UNCTIONAL PERFLUOROPOLYETHERS AS NOVEL MATERIALS FOR MICROFLUIDICS AND SOFT LITHOGRAPHY

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Introduction

Microfluidic devices developed in the early 1990s were fabricated from silicon and glass using photolithography and etching techniques.[1,2] These processes were costly, required clean-room conditions, were labor intensive, and posed several disadvantages from a materials standpoint. For these reasons, soft materials have emerged as excellent alternatives for microfluidic device fabrication. Soft materials make possible the easy manufacture and actuation of devices containing valves, pumps, and mixers.[1-4]

Soft lithographic processes such as Imprint Lithography have emerged as leading methods for producing nanostructures (< 100nm) as well as a promising alternative to traditional photolithography for generating microchips with features smaller than 30 nm.[5] Such techniques are based on the molding of resist materials with patterned stamps.

Poly(dimethylsiloxane) (PDMS) has rapidly become the material of choice for many microfluidics and soft lithography applications.[2-5] PDMS offers numerous attractive properties in relation to these technologies. Upon crosslinking, it becomes an elastomeric material with a low Young's modulus of ~750 kPa.[3] This enables it to conform to surfaces and form reversible seals. It is also readily available, UV transparent and displays low toxicity. Despite the advantages of PDMS for these technologies, this material suffers from a serious drawback in that it swells in most organic solvents. Whitesides *et al*. have recently reported in detail on the limited compatibility of PDMS-based microfluidic devices with various organic solvents.[6] Among those that greatly swell the material are hexanes, ethyl ether, toluene, dichloromethane, acetone, and acetonitrile.[6] The swelling of PDMS-based microfluidic devices makes it impossible for organic solvents to flow inside microfluidic channels. It has been proposed that those applications requiring the use of organic solvents will need to revert back to first-generation systems using glass and silicon.[6]

Additionally, the swelling of PDMS by organic solvents severely limits its versatility in many soft lithographic approaches. In particular, imprint lithography cannot be performed with common monomers or oligomers that will swell PDMS. Furthermore, the surface energy of PDMS is not low enough to facilitate release from molds. Often a surface fluorination step is employed. Finally the modulus of most commercially available PDMS is often low to generate stable features causing them to collapse. Some of these problems can be alleviated by using rigid materials such as fluorinated quartz or Teflon AF TM [7,8] however, these hard materials lack the flexibility required for easy mold release and conformal contact.

Our approach to these problems has been to utilize photocurable perfluoropolyethers (PFPEs). PFPEs are a unique class of fluoropolymers that are liquids at room temperature, exhibit very low surface energy, low modulus, high gas permeability, and low toxicity with the added feature of being extremely chemically resistant. We have recently reported on the fabrication of the first elastomeric microfluidic device compatible with organic solvents.[9] Herein, we expand our previous work in microfluidics and introduce soft lithographic techniques that have been performed with these materials.

Experimental

Microfluidic device fabrication. The synthesis and photocuring of the methacrylate-functionalized PFPE has been reported previously.[9] In a typical fabrication, PFPE DMA containing photoinitiator (2,2-dimethoxy-2-phenylacetophenone) was spin coated to a thickness of 20 μm (800 rpm) onto a Si wafer containing the desired photoresist pattern. This wafer was then placed into the UV curing chamber and irradiated for 6s. Separately, a thick layer (~5 mm) of the material was produced by pouring the PFPE DMA containing photoinitiator into a mold surrounding the Si wafer containing the desired photoresist pattern. This wafer was irradiated with UV light for 1min. Following this, the thick layer was removed and inlet holes were carefully punched in specific areas of the device. The thick layer was then carefully placed on top of the thin layer such that the patterns in the two layers were precisely aligned, and then the entire device was irradiated for 10 min. Once complete, the entire device was peeled from the wafer with both layers adhered together. These curing times were determined to be the optimal exposure times to achieve a good balance between structure failure and proper adhesion of the two layers.

