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PDMS and its Suitability for Analytical Microfluidic Devices

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***Abstract*—Poly(dimethylsiloxane) also known as PDMS is used in a wide range of biomedical applications. These range from implants through catheters to soft contact lenses. Therefore, it is understandable that PDMS has been extensively tested for these purposes.**

In past years, the microfluidics has moved from predominantly silicon and glass structures towards polymers due to their ease of manufacturing and moderate cost. PDMS has gained a lot of attention in various analytical applications. However, the testing of its suitability for such applications has not been as thorough as in the biomedical applications, perhaps relying on the experiments from that field.

Microfluidic PDMS structures are more and more popular in various analytical devices. Such devices consume less reagents and can work with lower sample volumes. On the other hand, the surface-to-sample-volume ratio becomes larger. That increases the influence of material properties on the actual measurement. Some of the challenges include adsorption, diffusion, surface rougness, permeability and elasticity of PDMS, which are discussed in this paper.

I. Introduction

POLY(DIMETHYLSILOXANE) known as PDMS has become an important material in various fields over the years. Some of its applications include mold-release agents, waterproofing, and biomedical products [1]. Lately, it became a popular material also in the microengineering. It was discovered as a stamping tool for micropattern transfer during soft lithography and as a fast prototyping material. The latter application has brought it to attention of various BioMEMS developers and nowadays many of the devices are actually manufactured in PDMS. Some of the PDMS applications in BioMEMS include PCR [2], DNA microarrays [3], capillary electrophoresis (CE) [4], and various other separation and point-of-care devices. A good review of PDMS applications is in [5].

As PDMS has a long history in biomedicine for instance as a soft lens material, there has been many tests performed covering its performance in these applications. However, its influence on microfluidic analytical devices has not been so thorough, although this area is blossoming now.

In microfluidic analytical systems, the PDMS typically serves as a material, in which the microchannels are manufactured [6]-[9]. The substance of interest is pumped through the microchannels (either electrokinetically or using pressure difference), usually mixed with other components and finally quantified. Quantification in PDMS has to be carefully considered with regard to following issues.

Microfluidic devices use minute volumes of samples (and that way allow savings of reagents and speed up the analysis time). Due to tendency to use easy to fabricate as well as low cost mixing approaches, the mixing is typically performed by diffusion, requiring a narrow and a long microchannel. That in turn means that the surface of the channel versus the volume of sample is large. Therefore, as the empty channel is gradually filled with sample, the empty hydrophobic sites at the surface of PDMS bond with parts of the sample and thus, change the content of the sample. In order to avoid this problem, one has to understand which molecules are adsorbed to PDMS and thus, which cannot be quantified reliably, or take other precautions (such as surface modifications).

Other less considered influences include the high permeability of the material, its elasticity and surface properties.

This paper firstly shortly reviews the nomenclature and structure of PDMS in Chapter II (Section A), followed by PDMS processing for microfluidics (Section B). The paper then focuses on properties of PDMS in Chapter III starting with general properties in Section A, and further permeability in Section B, elasticity in Section C and finally surface properties in Section D. This section covers contact angle, surface rougness and adsorption. The paper concludes in Chapter IV.

II. Poly(dimethylsiloxane)

A. Nomenclature and Structure

PDMS belongs to group of siloxanes. This organosilicon chemistry area succeeded in mid-20th century. At first, the group of new materials was called silicoketones or silicones, but as they did not contain a double Si=O bond, the misnomer was replaced by the name siloxanes or polysiloxanes.

From the siloxane group, PDMS presents one of the most studied one.

The skeletal atoms of PDMS consist of an inorganic siloxane group and bear side groups of methyl. The repeating unit (the simplest repetitive structure) is depicted in Fig. 1 and can be rewritten as [-Si$(CH_3)_2$O-].

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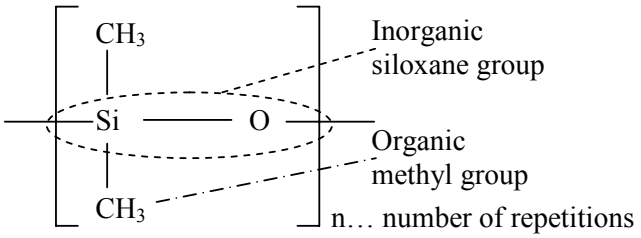

Fig. 1. The structure of a poly(dimethylsiloxane) combines both organic and inorganic groups. Adapted from [1].

B. Processing of PDMS for Microfluidics

In BioMEMS, researchers typically use PDMS Sylgard® 184 (Dow Corning Corporation, [10]), which is a two-part heat curable PDMS. The pre-polymer is usually cross-linked with the curing agent in the ratio 10:1 of weight (other ratios have been studied too resulting in different mechanical and chemical properties).

