficient mode the contact angle on various polymers including the PDMS. Argon plasma at 100 W was successfully used by Pinto to improve the wetting properties of PDMS for bio-applications [27]. Results reported in literature indicate that low-pressure plasma, in particular oxygen plasmas, is an efficient tool to activate polymer surfaces [28, 29]. Fig. 1 shows as oxygen plasma treatments reduced the contact angle on PDMS. The contact angle of cleaned PDMS was 107° as reported in the literature [9, 10]. After all plasma treatments, the surface becomes more hydrophilic than native PDMS, (contact angles < 90°).

In the oxygen plasma used in this work the working pressure treatment played an important role in the modification of the PDMS surface since pressure increase from 0.1 to 0.4 mbar leads to a decrease in the surface contact angle. A super-hydrophilic surface (ca. < 10°), in particular, was obtained only at 0.4 mbar. The reduction of water contact angle indicates an increase of water – PDMS interaction that can be thermodynamically estimated by work of adhesion, (1). The adhesion of water on native PDMS was only 52  $\text{mJ/m}^2$  while on treated PDMS the work of adhesion was >110  $\text{mJ/m}^2$ . This indicates that chemical species of this low power plasma are enough energetic or chemical active to produce polar groups on the PDMS surface and therefore help the water-polymer interaction. To better understand the plasma chemistry the OES has been used. This type of diagnostic is not invasive and using an optical fibre a specific region of the plasma discharge

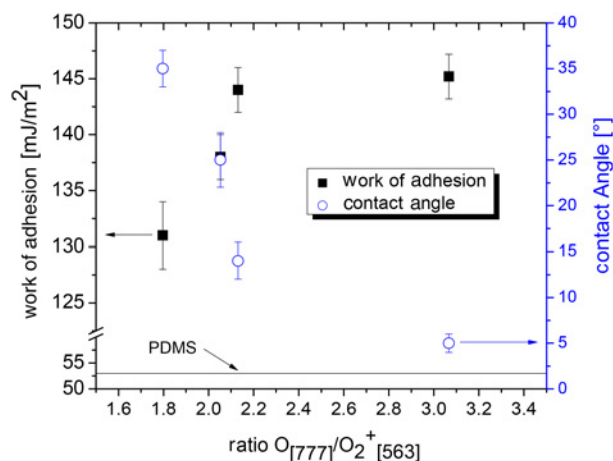
can be analysed. In this experiment, the optical signal of the plasma in the region near the PDMS surface has been collected. (Section area near the surface 4 cm). The OES of the plasma showed the presence of the line of atomic oxygen (777.4 nm) and the bands of  $\text{O}_2^+$  species (500–700) [30]. Moreover, the  $H_\alpha$  and  $H_\beta$  lines at 656.3 and 486.1 nm have been detected, respectively, more probably due to the presence of water on the wall of the plasma reactor [31, 32]. In Fig. 2, we report the water work of adhesion, estimated using (1), as a function of the ratio of the intensity of atomic oxygen on the intensity of molecular ionised oxygen,  $\text{O}/\text{O}_2^+$ . The water work of adhesion, increases monotonically with the increase of  $\text{O}/\text{O}_2^+$  ratio. The adhesion of water on the treated PDMS surfaces increases from 120 to 145  $\text{mJ/m}^2$ . The increasing water adhesion is proportional to the increasing of atomic oxygen in the plasma discharge. The work of adhesion increases of 270% when the PDMS surface is treated with oxygen plasma at 0.4 mbar (super-hydrophilic conditions), indicating that atomic oxygen is extremely efficient in the activation of the surface. We tested directly on the microchannel the effect of oxygen plasma treatments. Fig. 3a, show the picture of water in the reservoir of PDMS microchannel (without treatment). No spontaneous flow was detected. The water remains in the ‘load’ well of the device. In Fig. 3b we report the picture of a microchannel after oxygen plasma treatment at 0.4 mbar. by capillarity, the water immediately flows in the microchannel.

The super-hydrophilic treatment clearly shows excellent benefit regarding spontaneous capillary flux inside the microchannel, in fact water passes through the microdevice almost instantly (length 1.8 cm). Figs. 3c, d shows the picture of a micro-device where the microchannel is connected to PCR reaction area. The water flux in this region is clearly divided into two branches because the water tends to stay adhered to the wall of the microdevice.

