Proceedings of the ASME 2010 3rd Joint US-European Fluids Engineering Summer Meeting and
8th International Conference on Nanochannels, Microchannels, and Minichannels
FEDSM-ICNMM2010
August 1-5, 2010, Montreal, Canada

FEDSM-ICNMM2010-31243

# EFFECTS OF HYDROPHOBIC RECOVERY OF PLASMA TREATED PDMS MICROCHANNELS ON SURFACE TENSION DRIVEN FLOW

**Zeyad Almutairi**
Department of Mechanical and Mechatronics Engineering
University of Waterloo
Waterloo, ON, N2L 3G1
Canada
Email: zalmutai@uwaterloo.ca

**Carolyn Ren***
Department of Mechanical and Mechatronics Engineering
University of Waterloo
Waterloo, ON, N2L 3G1
Canada
Email: c3ren@mecheng1.uwaterloo.ca

**David Johnson**
Department of Mechanical and Mechatronics Engineering
University of Waterloo
Waterloo, ON, N2L 3G1
Canada
Email: da3johns@mecheng1.uwaterloo.ca

## ABSTRACT

*Surface tension driven flow is used in numerous microfluidic applications. It is considered a passive pumping technique which doesn't require any external energy, aside from the interfacial surface energy between the fluid and walls. Thus, it is preferred in applications where the goal is fluid and sample transport. In many applications PDMS (Polydimethylsiloxane) is the most adapted material for chip manufacturing in microfluidics. PDMS has several aspects that make it favorable for microfluidic applications. Ease of chip fabrication, cost effectiveness, chemical stability, and good optical properties are features offered by PDMS and desirable for microfluidics. On the other hand, PDMS has some shortcomings. One of importance is that PDMS is naturally hydrophobic. For this reason it is hard to achieve surface tension flow in native PDMS for various fluids used in microfluidics. Thus, native PDMS must be treated to get hydrophilic surface properties.*

*The most used method for altering PDMS properties to a hydrophilic state is by plasma treatment. This treatment has several aspects where it enhances the attachment of PDMS to substrates, it alters the surface from a hydrophobic to a hydrophilic state, and it increases the electrokinetic properties of PDMS. As a result, after plasma treatment surface tension pumping can be achieved in PDMS, unlike native PDMS. However, plasma treatment is not permanent due to the diffusion of non-cured PDMS species to the surface of microchannels, as is well documented in the literature. The change of plasma treated PDMS with time will affect both the electrokinetic and surface tension driven flow. To our knowledge, researchers have quantitatively documented the time effect on plasma treated PDMS microchannels (aging of PDMS) for electrokinetic flow, but not for surface tension driven flow. Therefore, a quantitative examination of the time effect on surface tension driven flow for plasma treated PDMS gives valuable information on both regaining the hydrophobic properties in PDMS and changes in the passive flow conditions.*

*In this work a quantitative study on the hydrophobic recovery for oxygen-plasma treated PDMS and its effects on surface tension flow was examined. The study was performed with a quantitative flow visualization technique (micro particle image velocimetry). It was found that the aging of PDMS will strongly affect surface tension flow of water based solutions in PDMS microchannels. This study gives important information on the effectiveness of surface tension driven flow for oxygen plasma treated PDMS microchannels.*

## INTRODUCTION

Microfluidics is an area that aims to combine and integrate different processes in one small device for numerous applications [1]. One of the major processes that must be achieved is flow and sample transport through microchannels. There are a

*Address all correspondence to this author.

number of flow techniques utilized in microfluidics, the major pumping approaches are: pressure driven, electroosmotic, and surface tension driven flows [2]. Each type of flow has its advantages and limitations [2]. For this reason the proper choice of flow pumping mechanism is an essential step in microfluidic chip design. Surface tension driven flow received attention since it offered a passive pumping technique. Thus, it has advantages compared to other pumping techniques if only flow pumping and sample transport and handling is required. It has been applied in a number of microfluidic and microscale applications such as epoxy underfill flow [3], transporting blood samples in microchannels [4, 5], and performing chemical reactions in small microchannels [6].

In the literature surface tension driven flow is associated with two types of flows. The first one originates from the surface tension properties of fluids [7–9]. This liquid surface tension occurs when liquids attain a meniscus shape which creates a pressure difference, also known as Laplace pressure [7]. In microscale Laplace pressure is sufficient to create flow through microchannel networks. The other type of surface tension flow, also referred to as capillary flow, occurs at the walls of capillaries and microchannels. The attraction of some materials to liquid molecules creates a flow. This is due to the viscous drag between the liquid molecules close to the wall and others far from the wall. In this work the latter type will be our main focus.

