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# Fabrication and Characterization of a Hybrid Valve for Microfluidic Applications

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**Abstract-** A hybrid valve for lab on chip applications is presented. The valve is assembled by bonding poly (methyl methacrylate), PMMA, and silicon based elastomers. The process used to promote the hybrid bonding is based on the deposition of an organosilane (TMSPM) on the thermoplastic polymer which acts as interface with the elastomers. An elastomer membrane has been bonded in correspondence of the end of two microfluidic channels of a fabricated PMMA chip. Prior the bonding, a plasma etching process has been used to remove the TMSPM in specific areas of the PMMA allowing to bond only the edge of the elastomeric membrane while it is free to move in the central part. Actuating the membrane with an external pressure or vacuum is possible, respectively to obstruct or to connect the microfluidic channels of the chip. The microvalve is easy to integrate in microfluidic devices and allows the control of microvolumes of fluids in processes such as transport, separation and mixing. The deposition of the TMSPM, the bonding of the valve and its actuation has been characterized and tested. The flow rate control of liquids through the valve has been characterized. The results have been discussed and commented. The valve can stand up to 14 psi without showing leakages.

## I. INTRODUCTION

In recent years, microfluidic systems for biomedical analysis have been developing to accelerate the speed of analysis, reducing the use of expensive reagents and allowing the creation of point of care apparatus [1, 2].

In order to produce such systems, it is important to miniaturize functional elements like reaction chambers, sensors, pumps and valves which allow to handle samples to be analysed [3, 4].

Traditionally, the valves have been fabricated processing a variety of materials including elastomers, such as polydimethylsiloxane, PDMS, [5], silicon [6], SU-8 [7].

But valves realized using these materials show different disadvantages: elastomeric valves do not ensure structural rigidity and due to the porosity and hydrophobicity are often incompatible with biochemical fluid; silicon and SU-8 valves require complex and expensive fabrication processes and they are hard to integrate.

Recently, a pneumatically actuated valve has been presented and the importance of using hybrid materials like elastomers and thermoplastic polymers has been emphasized [8].

Albeit, the possibility to perform irreversible bond between elastomers and thermoplastic polymers is still undiscovered. Combining elastomers and methacrylic plastics through an irreversible bond allows exploiting the advantages and overcoming the drawbacks which the single materials show and allows the fabrication of hybrid systems with enhanced properties, inexpensive and easy fabrication and integration.

Our valve consists of a microfluidic network embedded in a PMMA substrate with an inlet and an outlet channel [9] and an elastomeric membrane fabricated in ELASTOSIL®.

A thin layer of 3-(trimethoxysilyl) propyl methacrylate, TMSPM, coated over the PMMA substrate promotes the irreversible chemical bond between the PMMA and the elastomeric membrane.

## II. MATERIALS AND METHODS

3-(trimethoxysilyl) propyl methacrylate, TMSPM, was purchased from Fluka (Italy) and used as received.

Elastomeric membranes were fabricated in ELASTOSIL® (Waker). Poly(methyl methacrylate) (PMMA) sheets with a thickness of 1.5 mm were purchased from Rohm (Italy) and cut to circular discs of diameter 100 mm.

The modification of the PMMA surface chemistry was observed using the Fourier Transform Infrared (FTIR) spectroscopy (Jasco Italy).

The FTIR spectra were collected from 3 measurement scans at a resolution of 4 cm<sup>-1</sup> within the wavenumber range of 2000-1000 cm<sup>-1</sup>. Grazing angle holder was used for holding the sample during the measurements.

Contact angle measurements were performed by using a Kruss DSA 100 which had a measurement accuracy of ±1°. Deionized water was used as the probe liquid in all measurements. The advancing water contact angles presented come from an average of 3 measurements.

PMMA microfluidic chip were machined with a micro-milling machine (Mini-Mill/3Pro, Minitech Machinery Corporation, Georgia, USA). For the grooves, milling bits with a diameter of 0.5 mm (Performance Micro Tool, Wisconsin, USA) were used at a spindle rotation of 10'000 rpm.

A Plasma reactor MF (Gambetti Italy) was used to etch and for the ozonization of the PMMA.

Peristaltic pumps from Watson Marlow, model 102R, allowed applying pressure or vacuum. They have been used to create pressure inside the microfluidic circuit of the microvalve and vacuum and pressure in the pneumatic circuit which allowed actuating the valve.

