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Light Observation in Polymer:A Study of Silicon-Based Organic Polymer Using Visible Spectroscopy

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Abstract: As advancement in nano laboratory on chip is moving at the speed of light, microfluidic devices which consist of Polydimethylsiloxane (PDMS) are used extensively for the production of fluidic devices through the use of various structural engineering and on-chip photo polymerization and photolithography. However, in the current existing methods, the integration of device in confinement of the photochemical structure is impaired by lack of proper consideration of the light absorption inside the PDMS elastomers, which if not taken care of properly, a heat will be generated there causing the sensing element behaving abnormally . Hence, we present a study on the degree of light absorption in PDMS microfluidic devices and also presented is the current state of the art by studying recent advancement on hydrophilization and hydrophobic recovery of PDMS by oxygen plasma, thermal aging technique and effects of functional group modifications on the conformational behaviour of chains at the interface with brief presentation on chemistry of the creation of silanol groups on the active surface and presentation of brief summary of some important properties of Polydimethylsiloxane (PDMS).

Key words: PDMS; Photoligraphy; elastomers; Thermal aging; functional group

INTRODUCTION

Poly (dimethylsiloxane) (PDMS) is a silicon-based organic polymer that is widely used in microfluidic fabrication after glass. However, unlike other plastic, PDMS acts like an elastic solid. The tensile strength of PDMS can be up to 7.1 MPa, however, the number can be varied with preparation conditions. The chemical formula of PDMS is form of a number of repeating monomer $[SiO(CH_3)^2]$ units. PDMS is one of the thermoset polymers which will polymerize or crosslink once heated. The shape of the PDMS is relied on the mould used for the polymerization. Therefore, by having the master mould, PDMS can be used in casting shapes and replicas. As this material is generally inert, non-toxic and easy to use, thus it was utilized as the platform for microfluidic devices. PDMS has been applied in membrane technology for a long time as it is highly permeable to oxygen and also biocompatible (Duffy, D.C., *et al*., 1998). The first report about PDMS used in microfabrication was in 1997 by Effenhauser, where this flexible micro device was used for single DNA detection and analysis (Fiorini, G.S., *et al*., 2003; Kangil Kim1, 2010; Lee, J.H., *et al*., 2008; Kevin S. Lee, Rajeev J. Ram, 2009; Mair, D.A., *et al*., 2006). Since then PDMS has dominated the fabrication of microfluidic device (Eijkel, J.C.T., *et al*., 2004; Jong, J.D., 2006; Effenhauser, C.S., *et al*., 1997; Jo, B.H., *et al*., 2000; Ng, J.M.K., *et al*., 2002). Rapid prototyping has been developed and introduced for the fabrication of microfluidic device using PDMS (Chow, W.W.Y., *et al*., 2006), where it took no longer than 24 hours to make a ready to use device. PDMS can bond irreversibly to glass by oxygen plasma treatment on the surface. Oxidizing the surface of the PDMS and glass creates $-O_nSi\ (OH)_{4-n}$ which allow irreversible covalent siloxane bonds between the PDMS substrates by a reaction (Chaudhury, M.K. and G.M. Whitesides, 1992; Cha, J., *et al*., 2006; Patrito, N., *et al*., 2007; Chow, W.W.Y., *et al*., 2006). PDMS was reported to be usable as an adherence agent for bonding other plastic (Patrito, N., *et al*., 2007) and has also successfully bonded to polystyrene substrate (Chow, W.W.Y., *et al*., 2006). PDMS was often used for making master replica or moulding due to the ease of handling and inert to other polymers such as casting acrylic glass and thermoset polyester (Effenhauser, C.S., *et al*., 1997). Due to high back pressure from the pump and pack column, this material will expense and deform. Therefore, solid and hard polymers are the alternatives. However, as PDMS is inert to chemicals, PDMS was used in preparing replica for the polyester casting

A. Surface Treatment by Thermal Aging Technique:

Thermal aging on Polydimethylsiloxane (PDMS) is often done exposing it to an oxygen plasma to render its surface hydrophilic and form permanent bonds between activated surfaces (Wu, H., 2005). In certain instances, hydrophilic surfaces promote cell adhesion and facilitate channel filling with aqueous solutions making the