The origins of surface tension driven flow are from the interaction between the liquid molecules and the solid materials [7]. Most researchers have studied the interaction phenomenon between liquids and solid materials with static approaches, mainly static contact angle measurement. This measurement finds the angle formed between a small droplet on a horizontal surface [7,10]. However, the measurement is very sensitive and suffers from many error sources [10]. Although static contact angle of liquids offers information about applicability in using materials for surface tension driven flow, it doesn't probe the dynamic aspects of the flow in microchannels and small capillaries. This is due to the fact that the dynamic contact angle formed in surface tension driven flow differers from the angle measured under static conditions [11]. For this reason the interest in examining the dynamic behavior of surface tension driven flow received great interest by researchers.

There are several approaches used in examining the dynamic angles formed between liquids and solids [11–15], but the one of interest to us is tracking the leading edge for liquid flow in microchannels and capillaries [15–17]. The main two parameters that are studied in the leading edge of the flow are the angle formed between the wall material and the liquid (the dynamic angle) and the speed of the leading edge. These two parameters give information on the surface tension driven flow properties. Although this approach examines the dynamic properties of surface tension flow, it suffers from some drawbacks. One important drawback is that it is sometimes hard to accurately measure the dynamic contact angle due to its small magnitude [1]. Thus, researchers used the angle formed between the leading edge meniscus and the channel material as an approximate dynamic angle [16].

In the literature researchers examined the leading edge in different surface tension driven flow conditions and configurations [16, 17]. Chen et al. [16] examined the effects of channel shape changes on surface tension flow for open channel conditions. In their work they adapted tracking the leading edge for examining surface tension driven flow. It was found that the flow decelerates before turns and then accelerates after the channel turns and regains its original speed. Chen et al. [16] also performed numerical analysis of the flow and good agreement with experimental results was achieved.

Zhu and Duran [17] examined capillary driven flow in different materials. In their work they examined the speed and shape of the leading meniscus for different channel geometries and conditions. It was found that leading edge properties of water differs with the channel materials. Glass capillaries and microchannels gave the highest speeds (ranging from 21.5 to 2.5 mm/s) according to the size. Also, it was observed that the capillary speed for plasma treated microchannels changes with time.

PDMS is the most adapted material in microfluidics for chip manufacturing [18]. PDMS is hydrophobic by nature and in most applications hydrophilic properties are desired. Thus, surface treatments of PDMS are widely used in microfluidics. One of the most adapted approaches is the plasma treatment. However, this treatment is not permanent due to the diffusion of non-cured PDMS to the surface of microchannels under dry storage conditions [19, 20]. This phenomenon has been studied for electroosmotic flow. But there is still some lack of information on the PDMS aging effects in surface tension driven flow. Therefore, the examination of PDMS aging with dynamic conditions is important.

In this work a quantitative velocity measurement study of surface tension (capillary) driven flow in PDMS microchannels is presented. The study is performed to examine the velocity of both the wetting region and the leading edge in surface tension driven flow. The effect of PDMS aging on these two parameters will be examined. Unlike other studies tackling this phenomenon other sources of errors were eliminated, such as undesired pressure driven flow. A detailed description on the approach and the experimental setup used in this work is next.

[1]The actual dynamic angle is the angle formed by the liquid wetting and dispersing on the wall. The liquid is forms a very thin film and spreads on the wall. The scale of this liquid region is very small and it is hard to exactly measure the angle formed.

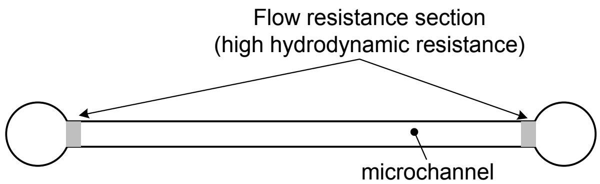


Figure 1. A SCHEMATIC IMAGE OF A MICROCHANNEL INDICATING THE REGIONS WITH PRESSURE RESISTANCE.

