

# ON-CHIP LIQUID CONTROL USING STRIPED SURFACE TOPOGRAPHY FABRICATED BY POLYMER INJECTION MOLDING

Karen S. Sørensen<sup>1,2</sup>, Peter F. Østergaard<sup>1</sup>, Rafael J. Taboryski<sup>1</sup>, and Mikkel F. Hansen<sup>1</sup>

<sup>1</sup>Department of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345B, DK-2800 Kongens Lyngby, Denmark

<sup>2</sup>Center for integrated Point of Care technologies (CiPoC), DELTA, Venlighedsvej 4, DK-2870 Hørsholm, Denmark

## ABSTRACT

We present a new approach to control the pathways of water-based liquids in microfluidic systems fabricated by injection molding. The top or bottom of a chamber forming the fluidic system is patterned with parallel micro-sized ridges, which result in appreciable anisotropic wetting behavior. With the presented surface structures we have demonstrated the possibility of creating microfluidic channels with virtual side walls and channels with capillary stops fabricated in a polymer that otherwise exhibits a hydrophilic wetting property when no surface structures are present.

## KEYWORDS

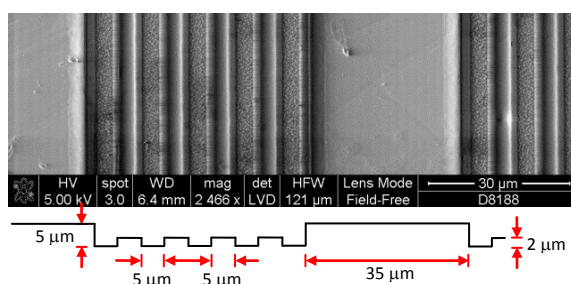
Injection molding, surface structures, contact angle, wetting anisotropy, microfluidics.

## INTRODUCTION

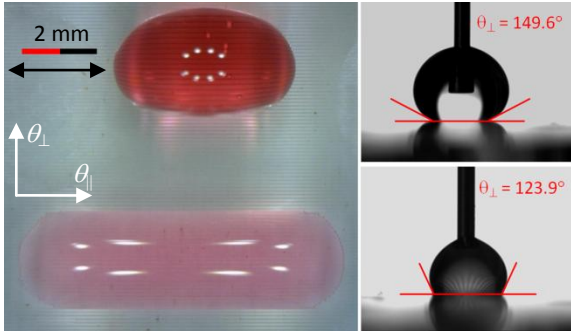
The vision of inexpensive lab-on-a-chip systems for diagnostics and chemical analysis includes the need for simple methods for on-chip liquid control that are compatible with mass-production techniques. The fabrication cost of a lab-on-a-chip system can greatly be reduced if active pumps can be substituted by automatic liquid filling using capillary forces. When controlling liquid movement using capillary force, the wetting behavior of the inner surfaces of the on-chip microfluidic channels has to be controlled, and this is done by controlling the contact angle of the used liquids to the inner surfaces. Moreover, for some applications it is desirable to have anisotropic wetting properties to allow liquid movement only in some directions.

In the literature, the anisotropic wetting of pure water on a striped substrate has been studied for PDMS with controlled wrinkles [1] and for chemical patterning of silicon [2]. These studies compared experimental results with theoretical models for the wetting of pure water droplets on a flat substrate. A chemical patterning of the intrinsic contact angle on a polymer substrate induced by oxygen plasma treatment has previously been used to define on-chip wall-less channels [3]. On-chip hydrophobic stops have been created by variations of the channel cross-section [4] and by deposition of a material with high contact angle such as Teflon [5]. Anisotropic wetting properties can therefore be achieved both by modification of the surface topography and by chemical patterning. However, chemical patterning is less favorable as it is not a batch fabrication process and is expected to have a limited shelf time [6].

In this work, we study the effect of micro-sized parallel ridges in the surface of either the top or bottom of a polymer microfluidic channel fabricated by injection molding Cyclic Olefin Copolymer (COC) TOPAS<sup>®</sup> grade 5013 (TOPAS Advanced polymers GmbH, Germany). Figure 1 shows the geometry of the stripes. We show that such stripes introduce highly anisotropic wetting properties for both pure water and the biologically relevant buffer 1×Phosphate Buffered Saline + 0.05% Tween-20 (abbreviated PBST), which is commonly used in DNA extraction and amplification [7]. In PBST, Tween-20 functions as a detergent decreasing the surface tension of the liquid/air and liquid/solid interfaces, which results in a lower intrinsic contact angle. Moreover, we demonstrate the guiding of these liquids in a wall-less channel as well as the use of the structures for a capillary stop in a fluidic channel. The presented approach is easily integrated in polymer chips fabricated by injection molding and it eliminates the need for chemical surface patterning to vary the wetting properties.



**Figure 1:** Top: Scanning electron micrograph of the surface structures on the injection molded polymer chip. Bottom: Sketch of surface structures with dimension sizes indicated.



**Figure 2:** Left: Red dyed 10  $\mu\text{L}$  water droplet (topmost) and PBST droplet (lowest) deposited on the structured TOPAS. The black arrow indicates stripe orientation. Right: Side view of the droplets while measuring the advancing contact angles perpendicular to the stripes. No difference was observed between liquids with and without the dye.