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hydrophilic surface advantageous, the nature of hydrophobic PDMS surface can be rendered hydrophilic through exposure to an oxygen plasma. However, in the hydrophobic recovery since larger volumes have larger reservoirs of LMW chains. Therefore, the thermal aging can be modified 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 ^{0}C (Bubendorfer, A.,) since the PDMS will begin to break down above this temperature (Wu, H., 2005; Bubendorfer, A.,), it was reported by Bubendorfer, A., that the PDMS network without low molecular weight species will retain its hydrophillicity for a much greater time and it further found out that the samples cured under standard conditions (85 ^{0}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 as shown in (fig. 2a). the PDMS regains its hydrophobicity within minutes. Another important information was obtained the same for the verification of this phenomenon (Jo, B.H., *et al*., 2000; David T. Eddington, 2006) and the they claimed that low molecular weight PDMS chains migrate to the surface to cover up the thermodynamically unstable hydrophilic surface. Where, a polymer with fewer low molecular weight species would remain hydrophilic longer. This claim 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

B. Surface Treatment by Oxygen Plasma:

Plasma treatment of PDMS is a useful way of increasing wettability for its enhanced adhesion and 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 oxygen plasma. Hydrophilic microchannels are sometimes advantageous over hydrophobic microchannels due to increased cell adhesion or increase in electro osmotic flow (EOF) leading to ease of liquid filling in microchannels. However, the hydrophilic surface is unstable and that low molecular weight (LMW) chains diffuse from the bulk of the PDMS and cover up the thermodynamically unstable surface. This is one reason for the hydrophilic instability of PDMS. Else where a study was report on bonding strength and surface wettability of PDMS, the self-assembled layer of silane radicals was used for the bonding of PMMA and PDMS.In order to find the factor affecting the bonding strength, and analysis was conducted on the surface using the contact angle measurement and the XPS. The analysis results confirmed that the oxygen plasma treatment of PMMA, the self-assembled layer formation using 3-APTES, and corona discharge treatment of the self-assembled layer are required (fig.3). The samples were treated in various surface treatment combinations and the tensile bonding strength and the leakage bonding strength were measured. The bonding strength test results prove that the optimal process is to form the self-assembled layer on the PMMA and PMDS surface treated with oxygen plasma, the tensile bonding strength obtained from the optimal bonding process is 2.5 MPa and this value is larger than those reported by others as claimed by (Kangil Kim1, 2010).

Important Properties of Polydimethylsiloxane (PDMS):

C. Permeability:

Permeability is the product of *solubility* (*partition*) of a gas in polymer and its *diffusivity*. Permeability of siloxanes is much higher than the one of most other elastomeric materials (David T. Eddington, 2006). The permeability of PDMS with O2 is 6 cm3 (STP) cm/(cm2·s·cm·Hg), while with N2 it is 3.1 cm3(STP)cm/(cm2·s·cm·Hg). That gives a ratio of the Permeabilities 1.9 (O2/N2) (Fiorini, G.S., *et al*., 2003). With higher temperatures, the diffusion is faster, the solubility lower, and the permeability decreases [261]. Further reading on diffusion and partition coefficients can be found in (David T. Eddington, 2006). Although permeability is advantageous for instance in gas separation membranes, artificial skin coatings for burns,soft contact lenses or oxygenators, in Microfluidics analytical devices it may hamper the results for instance due to vapour losses or changes of pH due to CO2 diffusion (Jo, B.H., *et al*., 2000). Evaporation is a threat to applications handling minute volumes of samples. Some groups try to avoid evaporation by pre-saturating the PDMS with a liquid and/or changing the mixing ratio of the base and curing agent (Yevgeny Berdichevsky, 2004), which also changes the stiffness of the PDMS. Another group has reported coating (e.g. polyethylene) of PDMS, which reduces the evaporation problems, but which typically increase the rigidity of the material (Kangil Kim1, 2010). Most organic solvents are soluble in bulk PDMS and swell the polymer (David T. Eddington, 2006). The fig1 below further illustrate the permeability of PDMS that could permit interaction between the inner structure with the environment but could have negative impact on the devices performance due heat development.