## Experimental Setup

### Channel Manufacturing

Straight microchannels with pressure resistance sections close to the reservoirs were used in the current study. The pressure resistance sections were adapted to eliminate pressure driven flow in the microchannels from height or meniscus droplet formation at the inlet reservoir. Thus, it is reasonable to assume that the flow in the microchannels is due to surface tension. Figure 1 presents the configuration of the microchannel and its pressure resistance regions. The microchannels were manufactured with replica molding of SU8 structures. The SU8 structures were fabricated on silicon wafers with soft lithography manufacturing approaches [18]. The microchannels had a square cross section $100 \times 100\ \mu m^2$ and a total length of $5cm$ between reservoirs.

PDMS microchannels were made by mixing the PDMS base and curing agent (Sylgard 184 PDMS kit, Dow Corning) with 10:1 ratio. Then, the liquid PDMS was poured on the silicon wafers that contains hard SU8 structures of the microchannels. PDMS was degassed under -170 kPa in a vacuum oven for 1 hr. Afterwards, the silicon wafers covered with liquid PDMS were cured over a hot plate ($140^oC$) for 3 hrs. This was done to assure full curing of PDMS. Afterwards, access holes (Diameter = 2 mm) were punched through cured PDMS at the reservoirs.

The microchannel substrates were made from glass slides coated with PDMS. The PDMS coating was done in the next steps. Liquid PDMS (10:1 ratio) was spun coated on the glass slides. This was done with a speed of 1,500 rpm for 1 min. Then the coated slides were cured over a hot plate (100 C) for 15 min.

Prior to bonding the microchannels to the substrates, all the samples were cleaned with acetone, deionized water and dried with nitrogen gas. The PDMS microchannels and substrates were bonded with the aid of an oxygen-plasma cleaner. The samples were treated for 20 s with $-66.6 \times 10^{-3}\ kPa$ (-500 mTorr). After bonding the microchannels were left in dry conditions until the time of the experiment.

### Optical and Imaging Systems

In the current study an optical velocity measurement approach was used to find the velocity fields and the leading edge properties in surface driven flow in oxygen-plasma treated PDMS microchannels. The technique is known as micro-PIV (micro particle image velocimetry) [21]. A Nikon (TU-2000) inverted microscope was used to view the region of interest in the microchannel. All the measurements were done with a 20X objective (CFI-S PlanFluor ELWD, NA 0.45). A double head Nd:YAG laser was used to illuminate the flow that contains fluorescent tracking particles. The laser emits light at 532 nm with duration of 3-5 ns. The light is guided through a liquid light guide assembly to the microscope filters and optics to be focused on the area of interest in the microchannel.

To have consistent measurement the region of interest was similar in each test. The imaged region of interest is located 4 cm from the inlet reservoir. Fluorescent particles (1 $\mu m$, Carboxylate modified microspheres, Invitrogen) diluted in water were used in the experiments. The flow images were recorded with a CCD camera (HiSense, Dantec Dynamics). The velocity fields were calculated with an adaptive correlation analysis on the captured images (DynamicStudio,Dantec Dynamics).

### Experimental Procedure

Experiments were done in the following procedure. The scale factor was calibrated between the physical measurement and the image recorded by the CCD camera. Afterwards, focusing was done on the area of interest located 4 *cm* from the inlet reservoir. The micro-PIV system was operated (the laser and image recording). Then, water containing fluorescent particles was introduced at the inlet reservoir. Surface tension causes flow from the inlet reservoir to the outlet reservoir passing the area of interest. A successful trial happens when the leading edge is imaged while it crosses the area of interest. If the leading edge wasn't imaged, another experiment was done with a new chip and the same procedure presented above. A new chip was used in each experiment to avoid cross contamination between different runs, and to avoid errors from fluorescent particles adsorbed at the PDMS walls after each experiment.

After recording the desired images of the leading edge two types of analysis were done. First the images of the leading edge were enhanced with different filtering approaches to improve the contrast of the leading edge. The dynamic contact angle was found with a contact angle approach [10]. This was done with a free contact angle software [10]. The second analysis of the recorded images were done with DynamicStudio (Dantec Dynamics) to find the velocity fields along the interface.

