Analysis of a Simple Method to Change the Wettability of the PDMS Surface for Biomicrofluidic Applications

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Abstract: One of the most often utilized materials for making microfluidic devices is polydimethylsiloxane (PDMS). Organs-on-a-chip (OoC) is a novel class of devices that blends cell culture with microfluidic technology. These devices replicate the microphysiological characteristics of the human body to make it easier to research both healthy and unhealthy conditions. Due to its mechanical and chemical characteristics, as well as the fact that it is a biocompatible and inert substance, PDMS is one of the materials of choice to manufacture OoC. However, PDMS has the tendency to promote the adsorption of non-specific molecules due to its hydrophobic properties, which may impede cell culture adhesion and growth and reduce the specificity of several biochemical tests. It is also necessary to use external sources for flow control, such as syringe pumps, due to the hydrophobicity of the materials' potential effects on fluid flow within the microchannels of microfluidic devices. Oxygen plasma treatment is one of the frequently used methods for enhancing the wettability of the PDMS surface. This strategy is, however, only effective for a limited time. Another tactic is to add ingredients like surfactants during manufacturing to change the bulk of PDMS. In this study, PDMS was mixed with a variety of surfactants at a concentration of 1% wt. The wettability changes were examined on the day the samples were collected and one week later. A week after manufacture, two surfactants continued to improve the wettability of the PDMS surface to a hydrophilic behavior.

1 INTRODUCTION

The organic polymer polydimethylsiloxane (PDMS), which has physicochemical and mechanical qualities like optical transparency, gas permeability, nontoxicity, and biocompatibility, is frequently used in the biomedical sector. Additionally, its fabrication is a quick and inexpensive procedure (Gokaltun et al., 2017). The evaluation and research of blood phenomena, such as the behavior of red blood cells or the emergence of aneurysms, is one of its applications (Miranda et al., 2021; Pinho et al., 2020).

Lab-on-a-chip (LoC) and organ-on-a-chip (OoC) technology has also utilized PDMS for the manufacture of the respective devices (Carvalho et al., 2021; Gonçalves, Carvalho, et al., 2022; Gonçalves, Rodrigues, et al., 2022; Miranda et al., 2021; Vlassov et al., 2018). Although the hydrophobicity of the polymer, due to a contact angle with water of around 108º ± 7º (Gokaltun et al., 2017; Klasner et al., 2009), helps the substance be removed from molds, it can be detrimental for its use in medicine because it promotes undesired, non-specific protein and small molecule adsorption. This might impact analyte mobility and lessen the sensitivity of

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the detection (Gokaltun et al., 2017; Han & Lee, 2018). Since it is challenging to move a fluid across the surface of the polymer due to its hydrophobicity, external pumping sources are necessary for microfluidic research (Kim et al., 2010; Litwinowicz et al., 2021).

Numerous techniques have been used to increase the wettability of PDMS. These tactics could comprise modifications to the surface and to the bulk of the material. (Hu et al., 2020) The oxygen plasma treatment is one method of surface modification that is frequently employed (Han & Lee, 2018; Seo & Lee, 2006). The hydrophilicity produced by this method is just momentary, whereas the PDMS quickly regains its hydrophobicity (Hu et al., 2020; Kim et al., 2010). The optical and mechanical properties of the polymer may be better maintained with surface changes. However, their processes are frequently challenging. Adding hydrophilic moieties or surfactants to the polymer surface is another option since surfactants lower the substance's surface tension, promoting aqueous solutions to scatter more broadly. (Hu et al., 2020; Litwinowicz et al., 2021; Seo & Lee, 2006)

The composition of the material used in this study was changed by combining PDMS with various surfactants. The wettability of the surfaces was then evaluated and compared over a week. The transparency of the most promising samples was also evaluated. Lastly, preliminary microfluidic studies were performed using altered PDMS.