D. Elasticity:

Good elasticity is given by the fact that PDMS exists in a highly coiled conformers. As the material is stretched, the polymer unwinds and as the tension is released, the polymer recoils. Elasticity thus relies on the ability of adjacent polymer regions to slip past each other (Mair, D.A., *et al*., 2006). The elasticity is directly

influenced by the amount of cross linking (Mair, D.A., *et al*., 2006). The more the PDMS is cross linked, the less it is elastic (Mair, D.A., *et al*., 2006). Elasticity serves well for instance in applications, where the material should be bended or twisted, however, in Microfluidics, it is a both-sided coin. Depending on the pressures used for the fluid transport, the walls of the micro channels deform and therefore, accommodate part of the pressure and thus, decrease the flow-rate in the area. The degree of deformation is given by the pressure on the wall, the degree of cross-linking of the polymer, but also by the thickness of the wall. This property has to be taken into account in systems, where volumes should be determined in-line or where constant flow-rate is of essence (Mair, D.A., *et al*., 2006). In high aspect ratio structures, the PDMS tends to stick onto adjacent structures as it cannot support itself sufficiently due to its elasticity. The elasticity can be on the other hand utilized for various PDMS based pneumatic valves (Kangil Kim1, 2010) and pumps.

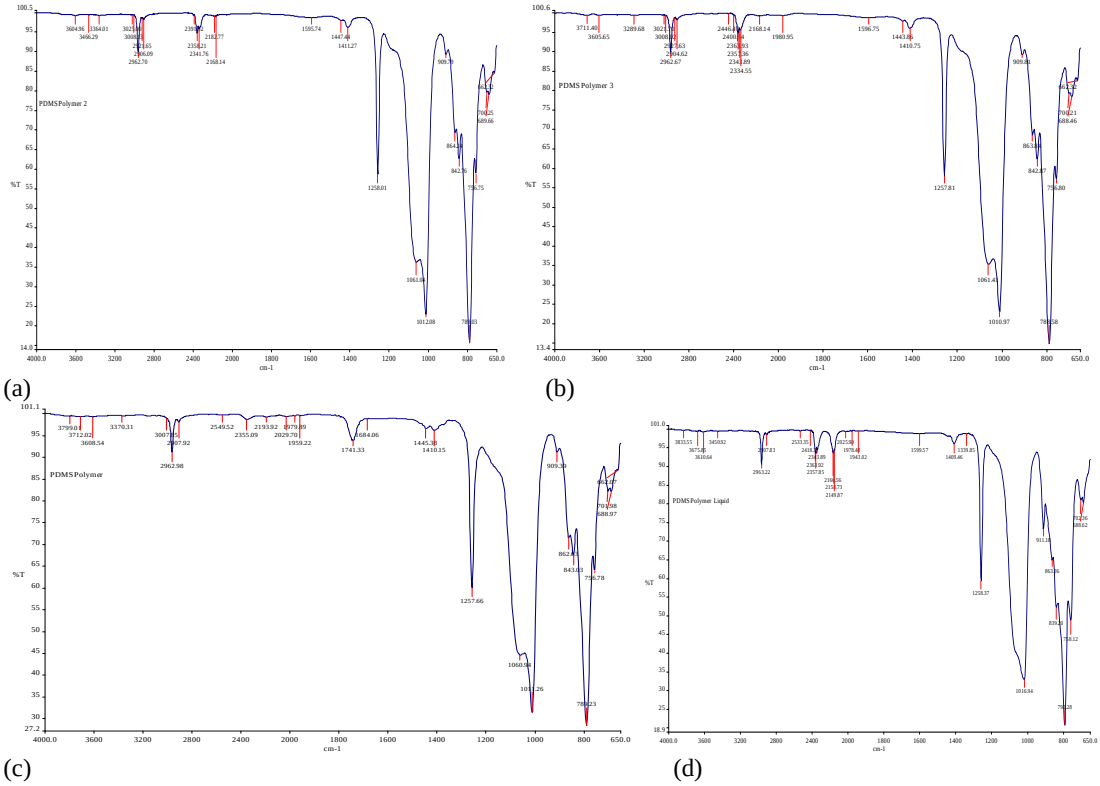

Fig. 1: (a) XRD Absorption spectroscopy of cured pdms before treatment XRD (b) Absorption spectroscopy of cured pdms after treatment (c) XRD Absorption spectroscopy of uncured pdms before treatment (d) XRD Absorption spectroscopy of uncured pdms after treatment.

E. Contact Angle:

Depending on the post-processing of the PDMS, the surface can have varying properties (Mair, D.A., *et al*., 2006). One of such examples is the contact angle (or hydrophobicity) of the structure, which is a crucial property not only for bonding of the Structure, but also for capillary driven devices and affects also level of absorbance. As already mentioned in Section B, oxygen plasma can be used to decrease the contact angle, however such hydrophillicity is unstable in air and fades away with time (circa 30 min) (Mair, D.A., *et al*., 2006). Other ways to change surface are discussed later. Changes in contact angle in connection with various chemicals involved in the MEMS processes have been tested in (Patrito, N., *et al*., 2007; David T. Eddington, 2006).