Typical images of the leading edge at different times are presented in Fig. 2

## Results and Discussions

Surface tension driven flow was examined for oxygen-plasma treated PDMS microchannels. The aim of the study was to find the effect of time on oxygen-plasma treated PDMS mi-

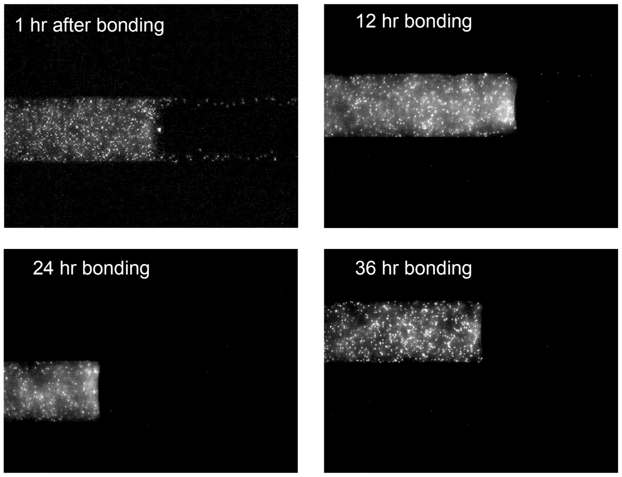


Figure 2. IMAGES OF THE LEADING EDGE FOR SURFACE TENSION DRIVEN FLOW IN MICROCHANNELS. EACH IMAGE PRESENTS THE LEADING EDGE FOR A MICROCHANNEL AND THE STORING DURATION PRIOR TO THE EXPERIMENT, AS LABELED IN THE FIGURES.

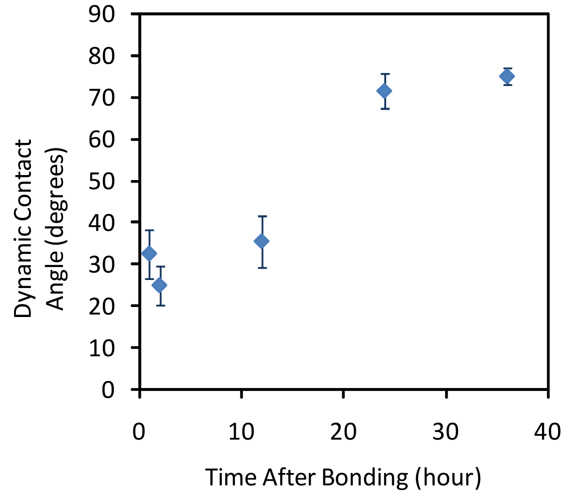


Figure 3. THE LEADING EDGE DYNAMIC CONTACT ANGLE CHANGE WITH TIME.

crochannels. Changes in the surface tension properties are used to examine the effect of PDMS aging. This is done with an optical measurement approach of the leading edge. There are three major phenomena that are examined in this study:

* The shape of the leading edge.
* The dynamic contact angle formed in between the meniscus and the channel walls.
* The speed of the leading edge.

### The Shape of the Leading Edge and Dynamic Angle

Examining the shape of the leading edge gives information on the channel walls attraction to liquid molecules. If the attraction is high the leading edge will have a concave shape and forms a small angle between the leading meniscus and the channel walls. The concave shape of the leading edge causes fluid motion through the microchannel because it is under continuous attraction from the walls. It is clear from Fig. 2 that meniscus shape of the leading edge changes with time. This is observed from Fig. 2 *one hour after bonding* to *36 hr after bonding* where the meniscus shape flattens with time. This is an indication that the surface tension driven flow is decreasing with time for oxygen-plasma treated microchannels under dry storage conditions. The main cause for changes in the leading edge shape is that PDMS is losing surface energy with time. This is due to the changes of the surface properties of treated PDMS from a hydrophilic to a hydrophobic state. It is well accepted that this change is due to the diffusion on non-cured PDMS species in the bulk PDMS to the surface of the microchannel.

The contact angles formed between the leading edge and the channel walls were measured with a static contact angle approach. This was done on a single frame image of the leading edge, similar to images presented in Fig. 2. Due to the symmetry of the meniscus the angle should be the same. However, due to human experimental errors and image quality issues the angle was measured at both sides of the microchannel. The presented results are averaged for both measured angles at the different walls. Open source software was used for finding the angles [10]. The change of the dynamic contact angle with time is shown in Fig. 3.

As shown in Fig. 3, the dynamic contact angle increases with time. The angles changed from around $25^o$ an hour after bonding to $75^o$ after 36 hrs. This indicates the change of PDMS properties with time. However the results from the dynamic contact angle must be taken with great caution. This is due to the fact that the actual contact angle between the liquid and wall wasn't measured but inferred from the meniscus shape. The actual contact angle must be measured close to the microchannel walls. Due to the optical limitations of the current system and the florescence imaging approach used in this work this measurement couldn't be done. On the other hand, inferring the dynamic angle from the meniscus shape has been previously used in surface tension driven flow [16]. This justifies our approach and gives creditability to the findings.