**Table 1:** Contact angles using water and PBST on both the unstructured and structured TOPAS. It has not been possible to measure static contact angles for PBST since the droplet continues to flow in the direction parallel with the stripes after end deposition.

Static	$\theta_{\text{flat}}$	$\theta_{\perp}$	$\theta_{\parallel}$	$\Delta\theta$
Water	87.4°	149.6°	94.9°	54.7°

Advancing	$\theta_{\text{flat}}$	$\theta_{\perp}$	$\theta_{\parallel}$	$\Delta\theta$
Water	96.6°	150.2°	100.4°	49.8°
PBST	63.7°	123.9°	53.2°	70.7°

## THEORY OF CONTACT ANGLES

The intrinsic contact angle,  $\theta_Y$ , of a liquid on a solid depends only on the surface tensions associated with the liquid/air, liquid/solid, and solid/air interfaces. However, the observed contact angle may differ from  $\theta_Y$  due to surface roughness and is therefore called the apparent contact angle,  $\theta_A$ . When a rough surface is fully wetted, the Wenzel model predicts that  $\cos(\theta_A) = r \cos(\theta_Y)$  where the roughness  $r \geq 1$  is the ratio between the solid-liquid contact area and the projection area of the droplet on the surface [8]. This implies that in the Wenzel regime (which assumes equilibrium), roughness can only increase the hydrophilicity or hydrophobicity of a surface [9].

## CONTACT ANGLE MEASUREMENTS

The wetting properties of the structured surface were characterized by measuring both the apparent advancing and static contact angle for water on the unstructured surface and both perpendicular and parallel to the ridges on the structured surface. For PBST, only the advancing contact angle could be measured since PBST continues to wet along the parallel direction of the ridges after the droplet has been deposited. The contact angles were measured using the DSA-10-Mk2 Drop Shape Analysis System (Krüss GmbH, Germany). Measurements started with a drop size of 2  $\mu\text{L}$  that was expanded up to 10  $\mu\text{L}$  at a dispensing rate of 15  $\mu\text{L}/\text{min}$  while measuring the advancing contact angle. Results of the contact angle measurements shown in Figure 2 and Table 1, reveal contact angle anisotropies,  $\Delta\theta$ , for the advancing contact angle of 49.8° and 70.7° for pure water and PBST, respectively. Furthermore, for PBST, the surface changes from being hydrophilic (liquid-loving [8]) with  $\theta_{\text{adv}} = 63.7^\circ$  for the flat TOPAS surface to being hydrophobic (liquid-repellent [8]) with  $\theta_{\text{adv},\perp} = 123.9^\circ$  for the structured surface in the direction perpendicular to the surface ridges.

For the parallel direction, the roughness can be estimated from Figure 1 to  $r \approx 1.33$ . Assuming that the Wenzel model is valid also for the advancing contact angle, it predicts the apparent advancing contact angles along the ridges to be  $\theta_{\text{adv},\parallel} \approx 54^\circ$  (PBST) and  $\theta_{\text{adv},\parallel} \approx 99^\circ$  (water) in good agreement with the measured results,  $\theta_{\text{adv},\parallel} = 53.2^\circ$  (PBST) and  $\theta_{\text{adv},\parallel} = 100.4^\circ$  (water). Thus, the observations in the parallel direction agree with the predictions by the Wenzel model.

In the perpendicular direction, the theory by Wenzel is clearly inadequate for predicting the observations. In that direction, the periodic surface structures create small barriers in the free energy as function of contact angle. These introduce many metastable states for the droplets, which prevent the droplet meniscus from advancing. Hence, for the advancing droplet, the droplet will be in the metastable state with the highest contact angle whereby the apparent contact angle will always be larger than predicted by Wenzel [9]. From close-up side views of the droplets (not shown) it appears that both water and PBST completely fill the grooves between the ridges in the surface. This is consistent with the highly elongated drop shape in Figure 2 as a more symmetric droplet shape is expected if the grooves are not filled [10].

## ON-CHIP LIQUID CONTROL

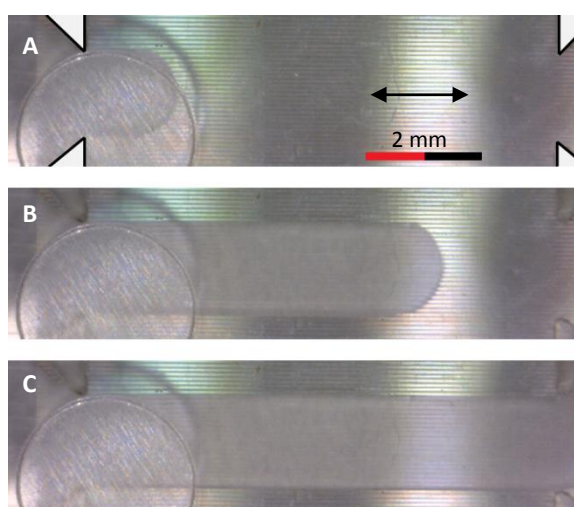
Next, we present proof-of-concept of on-chip liquid control utilizing the anisotropic wetting properties of the structured TOPAS substrate when it is used as the top in a fluid chamber with a flat TOPAS bottom. The two substrates are separated by a tape spacer of thickness 125  $\mu\text{m}$ . The top piece of the system is constructed with a top with tapered Luer fittings described in [11]. The Luer fittings are used to inject the liquid as well as working as air outlets. For visualization, the PBST is dyed red and no difference can be observed between PBST with and without dye. The same observation is made for water. Furthermore, no difference in contact angles can be observed between water and PBS (PBST without Tween-20) indicating, that the detergent Tween-20 is fully responsible for the observed changes in contact angles for PBST compared with water.

