

A Simple Method to Modify the PDMS Surface Wettability for Biomicrofluidic Applications

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ABSTRACT

Polydimethylsiloxane (PDMS) is one of the most used materials for the manufacture of microfluidic devices. Recent studies have combined microfluidic devices and cell cultures to originate a new group of devices, the organs-on-a-chip (OoC). These devices replicate the microphysiological features that can be found in the human body so that healthy and pathological conditions can be easily studied. PDMS is also one of the materials of choice for the manufacture of the OoC, due to its mechanical and chemical properties, and due to the fact that it is a biocompatible and inert material. However, the hydrophobic behavior of PDMS leads to the adsorption of unspecific molecules, hinders cell culture attachment and growth, and decreases the specificity of certain biochemical tests. Additionally, the hydrophobicity of microchannels walls of microfluidic devices difficult the fluid flow, making necessary the use of external sources for the flow control, such as syringe pumps. A common strategy to improve the wettability of the PDMS surface is to apply oxygen plasma. However, the effects of this technique only last a few hours. Another strategy is to alter the bulk of PDMS during manufacture by adding components such as surfactants. In this work, different compounds were combined with PDMS in concentrations of 1 and 2 wt.%. The changes in the wettability were verified on the day of sample manufacturing and one week later. Since the optical properties of PDMS can be important for some microfluidic studies, the changes in the transparency of the samples were also evaluated by measuring the respective transmittance spectrum. The results showed that two tested surfactants can improve the wettability of the PDMS surface to a hydrophilic behavior remaining for at least one week after fabrication. The transparency of the PDMS shows to be affected by one of those two surfactants while the other only led to a small decrease when used the higher concentration.

1. Introduction

The organic polymer polydimethylsiloxane (PDMS) is commonly used in the biomedical field due to its physicochemical and mechanical properties, such as optical transparency, gas permeability, nontoxicity, and biocompatibility. Also, the device fabrication using PDMS is a simple and low-cost process. (Gokaltun et al., 2017). One of its uses is the microfluidic assays for the visualization and study of blood phenomena, such as the behavior of the red blood cells or aneurysms (Miranda et al., 2021; Pinho et al., 2020). PDMS has also been used for the development of lab-on-a-chip devices and, in more recent studies, organ-on-a-chip devices (Carvalho et al., 2021; Gonçalves, Carvalho, et al., 2022; Gonçalves, Rodrigues, et al., 2022; Miranda et al., 2021; Vlassov et al., 2018). One characteristic of that polymer is its hydrophobicity, presenting a contact angle of around $108^\circ \pm 7^\circ$ with water (Gokaltun et al., 2017; Klasner et al., 2009). This characteristic is favorable for a better demolding of the material but can be detrimental for biomedical applications, since it promotes undesirable nonspecific adsorption of proteins and small molecules. This can affect analyte transportation, reducing detection sensitivity (Gokaltun et al., 2017; Han & Lee, 2018). Another issue caused by the hydrophobicity of the polymer is the difficulty in moving fluid through the surface and, consequently, the need for external pumping sources for microfluidic studies (Kim et al., 2010; Litwinowicz et al., 2021).

To enhance the wettability of PDMS, different methods have been studied. Those methods can comprise surface modifications and bulk modifications (Hu et al., 2020). One common surface modification used is the oxygen plasma treatment. However, the result is unstable and the PDMS recovers its hydrophobicity after a few hours (Hu et al., 2020; Kim et al., 2010). Surface modifications were demonstrated to be a better option to maintain the optical and mechanical properties of the polymer. However, their procedures are usually complicated. Thus, another possible strategy is the addition of hydrophilic moieties or surfactants to the polymer surface. Surfactants lead to the reduction of the surface tension and, consequently, increase the spreading of aqueous solutions (Hu et al., 2020; Litwinowicz et al., 2021; Seo & Lee, 2006).

For this work, the bulk of PDMS was changed by the addition of different surfactants and polymers, both liquid and solid, in different concentrations. The wettability of the surfaces was then evaluated and compared. The effects of the modification on the bulk of PDMS on its transmittance properties were evaluated using spectrophotometry.

