

Thermal aging and reduced hydrophobic recovery of polydimethylsiloxane

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Abstract

Rapid prototyping of polydimethylsiloxane (PDMS) is frequently used to build microfluidic devices. PDMS is inherently hydrophobic; however, the surface can be temporarily rendered hydrophilic by exposing the surface to an oxygen plasma. Hydrophilic microchannels are sometimes advantageous over hydrophobic microchannels due to increased cell adhesion to hydrophilic surfaces or less air bubble trapping during filling with aqueous solution. However, the hydrophilic surface is unstable and low molecular weight (LMW) chains diffuse from the bulk of the PDMS and cover up the thermodynamically unstable surface. However, eliminating LMW species through thermal aging allows the hydrophilic surface to be more permanent.

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1. Introduction

Polydimethylsiloxane (PDMS) is often exposed to an oxygen plasma to render its surface hydrophilic and form permanent bonds between activated surfaces [1]. In certain instances, hydrophilic surfaces promote cell adhesion and facilitate channel filling with aqueous solutions making the hydrophilic surface advantageous. The surface can also be selectively activated by masking with glass or a PDMS stencil creating a precisely defined pattern of hydrophilic and hydrophobic surfaces on the same substrate. However, the thermodynamically unstable hydrophilic surface regains its hydrophobicity in less than an hour [1], as a result of low molecular weight (LMW) chains diffusing to the surface [2,3]. The LMW species are either uncrosslinked linear PDMS chains or residual crosslinking agent. These LMW species can be volatilized and removed from the bulk through

thermal aging. A PDMS network without LMW species will retain its hydrophilicity for a much greater time. This paper describes experiments to quantify the hydrophobic recovery with time as a function of extended curing. The Sessile drop method will be used to measure the contact angle of a drop of water to quantify the hydrophobic recovery rate of the PDMS specimens with respect to time following oxygen plasma activation.

2. Methods

2.1. Extended curing

Samples (3 in. diameter, 5 and 2.5 mm thick) were prepared from Sylgard 184 kits and cured at 85 °C for 100 min on a hotplate. These samples were removed from the hotplate and thermally aged in an air oven at 100 °C for 2, 4, 7 and 14 days. The samples were hung in the oven to ensure all the surfaces of the sample were exposed to the oven environment. Following thermal aging, the samples were exposed to

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oxygen plasma and the contact angle was measured daily for 14 days to monitor the hydrophobic recovery rate.

2.2. Hydrophobic recovery analysis

Once the thermal aging was completed, the samples were placed in a reactive ion etching system and exposed to an oxygen plasma at 70 W for 12 s. The time and energy was chosen based upon standard laboratory practices. Previous experiments report bending the activated surface will increase the hydrophobic recovery [3]; therefore, before plasma activation each specimen was mounted on a 3-in. pyrex wafer to prevent the surface from bending. Upon completion of the plasma activation the specimen was exposed to a 5 μL droplet of water. Each contact angle was measured in three different locations and the droplet was blown off the surface with nitrogen following the measurement. The locations of the measurements were marked to ensure the surface analyzed had never been exposed to water. The contact angle was analyzed using a goniometer (Ramé-Hart, Inc., Model 200-00) over a period of 14 days.

3. Results and discussion

A hydrophobic PDMS surface can be rendered hydrophilic through exposure to an oxygen plasma. However,

the PDMS regains its hydrophobicity within minutes. Recent work investigated this phenomenon [2,3] and hypothesized that LMW PDMS chains migrate to the surface to cover up the thermodynamically unstable hydrophilic surface. Therefore, a polymer with fewer LMW species would remain hydrophilic longer. This hypothesis was tested with two thicknesses of PDMS (5 and 2.5 mm) by thermal aging the samples for 0, 2, 4, 7 and 14 days and then treating with oxygen plasma. The contact angle was then analyzed using a goniometer (Ramé-Hart, Inc., Model 200-00) daily as shown in Fig. 1.

These results show samples cured under standard conditions (85 °C for 100 min) without extended thermal aging recover their hydrophobicity in roughly 15 min, while thermally aged samples never fully regain their hydrophobicity under the times investigated. Plotting the time to reach 45° with respect to extended curing time allows a clearer visualization of the differences between the two thicknesses of the samples. A contact angle of 45° represents the midway point between hydrophilic and hydrophobic. The thinner samples recovers quicker than the thicker samples as shown in Fig. 2. The reason for the difference in recovery rates is most likely due to a larger depot and longer diffusion times for the LWM species in the thicker samples.

