Microfluidic channels fabricated from poly(vinylmethylsiloxane) networks that resist swelling by organic solvents†

Robin L. Mays, Michael D. Dickey* and Jan Genzer*

This paper describes the use of poly(vinylmethylsiloxane) (PVMS) networks for fabricating microfluidic channels that resist swelling in the presence of organic solvents, thus providing a versatile alternative to poly(dimethylsiloxane) (PDMS). In particular, we demonstrate that in contrast to PDMS microchannels, the UV-treated PVMS structures exhibit high resistance to swelling by toluene.

Introduction

This paper describes the use of poly(vinylmethylsiloxane) (PVMS) as an alternative material for constructing microfluidic channels. Microfluidics involves the manipulation of small volumes of fluid typically accomplished with micro-scale channels. Microfluidic channels are commonly fabricated in poly(dimethylsiloxane) (PDMS) because of numerous favorable properties, including optical transparency, ease of sealing, and chemical inertness. However, PDMS can contaminate microfluidic solutions with unreacted oligomers, absorb organic molecules from solution, and swell upon exposure to most organic solvents. Alternative polymeric materials, such as perfluoropolyethers and thiol-enes, have also been explored as replacements for PDMS. While some of these materials overcome the organic solvent swelling drawback of PDMS, sealing these devices can be problematic or cumbersome.

Another drawback of PDMS is that the methyl side groups are notoriously difficult to modify chemically. In contrast, a PVMS surface is easy to modify due to the presence of reactive vinyl bonds. It is often desirable to chemically tune the interface of microfluidic channels to achieve a specific wettability, or to pattern the local wettability in a channel. In many biological applications, sensing and screening depends on the attachment of enzymes, ligands, or proteins to desired regions of the channel. Extensive research exists on altering the surface properties of PDMS chemically, physically, or through grafting of polymers. Here, we demonstrate the utilization of PVMS, a material which can be chemically and mechanically modified, as a suitable drop-in replacement for PDMS. Previous applications of PVMS have included cell studies, chemically responsive surfaces, optically responsive materials, and mechanically tunable networks. The vinyl groups on PVMS provide opportunities for applying thiol-ene click chemistry, cross metathesis, as well as free radical reactions to endow the base materials with useful new chemical functionalities. Like PDMS, PVMS can be end-group cross-linked to form elastomeric networks that behave similarly to PDMS networks, exhibiting low surface energy, low modulus, mechanical flexibility, optical transparency, and hydrophobicity. PVMS can be replica-molded into microchannels and sealed using methods identical to those employed in fabricating microchannels composed of PDMS.

By UV treating microchannels constructed from PVMS networks, we demonstrate siloxane-based microchannels that resist swelling in toluene. Although other research groups implement photo-sensitive PDMS in coatings or adhesive applications or as photo-resists, little work has been done on modifying photo-sensitive PDMS microchannels in situ. PVMS homopolymers have not, to our knowledge, been used to construct microchannels. In our system, reactive hydroxyl end-groups on the synthesized polymers create a siloxane network, while the vinyl side groups remain available for further reactions in a later step. This method enables the localization of modifications by selectively delivering photoinitiator to specific regions of the polymer (in this case, the walls of the channel) for subsequent treatment with UV light. These reactions can change the local...
interfacial energy and chemical composition, mechanical properties, and permeability.

Results

We synthesized the PVMS used for microchannel fabrication by either step-growth polymerization or one-pot anionic ring opening polymerization (ROP) to obtain hydroxyl-terminated polymers. Using poly(vinylmethoxysiloxane) (PVMES; Gelest) as a cross-linker and tin(II) 2-ethylhexanoate (Sigma-Aldrich) as the catalyst, we made PVMS networks. Microchannel fabrication follows the same basic steps used when working with a commercial Sylgard-184 kit; we use a master mold made by photolithography to create channels and seal those channels to either glass or flat PVMS networks after treatment with oxygen plasma.

Modification of the PVMS channels involves a two-step process (cf. Fig. 1b). First, pumping a solution of 2-hydroxy-2-methylpropiophenone photoinitiator (HMPP, VWR International) in ethanol through the channel over the course of 30–60 min causes it to diffuse into the walls of the PVMS. Exposing the initiator-infused PVMS to UV light causes the vinyl groups present in PVMS to participate in radical reactions, creating additional crosslinks that increase the rigidity and solvent resistance of the walls.

We sought to demonstrate some of the advantages of UV treated PVMS relative to Sylgard-184. The images in Fig. 2 depict the performance of Sylgard-184 and UV-treated PVMS under prolonged periods of exposure to toluene (flow rate of 1 mL h⁻¹). We chose toluene as a solvent because toluene diffuses into PDMS and swells it significantly. As toluene loaded with red dye flows through the channel, the dye diffuses into the PDMS matrix around the channel (cf. Fig. 2a–b). In contrast, the UV-treated PVMS shows essentially no leaching (cf. Fig. 2c–d), even after two hours (cf. Fig. S2 in the ESI†). Despite the apparent difference in intensity of the red color, the concentration of red dye for both systems remains the same. The difference in color is likely due to the rapid absorption of red dye into the top and bottom walls of the PDMS channel, which is not seen in the treated PVMS channel even after an hour of exposure. Model PDMS (containing no silica particle fillers) and untreated PVMS channels both show swelling in toluene, behavior indistinguishable from Sylgard-184. Likewise,
when we treat Sylgard-184 with photoinitiator and UV light, we see the same swelling behavior as pristine Sylgard-184.

