TEFLON-CARBON BLACK AS NEW MATERIAL FOR THE HYDROPHOBIC PATTERNING OF POLYMER LABS-ON-A-CHIP

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ABSTRACT

We provide a new method for the selective surface patterning of microfluidic chips with hydrophobic fluoropolymers which is demonstrated by the fabrication of hydrophobic valves. It enables efficient optical quality control for the surface patterning thus permitting the low-cost production of highly reproducible hydrophobic valves. Specifically, a fluoropolymer-solvent-dye solution based on carbon black (CB) is presented which creates superhydrophobic surfaces (contact angle = 157.9°) on chips made from cyclic olefin copolymer (COC). It further provides good visibility for the quality control (QC) in polymer labs-on-a-chip and increases the burst pressure of hydrophobic valves. Finally, an application which aims for the amplification of mRNA on-chip and relies on the defined flow control by hydrophobic valves is presented. Here, the QC in combination with the Teflon-CB coating improves the average standard deviation of the burst pressures from 14.5% down to 6.1 % compared to solely Teflon-coated valves.

KEYWORDS

hydrophobic valves, flow control, superhydrophobic, quality control, low-cost

INTRODUCTION

The ongoing trend towards point-of-care technologies in medical diagnostics has stimulated the development of miniaturized "lab-on-a-chip"-systems [1]. These labs-on-a-chip feature a set of basic unit operations such as sample injection, metering, and mixing to integrate and thus automate full diagnostic test protocols on a typically credit card sized microfluidic substrate. Further, to conduct complex protocols of unit operations, the liquid flow has to be controlled in a defined manner. This can be realized by the integration of valves whereas it is highly desirable to use passive valves to reduce the costs of the lab-on-a-chip.

A simple way for retaining liquids is the use of hydrophobic patterns due to the change in contact angle [2]. Another approach utilizes capillary valves, i.e. geometrical restrictions to pin liquid plugs at defined positions due to a pressure drop [3]. Both concepts can be combined in the form of hydrophobic valves [4], i.e. capillary valves featuring a hydrophobic coating which provide higher retention forces.

For some time, there has been a strong trend towards polymer labs-on-a-chip [5] specifically due to their amenability for low-cost mass-production and chips comprising hydrophobic valves have already been reported [6]. As the precise coating of the capillary valve, i.e. the hydrophobic patterning is of great importance for the valve functionality, suitable quality control procedures are required. In this paper, a fluoropolymer-solvent-dye solution enabling the visual inspection of the localized coating and with it a quality control of the hydrophobic patterning is presented.

This paper is structured in the following way. We first describe the principle of a hydrophobic valve and different means of patterning. Next, a possible dye for fluoropolymer solutions is presented which enables a visual inspection of the hydrophobic patterning. Then, we present an application example for the hydrophobic patterning based on the given coatings. Finally, we discuss the results of the quality control as well as the measured burst pressures and conclude.

HYDROPHOBIC VALVES & VALVE COATING

Passive hydrophobic valves generally comprise a geometrical restriction with a hydrophobic surface coating (Fig. 1). They feature a high burst pressure, i.e. the pressure which has to be applied for the liquid to pass the valve structure as it is impacted by the valve geometry as well as the difference in contact angle. Hydrophobic coatings can be applied by various means, e.g. by pipetting, the use of a felt pen [7], or by dispensing [8]. Depending on the dimensions of the capillary valve to be coated, a tight control of the applied volume is required to minimize the risk of overflow or insufficient coverage which would render the valve non-functional. Further, hydrophobic coatings exhibit an insufficient visibility especially in transparent polymer labs-on-a-chip. As measuring each burst pressure for different patterning parameter settings is an inefficient approach for complex fluidic structures, enabling a rapid visual inspection with the use of dyes is a highly preferable method for quality control.

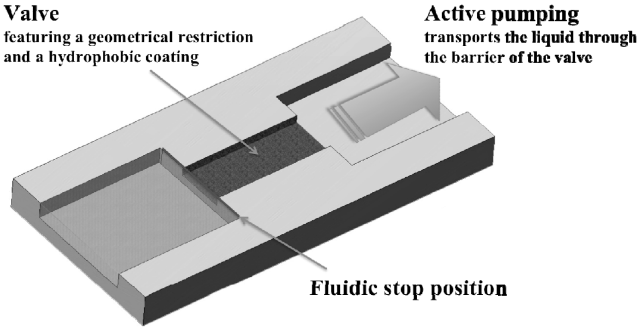

Figure 1: Principle of a hydrophobic valve comprising a geometrical restriction and a hydrophobic coating. A liquid plug can be pulled over the valve by a static or transient pressure gradient.