Figure 3 shows the system geometry and demonstrates the PBST filling of a wall-less channel defined by the surface ridges. The width of the inlet to the left in the picture in Figure 3 defines the width of the channel. Figure 4 demonstrates the use of the stripe geometry as a hydrophobic stop when PBST is introduced in a liquid inlet. With no surface structures the PBST experiences a low contact angle with TOPAS and the width of the capillary stop in Figure 4 is too wide in order to stop the PBST from passing through. However, with the structured surface in top of the channel, the advancing contact angle of PBST increases to above  $90^\circ$  and PBST stops at the constriction.

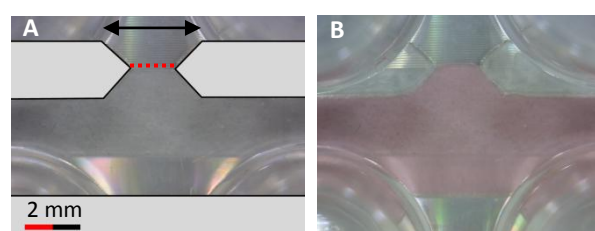
Due to the low advancing contact angle of PBST parallel to the surface stripes as well as for the unstructured TOPAS, PBST experiences capillary filling in the channels. Active pumps are therefore not necessary to fill the micro fluidic channel and this further makes the system inexpensive and simple to operate in accordance with the wish for inexpensive lab-on-a-chip systems.

## CONCLUSION

The present study constitutes one of the first implementation of an injection molded structured substrate for the control of liquids in a chip system. We have demonstrated the use of the structures for defining an on-chip wall-less channel and an on-chip capillary stop for PBST, which is much more relevant for biological experiments than pure water. In conclusion, we have demonstrated a simple approach to liquid handling in a microfluidic system that easily can be integrated with mass-production techniques such as injection molding.



**Figure 3:** “Wall-less” channel. A: Black marks indicate the tape spacer. The channel runs from an inlet to the right to an outlet to the left. The round object to the left in the picture is a mark from the injection molding on the upper surface of the top. The arrow indicates stripe orientation. B: Picture of the same channel as in A, but taken 2 s later. C: Picture of the same channel as in A, but taken 6 s later.



**Figure 4:** Enhancing capillary stop. A: Black marks indicate the tape. To the left is the inlet and to the right the outlet. The stripes are above the red dotted line and the arrow indicates stripe orientation. B: Red dyed PBST fills the channel without bursting through the opening. Without stripes, PBST easily flows through the opening.

## REFERENCES

- [1] C. Bukowsky, J.M. Torres, and B.D. Vogt, *J. Colloid Interface Sci.*, **354**, 825 (2011).
- [2] H.P. Jansen, O. Bliznyuk, E.S. Kooij, B. Poelsema, and H.J.W. Zandvliet, *Langmuir*, **28**, 499 (2011).
- [3] S. Bouiadat, O. Hansen, H. Bruus, C. Berendsen, N.K. Bau-Madsen, P. Thomsen, A. Wolff, and J. Jonsmann, *Lab Chip*, **5**, 827 (2005).
- [4] C.G. Cooney, D. Sipes, N. Thakore, R. Holmberg, and P. Belgrader, *Biomed. Microdevices*, **14**, 45 (2012).
- [5] L. Riegger, M.M. Mielnik, A. Gulliksen, D. Mark, J. Steigert, S. Lutz, M. Clad, R. Zengerle, P. Koltay, and J. Hoffmann, *J. Micromech. Microeng.*, **20**, 045021 (2010).
- [6] S.T. Larsen and R. Taboryski, *Langmuir*, **25**, 1282 (2009).
- [7] M. McPherson and S. Møller, “PCR”, Taylor & Francis Group, second edition (2006).
- [8] A. Marmur, *Langmuir*, **24**, 7573 (2008).
- [9] J.Y. Chung, J.P. Youngblood, and C.M. Stafford, *Soft Matter*, **3**, 1163 (2007).
- [10] W. Li, G. Fang, Y. Li, and G. Qiao, *J. Phys. Chem. B*, **112**, 7234 (2008).
- [11] K.Ø. Andresen, M. Hansen, M. Matschuk, A.T. Jepsen, H.S. Sørensen, P. Utko, D. Selmeczi, T.S. Hansen, N.B. Larsen, N. Rozloznik, and R. Taboryski, *J. Micromech. Microeng.*, **20**, 055010 (2010).