Pressure sensor from Sensor technics (model BSDX1000D4D, 5% of accuracy) have been used to detect the pressure inside the fluidic and pneumatic network of the experimental set-up. A precision balance has been used to measure the weight of the waste in the time to calculate the flow rate flowing in the microvalve.

Silicone tubes from Watson Marlow have been used to create the pneumatic and fluidic circuit for connecting the pumps, the pressure sensors and the microvalve.

### III. FABRICATION OF THE VALVE

The microvalve fabrication process is outlined in Figure 1.

#### A. Microfluidic chip fabrication

PMMA microfluidic chips were fabricated by micromilling grooves (500  $\mu\text{m}$  in width and 250  $\mu\text{m}$  in height) and through holes (500  $\mu\text{m}$  in diameter) in a substrate. The high precision of the micromilling machine used combined with optimized parameters of spindle velocity and feed rate allowed to obtain very smooth channels. Average roughness as low as 200- 250 nm can be achieved [10, 11].

After the microchannels were milled, the chips were placed in an ultrasound bath for 5 minutes to remove dust and debris. They are then dried by using a Nitrogen flux.

The microchannels were sealed by bonding a PMMA lid on the substrate in correspondence of the side where the channels were machined.

The bonding was performed by a solvent assisted process. The PMMA plates were immersed in a mixture Ethanol-water (95 v: v %) for 5 minutes. The plate where the microchannels are machined and the lid were then placed in a press and pressed together using a pressure of 10 kPa. The press was placed in an oven at a temperature of 40°C. After 5 minutes the plates are removed from the press and the remaining Ethanol was dried by using Nitrogen flux (Step 1).

The Ethanol reacts with PMMA reducing further the roughness of the surface of the microchannels.

#### B. Elastomeric membrane fabrication

The ELASTOSIL® elastomer and curing agent were mixed in a ratio of 10:1 to yield a prepolymer solution.

The prepolymer was degassed in vacuum for 1 hour after being poured in a metallic mould.

The mould was machined to obtain the negative shape of the membrane which reproduced a disk. The disk had a diameter of 10 mm with a central thinner part (0.2 mm thick) having a diameter of a 4 mm. It also incorporated an outer ring 0.8 mm thick which made easier to handle and align the membrane to the microfluidic chip.

The ELASTOSIL® membrane was then completely cured at 65°C for 4 hours.

The replica was subsequently peeled off the mould.

#### C. Selective, hybrid bonding

Step 2 shows the surface functionalization of the PMMA chip.

The TMSPM was deposited by vapour on the microfluidic PMMA chip on the side where the ends of the microfluidic channels (through holes) were machined.

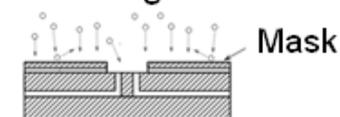
#### 1. Microfluidic PMMA substrate



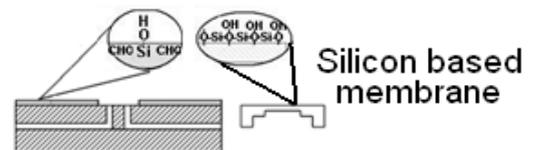
#### 2. TMSPM deposition



#### 3. Plasma etching



#### 4. Plasma for radical activation



#### 5. Bonding

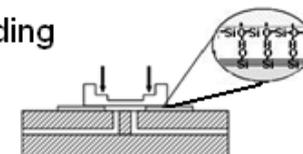


Fig. 1: Schematic representation of the fabrication process of the valve.

Silanes have been applied to substrates under dry aprotic conditions by chemical vapor deposition. This method favors monolayer deposition. Vapor deposition was performed by heating 5 ml of the TMSPM to 100°C. Heating was performed in an oil bath, and the chamber of the deposition was closed. Vapor pressure inside the chamber has been measured 2 torr. Deposition of organosilane molecules occurred placing the chip surface at 20 mm from the liquid and exposing it for 10 minutes.

Drying was performed in a ventilated oven at 40°C for 2 hours.

In order to remove the TMSPM and to selectively bond the elastomeric membrane, the PMMA chip has been etched in O<sub>2</sub> plasma oven. The power was set at 140W and the voltage at 240V, while the pressure was kept at 0.9 mbar. The process has last 3minutes.