2 MATERIALS AND METHODS

Six distinct samples were prepared for this work. All samples were produced starting from a 1:10 mixture of the pre-polymer and PDMS curing agent. On five of the samples, polyethylene glycol (PEG), PDMS-b-ethylene oxide (PDMS-b-PEO), Triton X-100 (TX100), Leophen ML, or Leophen BN were added at a concentration of 1% wt. The surfactants PEG, PDMS-b-PEO and TX-100 were selected since previous works showed that non-ionic surfactants can present antimicrobial properties and have improved PDMS wettability (Litwinowicz et al., 2021; Madadi & Casals-Terré, 2013). Leophen ML and BN are non-ionic emulsifiers used as wetting agents in the textile field. Each sample was placed into a rectangular mold and cured in an oven set to 80 °C for three hours. After curing, the samples were taken out of the mold, and the static contact angle between a 5 µL drop of distilled water and the surface was measured to evaluate the wettability of the surfaces.

Contact angles were determined on the optical tensiometer THETA (Attention) by processing the captured images of the profile of the droplet deposited on the samples' surface. 640 × 480 pixels were evaluated during the image capture (corresponding to 240 images per test). The spatial resolution for the system's optical configuration that was used is 15.6 µm/pixel. The images were post-processed using a drop detection method based on the Young-Laplace equation (One Attension software). According to (Cheng et al., 1990), the algorithm's precision is in the range of ±0.1°. After one week, the same approach was used to evaluate the samples' contact angles once more.

After the samples dried from the contact angle readings, the transmittance spectrum was determined. The UV-2600 spectrophotometer (Shimadzu, Japan) and associated software were employed. A wavelength between 200 and 800 nm was used for the measurements.

In summary, the sample was introduced into the apparatus after being placed in a holder. Using a grating, the monochromator divides the light from the emitting source into various wavelengths, allowing only one beam at a single wavelength to pass through the sample. The amount of light detected by the detector on the other side then determines the sample's transmittance. Depending on the user-selected range, the beam's wavelength varies.

Preliminary microfluidic assays were performed using unaltered PDMS and PDMS altered with PDMS-b-PEO. Two types of microchannels were used, as presented in Figure 3. One of the channels presented a constriction in width while the other was a linear channel, without any change in the geometry.

For the microfluidic assays, a blood analog fluid was prepared as described in (Carneiro et al., 2021). In brief, a PDMS pre-polymer mixed with a curing agent in a ratio of 6:4 (Corning Sylgards 184 kit) and added to an aqueous solution of sodium dodecyl sulfate (SDS) 4% w/w. After vortex stirring the solution was filtered using a filter with a hydrophilic membrane, with 10 µm pore size (Versapors Acrodiscs Syringe Filter, PALL). The filtered solution was then left to cure in an oven at 80 ºC for three hours. Lastly, a solution with 1% particle concentration was prepared to be used for the microfluidic assays.

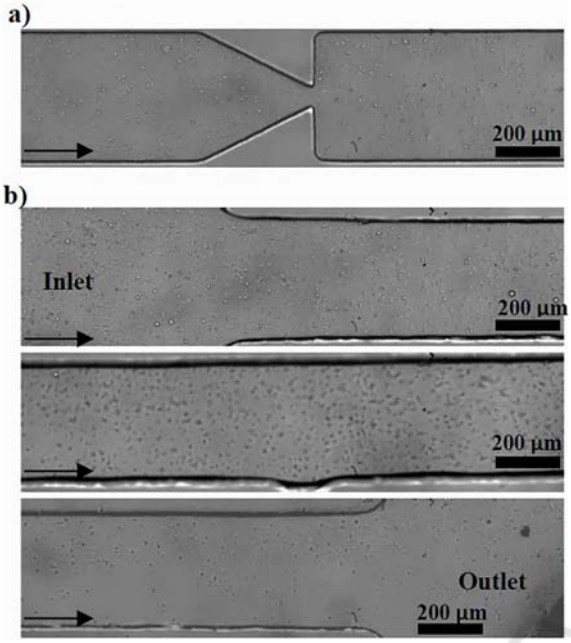

Figure 1: Microscopy images of the microchannels used for preliminary microfluidic assays: a) constriction channel and b) linear channel.