Due to the fluorinated or perfluorinated nature of solvents (e.g., Fluorinert FC-77, 3M) used for dissolving fluoropolymers (e.g., Teflon AF 1600, Du Pont), standard dyes (chromophores and fluorophores) as well chromophores featuring non-polar groups are inapplicable for fluoropolymer solutions. Thus, alternate possibilities for dying the fluoropolymer solution have been researched. Carbon black (Type 901, Degussa) was identified as a possible dye which in the combination with Teflon is mainly used in fuel cells. If ultrasonicated in a fluoropolymer solution, a dispersion is created. Upon drying and evaporation of the solvent, a Teflon-carbon black layer is formed comprising carbon black particles with a size of roughly 500 nm encased in Teflon. This not only provides a very good visibility but also superhydrophobic properties (contact angle > 150°, Fig. 2) if a high enough particle density (i.e., total applied volume per surface area) is deposited (> 11 ng/mm²). A suitable composition and the respective water contact angle in contrast to a Teflon-only solution is given in Tab. 1.

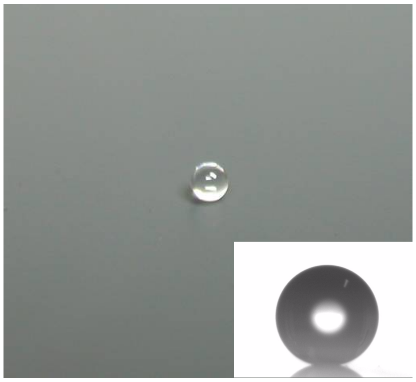

Figure 2: DI-water droplet on a Teflon-CB coated surface exhibiting a strong water- repelling property.

Table 1: Table presenting two suitable fluoropolymer solutions and the respective water contact angles. With the use of carbon black (CB) as dye, superhydrophobic surfaces can be created.

Patch Material	Solvent	Contact Angle [°]
0.5 wt% Teflon AF 1600	3M Fluorinert FC-77	119.5 +/- 0.8
0.5 wt% Teflon AF 1600 0.25 wt% carbon black	3M Fluorinert FC-77	157.9 +/- 2.1

APPLICATION: RNA AMPLIFICATION CHIP

As proof-of-principle, the RNA amplification chip (Fig. 4-A) of the research project Microactive [9] which has been fabricated by injection molding is patterned with the proposed fluoropolymer solutions. The chip, made from COC (type 5013, Ticona), comprises 8 parallel channels with 3 hydrophobic valves (Fig. 4-B) each, one valve for metering of the sample, one valve for confining the sample during the rehydration of dried reagents and one valve for the confinement in the amplification chamber. The consecutive valves feature increasing burst pressures due to decreasing dimensions in width and depth of the structures thus permitting sequential transfer of the sample plugs. To permit a capillary priming of the single channels, the chip features an overall hydrophilic surface coating with PEG (P2263, Sigma-Aldrich). Further, the chip is sealed with a polyolefin foil featuring a pressure-sensitive, silicone-based adhesive (Advanced Polyolefin Microplate Sealing Tape 9795, 3M).

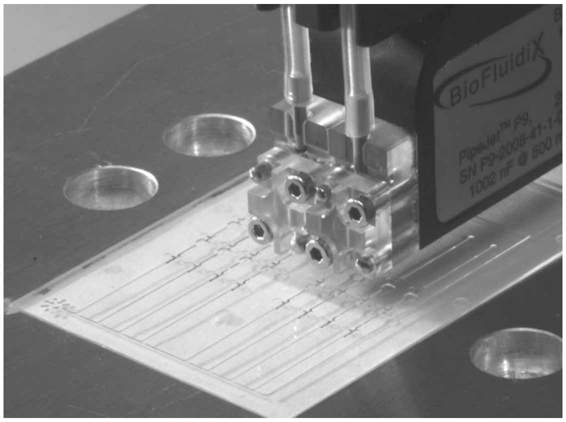

Figure 3: Patterning the RNA amplification chip of the research project Microactive [9]. The nL-Dispenser is moved in parallel over the valve structures and a dispensing is triggered during movement.