A stainless steel mask was used to expose to the gas plasma only a small area, 4 mm in diameter, of the PMMA chip in correspondence of the end of the microfluidic channels (through holes) (Step 3).

A silicone gasket was put between the mask and the PMMA chip to isolate the heat of the mask from the chip, developed during the plasma etching process.

The bonding of the elastomeric valve and the microfluidic chip was, finally, achieved by activating both the surfaces. At this purpose the surfaces were exposed to the plasma O<sub>2</sub>. Power was set at 40 W, voltages at 360 V while the pressure was kept at 0.3 mbar. The process was performed for 20 seconds, to perform the radical attack and ozonation of both surfaces, respectively (Step 4).

Finally, the PMMA substrate and the ELASTOSIL® membrane were brought in contact and pressed together at room temperature and applying a pressure of 5 kPa for one hour (Step 5).

The organosilane TMSPM thin film was the functional film which promoted the adhesion between the PMMA chip and the elastomeric

In fact, chemical interactions occurred when both the parts were put in contact between the oxydrilic part and make irreversibly sealed the elastomeric membrane and the microfluidic chip.

Both the center of the membrane and of the etched area on the PMMA substrate were aligned before they were pressed together. In this way, since the diameter of the elastomeric disk was bigger than the diameter of the etched area, the boundary of the elastomeric disk was bonded to the methacrylic substrate, while the central part remained free to move during the actuation.

#### D. Microvalve fluidic interconnections

The microvalve has been interconnected to the silicone tubes of the experimental set-up by gluing a needle to the inlet and outlet of the microvalve.

The needle was then fixed to the silicone tubes by interference since the outer diameter of the needle was slightly bigger than the inner diameter of the silicone tube.

### IV. ACTUATION OF THE VALVE

Once the valve is assembled, it can be pneumatically actuated as shown in Figure 2.

The actuation was easily performed by applying vacuum or pressure in the middle of the membrane by means of a nozzle which fits into it.

The nozzle was made in PMMA by micromilling in a similar way as it has been done for the microfluidic chip.

After aligning the nozzle to the center of the membrane, it can be kept attached to the valve by using a double-side tape.

The pressure or vacuum can be applied by connecting the nozzle to a peristaltic pump by means of a silicone tube attached to it in a similar way as described in the previous section.

The vacuum permitted to suck the membrane creating a volume which connected the channels of the PMMA chip,

while, applying pressure, the channels were obstructed by the membrane.

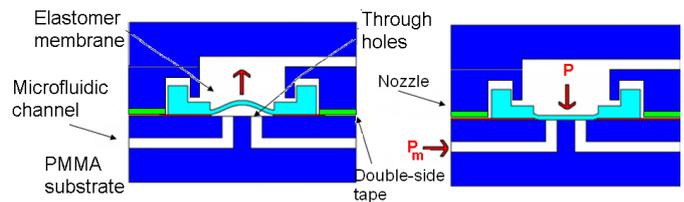


Fig. 2: Schemes of the actuation principle of the valve: open condition by applying vacuum (left); close condition by applying pressure (right).

A schematic representation of the set-up used for conducting the bonding experiment is shown in Figure 3.

For testing the bonding strength between the elastomer membrane and the PMMA microfluidic chip in the valve, a pneumatic circuit has been connected between the inlet of the microfluidic chip and a peristaltic pump. The circuit has been connected in parallel with a pressure sensor by means of a 'T' junction to detect the pressure inside the valve. The outlet of the microfluidic system has been connected to a tube which outlet has been clogged by using glue. The valve has then immersed in a transparent box filled with water. At this point, the peristaltic pump has been actuated to pressurize the microfluidic circuit until a leakage in the valve is detected by air bubble formation in the water. The pressure at which the valve exhibits a leakage has been detected by the pressure sensor. A dedicated software made in Lab View® allowed to interface the pump and the sensor through a PC.

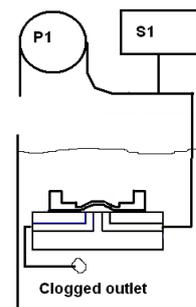


Fig. 3: Schematic representation of the set-up used for testing the bonding strength between the PMMA substrate and the elastomeric membrane. The valve is connected in inlet with a peristaltic pump (P1) and a pressure sensor (S1) and in outlet with a tube clogged with glue. It is, then, immersed in water for detecting leakage when the peristaltic pump increases the pressure in the microfluidic circuit.

