A Brief Discussion on PDMS Surface Wettability Enhancement Methods for Microfluidic Applications

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Abstract: This position paper examines recent advancements in surface modification techniques for polydimethylsiloxane (PDMS) to improve its inherent hydrophobicity and enhance its application in microfluidic devices. While PDMS is valued for its transparency, biocompatibility, flexibility, stability, and non-toxicity, its hydrophobic nature limits fluid handling capabilities, which is essential for efficient microfluidic performance. Various methods, including oxygen plasma treatment, UV irradiation, and chemical Layer-by-Layer (LBL) deposition, have been explored to improve PDMS wettability. Surfactant-based modifications have shown promising results for achieving long-term hydrophilicity with straightforward application. Studies demonstrate that methods such as Polyethylene Glycol (PEG) coating and surfactant incorporation enable continuous capillary-driven flow without external pumps and improve sample purity by minimizing issues like bubble formation and cell aggregation. These advancements hold great potential of PDMS modifications to create more efficient and reliable microfluidic devices, and consequently to expand its applications in the biomedical and microfluidic fields.

1 INTRODUCTION

The development of materials with customized properties to meet the specific demands of microdevices has been crucial for advancing the field of microfluidics. Polydimethylsiloxane (PDMS) ranks among the most utilized materials in this area due to its characteristics, including biocompatibility, flexibility, stability, and non-toxicity. However, the naturally hydrophobic surface of PDMS poses challenges for fluid handling applications, compelling modifications to improve its wettability and allow efficient liquid flow without compromising the structure or functionality of the device. With increasing research on surface treatments to enhance these characteristics, various techniques have emerged, including gas-phase processes, chemical methods, and surfactant modifications. These methods aim not only to optimize flow in microfluidic devices but also to improve separation efficiency and reduce issues such as bubble formation and particle aggregation.

2 ENHANCING PDMS SURFACE WETTABILITY FOR MICROFLUIDIC APPLICATIONS

Given the growing application of surface treatments to modify PDMS wettability in microfluidic devices, recent studies have investigated effective methods to enhance this property. PDMS is widely used in

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microfluidics due to its biocompatible, non-toxic, stable, and flexible properties (Neves et al., 2024). However, its hydrophobic nature poses limitations for fluid handling, prompting the development of various surface treatment methods. Among the most studied methods are gas-phase treatments such as oxygen plasma (Long et al., 2017; Peterson et al., 2005; Vickers et al., 2006) and UV irradiation (Zhou et al., 2010), as well as chemical methods, such as Layer-by-Layer (LBL) deposition (Zhou et al., 2010). Surfactant modification has shown promising results, offering a straightforward and effective solution for creating long-lasting hydrophilicity without requiring complex procedures (Lin & Chung, 2021; Trantidou et al., 2017).

Long et al. (Long et al., 2017) applied oxygen plasma followed by a Polyethylene Glycol PEG coating to increase PDMS hydrophilicity. The microfluidic device performance was evaluated using rhodamine droplets, resulting in complete channel filling within 13 seconds, whereas untreated PDMS showed no flow within the first 60 seconds, as depicted in Figure 1. This method proved effective for achieving a sustained hydrophilic state, allowing continuous flow without the need for external pumping for up to 420 hours.

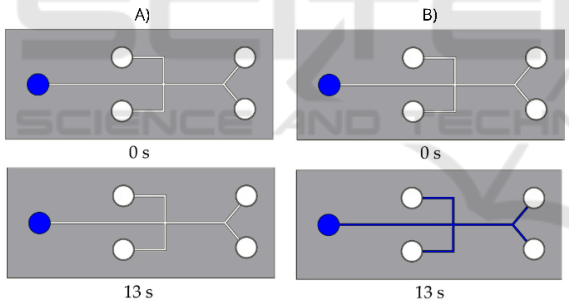

Figure 1: Schematic diagram of a capillary test on PDMS after 420 h of treatment by O_2-plasma-PEG based on the work of Long et al. (Long et al., 2017). The images make it clear that B) at 13 s the channels were completely filled and A) with untreated PDMS, no flow was observed at least during the first 60 s. Adapted from (Neves et al., 2024).

Peterson et al. (Peterson et al., 2005) examined the performance of native and ox-PDMS coatings in glass-silicon microfluidic devices. The ox-PDMS coating maintained a consistent flow rate for over 14 minutes, while untreated PDMS showed a significant reduction, with flow rates nearly 40% lower.

Holczer et al. (Holczer & Fürjes, 2017) applied surfactants to modify PDMS surfaces and develop autonomous microfluidic systems for bioanalytical devices. Vilčáková and colleagues (Vilčáková et al., 2012) also tested Carbon Nanotubes (CNT)-based composites with various surfactants such as Dodecylbenzene Sulfonic Acid (DBSA) and Cetyltrimethylammonium Bromide (CTAB), using mechanical mixing and sonication to ensure even distribution in PDMS.

