



# Practical strategy to realistically measure the swelling ratio of poly(dimethylsiloxane) without underestimation due to the solvent volatility



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## ABSTRACT

We present an experimental method for measuring “realistically” the swelling ratio in terms of weight ( $SR_W$ ) of PDMS, where “realistically” means without the underestimation involved by the standard protocol (weight-measurements in open environment with time-delay incompatible with fast solvent evaporation rate). Comparison with the literature demonstrates that misleading conclusions can result under application of the standard protocol to very volatile solvents. To discuss this point, we develop a mathematical expression of  $SR_W$  including solvent properties and the effective amount of sorbed solvent determining a weight gain, consider two solvents with different volatility that severely swell PDMS (i.e., toluene and dichloromethane), check that the results of our measurements are consistent with theoretical predictions, demonstrate that our protocol rules out any dependence of  $SR_W$  on the solvent volatility and its reliability to measure and compare  $SR_W$  values of PDMS (or any swelling polymer/soft material) in the case of solvents with very different volatility.

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## 1. Introduction

Poly(dimethylsiloxane) (PDMS) is a silicon-based soft elastomeric material widely used in microfluidic platforms for biomedical applications due to its many advantageous properties (low-temperature polymerization, low cost, flexibility and reversible deformation under mechanical stress, porous structure with tunable permeability to liquids and gases, optical transparency, chemical inertness and non-toxicity, biocompatibility, tunable wettability, ability to adhere to various kinds of substrates by surface plasma-processing) [1–5]. Also, easy accurate patterning by soft-lithography makes PDMS a proper choice for the fabrication of microfluidic devices with large-scale integration [2,6–9]. Despite its attractive properties, PDMS swells in contact with several solvents [10]. All of this can involve deformation by geometry loss, distortion and collapse of PDMS micro-channels as well as blockage of the fluid flow [11,12]. Since treatment with different chemicals is routinely applied to synthesize compounds in PDMS micro-reactors

[6,13,14], measuring the swelling behavior of un-treated and functionalized PDMS with respect to a solvent as much carefully as possible is critical.

The swelling attitude of PDMS with respect to a solvent can be calculated by the fractional change in weight with respect to the starting weight, that is  $SR_W = (W - W_0)/W_0$ , where  $W$  and  $W_0$  indicate the weight of the swollen and dry sample, respectively.

Routinely,  $SR_W$  is evaluated by putting the PDMS sample in contact with the solvent of interest (usually to achieve volume saturation), then the sample is blow-dried to remove the residual surface solvent and weighted fast to limit weight-loss by solvent evaporation [15]. The protocol is usually not well described since the sample is immersed or simply wet by the solvent and drying time/intensity as well as weighting conditions are not well detailed [15–17]. Since the evaporation of very volatile solvents (such as dichloromethane, DCM) from the swollen PDMS sample begins by a few seconds, underestimation of the weight-gain and unreliable comparison between the effects of solvents with different volatility can result from standard measurements of  $SR_W$  inherently involving time-delay with respect to solvent evaporation rate.

The seminal paper of Whitesides et al. [10] discusses the compatibility of PDMS with respect to common solvents by

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identification of the key parameters and contributions (i.e., solubility parameter, Flory-Huggins interaction parameter, dipole moment and polarity) for swelling to occur on a fundamental basis and, in practice, to solve for the drawback of the evaporation of the solvent, it proposes to measure the swollen length, rather than the swollen weight, of PDMS samples under saturation conditions once submersed in the solvent of interest.

In this paper, starting from the pivotal work of Whitesides et al. [10], we try to give our original contribution on the problem of the accuracy in the measurement of the swollen weight of PDMS in contact with volatile solvents. We present an experimental method that gets a global information, i.e., PDMS swells or doesn't swell in a certain solvent and if it swells what the accurate degree of swelling is based on  $SR_W$ . To quantify the swelling behavior of PDMS realistically, we developed a practical protocol for measuring the swollen weight of PDMS in contact with solvents of different volatility, rather than the swollen length that, instead, we relate to the swollen weight mathematically. "Realistically" means that our measurement strategy is properly designed to avoid the solvent-loss by evaporation and, as a consequence, the drawback of a systematic underestimation of the weight-gain involved by the standard protocol in the case of very volatile solvents. Preliminary experimental tests were necessary to assess how time-delay and the configuration of the PDMS-solvent contact critically affect the measurement of the weight-gain of PDMS samples treated with a volatile solvent. Also, we related mathematically  $SR_W$  to the solvent properties and effective sorbed volume. Carefully chosen solvents swelling PDMS are considered (i.e., toluene and DCM) to carry out the predictions of our protocol, to demonstrate the critical influence of the solvent volatility on measurements of  $SR_W$  and to point out the misleading conclusions involved by lack of control on the weight-loss by solvent evaporation of the swollen sample in the case of very volatile solvents. The obtained estimations, once compared and discussed based on both experiments and literature reports, are fully consistent with the literature. Our developing and discussing both experimental and theoretical frameworks point out the misleading results and conclusions involved by standard approaches based on measurements of weight-gain in open environment, that is with poor control on the solvent-loss by evaporation.

