



Protocol of thermal aging against the swelling of poly(dimethylsiloxane) and physical insight in swelling regimes

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ABSTRACT

In this paper, an unprecedented inspection of the effects of thermal aging on swelling and wettability of PDMS as a function of the interplay between temperature (from 100 to 180 °C) and duration (from 20 min to 24 h) of the treatment is presented. Dichloromethane was used as sample swelling solvent and the swollen weight was measured by a method properly designed to avoid underestimation related to the volatility of the solvent.

This study: i) provides practical guidelines for performing optimal thermal aging treatments of PDMS against swelling (for example, in microfluidic platforms to synthesize cancer tracers), and ii) contributes to the fundamental understanding of the swelling process of soft matter systems. An interpretative model has been developed of the observed swelling regimes based on heating-promoted crosslinking and chain reorganization (inter-chain mobility) at short-lasting heating timescales and conformational changes (intra-chains transitions) at long-lasting heating timescales.

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1. Introduction

Since its introduction in the 1990s, the rubbery polymer poly(dimethylsiloxane) (PDMS) [1] has become the preferred material for the fabrication of micro- and nano-fluidic as well as biomedical multi-functional platforms [2–5] owing to its many advantageous properties (low cost, optical transparency, polymerization at low temperature, thermal and chemical stability, aging resistance, biocompatibility, easy surface activation by chemical and physical methods, permeability to liquid and gases, flexibility, tunable adhesion and bonding to many kind of substrates, oxidative stability and low glass transition temperature) [6] and easy prototyping in soft-lithography technology [7–10] and custom 3D-printed stamps [11].

Despite its numerous advantages, PDMS exhibits a few weaknesses, such as high compliancy, high sticking and permeability-induced swelling attitude, that introduce serious limitations in applications involving (i) high aspect ratio PDMS channels crossed by pressure-driven liquid flows [12–15], (ii) PDMS demolding from

masters in double casting microfabrication process [16,17] and (iii) contact between PDMS and weakly compatible solvents (commonly, nonpolar or only slightly polar solvents) [18]. This adverse interaction is particularly limiting in application areas, such as microfluidics and diagnostics, where chemical processes and analyses are performed in PDMS-based elements (channels and reaction chambers) exposed to organic solvents that can deform and damage pristine PDMS leading to disruption of microscale features, leaks, chemical contaminations and loss of active solute [18]. Despite such drawbacks, the advantages offered by PDMS substrates and components over harder materials in terms of micro- and nano-fabrication outweigh the disadvantages and have prompted searching of strategies to mitigate or overcome such disadvantages.

Among the numerous attempts to solve for the mentioned weaknesses of PDMS [19–32], post-cure heating (thermal aging) and/or changes of the standard composition [33–37] let avoidance of chemical treatments, specific solutions, multistep approaches and the introduction of foreign materials to the host PDMS.

Indeed, PDMS polymerizes following first mixing of a pre-polymer (vinyl-terminated $-\text{Si}(\text{CH}_3)_2\text{O}-$ repeating units, termed base) with a cross-linker (a mixture of a metal catalyst and short monomers with Si-H silicon hydride groups, termed curing agent)

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and then heating of the two-component liquid mixture [38]. In principle, a one-to-one reaction between Si-H and CH-CH₂ (vinyl) groups along the chains of the base would involve a perfectly cross-linked network. In practice, because of the intrinsically low cross-link densities of PDMS [18,39,40], the reference weight ratio base-to-curing agent is different from 1:1 and is suggested by the producer as the one optimized to assure a minimal amount of defects and unreacted low molecular weight chains. Hence, changes in the standard PDMS composition (usually 10:1 mass ratio of base-to-curing agent) can affect inter-chain bonding and density of free volumes of the polymer network with consequences on stiffness, hardness, permeability and degree of swelling (the amount of imbibed solvent) [34,41–46].

Since the presence of freely diffusive chains of the curing agent is inherently unavoidable in the standard polymerization of PDMS (i.e., 10:1 mass ratio of base-to-curing agent and polymerization for tens of minutes (35, 20 or 10) at high temperature (100, 125 or 150 °C, respectively) or 48 h at room temperature), post-cure heating acts as an extended curing process that can control order and density of the polymer network [41,47] as well as influence the hydrophobic recovery of oxidized PDMS48 and make PDMS less hydrophobic than its as-prepared counterpart [33].

Since changing the standard polymerization conditions introduces imbalance in the optimal quantity of the reactive groups, resulting in defects and dangling bonds of the crosslinked network, it could be better to act on PDMS swelling attitude by applying a moderate post-cure thermal treatment that doesn't degrade the polymer [33], avoids preparing multiple compositions as well as increases density, by reduction of free volumes, and cross-linking of the polymeric network [34]. In practice, post-cure treatment is also more convenient with respect to the assembly of PDMS microchips since the adhesion and compliancy properties of just cured PDMS are preserved during the bonding and assembly steps [49]. Hence, post-assembly thermal aging can enhance the chemical endurance of PDMS without structural damage or de-sealing of the assembled device, which is beneficial for multiple usage and long-term durability of devices.