Once both parts are well mixed, the mixture is poured or spun over a mold (made for instance of SU-8 or silicon) and thoroughly degassed. The mold with PDMS is then cured by heat for several hours.

De-molded PDMS is typically sealed with a substrate. The bonding can be either reversible (e.g. van der Waals contact of PDMS-PDMS or PDMS-glass) or irreversible (with the assistance of plasma oxidation or bonding of pre-cured PDMS to a fully cured PDMS [11]). The reversible seal is fast and occurs at room temperature, however does not withstand high pressures (>30 kPa) [5]. The irreversible sealing can be done with a number of substrates (PDMS, glass, Si, SiO_2, quartz, polystyrene, polyethylene), but does not work with polyimide, poly(methylmethacrylate) or polycarbonate [12]. Such seal withstands pressures up to 200 kPa [5],[12]. Adhesion of PDMS is further discussed in [13].

Devices to be used in biomedicine have to be also sterilized.

Some examples of PDMS devices fabrication recipes are in [2],[5],[14]–[19].

III. Properties of PDMS

A. General Properties

The PDMS is an elastomer having a good thermal stability, low surface tension and good transparency (down to 280 nm [5]). The refractive index is 1.430 [10]. The glass transition temperature of PDMS is -125ºC. The thermal conductivity is 0.18 W/m·K [10]. Although durable at high temperatures, the polymer degrades completely and relatively fast in natural environment and therefore, does not present any significant environmental problem [1].

Other interesting properties of PDMS include atypically low characteristic pressure, bulk viscosity, and entropies of dilution. From biomedical point-of-view, PDMS is valued for its inertness, stability, flexibility and non-fluorescent properties [20].

However, considering the microfluidic devices, where quantifications of chemical substances are involved, the most important properties are elasticity, permeability and surface properties.

B. 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. The permeability of PDMS with O_2 is 6 cm^3(STP)cm/(cm^2·s·cm·Hg), while with N_2 it is 3.1 cm^3(STP)cm/(cm^2·s·cm·Hg). That gives a ratio of the permeabilities 1.9 (O_2/N_2) [1]. With higher temperatures, the diffusion is faster, the solubility lower, and the permeability decreases [21]. Further reading on diffusion and partition coefficients can be found in [21].

Although permeability is advantageous for instance in gas separation membranes, artificial skin coatings for burns, soft contact lenses or oxygenators, in microfluidic analytical devices it may hamper the results for instance due to vapor losses or changes of pH due to CO_2 diffusion [22].

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 [33], 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 [2].

Most organic solvents are soluble in bulk PDMS and swell the polymer [5].

C. 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. The elasticity is directly influenced by the amount of crosslinking. The more the PDMS is crosslinked, the less it is elastic.

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 microchannels 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.

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 [2],[11],[23],[24] and pumps

[2],[24], which makes the systems more compact.

D. Surface Properties

1) Contact Angle

Depending on the post-processing of the PDMS, the surface can have varying properties. 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 adsorbance. 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) [5]. 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 [25].

2) 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 microfluidic PDMS devices, one cannot always assume laminar flow as there might be local eddy currents and pressure losses [26].

3) 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-to-polar interaction [21]. Analytes containing methyl or alkyl groups can interact with PDMS due to van der Waals forces [21]. The force is proportional to the number of methyl groups or to the length of the alkyl chain [21].

As already mentioned, one of the driving market forces for microfluidic devices is their reduction of sample volume needed for an analysis. On the other hand, in many of the microfluidic 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. This 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 microchannel [27] and thus, changes in the flow properties.

Components easily disturbed by PDMS unfortunately include some fluorescent dyes [22] utilized as labels in many standard experimental procedures. Also proteins are avidly adsorbing at PDMS [27]–[29].

The researchers in [30] elaborate on the fact that proteins are adsorbed on the surfaces. That means that if for instance blood is being analyzed in a microfluidic device, the platelets adhere as well and activate along coagulation pathways.

Also [14] 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.

4) 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 microfluidic system in order to block this undesirable binding [28].

A review of surface modifications of PDMS can be found in [31]. 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 vapor deposition, phospholipid bilayer, and proteins.

While devices from native PDMS exhibit good repeatability [32], the PDMS devices treated for instance by plasma oxidation demonstrate considerable systematic drift [22]. That may represent a problem even for disposable systems. Therefore, some of the researchers recommend using of each PDMS chip only once [22].

Properties of oxidized PDMS are revealed in [12].

IV. Conclusion

PDMS has become a popular material in microfluidic applications. Many researchers are using it for its ease of use and moderate cost. However, many of them are not aware of the challenges associated with its use especially in analytical applications.

This paper has identified some of the critical areas associated with PDMS. These include permeability, elasticity and surface properties.

More studies of PDMS properties are necessary in order to fully understand the processes in the microchannels.

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