Since our study addresses the basic general principles underlying an accurate measurement of swollen weight it focuses on both fundamental knowledge and can impact on specific applications in the field of soft material properties, interfacial processes as well as design and functional characterization of microfluidic channels and synthesis chips. In this respect, measurements of swollen weight would be a more practicable and easy strategy than measurements of swollen lengths.

## 2. Materials and experimental methods

### 2.1. Materials

The developed our protocol and its experimental implications were tested and discussed by considering two solvents with different volatility that severely swell PDMS, such as toluene (boiling point 111 °C at 25 °C, density  $\rho_{\text{tol}} = 0.865$  gr/mL) and DCM (boiling point 36.6 °C at 25 °C, density  $\rho_{\text{DCM}} = 1.325$  gr/mL) purchased from Sigma Aldrich.

Cross-linked PDMS was prepared by the two-component kit PDMS Sylgard® 184 (Dow Corning Corporation): polymer base and curing agent were thoroughly mixed with the weight ratio 10:1 (as suggested by the producer) and, after degassing under vacuum conditions, curing was conducted at 65 °C for 2 h in an oven. The peeled off cross-linked PDMS was cut to prepare 2 mm-thick

diskettes with diameter of 10 mm to be used in our preliminary test experiments and cubes with side of nearly 2-mm to be immersed in toluene and DCM up to 24 h for swelling tests. All of the cubic samples were weighted before their dipping in the solvent of interest to quantify their starting weight  $W_0$  that was estimated to be  $W_0 = (0.10 \pm 0.01)$  gr.

### 2.2. Experimental methods

To systematically study the issue of the underestimation of the weight-gain of the swollen sample related to the solvent volatility, we performed preliminary experiments (termed "Experiment\_1" and "Experiment\_2", hereafter) that are not part of our protocol (termed "Protocol\_ $SR_W$ ", hereafter) but were planned just to point out how the configuration of the PDMS-solvent contact critically affect the measurement of the weight-gain of PDMS and to recognize the effects involved by the volatility of the solvent in measuring the swollen weight in open environment. To perform our preliminary experiments we used DCM, which is more volatile than toluene.

**i) Experiment\_1:** Some drops (nearly 1.0 mL) of DCM were dispensed by a Pasteur pipette on silica glass slides and PDMS diskettes were placed in contact with DCM for times ranging from 1 to 10 min at room temperature (about 20 °C). In these experiments only one surface of each PDMS diskette got in contact with the solvent and the confinement due to the silica glass favored diffusion of the solvent through PDMS with reduced loss by evaporation. Once elapsed the designed PDMS-DCM contact time, the PDMS diskettes were turned upside and the solvent was allowed to evaporate for 1, 3 and 5 min before weighting the samples. A similar experimental procedure is reported in the literature to measure the swelling behavior of PDMS in toluene [16,17].

**ii) Experiment\_2:** To further investigate any practical implications of the fast rate of solvent evaporation we designed another class of experiments according to the following procedure (sketched in Fig. 1). After dispensing a few drops (nearly 1.0 mL) of DCM on a clean silica glass slide, PDMS diskettes were put in contact with the wet region of the silica glass slide for 1, 3 and 5 min

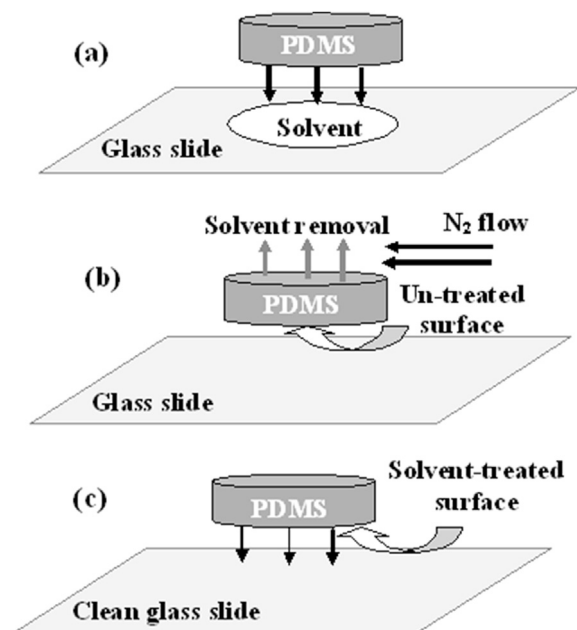


Fig. 1. (a)-(c) Sketch of the several steps of the preliminary experimental method applied to assess the influence of DCM volatility on the weight-gain of PDMS.

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