Flow characteristic of the valve was evaluated as a function of the actuation pressure (P) using the setup depicted in Figure 4.

The actuation pressure inside the valve was changed by connecting the nozzle of the valve to a peristaltic pump (P2) through a pneumatic circuit and it has been controlled by connecting in parallel of the pneumatic circuit a pressure sensor (S2).

A second peristaltic pump (P3) and a sensor (S3) have been connected to a closed reservoir filled with DI water.

The DI water of the reservoir has been in contact with a tube connected to the inlet of the microfluidic valve. The outlet of the valve has been connected to a beaker placed on a precision balance by a tube.

When the peristaltic pump (P3) applies a pressure (Pm) the DI water is pushed through the valve and drops in the beaker placed on the balance.

The flow rate of the water through the valve has been calculated measuring the weight of the water dropping in the beaker as a function of the time.

A dedicated software made in Lab View® allows interfacing the set-up through a PC, to change the pressure inside the peristaltic pumps, to control the pressure by means of pressure sensors and to keep constant the actuation pressure, and the pressure of the liquid inside the system to chosen values.

To characterize the behavior of the valve, experiments have been conducted by flowing the fluid at specific pressures inside the valve to characterize the flow rate as a function of the actuation pressure. Three different values of fluid pressure were selected, ranging from 1 to 4 psi. The valve leakage is then reported as a function of the applied air pressure.

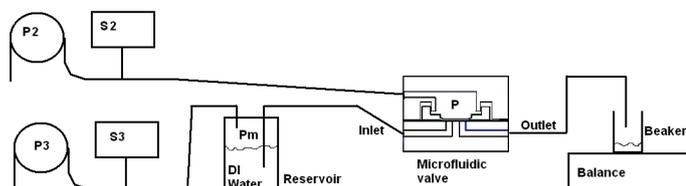


Fig. 4: Schematic representation of the set-up used to characterize the flow rate inside the valve as a function of the actuation pressure. The peristaltic pump (P2) and the pressure sensor (S2) allow controlling the actuation pressure inside the valve (P). The peristaltic pump (P3) and the sensor (S3) allow to control the pressure (Pm) of the liquid flowing from the reservoir in the microfluidic valve. As a function of the actuation pressure (P) and the pressure of the liquid (Pm), the flow rate through the valve can be calculated by measuring the weight of the liquid dropping in the beaker placed on top of the balance in the time.

## V. RESULTS

Figure 5 shows the FTIR spectra of native PMMA and of the TMSPM treated surface. Vapour deposition of the TMSPM modified the chemical functional groups present on top of the microfluidic PMMA chip.

The FT-IR spectrum of PMMA indicates the details of functional groups present in the plastic sheet. A sharp intense peak at  $1711\text{ cm}^{-1}$  appeared due to the presence of ester

carbonyl group stretching vibration. The broad peak ranging from  $1260\text{--}1000\text{ cm}^{-1}$  can be explained owing to the C-O (ester bond) stretching vibration.

In the IR spectrum of TMSPM thin film, that coats the surface of the PMMA, the relative intensity of the band recorded in the range between  $1000\text{--}1150\text{ cm}^{-1}$  of PMMA-TMSPM is much higher and broader than the intensity recorded in the same range for the PMMA only. This observation could be attributed to the presence of Si-O-C bonds in PMMA-TMSPM. While, the TMSPM characteristic peaks appeared at  $1254\text{ cm}^{-1}$  (-SiOCHn-), as underlined by the red area in the figure 5. The absorption band at  $1711\text{ cm}^{-1}$  (C=O of the ester group stretching vibration) can be detected from the spectrum of PMMA-TMSPM as well.

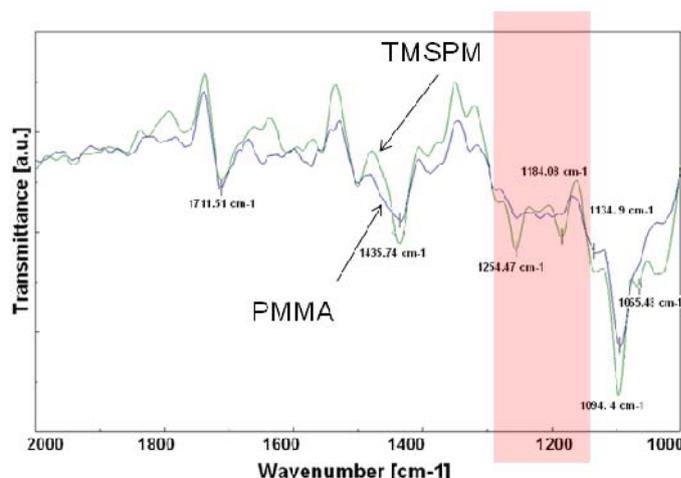


Fig. 5: FTIR analysis of the PMMA surface and of TMSPM thin film. The red area underlines the characteristic peaks of TMSPM.