The microfluidic devices used for the assays were placed on an inverted microscope (IX71, Olympus, Tokyo, Japan) connected to a high-speed camera (Fastcam SA3, Photron, San Diego, CA, USA) for the visualization and record of the particle flow. To control the fluid flow in the devices a syringe pump (CetoniNEMESYS Syringe Pump) was used. The set-up for the microfluidic assays is shown in Figure 4.

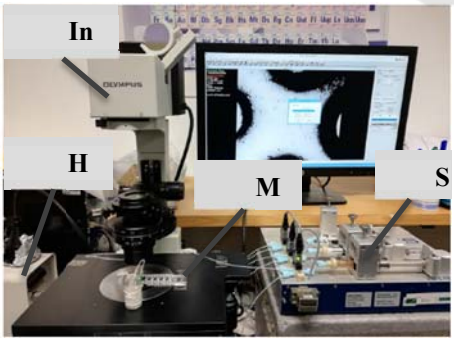

Figure 2: Experimental apparatus used to perform the preliminary microfluidic assays. In: Inverted microscope; H: High-speed camera; M: Microfluidic device; S: syringe pump.

The fluid flow values used for the constriction channel were 10, 20, 30 and 50 µl/min while for the linear channel the fluid flow was kept constant at 30 µl/min. The recording of the flow was performed at 3000 frames per second and using an objective with a magnification of 10x and an aperture of 0.25. The acquired videos were analysed with an ImageJ plugin, the MTrackJ.

3 RESULTS AND DISCUSSION

3.1 Contact Angle Measurements

Unaltered PDMS had an average contact angle of 112º ± 5º, which is consistent with values reported in the literature. Figure 5 illustrates how the samples with a surfactant showed a reduction in the average contact angle compared to PDMS alone. The Leophen ML, Leophen BN and PEG modified samples had average contact angles that were 108.23º ± 1.48º, 103.86º ± 3.92º, and 104.55º ± 5.00º, respectively, immediately after manufacture. These values were higher than 90º, even though they were lower than the value found for unaltered PDMS, demonstrating that the samples still exhibit hydrophobic behavior. After manufacture, the samples treated with PDMS-b-PEO and TX-100 had average contact angles that were 61.35º ± 2.17º and 84.12º ± 1.56º, respectively. These values are under 90º, demonstrating the hydrophilicity of the samples. The samples continued to show a hydrophilic behavior a week later, with an average contact angle value that was similar to the value recorded on the day of manufacturing. When PDMS-b-PEO was used, the contact angle value reduction was more noticeable. The presence of PDMS in the PDMS-b-PEO structure enhanced the surfactant's compatibility with the polymer. For the desired hydrophilic behavior using the other substances, higher concentrations might be needed.

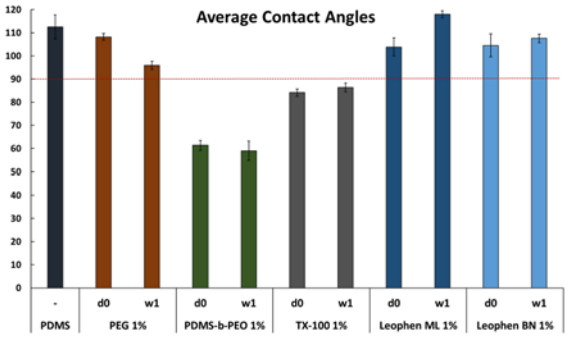

Figure 3: Contact angle measurements of PDMS and modified PDMS using distilled water. Bellow 90º the behavior is hydrophilic and above is hydrophobic.

3.2 Transmittance Spectrum

Since the modified PDMS has potential to be used on microfluidic assays that require optical analysis, the transparency of the samples is a relevant parameter to consider. The impact of the bulk PDMS alteration on the material's transparency was one challenge that was confirmed. As shown in Figure 6, the unaltered PDMS sample exhibits a transmittance of approximately 93% in the visible light spectrum.