2. Methods

Eleven different samples were prepared. All the samples started by mixing the PDMS curing agent and the pre-polymer in a ratio of 1:10. In ten of the different samples Dextran 40 (Dex40), polyethylene glycol (PEG), PDMS-b-ethylene oxide (PDMS-b-PEO), Triton X-100 (TX100), and Citric Acid were added at a concentration of 1 and 2 wt% to the bulk of PDMS. All samples were poured into a rectangular mold and left to be cured in an oven at 80 °C for 3 hours. After the curing, the samples were removed from the mold and the wettability of their surfaces was evaluated by measuring the static contact angle between a 5 μ L drop of distilled water and the surface at room temperature. Contact angles were measured by using an optical tensiometer THETA (Attension), presented in Fig. 1, and by processing the images of the droplet profile deposited on the surface. 640 $\times$ 480 pixels were analyzed during the acquisition time (corresponding to 240 images per test). The spatial resolution of the system for the current optical configuration is 15.6 μ m/pixel. The images were post-processed by a drop detection algorithm based on the Young-Laplace equation (One Attension software). The accuracy of the algorithm is argued to be of the order of $\pm 0.1^\circ$ (Cheng et al., 1990). After one week, the contact angles of the samples were measured using the same process.

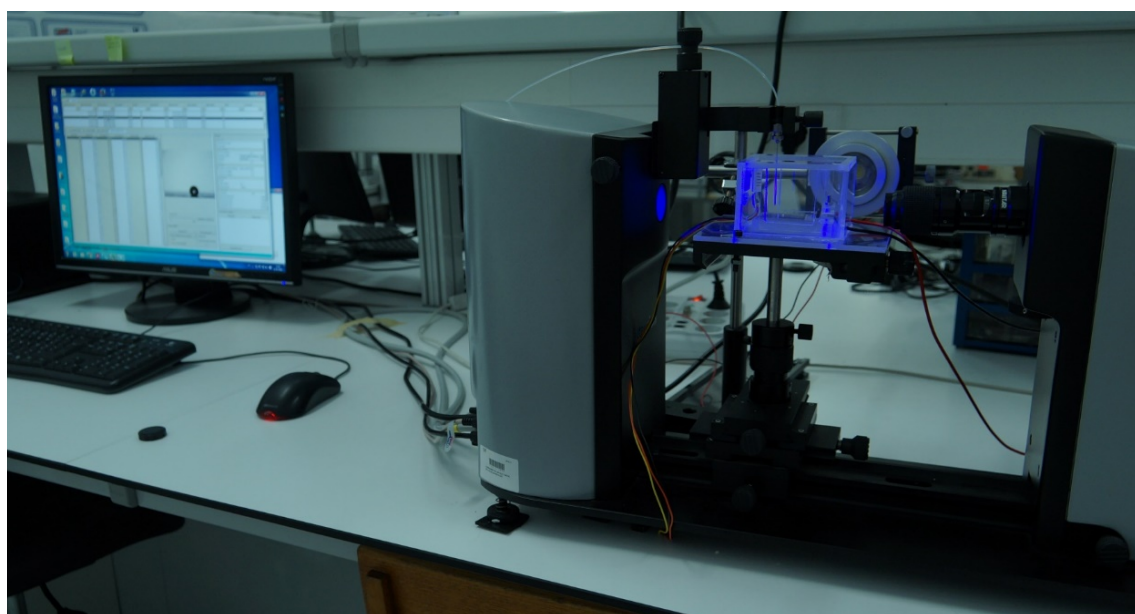


Fig. 1. Optical tensiometer used for contact angle measurements.

The transmittance spectrum was measured after the samples dried from the contact angle measurements. The Ultra-violet (UV) - Visible spectrophotometer UV-2600 (Shimadzu, Japan) and corresponding software, presented in Fig. 2, were used. The measurements were performed with a wavelength ranging from 200 to 800 nm.



Fig. 2. UV-Vis equipment for transmittance measurements.

