

Quantification of Hydrophobic Recovery and Temporal Bonding in Polydimethylsiloxane

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Polydimethylsiloxane is used ubiquitously in micro fluidics both as a mold and as a device in and of itself due to the polymer's distinct physical and chemical properties. This elastomer is intrinsically hydrophobic due to the methyl group that is a part of its chemical backbone. Hydrophilicity is induced by plasma activation but is short lived as this elastomer regains its hydrophobic nature as uncrosslinked PDMS chains start to reorient back to the surface. Quantifying the bonding time frame will prove invaluable for any and all research applications that revolve around PDMS.

Introduction

Polydimethylsiloxane (PDMS) is a polymer, specifically an elastomer with repeating monomers of Silicon Oxide and a methyl group - SiO(CH₃). This polymer is used extensively in a variety of fields due to its unique properties. It is the material of choice for micro fluidic devices.

The properties that make it so ideally suited to the field of micro fluidics are its surface chemistry, inherent optical transparency and its spontaneous adhesion onto flat surfaces.¹ The polymer's oxygen permeability and biocompatibility further allow it to be extensively used in the multidisciplinary field of biomedical engineering. PDMS replicates any form of submicron features allowing micro fluidic chips to be easily fabricated. PDMS microchips have been used for capillary gel electrophoresis¹ and have in turn proven to be a hundred and ten percent more efficient than standard industrial techniques currently employed for the same process. Other explorative research with PDMS has uncovered the polymer's uses in a glass hybrid micro reactor for cell free protein synthesis¹ which incorporates indium tin oxide transparent electrodes. One of the newer uses of PDMS is in the making of MLO (Multi layer bioreactor with an Oxygen Chamber) which is essentially as micro scale bioreactor which can achieve cell densities of $4 \times 10^7 \frac{\text{cells}}{\text{cm}^3}$ which is comparable to macro scale bioreactors.²

A majority of these applications are based on the polymer's adhesion to flat surfaces. Based on previous work, it is reasonable to hypothesize that this adhesion is only achieved when the polymer is hydrophilic as opposed to its intrinsic hydrophobic nature. In order to make PDMS hydrophilic, limited exposure to oxygen plasma will induce hydrophilicity for short periods of time.³ Oxygen plasma activation adds a hydroxyl group to the surface of the polymer resulting in the formation of a silanol group (SiOH). This happens when hydrogen atoms are first removed from the polymer after which the carbon radicals in the polymer combine with the plasma radi-

cals resulting in a functional hydroxyl group.⁴ Recent research also indicated that the surface of PDMS is permanently scarred.⁴ This alteration of the surface chemistry is what causes the change in the contact angle that has been widely documented. This window of hydrophilicity is short lived as PDMS regains its hydrophobic nature within an hour or so after plasma activation. This phenomenon is termed 'hydrophobic recovery' and is attributed to (a) The reorientation of non polar groups from the bulk to the surface (b) the diffusion of low molecular weight (LMW) chains from the bulk to the surface (c) condensation of the surface hydroxyl groups.⁵ LMW species are un-cross linked linear PDMS chains or residual cross linking agent left in the bulk of the polymer.³ The hydrophobic recovery of PDMS does repair the surface alterations caused by the plasma activation but the slab will never regain completely its original chemistry.² In other words, PDMS will never regain its original hydrophobicity.

Quantifying this time window of hydrophilicity and studying the effects of aging after plasma activation will reduce the ambiguity surrounding the bonding time frame of PDMS and will also clarify the effect that ageing after plasma activation has on the sample. If this form of ageing extends bonding time frames; a subsequent advantage will provide researchers longer periods of time during which the advantages of having a hydrophilic surface on an intrinsic hydrophobic substance can be exploited. Specifically in the case of micro fluidics, hydrophilic surfaces have been shown to increase cell adhesion and decrease air bubble trapping for aqueous solutions when compared to hydrophobic surfaces.³ The hydrophilicity also helps increase electro osmotic flow (EOF) leading to ease of liquid filling in micro channels.⁴

The goals of our experiment are threefold (1) Quantify bonding in PDMS after plasma activation (2) Determine if there is a correlation between bonding and the hydrophilic nature of the surface.