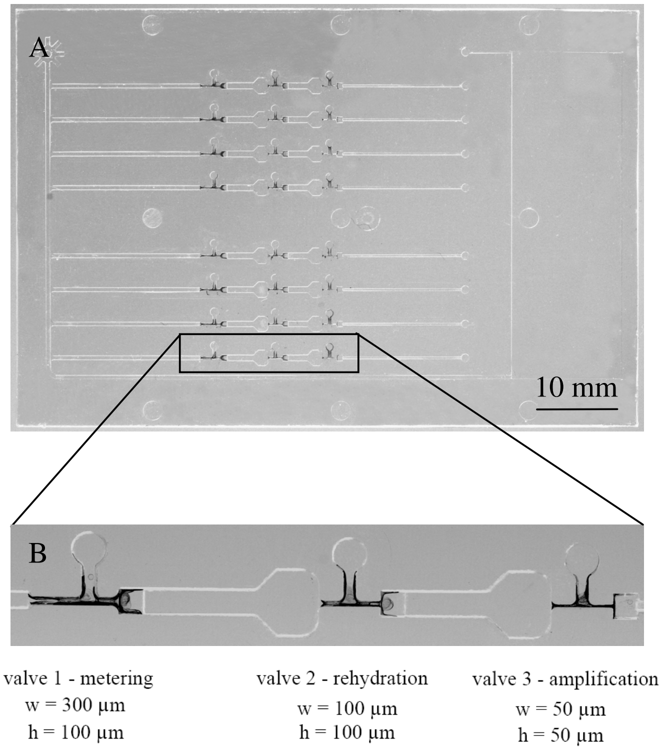

Figure 4: (A) RNA amplification chip of the research project Microactive [9] comprising 8 parallel channels with 3 valves each. (B) Close-up of the three high-quality coated valve structures which feature increasing burst pressures due to decreasing dimensions. The sample plug is moved via a static pressure gradient over valve 1 after the sample has been metered and over valve 2 after the reagents have been rehydrated and stays before valve 3 for the amplification reaction.

Due to the small dimensions of the valves, the solution cannot be applied by a standard pipette due to the high risk of overflow. Thus, the valves are coated with a commercial dispenser (PipeJet^{TM} P9, BioFluidiX) which enables precise dispensing of droplets in the lower nL range even for particle-containing liquids. Best patterning results are achieved by dispensing five to fifteen (depending on the valve) 10 nL droplets of the respective fluoropolymer solution in short succession (~ 1 Hz). To this end, the dispenser is moved in parallel by an automated stage (BioSpot^{TM}, BioFluidiX) over the valve structures (Fig. 3) with a velocity of 50 mm/s. Each time the actual coordinate matches one of the pre-programmed valve coordinates, a dispensing is triggered by the software. This procedure is repeated until sufficient coverage of the respective valve is ensured. Then, the dispenser moves to the next row of valves and continues with the patterning. A single chip can be processed in less than one minute.

QUALITY CONTROL AND EXPERIMENTAL RESULTS

Example images of negative cases for the quality control are depicted in Fig. 5-A, i.e. overflow for valve 1, fluidic shortcut by insufficient coating of the bottom wall for valve 2 and insufficient coverage at the inlet for valve 3. Positive cases are shown in Fig. 5-B. For a non-optimized patterning, most of the measurement channels failed to operate properly.