In brief, the sample was placed in a holder and inserted into the equipment. The monochromator diffracts, using a grating, the impinging light of the emitted source into several wavelengths, so a single beam at a specific wavelength passes through the sample. The transmittance of the sample is then determined by the amount of light that is detected by the detector on the other side. The wavelength of the beam changes accordingly to the range selected by the user. A representation of the process is presented in Fig. 3.

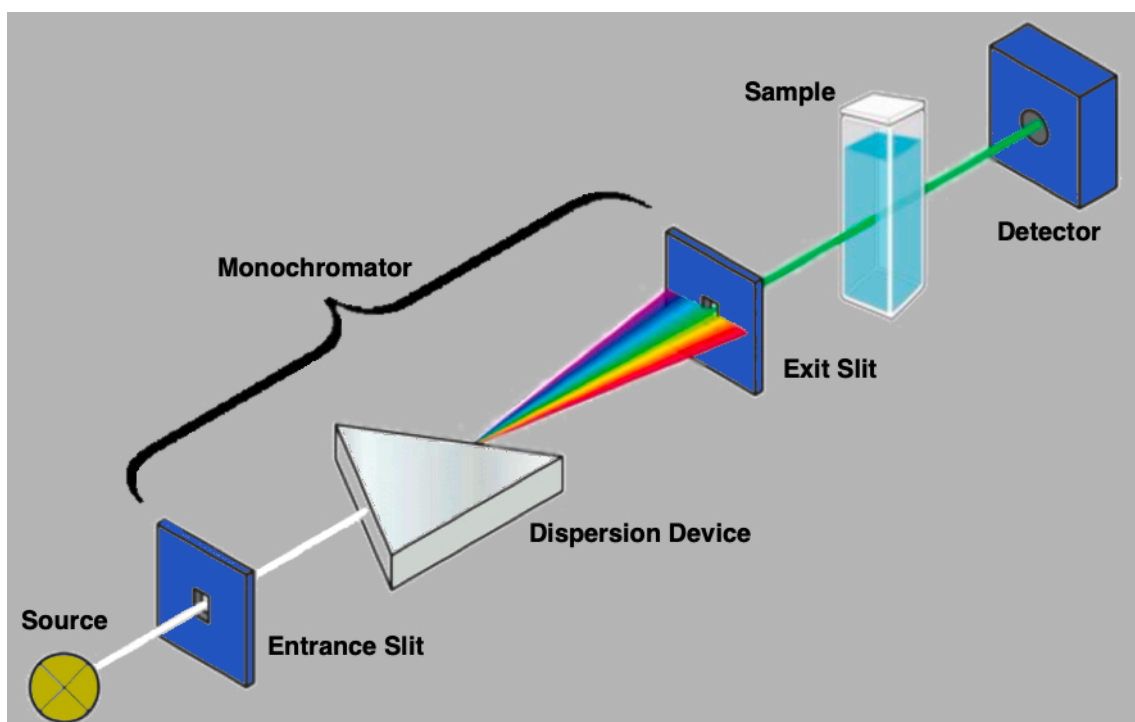


Fig. 3. Schematic representation of the transmittance apparatus. Reprinted from (Gohain, 2009).

3. Results and Discussion

The average contact angle obtained between water and unmodified PDMS was $112^\circ \pm 5^\circ$, which is to the values found in the literature [ref]. The samples with a mixture of PDMS and surfactant presented a reduction of the average contact angle when compared to PDMS alone, as seen in Fig. 4. For the samples modified with Dex40, PEG, and citric acid, the average contact angles right after manufacture were $101.91^\circ \pm 3.88^\circ$, $108.23^\circ \pm 1.48^\circ$, and $110.38^\circ \pm 0.94^\circ$ for the 1% wt. samples and $93.47^\circ \pm 2.15^\circ$, $104.97^\circ \pm 3.88^\circ$, and $108.97^\circ \pm 1.58^\circ$ for the 2% wt. samples, respectively. Despite being lower than the value obtained for unmodified PDMS, those values were still higher than 90° , which indicates that the samples still have a hydrophobic behavior. For the samples modified with PDMS-b-PEO and TX-100, the average contact angles obtained after manufacture were $61.35^\circ \pm 2.17^\circ$ and $84.12^\circ \pm 1.56^\circ$, for the 1% wt. samples, and $24.52^\circ \pm 4.37^\circ$ and $83.42^\circ \pm 1.43^\circ$, for the 2% wt. samples, respectively. Those values are lower than 90° , indicating that the samples were hydrophilic. One week later, the samples maintained their hydrophilic behavior, with an average contact angle value similar to the one registered on the day of the manufacture. The decrease in the contact angle value was more pronounced when using PDMS-b-PEO and the effect increased with the increase of its concentration. On the other hand, the effect on the contact angle was similar for both tested concentrations of TX-100. Since PDMS-b-PEO already presented PDMS on its structure, it enhanced the compatibility of the surfactant with the polymer. A higher amount of PEG might be required to achieve the intended hydrophilic behavior.

