Surface geometry based hydrophobicity of the PDMS for microfluidic devices

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Abstract. In this report, the surface hydrophobicity of PDMS was investigated using two methods of preparations. The first method was performed by changing the surface roughness through the use of different molds. The second method was performed by varying the reconstitution ratio (volume of elastomer base to volume of elastomer curing) of the PDMS. Variation in the hydrophobicity of the PDMS was characterized by measuring the contact angle of a liquid droplet against the surface of the PDMS. The results showed that both the surface roughness and the reconstitution ratio of the PDMS positively correlated with the contact angle measured regardless of the liquid used. The maximum and minimum contact angle obtained were $\theta_\text{max} = (138 \pm 3)^\circ$ and $\theta_\text{min} = (99 \pm 3)^\circ$, respectively. The results demonstrate a straightforward way of fabricating microfluidic devices using PDMS with controlled hydrophobicity.

1. Introduction
Microfluidic devices have driven considerable progress in the development of microsystems, predominantly for chemical, biological and medical applications. In the past years microfluidic devices has evolved from silicon and glass structures towards polymers. The commonly used polymer in this field is PDMS (polydimethylsiloxane) which generated interest due to its low cost and ease of fabrication and its properties which includes: thermal stability, transparency and its surface properties. However PDMS surface properties needs to be modified in order to achieve desirable functionality [1]. This modification leads to the degree of wetting of the PDMS, particularly its hydrophobic or hydrophilic nature. This property of the material can be altered by many ways ranging from different etching methods to chemical alterations. This can be characterized through the contact angle of a droplet with the surface of PDMS, these variations in the hydrophobicity of PDMS is essential in different applications, such as in cell culture, self-cleaning of the device and others [2].

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2. Theory and methodology

2.1. Fabrication

The main material used in this experiment was PDMS. This was reconstituted by mixing the elastomer base and the elastomer curing agent with a 10:1 ratio. In order to remove the unnecessary bubbles, the PDMS was degassed using a bell jar for a time interval of 4 hrs. Mold designs for the surfaces were made afterwards. The designs that were chosen were the molds for paper, vinyl sticker, and aluminum foil tape. These were made by cutting a part of each of the materials and pasting it on a glass slide. The elastomer was then poured into the design (which is attached to the slide) and was cured in an oven with a temperature of 80 °C for an hour. When the curing was done, the PDMS was peeled off the slide and the resulting surfaces for the three materials were obtained.

2.2. Characterization

Surface roughness was characterized by taking an image of the surface of the PDMS under a bright field microscope and a histogram of the gray level image was then obtained. By fitting the histogram to a Gaussian function and obtaining the FWHM (Full Width at Half Maximum) the distribution of the pixel value would then indicate the roughness of the surface.

Surface interaction between a solid medium and a liquid is often characterized by the degree of wetting of the surface, hence the contact angle of a liquid to the surface of a solid. The Cassie-Baxter equation for a heterogeneous surface is shown below [3],

\[
\cos \theta_r = rf \cos \theta - (1 - f)
\]

where \( \theta_r \) is the contact angle between the surface and the droplet, \( r \) is the roughness ratio, \( \theta \) is the contact angle of an ideal surface and \( f \) is the fraction of solid surface area wet by the liquid. If we decrease \( f \) we can see that \( \theta_r \) should increase, the decrease in \( f \) would imply greater roughness hence, as surface roughness increases the contact angle increases. A contact angle of \( \theta_r < 90^\circ \) is a hydrophilic surface and contact angle of \( 90^\circ \leq \theta_r < 150^\circ \) is a hydrophobic surface and a contact angle of \( \theta_r \geq 150^\circ \) is a super hydrophobic surface.

![Figure 1. (a)The experimental set-up consists of an optical caliper, an iron stand, a CCD camera connected to a computer installed with National Instrument Vision Assistant software, and a sample. (b) The contact angle of the sample droplet was obtained using the software ImageJ.](image)

After fabricating the surfaces, the next step was obtaining the contact angle of a droplet for each of the sample. The experimental set-up for the contact angle measurement is shown in figure 1a. The set-up consists of an optical caliper, a CCD camera connected to a computer with National Instrument Vision Assistant software, and a stand for the sample. A droplet of water with a volume of >5 µL was
placed on its surface using a pipette and an image of the droplet on the surface was taken. Using the software ImageJ, the contact angle of the droplet was obtained as shown in figure 1b. This was repeated for different liquids namely, Hydrochloric acid (1M), methyl orange, Sodium Hydroxide (1M), solution of HCl and methyl orange and distilled water. The PDMS was also reconstituted using a different elastomer base to elastomer curing ratios of 10:2, 10:1, 10:0.5 and 10:0.25. The surface of the paper and sticker was used as the mold for this part of the experiment and the only liquid use was water. The contact angle was also measured for the varied reconstitution ratio.

3. Results and discussions
From the FWHM of the different surfaces it can be inferred that the PDMS molded in paper proved to be the roughest surface, followed by the Al foil tape and sticker. The greater the FWHM the rougher should be the surface since the tendency of a rough surface is to scatter light in many directions hence the distribution of grey pixel value widens.

![Figure 2](image.png)

**Figure 2.** The histogram for each of the surfaces with their corresponding FWHM and image in 40x magnification. (a) surface of PDMS molded in Sticker, (b) surface of PDMS molded in paper (c) surface of PDMS molded in Al foil tape.

![Figure 3](image.png)

**Figure 3.** (a) The contact angle for different liquids used. (b) shows the contact angle for different reconstitution ratio, with paper as mold for a–d with 10:2, 10:1, 10:0.5 and 10:0.25 reconstitution ratio respectively and sticker as mold for e–f with 10:1 and 10:0.5 reconstitution ratio respectively.

From figure 3a below it can be inferred that even if the liquids are different, increasing surface roughness would still lead to increasing contact angle. This would imply that changing the material
used as a mold would directly correlate to a change in the hydrophobicity of the PDMS and holds true for a large number of liquid. However the effect in the interaction of different liquids with the surface of PDMS cannot be determined given the data, since the differences in the contact angles are inconclusive. From figure 3b below it can be inferred that by increasing the reconstitution ratio between the elastomer base and the elastomer curing, yields a positive correlation with the contact angle of the liquid and implies that the reconstitution ratio affects the hydrophobicity of the PDMS. This effect is attributed to the change in adhesion of the PDMS as the reconstitution ratio is changed.

4. Conclusion
The hydrophobicity of the PDMS was investigated using two methods, first by using different molds that would act as the surface of the PDMS, and the other was achieved by changing the reconstitution ratio of the PDMS. By combining the two methods, the maximum and minimum contact angle obtained are $\theta_r = (138 \pm 3)^\circ$ and $\theta_r = (99 \pm 3)^\circ$ respectively. The maximum contact angle was about $10^\circ$ less, to consider the surface as super hydrophobic while the minimum contact angle was about $10^\circ$ greater, to consider the surface as hydrophilic. These results demonstrate a straightforward way of fabricating microfluidic devices using PDMS with controlled hydrophobicity.

5. References
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