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Dye-based coatings for hydrophobic valves and their application to polymer labs-on-a-chip

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Abstract
We provide a method for the selective surface patterning of microfluidic chips with hydrophobic fluoropolymers which is demonstrated by the fabrication of hydrophobic valves via dispensing. It enables efficient optical quality control for the surface patterning thus permitting the low-cost production of highly reproducible hydrophobic valves. Specifically, different dyes for fluoropolymers enabling visual quality control (QC) are investigated, and two fluoropolymer-solvent-dye solutions based on fluorescent quantum dots (QD) and carbon black (CB) are presented in detail. The latter creates superhydrophobic surfaces on arbitrary substrates, e.g. chips made from cyclic olefin copolymer (COC, water contact angle = 157.9°), provides good visibility for the visual QC in polymer labs-on-a-chip and increases the burst pressures of the hydrophobic valves. Finally, an application is presented which aims at the on-chip amplification of mRNA based on defined flow control by hydrophobic valves is presented. Here, the optimization based on QC in combination with the Teflon-CB coating improves the burst pressure reproducibility from 14.5% down to 6.1% compared to Teflon-coated valves.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The ongoing trend towards decentralized point-of-care technologies in medical diagnostics has stimulated the development of miniaturized 'lab-on-a-chip'-systems [1–4]. For some time, there has been a strong trend towards polymer labs-on-a-chip [5, 6] specifically due to their amenability for low-cost mass-production. These labs-on-a-chip feature a set of basic unit operations such as sample injection, separation, metering and mixing to integrate and thus automate full diagnostic tests on a typically credit card-sized microfluidic substrate. To conduct complex protocols of unit operations, the fluid 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 disposable chips.

A simple way of retaining liquids is the use of hydrophobic patterns for flow control due to the change in surface tension [7–9]. Another approach utilizes capillary valves, i.e. geometrical restrictions to pin liquid plugs at defined positions due to a pressure drop [10, 11]. Both concepts can be combined in the form of a hydrophobic valve [12], i.e. a capillary valve featuring a hydrophobic coating. This provides a higher retention force than the purely capillary

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valve. Sophisticated polymer chips integrating hydrophobic valves have already been reported [13, 14]. To fabricate hydrophobic valves, the coatings are applied by various means, e.g. pipetting, the use of a felt pen [15], plasma processes [16, 17], spray coating [18] or dispensing [19, 20].

The typically micron-thick hydrophobic coatings exhibit insufficient visibility especially in transparent polymer labs-on-a-chip. As measuring each burst pressure for different patterning parameter settings is an inefficient approach, enabling a rapid visual inspection with the use of dyes is a highly preferable method for quality control. Further, 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. Thus, different means of application are more or less suitable depending on the boundary conditions.

In this paper, fluoropolymer-solvent-dye solutions enabling the visual inspection of the localized coating and with it a quality control for the hydrophobic patterning are presented. The novel Teflon-carbon black (CB) solution allows for the creation of superhydrophobic surfaces on arbitrary substrates and thus the fabrication of stronger hydrophobic valves. Further, we present an application where the favorite coating candidates are applied via nL-dispensing. Finally, we discuss the results of the measured burst pressures and conclude.

2. Dyes for fluoropolymer solutions

Due to the fluorinated or perfluorinated nature of solvents used for dissolving fluoropolymers, standard polar dyes (chromophores and fluorophores) as well as chromophores featuring non-polar groups are inapplicable. This can be explained by the highly non-polar nature of the solvents and by the absence of dipolar forces as well as the formation of hydrogen bonds in the solution.