TMSPM formed SAMs by vapor phase deposition processes. Usually, SAMs are due to a chemical (oxane) bond with the substrate which will be permanently modified.

The optimum performance of silane chain organization on the substrate happens in presence of siliceous substrates, while the organization of the chains is not well defined and controllable in presence of a different substrate. However FT-IR confirms the characteristic peaks of the organosilane and allows to assume a well organized chain of the organosilane over the substrate

Plasma etching, performed to remove selectively the TMSPM in a specific area drastically modifying the exposed surface. Figure 4.a shows the difference between the exposed and the masked area. In particular, captured image resembles the boundary between the etched and the un-etched area. Boundary effects were due to the mask and to the local increase of its temperature due to the plasma energy. A more accurate control of the temperature, by cooling the base of the sample, permits avoiding such thermal effects.

Contact angle measurements are also shown in Figure 6.a. Recorded contact angles of the etched and unetched area were

97.3° and 78.7°, respectively, (the native PMMA contact angle was 79.2°)

The plasma etching changed increasing the contact angle and the hydrophobicity of the treated area. Albeit, the wettability of the organosilane depended on the organization of its chains.

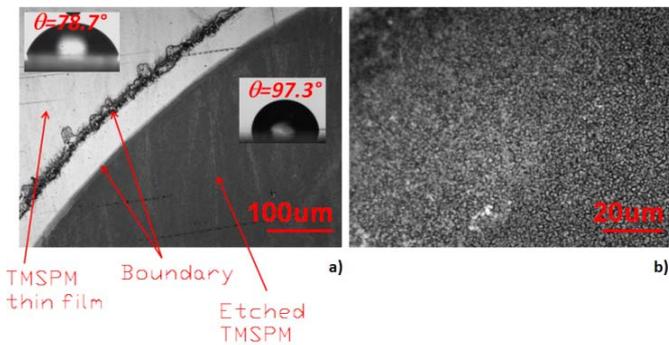


Fig. 6: Microscope images and contact angle measurements of a) boundary between TMSPM thin film and etched area; b) 100X magnification of etched area.

Figure 6.b, 100X magnifications, shows the aspect of the surface after the plasma process. Microroughness of this area increased and this can be an assumption of the cause of the increased contact angle.

The plasma etching process modifies the surface, and such modification was influenced by different parameters. The influences of power and total pressure on the etch rate represent the most crucial because of the opposing effects of resultant electron density, ion current and ion energy. The electron density, which increases with power, causes a larger degree of dissociation and a consequently larger radical concentration in the gas. Likewise, the higher energy transfer into the polymer surface by ion bombardment expedites surface reactions and stimulates desorptions of oxygen species and reaction products from the surface.

Higher total pressure decreases the electron density. Finally, the radical concentration results from the superposition of the two effects. The decrease in ion energy with pressure allows a higher surface density of adsorbed species and causes a lower energy transfer for the reactions.

Figure 7.a shows the measured flow rates of DI water samples through the valve as a function of the applied actuation pressure (P) for various inlet liquid pressure ( $P_m=1, 2, \text{ and } 4 \text{ psi}$ ). As it can be seen, the flow rate decreases by increasing the actuation pressure and decreasing the inlet liquid pressure. An actuation pressure 3 to 4 times higher than the liquid pressure inside the valve is necessary to reduce the flow rate to zero.

By using the set-up shown in Figure 3, no valve leakages have been observed by inflating the membrane with an applied air pressure of 14 psi. A top view of the inflated membrane is shown in Figure 7.b.