F. Surface Roughness:

The surface roughness is dependant on the processing and therefore, directly dependant on the processing of the mold as PDMS perfectly copies even the smallest holes. Increased surface roughness means increased surface area and thus, larger area for adsorption as well as for trapping of possible air bubbles in the system. It also means that in Microfluidics PDMS devices, one cannot always assume laminar flow as there might be local eddy currents and pressure losses (David T. Eddington, 2006).

G. Surface Modifications:

In order to avoid adsorption of sample onto the PDMS walls, one has to understand, which molecules are adsorbed to PDMS and thus, which cannot be quantified reliably or the process has to be taken into account. There are ways to coat the inner walls of the PDMS Microfluidics system in order to block this undesirable binding (David T. Eddington, 2006). A review of surface modifications of PDMS can be found in (Sia, S.K. and G.M. Whitesides, 2003; Duffy, D.C., *et al*., 1998; Chaudhury, M.K. and G.M. Whitesides, 1991; Chaudhury, M.K. and G.M. Whitesides, 1992; Cha, J., *et al*., 2006). These modifications include exposure to energy (such as oxygen plasma, ultraviolet light or corona discharge), charged surfactants, polyelectrolyte multilayers, covalent modifications (such as silanization), chemical vapour deposition, phospholipids bilayer, and proteins. While devices from native PDMS exhibit good repeatability (Duffy, D.C., *et al*., 1998), the PDMS devices treated for instance by plasma oxidation demonstrate considerable systematic drift (Yevgeny Berdichevsky, 2004). That may represent a problem even for disposable systems. Therefore, some of the researchers recommend Using of each PDMS chip only once (Yevgeny Berdichevsky, 2004). Properties of oxidized PDMS are revealed in (Duffy, D.C., *et al*., 1998).

H. Adsorption:

Native (untreated) PDMS is strongly hydrophobic and as such strongly interacts with polar samples either through hydrogen bonding between the siloxane group of PDMS and alcoholic/acid hydrogen of the analyte or through polar-topolar interaction (David T. Eddington, 2006; David T. Eddington, 2006). Analyte containing methyl or alkyl groups can interact with PDMS due to van der Waals forces. The force is proportional to the number of methyl groups or to the length of the alkyl chain (David T. Eddington, 2006). As already mentioned, one of the driving market forces for Microfluidics devices is their reduction of sample volume needed for an analysis. On the other hand, in many of the Microfluidics devices, the sample has to flow through a relatively long channel (for instance due to mixing). That results in a large surface that the sample has to run over and by doing so, part of the sample attaches to the free hydrophobic sites of the PDMS channel. Moreover, this process is selective and therefore, polar molecules are for instance more likely to attach than those, which are neutral. These unwanted filtering outcomes in analyzing of different sample than the one that has been introduced into the system on the beginning. (On the other hand, this filtering is used with an advantage in gas chromatography, where PDMS coatings are utilized.) Adsorption not only filters the sample, but may lead also to clogging of the micro channel (David T. Eddington, 2006) and thus, changes in the flow properties. Components easily disturbed by PDMS unfortunately include some fluorescent dyes (Yevgeny Berdichevsky, 2004) utilized as labels in many standard experimental procedures. Also proteins are avidly adsorbing at PDMS. The researchers in (Jo, B.H., *et al*., 2000) elaborate on the fact that proteins are adsorbed on the surfaces. That means that if for instance blood is being analyzed in a Microfluidics device, the platelets adhere as well and activate along coagulation pathways. Also (Chaudhury, M.K. and G.M. Whitesides, 1992) recognizes the challenge of using PDMS in analytical devices due to protein adsorption. In this paper, they modify the surfaces in order to reduce the non-specific protein adsorption, which would otherwise hamper the results.

Conclusion:

Two important PDMS temporarily or permanently treatment for hydrophilization and hydrophobic recovery is presented and as well as possible degree of heat development within fluidic delivery system is also presented, the current state of the art on oxidation of PDMS material and thermal aging for prolonging the hydrophobic recovery of oxygen plasma activated surfaces and presented also some of the essential properties of the PDMS.

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