### The Leading Edge Velocity

In this work the flow velocity across the microchannel was found with a micro-PIV system [21]. Typical images that were analyzed are presented in Fig. 2. The PIV analysis was done with

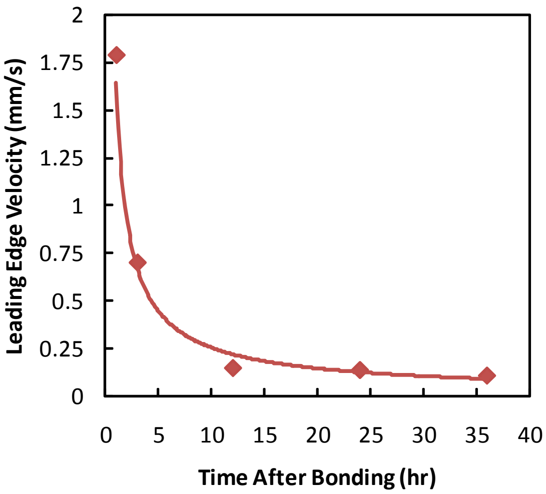


Figure 4. TIME EFFECT ON THE AVERAGE VELOCITY OF THE LEADING EDGE IN SURFACE TENSION DRIVEN FLOW.

cross correlation of two successive images for the flow [21]. Afterwards, the average axial velocity of the leading edge was calculated with an in house Matlab program (Mathworks) [2]. The average velocity changes of the leading edge with time is presented in Fig. 4.

As it is clearly shown in Fig. 4 the average velocity of the leading edge decreases greatly with time. The velocity changed from around 1.8 $mm/s$ an hour after bonding to around 110.0 $\mu m/s$ after 36 hours of bonding and dry storage conditions. Experiments after waiting 36 hrs failed and didn't show any significant surface tension driven flow. The leading edge velocity decreases rapidly in the first few hours (0 - 5 hrs). Then the change becomes less gradual, as observed in Fig. 4. The leading edge velocity represents the average velocity of surface tension flow in microchannels. This was confirmed previously in the literature with optical tracking of the leading edge [16, 17].

The decrease in the average velocity of surface tension driven flow with time coincides with observations from the leading edge shape and the the dynamic contact angle Fig. 2 & 3. These changes are due to one major phenomenon that occurs in oxygen-plasma and regular plasma treated PDMS, which is the regaining of the PDMS hydrophobic nature. Results from the average velocity measurements are the best indicator since it is the major strength of the micro-PIV system. The change of the average velocity of the leading edge with time can be approximated with logarithmic change. This change is very high and must be taken into consideration when plasma treated PDMS microchannels are used in this type of surface tension driven flow.

[2]The axial speed is a good representative of the leading edge speed. A comparison between the axial velocity and the average velocity of the leading edge showed that axial velocity contributes up to about 98 % of the average velocity in most cases. Thus, it reasonable to assume that the axial velocity represents the leading edge speed.

## Conclusions

Surface tension driven flow in oxygen-plasma treated PDMS microchannels was examined with a quantitative optical measurement technique. Aging of plasma treated PDMS was examined by finding the changes in surface tension driven flow. Three major aspects of the flow were examined in this study these are: the shape of the leading edge, the dynamic angle formed between the leading meniscus and channel walls, and the average velocity of the leading edge. The examined parameters were used as an indicator for PDMS aging.

It was found that PDMS attains high surface energy after oxygen-plasma treatment. This resulted in high leading edge speed (around 1.8 $mm/s$). The dynamic contact angle and the meniscus shape also agreed with this finding. The contact angle after bonding was around 24 degrees and the meniscus was concave. With dry storage conditions for the microchannels the average speed of the leading edge significantly changes with time ( 110.0 $\mu m/s$) after 36 hrs of dry storage conditions. This finding was confirmed by both the dynamic contact angle and the leading edge shape. After 36 hrs, no significant surface tension flow was observed.

This study shows the applicability of using micro-PIV studies for examining the dynamic aspects in surface tension driven flow. This was confirmed with studying changes in surface tension driven flow for oxygen plasma treated microchannels.

## ACKNOWLEDGMENT

The authors acknowledge the support of research grants of the Natural Sciences and Engineering Research Council, the Department of Mechanical Engineering at King Saud University for sponsoring Zeyad Almutairi, and Tomasz Glawdel for manufacturing the silicon master of the microchannels.

## REFERENCES

[1] Whitesides, G. M., 2006. "The origins and the future of microfluidics". *Nature,* ***442***(7101), July, pp. 368–373.