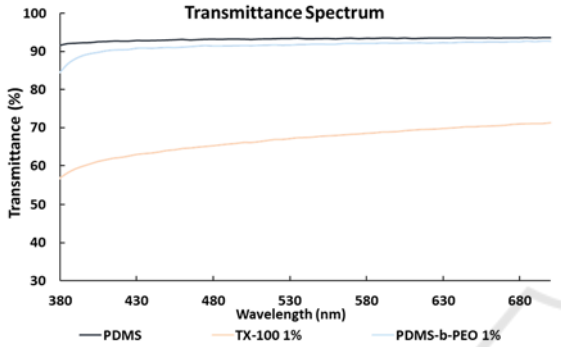

Figure 4: Transmittance spectrum of unaltered and modified PDMS.

While the sample containing 1% wt. of PDMS-b-PEO kept the value at 91%, the addition of TX-100 caused the transparency to drop to about 67%. The addition of TX-100 can drastically change the optical characteristics of PDMS despite the improvement in wettability. As PDMS-b-PEO only slightly reduced the material's optical characteristics, it demonstrated superior compatibility with the PDMS pre-polymer.

3.3 Microfluidic Assays

The maximum velocity of different particles passing through the constriction channel was measured and the average for each flow rate is presented in Figure 7. The velocity values increase with the increase of the flow rate, as expected, and are slightly higher on the microchannels with the altered PDMS. Also, the variation between the values is smaller on the altered PDMS channels.

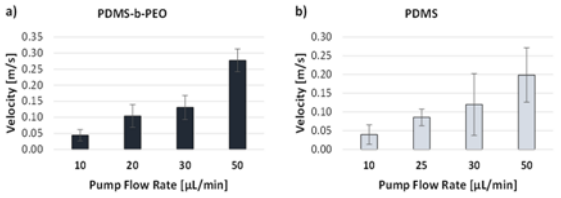

Figure 5: Maximum particle velocity for different flow rates on microchannels made using a) altered PDMS and b) unaltered PDMS.

On the linear channels, the average velocity of several particles was measured on three different regions of the microchannel: near the inlet, on the middle and near the outlet. The average of all the velocities on each region is presented in Figure 8. Higher velocities were registered on the microchannel with altered PDMS, and the variation between the values was also smaller than the ones presented on the microchannels with unaltered PDMS.

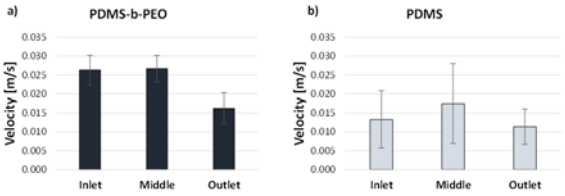

Figure 6: Average particle velocity in three different regions of the microchannel using a) altered PDMS and b) unaltered PDMS.

The results on both channels indicate an improvement regarding the flow on microchannels when using altered PDMS. However, the results are still insufficient to draw major conclusions regarding the benefits of changing the PDMS wettability through the proposed technique.

4 CONCLUSIONS

To improve the PDMS wettability, our current focus is on undertaking quantitative study with various surfactants and hydrophilic solutions. Using PDMS-b-PEO was the more effective technique to boost hydrophilicity while keeping transparency. By applying a small percentage of the surfactant, a hydrophilic behavior could be kept for over a week. Preliminary microfluidic studies showed a potential improvement of the fluid flow when using microchannels with altered PDMS. The modified PDMS will be optimized in the future to promote the manufacture of self-driven microfluidic devices. LoC and OoC devices could also be improved by such technology. Future studies will examine the wettability behavior of the modified PDMS in prolonged fluid contact, as well as the release of the surfactant into the fluid and its effects on cell culture. Biocompatibility and protein adsorption will also be analysed in future works to determine which type of PDMS will be better for each part of an OoC device.

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