Methods

A master slab of PDMS (using Sylgard 184 silicone elastomer kit) was created for each experiment using standard protocols. A ratio of one part activator/cross linker to ten parts base was added by weight and the mixture was then carefully mixed until an even texture was obtained. The compound was then placed in a vacuum desiccator for ten minutes in order to effectively remove all air bubbles introduced during mixing. After ten minutes any air residual bubbles on the surface was easily removed by light blowing with compressed air canisters. Fifteen grams of the polymer is then poured into a 3 inch Petri dish to obtain a thickness of 0.4 cm. The Petri dish must be uniform in shape with no structural abnormalities in order to ensure proper spreading of the polymer. Once the polymer in the Petri dish settled, the dish was placed on a perfectly level hot plate for two hours at seventy five degrees centigrade. Care was taken to ensure that the hot plate was level primarily as a level hot plate would ensure the uniform spreading of the polymer which in turn allows the PDMS slab to have a uniform thickness throughout - as previous research indicates varied thickness affects the rate of hydrophobic recovery.³ After the allotted two hours, the polymer was then gradually cooled to room temperature over a period of five to ten minutes. Vinyl gloves were used while handling the PDMS in order to prevent contamination of the surface with fingerprints. A stainless steel knife was used to cut out a six by six centimeter square out of the original slab. This square was then further cut into squares measuring two centimeters by two centimeters. The surfaces were then cleaned with cellophane tape and compressed air in order to remove any form of contaminants that normally adheres to the surface. The sample once cleaned was handled only by tweezers. The contact surface area between the tweezers and the samples was also kept to an absolute minimum.

Experiment: Quantifying Bonding in PDMS after plasma activation

In experiments involving contact angle, a microscope (Digital Blue QX - 5) was modified in house (Figure 1(b)) to serve the same ends as a goniometer. A PDMS slab was placed on the stage facing a microscope on its side. A one micro liter droplet of deionized water was placed at the edge of the slab and a horizontal snap shot was taken of the droplet and its general conformation. The contact angle was then measured using a NIH software known as ImageJ (Figure 1(a)). When capturing these pictures care was taken to ensure that the entire droplet was kept in frame so that the software could accurately render the contact angles based on angles from both contact points.

For all experiments involving bonding samples were carefully handled in order to prevent any form of non

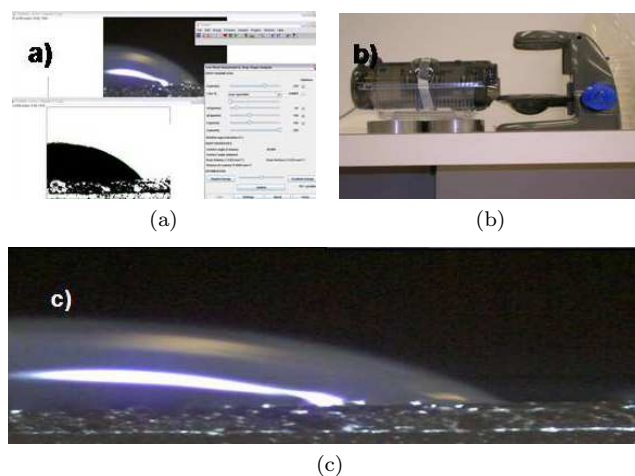


FIG. 1: a) Screenshot of ImageJ; b) In house instrument (replacement goniometer); c) $1\mu L$ water droplet on PDMS surface.

linear surface contortion, as bending has been shown to increase the rate of hydrophobic recovery.³ Samples were bonded to pre-cleaned 2.5×2.5 cm microscope slides that were also exposed to oxygen plasma to eliminate any form of organic residue on its surface. Once bonded, the sample was left for eight to ten hours in order to ensure proper bonding. Bonding was tested by physically trying to extricate the PDMS from the slide surface. Based on the difficulty of extrication and the residue on the slide after removal, a quantitative number from zero to ten was assigned to indicate the strength of the bonding (ten being the strongest bond and zero the weakest). Every step outlined thus far was carried out in a class one thousand clean room to eliminate dust as a possible confound during the course of experimentation.

Experimental

For the quantification experiment, the samples were not aged before or after plasma activation. The duration of bonding was measured after plasma activation to evaluate the length of bonding time without any aging/variable manipulation. The time frames chosen were from one to six hours (This was chosen after several previous experiments to accurately determine the right time frame to study. A larger time frame than the one chosen would have resulted in no bonding and hence it would not have been possible to determine the exact time frame that the ability to bond was lost or the relationship between contact angle and bonding). A different set of replicates were used for the same time frame to measure the contact angle. The more hydrophobic the surface is, the higher the contact angle. Both these results (bonding vs time and contact angle vs. time) were graphed for the better discernment of inherent patterns.) This experiment was repeated several times and till each time frame

for bonding and contact angle had a total of ten samples. This was done to reduce the variability obtained and to ensure proper statistical significance.

Results

Since plasma activation is central to all our experimentation, the first experiment that we carried out was the quantification of the plasma chamber. The experiment was carried out in hopes of finding specific region/regions in the chamber that received uniform distribution of plasma each time the machine was run. Conclusions about best regions were drawn based on contact angle measurements that we obtained for samples 3 hours after plasma activation. We were looking for regions which had the lowest hydrophobicity/ highest hydrophilicity and thus the ones with the lowest contact angle (Figure 3). Based on the results we obtained, we then used only those regions of the plasma chamber for the rest of our experimentation in hopes of eliminating the confound that presented itself in the form of non uniform plasma activation (this may be due to a variety of uncontrollable factors such as humidity, pressure variations from 98 - 100 *kPa* etc).