Previously reported thermal aging treatments for PDMS have relied upon a specific choice of conditions without a clear motivation for such a choice and a lack of a systematic consideration of intermediate possibilities or the occurrence of a threshold for the swelling behavior versus temperature and duration of the treatment. For example, it was reported thermal aging i) at 85 and 200 °C for 1 and 3 days by ramping the temperature to 300 °C for 120 min and keeping it at 300 °C for 30 min [33,34], ii) at 150 °C for 2 h [50], iii) at 100 °C for 2, 4, 7 and 14 days [48], iv) at 190 °C for 2 h [51] and v) at 85 °C over 3 days as well as at 250 °C for 30 min [52].

Recently, the interplay between temperature and duration of the thermal aging of PDMS heated at 100, 120 and 150 °C for short-time timescales (20, 30, 45, 60 min) as well as at 150 °C for 3, 10, 20, 24 and 48 h has been investigated [49]. Swelling tests were performed for PDMS channels heated at 150 °C (for 24 and 48 h) and 180 °C (for 24 h) that confirmed the effectiveness of long-lasting thermal aging in improving the chemical resistance of PDMS. Although practical guidelines were introduced for performing a post-cure long-term high-temperature treatment of PDMS channels effective in terms of reduced swelling degree, a comprehensive investigation of the evolution of the swelling attitude of PDMS depending on the conditions of the heating treatment (temperature and long-lasting versus short lasting heating) was not conducted. Moreover, no experimental evidence of the occurrence of different swelling regimes nor any insight in their occurrence were provided.

In this paper, the results of a systematic investigation of the effects of tuning the thermal aging conditions on the swelling

attitude of PDMS in contact with dichloromethane (also known as methylene chloride or briefly DCM) and their relationship with the chemical-physical structure of the polymeric network are presented. The findings of this comprehensive study demonstrate the occurrence of different swelling regimes for any sampled temperature (120, 150 and 180 °C). An almost constant swelling ratio was observed over heating interval lasting from a few hours to 20 h. This swelling ratio decreased exponentially for heating beyond 21 h. This experimental result is unprecedented and provides practical guidelines for performing optimal thermal aging treatment of PDMS as a function of swelling.

An interpretative model has been formulated that relates swelling, wettability and PDMS network structure in terms of heating-promoted crosslinking and chain reorganization (inter-chain mobility) at short-lasting (from 20 to 45 min) heating timescales and conformational changes (intra-chains transitions) at long-lasting (from 1 to 24 h) heating timescales.

While DCM is a very volatile solvent which severely swells PDMS [18], it may be expected that the studied conditions will be applicable for reducing swelling of PDMS with respect to solvents, less aggressive than DCM, such as toluene [18] and would require different calibration of temperature and duration in the case of solvents swelling PDMS more severely than DCM (such as hexane) [18]. The swelling behavior of both pristine and thermally aged PDMS has been determined by measuring the swollen weight accurately according to a method able to avoid any weight underestimation related to the volatility of the solvent [53].

2. Experimental

2.1. Materials

PDMS polymer was prepared by the two-component kit (base and curing agent) heat curable commercial PDMS Sylgard[®] 184 (Dow Corning Corporation). The polymer base and the curing agent were thoroughly mixed with the standard weight ratio 10:1 suggested by the producer for providing optimal conditions of cross-linking and minimal amount of defects in the network structure. The resulting liquid mixture was degassed in a vacuum chamber, then poured into a cleaned Petri dish and thermally cross-linked at 65 °C for 2 h. The cross-linked PDMS was peeled off and cut to obtain cubes with side of nearly 2-mm to be subjected to experiments of thermal aging and swelling as well as 1 cm × 1 cm plates to perform attenuated total reflection (ATR) Fourier transform infrared (FTIR) and wettability tests (see below).

Dichloromethane (DCM) purchased from Sigma Aldrich, was considered as example-solvent swelling PDMS. Prior to immersion in DCM for 10 min, all of the PDMS cubes were weighted and their mass was estimated to be (0.10 ± 0.01) gr without significant weight loss due to the heating treatment.

2.2. Thermal aging experiments

Thermal aging experiments were performed in two sets by probing different temperatures and heating timescales. First, the PDMS samples were heated at 100, 120 and 150 °C for 20, 30, and 45 min to select the more effective conditions of temperature for further experiments. In the second step, based on the findings of such preliminary investigation, heating temperatures of 120, 150 and 180 °C combined with thermal treatments lasting from 1 to 24 h were tested. Notably, 200 °C is the upper limit suggested by Dow Corning as curing temperature and thermal decomposition of PDMS was reported at temperatures exceeding 200 °C [54,55]. Heating at 150 °C for 48 h was also performed for comparison with the swelling performance treatment at 150 °C for 24 h. According to

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