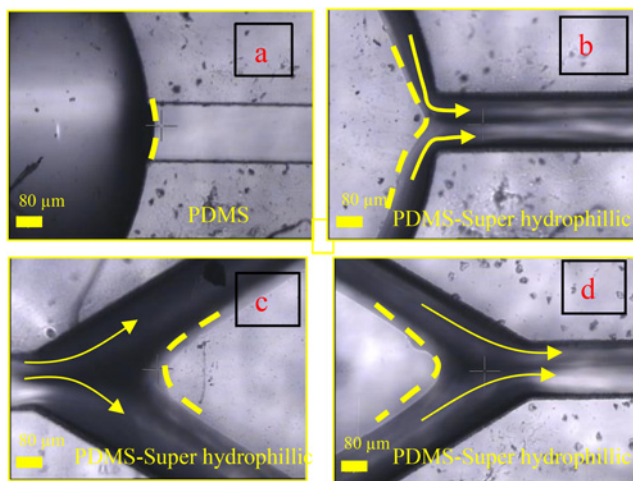
The water behaviour in Figs. 3b and c indicates that the walls of the microchannel are activated by plasma treatment, (higher active area) and this promotes the higher capillarity flux at the border of PCR zone. When the surface of the PDMS was only hydrophilic small spontaneous flux was detected. For instance, the PDMS microchannel with a surface with a contact angle of 40° shows a movement inside of the microchannel of only 5 mm in a minute. When the surface of the treated microchannel had a contact angle higher of 40°, the capillary flux was negligible. As shown in Fig. 2, oxygen plasma treatment induces an increasing of water work of adhesion. The enhancement of work of adhesion is due to change of the chemical bonds on the surface of the polymer, in particular, the formation of oxygen-containing polar functional groups (Si-Ox Si-OH, C-OH, COOH) on the surface [18, 33].



**Fig. 1** Contact angle of native PDMS and PDMS – treated with oxygen plasma at different plasma working pressure



**Fig. 2** Water work of adhesion of PDMS and contact angle as a function of the  $\text{O}[777]/\text{O}_2^+[563]$ , for each data the plasma pressure is reported



**Fig. 3** PDMS microchannel before (a) and after (b) super-hydrophilic oxygen plasma treatments. Water flux divided into two branches in the PCR reaction area (c) and (d)  
a PDMS  
b PDMS-Super hydrophillic  
c PDMS-Super hydrophillic  
d PDMS-Super hydrophillic

**Table 1** Elemental composition (% atomic) by XPS analysis of; PDMS as received and PDMS treated using oxygen plasma

	As received,%	Treated, %
C1s	48.5	24.65
O1s	28.5	40.5
Si2p	23.4	23.78

This is confirmed by the XPS analysis as presented in Table 1 that contains the atomic percentage of silicon, carbon and oxygen of the pristine and treated PDMS. An increase in the surface oxygen content can be observed for the treated PDMS, indicating the formation of the oxide groups.

The changing of surface chemistry improves wettability enhancing the capillary flow inside in the microchannel. The atomic oxygen promotes the Si-O<sub>x</sub> and Si-OH C-O and C-OH groups formation on PDMS surface. The atomic oxygen, in fact, is extremely reactive and it can easily react with PDMS surface, promoting in the presence of other species as hydrogen the formation of the polar groups on the surface. The presence of polar groups on the surface helps the interaction of surface with polar liquids, as water, and induces a spontaneous capillary flux in the microchannels. We observed that the distance covered by the water inside the microdevice can be tailored modifying the hydrophilic properties of the microchannel surface. The tailoring of hydrophilic properties of PDMS surface can easily be done using different pressure conditions of the oxygen plasma process, keeping the plasma power constant. We remark that the managing of the adhesion of the liquids and therefore the capillarity flux in the microchannel could be a crucial task also for the deposition of functional layers of materials on the wall of the microchannel using wet techniques.

**4. Conclusion:** In this work, we investigated on the wettability of PDMS surface after oxygen plasma treatments. We kept constant the power, the time and the distance for all processes, and we changed only the working pressure. We demonstrated that using oxygen plasma with low power (15 W) a super-hydrophilic surface can be obtained when the working pressure is 0.4 mbar. Using contact angle and Young–Dupre equation the water work

of adhesion has been calculated. The results show that the water adhesion of water on PDMS increase of 270% when the surface show the super-hydrophilic properties. The work of adhesion is directly proportional to the percentage of atomic oxygen present plasma discharge. The improving of water work of adhesion on PDMS surface, by plasma treatment, activates a spontaneous capillary flow in the microchannel of a microdevice. Super-hydrophilic PDMS microchannels, in particular, show the highest spontaneous capillary flow in the channels while the hydrophilic microchannel shows only a negligible capillary flow.

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