One possibility is the use of fluorinated azomethine dyes which have been synthesized by the group of Schrader [21, 22]. Different derivates of this type of dye have been mixed with the solvents containing fluoropolymers. For one derivate (type T 42), good solubility and similar hydrophobicity (∼120°) compared to the non-dyed fluoropolymer solution has been measured although the visibility in a microchannel is insufficient (i.e. low contrast with respect to the substrate). Another possibility for dyeing of a fluoropolymer solution is the use of a microemulsion based on Reichardt's dye and acetonitrile [23]. Again, the dried spots exhibit similar hydrophobicity but the visibility is again insufficient (refer to table 2). Fluorescent quantum dots (QDs) [24] are not soluble in perfluorinated solvents. Still, QDs (Lumidot 640, Sigma-Aldrich, Germany) disperse if mixed with different perfluorated solvents. The quality of the dispersion is not very reproducible, and there is a strong variation in relative fluorescence intensity for different types of QDs (i.e. emission wavelengths). Thus, the solubility has been tested in different fluorinated solvents and a fluorochlorocarbon (Freon-11, Sigma-Aldrich, Germany) has been found suitable for this application. The downside of using the fluoropolymer-QD-Freon solution is the difficult handling due to its very high volatility (i.e. its fast evaporation).

Table 1. Contact angle measurements (data represent at least six measurements per coating) of Teflon and Teflon-carbon black-coated chip surfaces (featuring a similar surface coverage). For the coating with the low carbon black content (0.1 wt%), the surface no longer exhibits superhydrophobic behavior and the contact angle is in the range of a solely Teflon AF-coated surface.

Surface coverage (nL mm^{-2})	Fluoropolymer & carbon black content in solution	Contact angle
100	0.5 wt% Teflon AF 1600	119.5° ± 0.8°
100	0.5 wt% Teflon AF 1600 0.1 wt% carbon black	124.4° ± 2.1°
100	0.5 wt% Teflon AF 1600 0.125 wt% carbon black	157.8° ± 3°
100	0.5 wt% Teflon AF 1600 0.175 wt% carbon black	159.0° ± 2.6°
100	0.5 wt% Teflon AF 1600 0.25 wt% carbon black	158.8° ± 2.5°
100	0.5 wt% Teflon AF 1600 0.5 wt% carbon black	156.1° ± 3.5°

Thus, alternate possibilities for dying the fluoropolymer solution have been researched. Carbon black (Type 901, Degussa, Germany) has been identified as a fourth possible dye which in combination with Teflon is mainly used in fuel cells. If ultrasonicated in a fluoropolymer solution, a stable dispersion is created. Upon drying and evaporation of the solvent, a fluoropolymer-carbon black layer is formed comprising carbon black particles with a size of roughly 50 nm encased in the fluoropolymer. This not only provides very good visibility but also superhydrophobic properties (contact angle > 150°) if a high enough particle density (i.e. total applied volume per surface area) is deposited (table 1).

The effect can be explained by the formation of a micro–nano binary structure [18, 25]. This provides the required surface roughness [26, 27] to create superhydrophobic surfaces with low surface energy polymers. The increase in hydrophobicity arises from an increase in the surface area that has to be wetted by water. Above a critical value of roughness, the drop contacts only with a small fraction of the surface, trapping air between the drop and the surface [26].

An image showing a 2 μL droplet not wetting a Teflon-CB surface as well as an AFM image of the Teflon-CB surface (table 2, solution 5) is depicted in figure 1. The latter shows distinct surface roughness with a roughness average (*Ra*) of 134 nm. In comparison, the injection-molded valves of the microfluidic chip presented in section 3 exhibit a roughness average of $Ra = 38 \pm 6$ nm.

To summarize, different fluoropolymer-dye solutions based on a 0.5 wt% solution of Teflon (Teflon AF 1600, DuPont, USA) have been investigated for contrast and hydrophobicity. The respective solution compositions, static contact angles as well as the relative contrast are summarized in table 2. The contrast has been determined by measuring the visible light transmission of a coated glass slide (100 nL mm^{-2} coverage). As devices, a standard microscope (Axiophot, Zeiss, Germany) and CCD camera (Axiocam MRc, Zeiss,