Wu and Hjor (Wu & Hjort, 2009)incorporated the non-ionic surfactant Pluronic F127 into the PDMS prepolymer before curing. After introducing water into the microchannels, Pluronic F127 molecules migrated to the PDMS-water interface, reducing surface energy and decreasing the contact angle from 99° to 63° after 24 hours, compared to the 104° contact angle of untreated PDMS.

A study, carried out between the research group at IN+, Instituto Superior Técnico, MEtRICS (University of Minho) and in collaboration with colleagues from Tokyo Medical and Dental University further explored the use of surfactants to alter PDMS during the manufacture process, by adding components, such as surfactants, combined with PDMS in concentrations of 1 and 2 wt.%. Sessile droplet method was used in an optical tensiometer (THETA from Attention), on the day of the fabrication and one week later. Given the relevance of assuring the optical access to many of the fabricated devices in biomedical applications, the potential changes in the transparency of the samples were also evaluated by measuring the respective transmittance spectrum, considering that studying PDMS transparency is crucial due to its wide application in optical, microfluidic and biomedical devices, where optical clarity enables observation and effective functioning in systems that require interaction with light. The transmittance spectrum was in dried samples with thickness of 2-3mm, using a Ultra-violet (UV) - Visible spectrophotometer UV-2600 (Shimadzu, Japan) and corresponding software.

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 associated software. The measurements were performed with a wavelength ranging from 200 to 800 nm.

Furthermore, understanding and optimizing transparency helps to tailor the material to specific requirements, ensuring efficiency in emerging technologies. Two tested surfactants were able to improve the wettability of the PDMS surface to a hydrophilic behavior remaining, for at least one week after fabrication, as shown in Figure 2. First column in each material represents the measures performed in the first day of fabrication, while the second represents the values of the contact angles measured one week later.

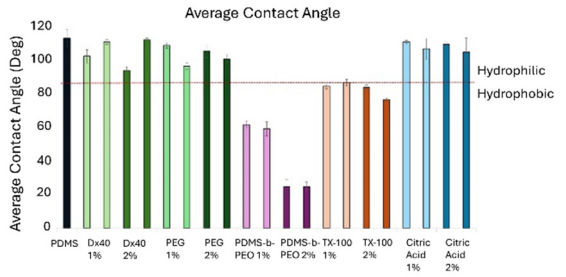

Figure 2: Average contact angle between PDMS and modified PDMS surfaces and distilled water measured at the day of manufacture (d0) and one week after (w1).

The transparency of the PDMS shows to be affected by one of those two surfactants, while the other only led to a small decrease with the highest concentration. Hence, while incorporating 1or 2 wt.% of PEG in the bulk of PDMS was observed to have 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 (Figure 3). Other surfactants such as 1 wt.% Polydimethylsiloxane-block-Poly(ethylene oxide) (PDMS-b-PEO) maintained the transparency around 91%.

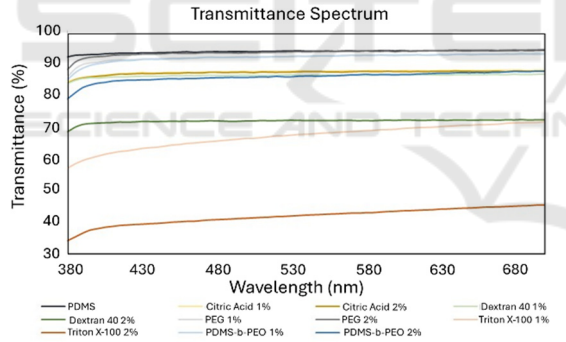

Figure 3: Transmittance spectrum of PDMS and modified PDMS additivated with various surfactants.

Details on the measurements procedure can be found in Gonçalves et al. (2024a).

More recently, Gonçalves et al. (Gonçalves et al., 2024b) investigated PDMS surface modification using surfactants Pluronic® F127, PEG, and PEO. Notably, PEO at a concentration of 2.5% proved highly effective in improving blood plasma separation within microfluidic devices. This modification promoted smoother fluid flow, minimized cell clustering, and reduced air bubble formation, leading to higher sample purity.

These studies highlight the promising results of surface modification methods to improve PDMS performance in microfluidic devices, especially in applications that demand accurate fluid flow control and effective biomolecule interaction.

3 CONCLUSIONS

Several PDMS surface modification approaches have shown significant potential in addressing the limitations associated with its hydrophobicity, enabling the development of more efficient and adaptable microfluidic devices. Recent studies highlight the effectiveness of oxygen plasma treatments, surfactant coatings, and polymer-based methods in achieving long-term hydrophilicity. By integrating straightforward and effective modification techniques, such as surfactant incorporation, it is possible to enhance fluid control and sample purity, benefiting the use of PDMS in biochemical and medical analysis microdevices. These advances emphasize the importance of ongoing research to optimize PDMS performance, expanding its potential in microfluidic solutions for biomedical applications.

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