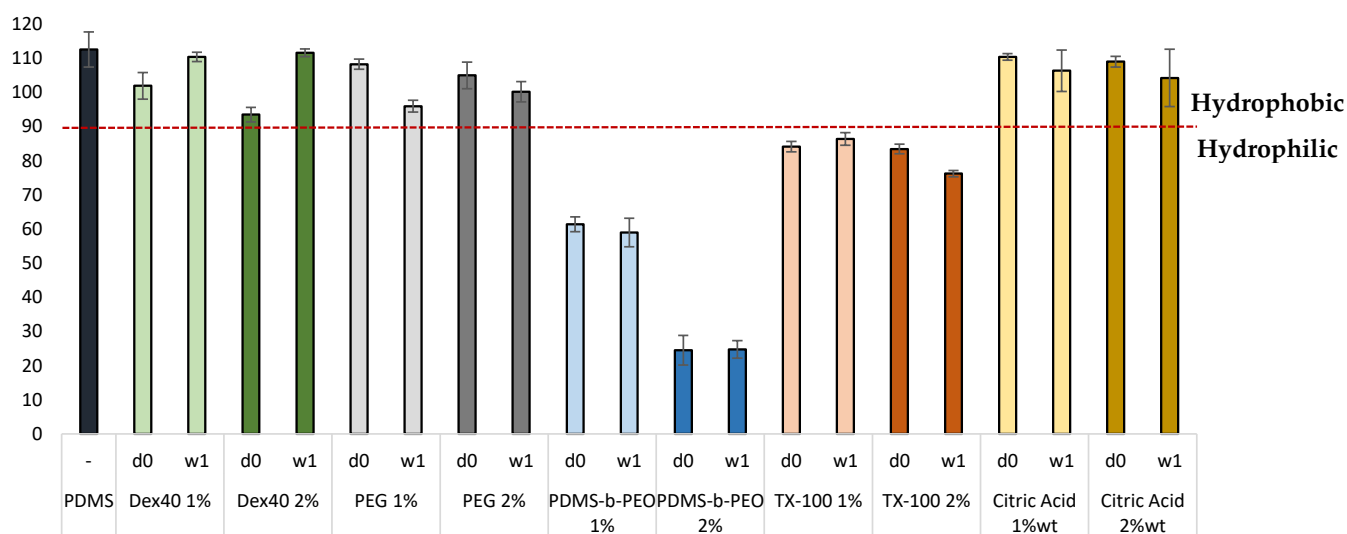


Fig. 4. The average contact angle between PDMS and modified PDMS surfaces and distilled water measured on the day of manufacture (d0) and one week after (w1).

One challenge that was verified, associated with the modification of the bulk PDMS, was the effect on the transparency of the material. As can be seen in Fig. 5, the unmodified PDMS sample presents a transmittance of about 93% in the wavelength of visible light.