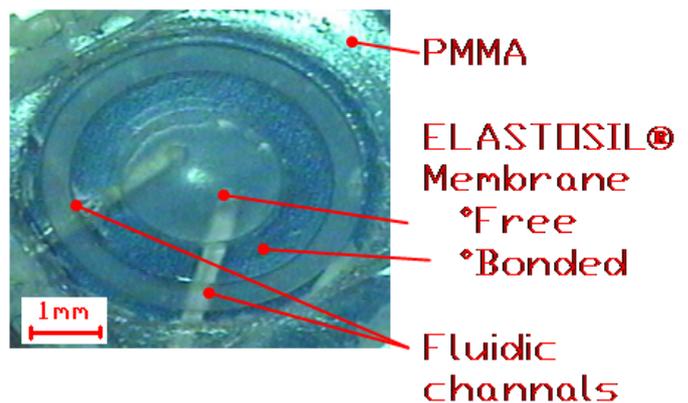
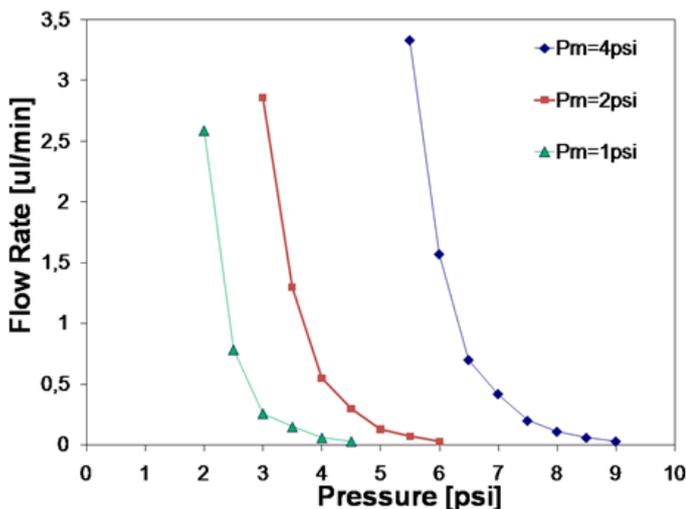


Figure 7: a) Measurements of the flow rate passing through the valve for specific values of liquid pressure  $P_m$  as a function of the pressure which actuates the valve. It can be seen that as the actuation pressure increase, at specific pressure of the liquid passing through the microfluidic network, the flow rate of the liquid decreases. It should be applied a pressure which is three or four times higher than the pressure of the liquid to block the flow rate of the liquid; b) top view of the inflated membrane. The membrane is inflated by connecting the inlet of the microfluidic channel to a peristaltic pump and clogging the microfluidic channel connected to the outlet with glue. It can be clearly seen that the central part of the membrane is free to move and, in fact, it is deformed and blew up when the nitrogen pressure is applied by the pump while the rest is constrained by the hybrid bonding between to the PMMA and the Elastosil.

## VI. CONCLUSIONS

The importance of microfluidic systems in the biomedical field is becoming always more evident. The necessity of miniaturize functional elements such valves to allow a proper functioning of those systems is crucial.

A hybrid valve adaptable for a generic polymer microfluidic system was presented.

The assembling has been obtained by a novel method of irreversible selective bonding between polymethacrilics and silicon based elastomers. The bonding has been allowed by depositing on the plastic substrate a layer of organosilane which creates affinity with the elastomer material used as membrane of the microvalve. Plasma etching allowed removing the organosilane away from the area where the membrane should be free to move in correspondence of the end of two microfluidic channels. The membrane was actuated by an external pressure and vacuum source. Applying pressure to the membrane the microfluidic channels could be obstructed while applying vacuum the channels were connected together. The deposition of the organosilane has been characterized by an FTIR analysis which showed the typical peaks of the silane at 1254 cm<sup>-1</sup>. The selective removal of TMSPM and the surface modification due to the plasma etching was characterized by contact angle measurements. Contact angles of 97.3° and 78.7° were measured for, respectively, the etched area and the unetched area showing that the TMSPM was totally removed from the etched area. Microroughness created by the plasma etching contributed to achieve a proper selective bonding of the valve.

The bonding strength between PMMA and Elastosil was pneumatically tested. It resulted that the bonding can stand high pressures up to 14 psi without exhibiting any leakage.

The flow rates of liquid samples through the valve have been characterized as a function of the applied actuation pressure for various inlet liquid pressures. By increasing the actuation pressure and decreasing the inlet liquid pressure the valve leakages substantially decreased. For not having leakages in the valve, an actuation pressure 3 to 4 times higher than the liquid pressure inside the valve was necessary.

## ACKNOWLEDGMENT

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