The hydrophobic recovery of a hydrophilic PDMS surface can be extended from minutes to days following a thermal aging step. In addition, the volume of PDMS also plays in a role

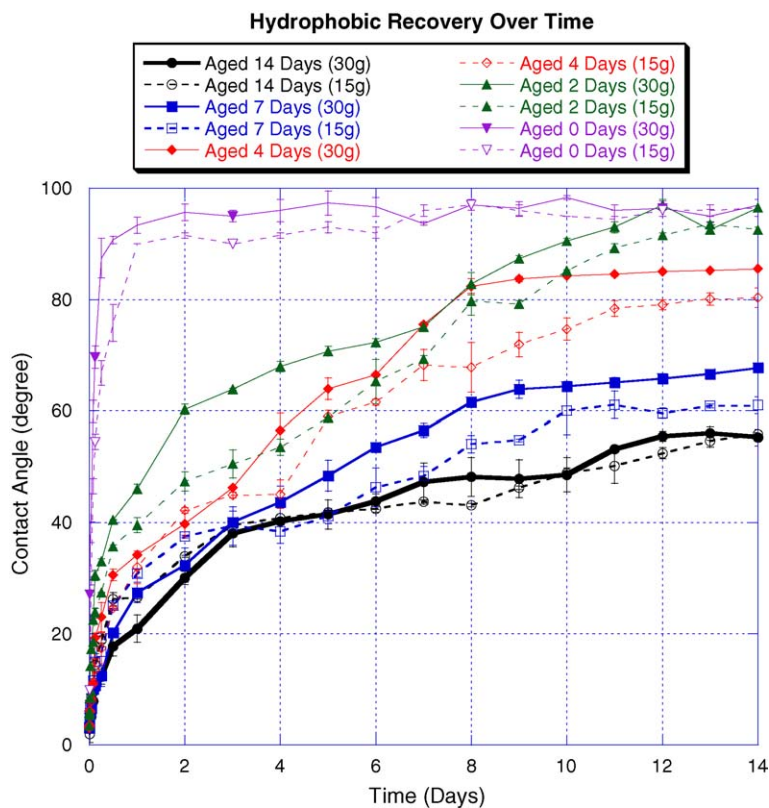


Fig. 1. Plot of contact angle with respect to time for oxygen plasma exposed PDMS. Each data point is the mean of five measurements taken in different locations. The inset plot shows the time points up to 14 days for both the 5 mm (solid) and 2.5 mm (dashed) samples.

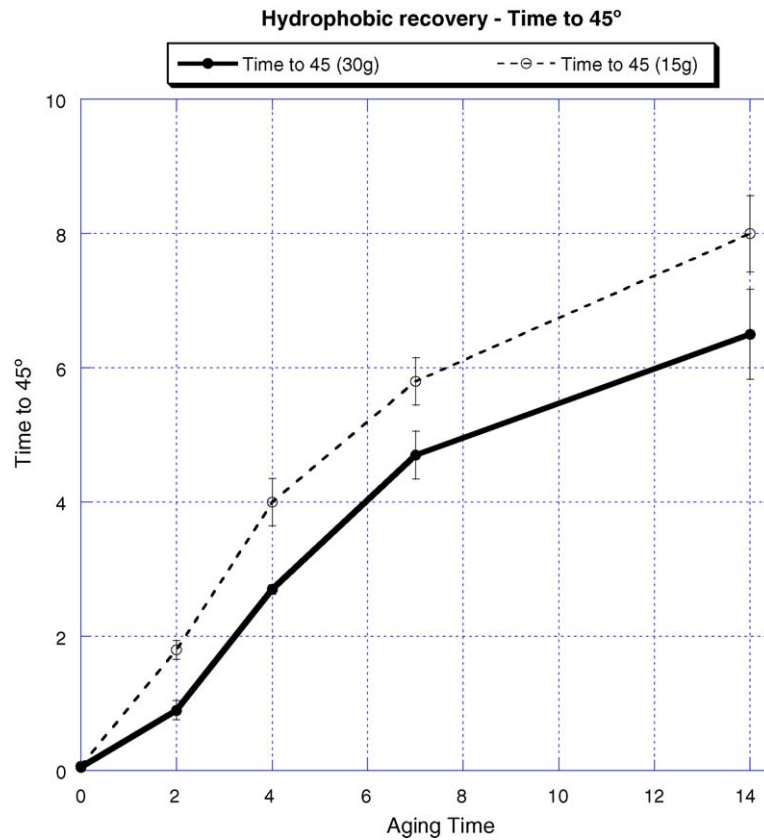


Fig. 2. Plot of time when the contact angle reached 45° after plasma exposure with respect to each samples extended curing time.

in the hydrophobic recovery since larger volumes have larger reservoirs of LMW chains. Therefore, the thermal aging can be tuned to prevent hydrophobic recovery by adjusting the length of the aging based upon the volume of the PDMS. The thermal aging temperature could also be increased to achieve the same effect with less time; however, the temperature should not be more than 200°C since the PDMS will begin to break down above this temperature.

4. Conclusions

Thermal aging delays the hydrophobic recovery of oxygen plasma activated surfaces. This may be advantageous in certain applications requiring hydrophilic surfaces. This

hydrophilic surface could be further stabilized by storing in nitrogen. These findings prove promising for applications requiring a surface patterned hydrophilicity.

References

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