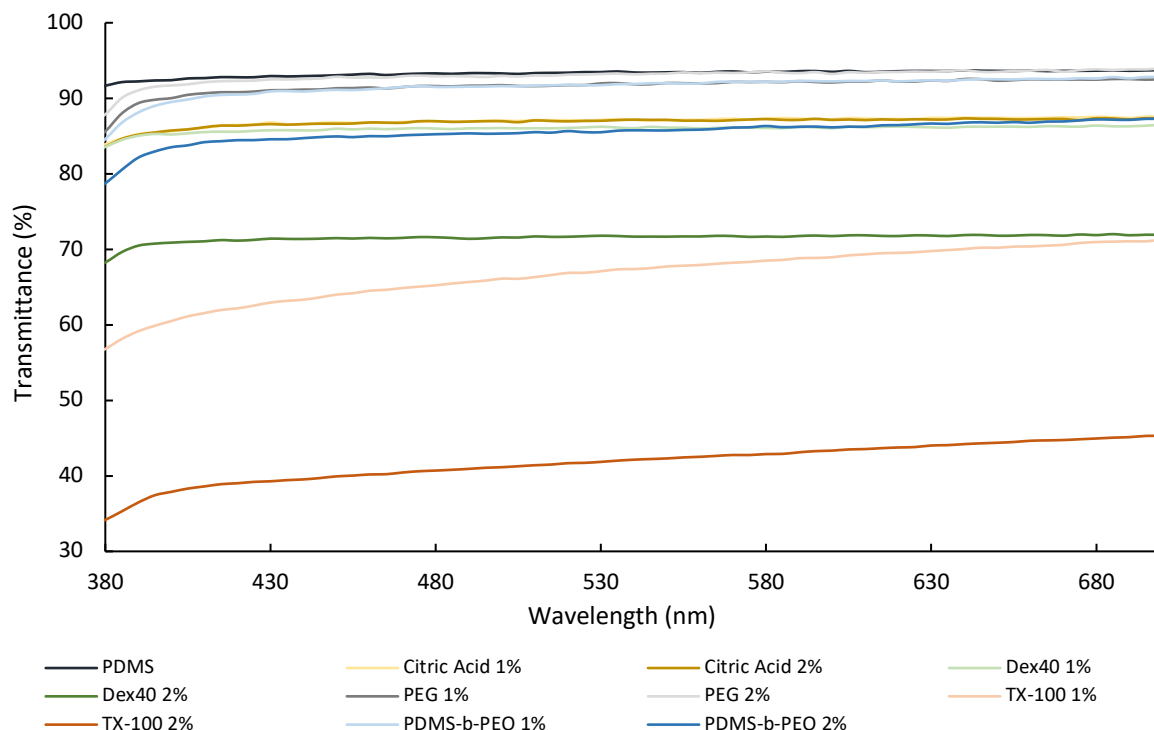


Fig. 5. Transmittance spectrum of PDMS and modified PDMS.

The incorporation of 1 or 2 wt.% of PEG in the bulk of PDMS had no significant effect on the transparency of the PDMS. The addition of citric acid reduced the transparency to around 87% when using each of the concentrations. For the other compounds, the increase in concentration results in a more pronounced effect on the transparency. The sample with 1 wt.% of PDMS-b-PEO maintained the value around 91% while for the 2 wt.% sample the value decreased to around 85%. The samples with Dex40 decreased the transparency of PDMS to around 86%, using the lower concentration, and around 71%, using the highest concentration. The particles of Dex40 are smaller and lighter than the ones of citric acid so a higher amount was required for the same concentration. Consequently, more spots on the sample were interfering with the light passage resulting in lower transparency. The incorporation of TX-100 led to a reduction of transparency to around 67% and 42%, using the lowest and the highest concentrations respectively.

Despite the improvement in wettability, the incorporation of TX-100 can significantly affect the optical properties of PDMS. PEG and PDMS-b-PEO presented better compatibility with the PDMS pre-polymer since they led to only a small reduction of the optical properties of the material.

4. Conclusions

Currently, we are performing quantitative analysis with different surfactants and hydrophilic solutions, to improve the PDMS wettability without compromising its optical properties. Using the non-ionic surfactant Triton X-100, a hydrophilic behavior can be achieved. However, the optical properties were significantly compromised. The use of 2 wt.% of PDMS-b-PEO proved to be the better strategy regarding the increase of hydrophilicity and maintaining PDMS transparency. The effects on the flow inside microchannel devices made with modified PDMS, as well as the visualization of particle flow, will be evaluated in future studies. The wettability behavior of the modified PDMS when in contact with fluid for long periods will also be evaluated, as well as the release of surfactant to the fluid and the respective consequences for cell culture.

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