[2] Pennathur, S., 2008. "Flow control in microfluidics: are the workhorse flows adequate?". *Lab on a Chip,* ***8***(3), pp. 383–387.

[3] Schwiebert, M. K., and Leong, W. H., 1996. "Underfill flow as viscous flow between parallel plates driven by capillary action". *IEEE transactions on components, packaging and manufacturing technology. Part C. Manufacturing,* ***19***(2), pp. 133–137. Compendex.

[4] Huang, W., Bhullar, R. S., and Fung, Y. C., 2001. "The Surface-Tension-Driven flow of blood from a droplet into

a capillary tube". *Journal of Biomechanical Engineering,* ***123***(5), Oct., pp. 446–454.

[5] Chakraborty, S., 2005. "Dynamics of capillary flow of blood into a microfluidic channel". *Lab on a Chip,* ***5***(4), pp. 421–430.

[6] Nag, A., Panda, B., and Chattopadhyay, A., 2005. "Performing chemical reactions in virtual capillary of surface tension-confined microfluidic devices". *Pramana,* ***65***(4), Oct., pp. 621–630.

[7] Probstein, R. F., 2003. *Physicochemical Hydrodynamics: An Introduction*, 2 ed. Wiley-Interscience, May.

[8] Walker, G. M., and Beebe, D. J., 2002. "A passive pumping method for microfluidic devices". *Lab on a Chip,* ***2***(3), pp. 131–134.

[9] Berthier, E., and Beebe, D. J., 2007. "Flow rate analysis of a surface tension driven passive micropump". *Lab on a Chip,* ***7***(11), pp. 1475–1478.

[10] Stalder, A., Kulik, G., Sage, D., Barbieri, L., and Hoffmann, P., 2006. "A snake-based approach to accurate determination of both contact points and contact angles". *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* ***286***(1-3), pp. 92–103. Compendex.

[11] Hoffman, R. L., 1975. "A study of the advancing interface. i. interface shape in liquid–gas systems". *Journal of Colloid and Interface Science,* ***50***(2), Feb., pp. 228–241.

[12] Marsh, J. A., Garoff, S., and Dussan, E., 1993. "Dynamic contact angles and hydrodynamics near a moving contact line". *Physical Review Letters,* ***70***(18), p. 2778. Compendex.

[13] Marsh, J. A., Garoff, S., and Dussan, E., 1993. "Dynamic contact angles and hydrodynamics near a moving contact line". *Physical Review Letters,* ***70***(18), p. 2778. Compendex.

[14] Gennes, P. D., Hua, X., and Levinson, P., 1990. "Dynamics of wetting. local contact angles". *Journal of Fluid Mechanics,* ***212***, pp. 55–63. Compendex.

[15] Ichikawa, N., Hosokawa, K., and Maeda, R., 2004. "Interface motion of capillary-driven flow in rectangular microchannel". *Journal of Colloid and Interface Science,* ***280***(1), Dec., pp. 155–164.

[16] Chen, Y., Tseng, F., ChangChien, S., Chen, M., Yu, R., and Chieng, C., 2008. "Surface tension driven flow for open microchannels with different turning angles". *Microfluidics and Nanofluidics,* ***5***(2), pp. 193–203. Compendex.

[17] Zhu, Y., and Petkovic-Duran, K., 2010. "Capillary flow in microchannels". *Microfluidics and Nanofluidics,* ***8***(2), Feb., pp. 275–282.

[18] Ng, J. M. K., Gitlin, I., Stroock, A. D., and Whitesides, G. M., 2002. "Components for integrated poly(dimethylsiloxane) microfluidic systems". *ELECTROPHORESIS,* ***23***(20), pp. 3461–3473.

[19] Chen, I., and Lindner, E., 2007. "The stability of Radio-Frequency Plasma-Treated polydimethylsiloxane surfaces". *Langmuir,* ***23***(6), Mar., pp. 3118–3122.

[20] Pittman, J. L., Henry, C. S., and Gilman, S. D., 2003. "Experimental studies of electroosmotic flow dynamics in microfabricated devices during current monitoring experiments". *Analytical Chemistry,* ***75***(3), Feb., pp. 361–370.

[21] Devasenathipathy, S., Santiago, J., Wereley, S., Meinhart, C., and Takehara, K., 2003/04/. "Particle imaging techniques for microfabricated fluidic systems". *Experiments in Fluids,* ***34***(4), pp. 504 – 14.