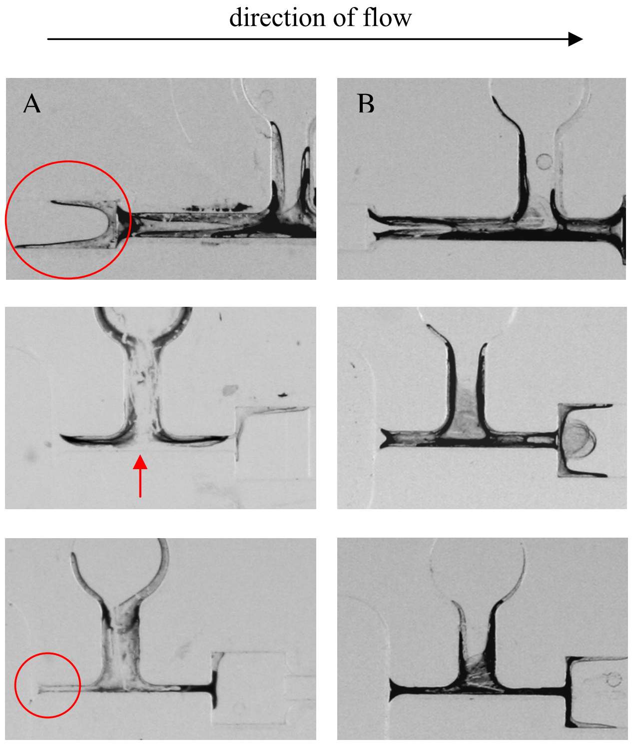

Figure 5: (A) Images of low quality valves detected by the visual quality control (all inlets are on the left sides of the structures). For valve 1 (upper left), an overflow into the metering channel at the valve inlet is observable which would lead to a falsely metered sample. For valve 2 (middle left), a fluidic shortcut would occur while for valve 3 (bottom left), the front end of the restriction is not completely covered which would reduce the burst pressure of the valve. (B) Images of high quality valves. It should be noted that the exit areas of the valves are intentionally covered to prevent pinning of the liquid meniscus during valve burst.

The measured burst pressure values for valves patterned using optimized parameters, i.e. single droplet volume, number of droplets, time between dispenses as well as spot position due to the quality control are summarized in Fig. 6. It can be seen that with the Teflon-CB coating, the highest burst pressures as well as the best reliability (CV < 4 % for valve 1, CV < 7 % for valve 2 and CV < 8 % for valve 3, respectively) can be achieved.

The deviation of the theoretical values indicates that the radius of curvature of the meniscus is limited which implies that a coating featuring a contact angle greater than 140° does not further increase the burst pressure of the valve. The higher CVs for the Teflon (CV < 12 % for valve 1, CV < 13 % for valve 2 and CV < 21 % for valve 3, respectively) reflect the inability to do an on-site quality control.

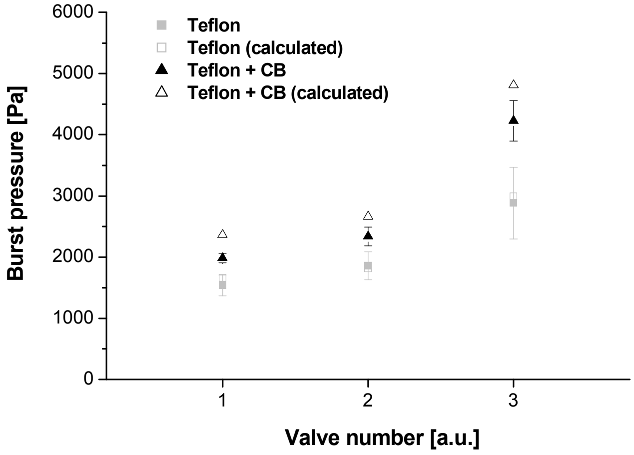

Figure 6: Measured and calculated burst pressures of the valves at the three positions for the two different coatings. Each average pressure and CV value represents data from ~ 15 valves. The highest burst pressures and the best reliabilities (mean CV = 6.1 %) are achieved with the Teflon-CB coating. The higher mean CV of 14.5 % for the Teflon-only coating can be explained by the inability to do an adequate on-site quality control. The deviation of the theoretical values for the Teflon-CB coating indicates that a coating exhibiting a contact angle greater than 140° does not further increase the burst pressure of the valve.

CONCLUSION

With the introduced fluoropolymer-dye solution, namely Teflon-carbon black, the hydrophobic patterning of microfluidic chips can be significantly improved. First, the good visibility of the dried material allows for efficient visual quality control. Second, the coating can create superhydrophobic surfaces (typical layer thickness: 2 µm) on arbitrary polymer substrate materials due to the highly wetting solvent as well as the strong adhesion of the coating. If applied on passive valve structures, it can largely increase the burst pressures of the valves.

As a consequence, strong and highly reliable hydrophobic valves can be rapidly produced by simple dispensing without the need of costly clean-room processes which is especially suitable for low-cost lab-on-a-chip systems based on polymer chips.

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