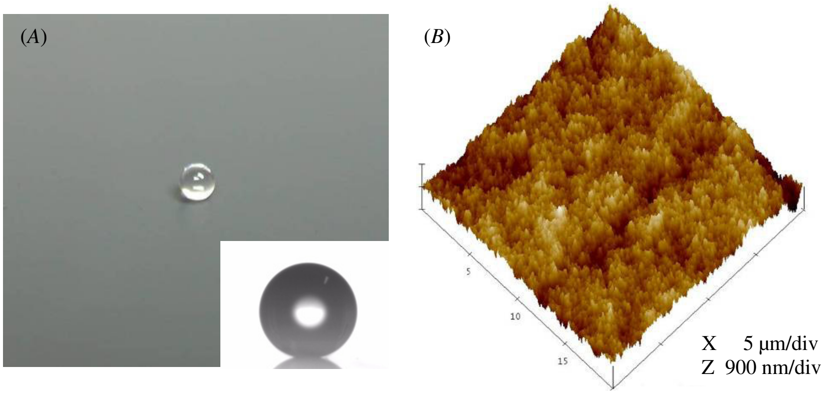

Figure 1. (*A*) DI-water droplet on a Teflon-CB-coated surface. (*B*) AFM image of a Teflon-CB surface (100 nL mm^{-2}, 0.25 wt% carbon black) exhibiting a roughness average Ra of 134 nm.

Table 2. Table presenting six fluoropolymer solutions (labeled 1–6), the respective water contact angles (data represent at least ten measurements per coating) and the relative contrast of the coating on a transparent surface.

No	Fluoropolymer and dye content	Solvent	Contact angle	Relative contrast	Image
1	0.5 wt% Teflon AF 1600	3 M Fluorinert FC-77	119.5° ± 0.8°	0%	
2	0.5 wt% Teflon AF 1600 1.0 wt% Reichardt's Dye	FC-77 2.0 wt% Acetonitrile	125.0° ± 1.6°	7%	
3	0.5 wt% Teflon AF 1600 0.025 wt% Lumidot 640	Freon-11	107.6° ± 2.5°	SNR $> 10^{*}$	
4	0.5 wt% Teflon AF 1600 0.125 wt% carbon black	3 M Fluorinert FC-77	157.8° ± 3.0°	87%	
5	0.5 wt% Teflon AF 1600 0.25 wt% carbon black	3 M Fluorinert FC-77	157.9° ± 2.1°	98%	
6	0.5 wt% Teflon AF 1600 0.5 wt% carbon black	3 M Fluorinert FC-77	156.1° ± 3.5°	100%	

Note: for the Teflon-QD surface, no contrast value but a signal-to-noise ratio (SNR) is given due to its use as a fluorescent dye. A mean SNR > 10 has been measured for the coated valves using the same setup as described above.

Germany) have been utilized. The mean gray-scale values have been normalized to the highest absorbing sample to result in relative contrast values.

When analyzing the results, the solution based on Reichardt's dye exhibits similar hydrophobicity compared to the Teflon-only coating. However, it does not feature good contrast (i.e. $\ll$50%) to enable visual quality control. Teflon-QD-coated surfaces provide adequate fluorescence intensity when compared to non-coated surfaces (SNR > 10 for the given setup) and can thus be easily discriminated. Still, this comes at the cost of reduced hydrophobicity. Differently diluted Teflon-CB solutions all feature good contrast (>50%). Additionally, Teflon-CB-coated surfaces are superhydrophobic for high surface coverage (refer to table 1).

3. Application: microactive RNA amplification chip

3.1. Chip principle and processing

As a proof-of-principle, the microfluidic chip (figure 2(*A*)) of the research project Microactive [28] is patterned with the proposed fluoropolymer solutions. The chip enables the parallel screening of purified patient samples for e.g. different HPV (human papilloma virus) types which are detected by NASBA (nucleic acid sequence-based amplification).

The chip is fabricated by injection molding from COC (type 5013, Ticona, Germany) and comprises eight parallel channels with three hydrophobic valves (figure 2(*B*)) each: valve 1 for a defined metering of the sample, valve 2 for confining the sample during the rehydration of dried reagents and valve 3 for the sample confinement in the amplification chamber during read-out. The consecutive