Soft Lithography Techniques..PFPE stamps were generated by pouring the material onto an etched silicon wafer patterned with 140 nm features followed by subsequent photocuring. Once the stamp was generated it was brought into contact with a small drop of uncured photopolymer resin containing photoinitiator (2,2-dimethoxy-2-phenylacetophenone) on a Si wafer. This resin is known to have excellent etch resistance, a rapid curing rate, and a high crosslink density.[10] A fixed pressure was exerted on the stamp with a modified Instron® to ensure conformal contact. UV light was then passed through the stamp for 1 minute fully curing the monomer in the desired pattern. The stamp was then easily peeled from the wafer revealing the patterned resist material. AFM micrographs were recorded in tapping mode on a Nanoscope III from Digital Instruments.

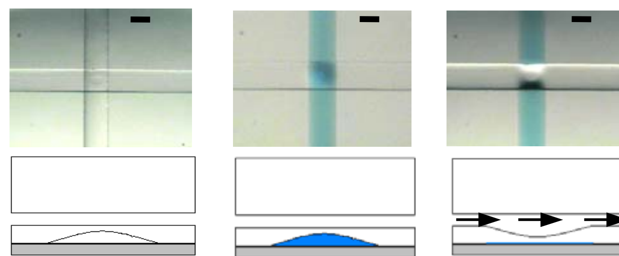

Figure 1. A.) Top-down view of microfluidic channels containing no solvent. The channels on the thin layer (fluid) run vertical, while those on the thick layer (air) run horizontal. **B.)** Thin layer channel filled with dyed solution of acetonitrile, dichloromethane, and methanol. **C.)** Valve actuation produced by introducing 25 psi of air into the thick layer channel. Beneath each picture, a cartoon representation of the valve cross-section is shown.

Results and Discussion

Swelling Experiments.To measure solvent resistance, tests using classical swelling measurements were performed on both the crosslinked PFPE DMA and Sylgard 184®. Sample weight was compared before and after immersion in dichloromethane for several hours. The data show that after 94 h the PDMS network had swelled to 109 % by weight, while the PFPE network showed negligible swelling (< 3%).

Mechanical Properties. Dynamic mechanical thermal analysis was performed on the fully cured materials. Both the PFPE and PDMS networks exhibited low-temperature transitions (-112 ºC and -128 ºC respectively) as evidenced by maxima in the loss modulus E''. This transition accounts for the similar elastic behavior of the two crosslinked materials at room temperature. Stress strain analysis shows that the tensile modulus of the fully cured PFPE-based elastomer is 3.9 MPa, slightly higher than that measured for fully cured Sylgard 184® (2.4 MPa).

Microfluidic Device Fabrication. Device fabrication was accomplished according to established procedures for PDMS-based devices. This method utilizes partial curing techniques to adhere the two layers without compromising feature sizes.[3]

To compare the solvent compatibility of devices made from the two materials, a dyed solution containing dichloromethane, acetonitrile, and methanol was introduced into both a PFPE and a PDMS channel by capillary action. The PFPE channels showed no evidence of swelling as the solution traveled easily through the channel. A pronounced reverse meniscus was observed indicating good wetting behavior. In contrast, no solution entered the PDMS device because the channel was plugged shut when it made contact with the droplet. As a control, a dyed methanol solution was easily introduced in the PDMS channel in the same manner.

Actuation of the valves was accomplished by introducing pressurized air (~25 psi) to small holes that were punched through the thick layer at the beginning of the channels. When the solution was present in the channel, valve actuation was easily observed (Figure 1).

Soft Lithography Techniques. PFPE-based stamps were generated as described above. The pattern transferred from the master to the stamp without any detectable defects. Furthermore, the stamp showed nearly flawless pattern transfer to the resin. This was verified by AFM. The flexibility and low surface energy of the stamps allowed for remarkably easy release from the imprinted resin. These materials posses the favorable properties of both hard and soft stamps in that they are flexible but also exhibit chemical resistance, low surface energy, and an ideal modulus for stamping techniques. The PFPE stamps were subjected to pressures up to 400 N and still exhibited excellent replication.

Conclusions

In summary, we present a novel solvent-compatible microfluidic device fabricated from PFPE-based elastomers. Photocuring decreases fabrication from several hours to a matter of minutes. The device showed a remarkable resistance to organic solvents. This work has the potential to expand the field of microfluidics to many novel applications.

We have further shown the utility of PFPE stamps in soft lithographic stamping techniques. PFPE-based stamps were used to replicate patterns with excellent feature integrity as verified by AFM. The materials showed ideal properties for stamping and molding techniques.

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