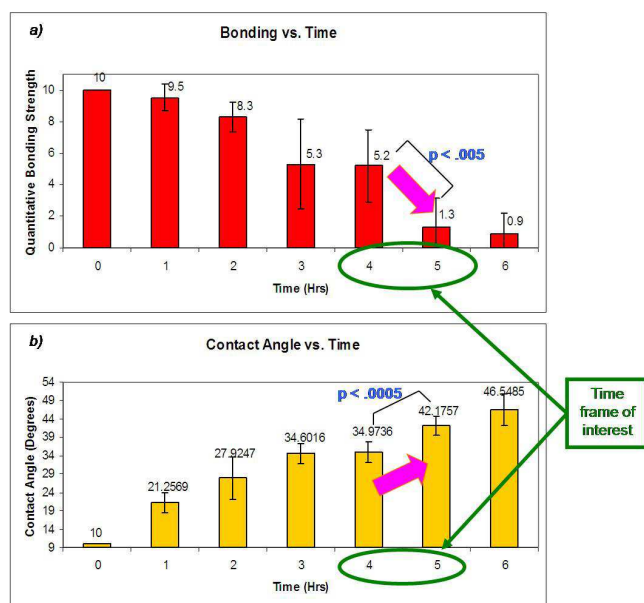


FIG. 2: a) Bonding time with respect to time. Ten samples were used for each time frame; b) Contact time versus angle.

The control experiment provided data that was scientifically unexpected. Empirically it was determined that PDMS lost its ability to bond about three to five hours after plasma activation. A careful look at the bonding during those time frames showed an interesting trend. Between four and five hours, there was a sudden loss in bonding strength (Figure 2a). When the contact angle graph is studied carefully; between four to five hours after

plasma activation, the contact angle shows sudden spike (indicating a sudden increase in hydrophobicity). This unusual spike is sharp and against the gradual increase that is observable in the graph up to that point (Figure 2b). When the two graphs are overlaid, it becomes clear that the sharp spike in hydrophobicity occurs during the exact same time frame during which bonding is lost.

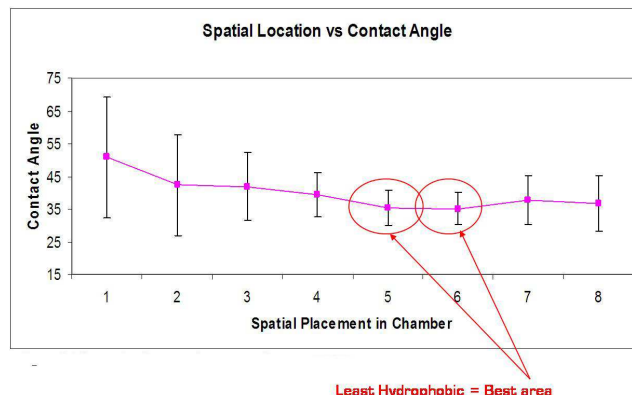


FIG. 3: Plasma chamber spatial contact angle measurements.

Discussion

From the overlaid graph, the following is definitively clear. (1) Since the bonding graph and the contact angle graph show the exact same trends except in reverse; bonding is inversely proportional to the hydrophobicity of PDMS; (2) Loss of bonding occurs between four to five hours; (3) The same unknown surface chemistry phenomenon is responsible for the sudden spike observed for both graphs. Theoretically it could be attributed to the sinusoidal structures that form on the surface of PDMS. These sinusoidal structures are believed to be formed as the oxidized surface of the PDMS has a lower coefficient of thermal expansion than the unutilized bulk PDMS.⁶ The cooling that results after plasma activation places the oxidized layer under compressive stress resulting in the formation of sinusoidal structures which act as entropic method of relieving that stress placed on the surface. However this line of reasoning is completely speculative but is probable as only a change in the composition of the sample's surface chemistry can account for the sudden spikes observed in the data.

Another general trend observable in the data is the low contact angle six hours after plasma activation which indicates that hydrophobic recovery in fact takes a much longer time than that which was suggested by previous reports.³ The variability in the data observed is due to the inherent inconsistency that presents itself with the remaking of PDMS samples from a day to day basis. Even streamlining of protocol cannot eliminate the variable LMW chains that result from personal changes in the way the sample is both stirred and made. Humidity

along with aging conditions has also been shown to affect the behavior of the polymer.⁵

Conclusion

PDMS is truly a versatile polymer whose varied applications make it a valuable tool to the research community. With the quantification data obtained from this experiment, researchers can now definitively change production methods of micro chips, biochemical assays etc which uses PDMS to maximize the hydrophobicity that they would want to have with respect to time. Furthermore with this data, bonding can be carried out at the

right time after plasma activation for desirable effects before the hydrophobic nature completely sets back in after which bonding will not be possible. From the experiments carried out thus far it is clear that PDMS loses its ability to bond between four and five hours after plasma activation and that hydrophobicity is irrevocably responsible for the loss in bonding.

Acknowledgements

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