We used Fourier transform infrared (FTIR) spectroscopy to quantify the chemical changes resulting from UV-induced surface modification of PVMS films (cf. Fig. 3). Because free radical reactions are inhibited by the presence of oxygen, we covered the samples used to produce the FTIR spectra with a quartz slide during UV treatment, limiting oxygen inhibition at the surface. Other work done on the degradation of silicone rubbers and siloxanes proposes a number of reactions due to UV or oxidation as an effect of UV. However, to our knowledge, little work has been done using a photoinitiator in a system with PVMS. While the exact mechanism of the reaction is unknown, the decrease in IR signal originating from the vinyl groups (1407 and 1598 cm$^{-1}$) indicates that a primary mechanism is the reaction involving those vinyl groups, resulting in additional crosslinks in the material. The appearance of a shoulder at 930 cm$^{-1}$ is assigned to the formation of a $-\text{Si-CH}_2-\text{CH}==\text{CH}-$ group.

As the polymer network crosslinks through the vinyl side groups, the material stiffens. Dynamical mechanical analysis (DMA) of 1 mm thick PVMS networks shows that infusing the networks with photoinitiator followed by UV exposure (treatment similar to the procedure used for microchannels, see ESI†) increases the storage modulus. As seen in Fig. 4, the modulus increases by two orders of magnitude within $\approx 10$ minutes of UV light exposure. Variability in the modulus at long UV treatment times is primarily due to the uncontrolled nature of a UV initiated free radical reaction as well as the dependence of the extent of reaction on sample thickness. Because of the variability in mechanical measurements, we caution that the values presented may differ with changes in PVMS molecular weight, UV lamp intensity, photoinitiator concentration, and sample thickness. Nevertheless, the results illustrate that the mechanical properties change significantly with exposure to light. The elastic modulus plateaus after $\approx 25 \text{ J cm}^{-2}$ ($\approx 7$ min exposure time with our UV lamp for a 10 wt% HMPP photoinitiator solution in ethanol).

The amount of photoinitiator and the dose of UV light determine the extent of reaction inside the microchannel and thus, the mechanical properties and permeability of the PVMS. The amount of photoinitiator embedded in the elastomer depends on the concentration of the HMPP/ethanol solution and the amount of time the solution flows through the channel. This diffusion-based process results in a gradient of photoinitiator from the channel into the surrounding matrix, similar to work done in PDMS channels. In a typical experiment, the UV-modified area extends into the surrounding matrix for $\approx 500$–600 $\mu$m (cf. Fig. S3 in the ESI†), as determined by optical microscopy of a cross-section of the channel.

Although the geometry of a PDMS microchannel changes with absorption of organic solvent, we did not see a corresponding deformation in UV-treated PVMS channels. To further demonstrate this effect, we observed the deformation of wells of both PDMS and PVMS in the presence of solvent (cf. Fig. S4 in ESI†). The features deform with solvent absorption in PDMS, swelling over 100% by volume, and untreated PVMS (swelling of untreated PVMS not shown), but the UV-treated PVMS features do not change significantly in dimensions with exposure to toluene. After UV modification of the PVMS surface, the siloxane networks maintain organic solvent wettability (cf. Fig. S5 in the ESI†); yet they do not swell in the presence of the organic solvent. A microfluidic chemical synthesis channel could make use of organic solvents without the concern that the solvent will leach into the surrounding network, thus changing the geometry of the channels (and therefore the flow profile) and the concentration of reactants inside the channel.

During replica molding, the PVMS occasionally tears due to the lack of filler. Commercial PDMS kits, such as Sylgard-184 contain as much as 30–60 wt% silica particle fillers that are employed to increase the tear strength. We chose to use the PVMS as is, although it is well known that adding fillers reinforces the network and increases tear strength. Tearing can sometimes be observed around the edges of the features (cf. Fig. S1a, c in the ESI†), although this can also be seen with features reproduced with Sylgard-184 (cf. Fig. S1d in the ESI†), as well as with the pure PDMS system (cf. Fig. S1b in the ESI†). Based on our preliminary results, adding fillers to the PVMS prevents tearing and increases tear strength to improve replica molding of PVMS channels.

**Conclusions**

PVMS is an attractive alternative material for microchannel fabrication that offers several benefits in comparison with PDMS. Like PDMS, PVMS is optically transparent, easy to process, and flexible. However, unlike PDMS, the ability to UV-modify the PVMS interface (e.g., the walls of microchannels, as.
shown here) allows the user to create flexible, transparent, molded elastomers that are compatible with organic solvents. The UV treatment is also capable of tuning the modulus by two orders of magnitude using light, which may be useful for other applications.

The most significant drawback of PVMS, however, is the lack of a commercially available material. We synthesized the materials used in this study in house; although the synthesis is straightforward, this additional step may be a deterrent to rapid implementation of PVMS devices. Another consideration is the poor tear strength of unfilled silicone rubbers (both PDMS and PVMS); commercial PDMS products are often loaded with silica particles to overcome this problem. Future work will focus on the improvement of mechanical properties for replica molding by including silica fillers like those used in commercial PDMS kits.

The UV treatment in this work is used primarily to modify the mechanical and diffusive properties of the material around the channel. However, it may be possible to introduce other chemical functionality by grafting molecules to or from the vinyl functional groups on the surface for further tailoring of the properties of PVMS microchannels. The versatility and tunability of PVMS show promise for use in other soft lithographic applications.

Acknowledgements

This work was supported by the NSF’s Research Triangle MRSEC (DMR-1121107).

Notes and references