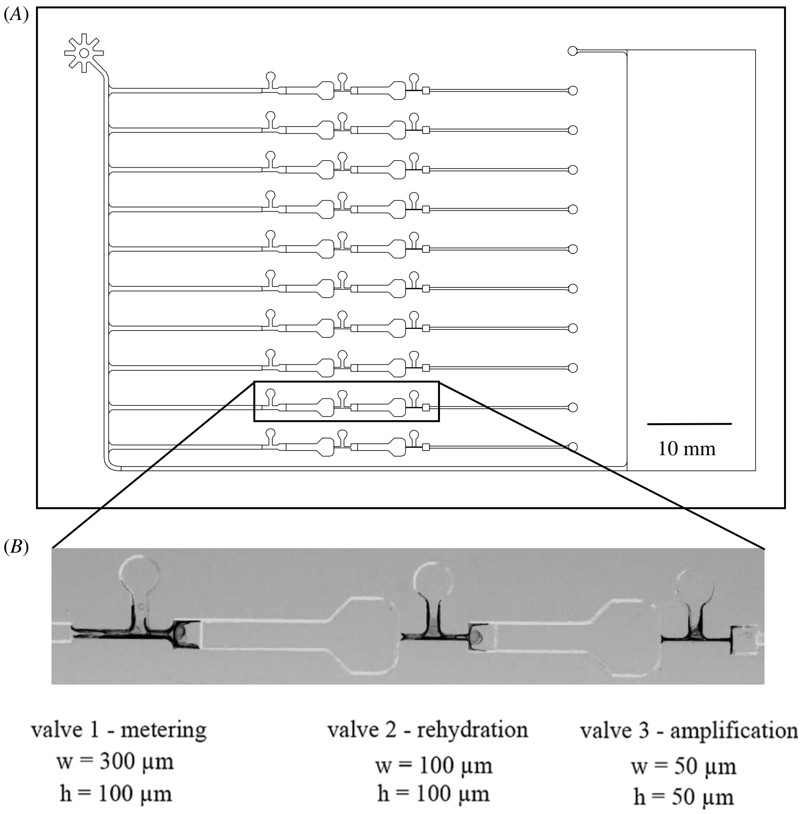

Figure 2. (*A*) RNA amplification chip schematic [28] comprising eight parallel channels with three valves each. (*B*) Close-up of the three high-quality coated valve structures which feature increasing burst pressures due to decreasing dimensions. The sample plug is moved via a static pressure gradient 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.

valves feature increasing burst pressures due to decreasing width and depth of the structures thus permitting sequential transfer of the sample plugs. To permit a capillary priming of the channels, the chip is coated by pipetting 60 μL of a 4.8 mg mL^{-1} PEG (mol. weight 15000–20000 Da, P2263, Sigma-Aldrich, Germany)-methanol solution into the channels. Further, the complete chip is sealed with a polyolefin foil featuring a pressure-sensitive, silicone-based adhesive (Advanced Polyolefin Microplate Sealing Tape 9795, 3M, USA). It should be noted that a low-quality sealing (i.e. sagging of the sealing foil into the restrictions) can have a strong impact on the burst pressures and should thus be prevented by, e.g., using a soft stamp to release the pressure-sensitive adhesive. Before priming the channels by a capillary action, the inlet as well as the outlets is opened with the use of a scalpel. A syringe pump for plug movement is connected via an adapter plate to the outlets.

3.2. *Fabrication of hydrophobic valves*

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$^{\mathrm{TM}}$ P9, BioFluidiX, Germany). The applied nozzle features a diameter of 200 μm which enables precise dispensing of droplets in the lower nL range even for particle-containing liquids while exhibiting a low risk of clogging during operation. The spotting is optimized by varying the following parameters: the single droplet volume, the number of dispensed droplets, the time between dispenses as well as the droplet target position(s). The boundary condition is the minimum coverage required to create a hydrophobic surface in the restriction which translates into a target volume. It would of course be desirable to coat each valve with a single dispense, only. However, as single droplets with volumes >50 nL can already lead to overflow, it is preferable to dispense a number of smaller droplets instead. Further, if the time between dispenses is set too short (which depends on the vapor pressure of the solvent), the droplets will merge and thus potentially clog the valve. The droplet target position primary impacts on the risk of overflow especially when adjacent to the beginning of the restriction.

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 by a spotter (BioSpot$^{\mathrm{TM}}$, BioFluidiX, Germany) in parallel over the valve structures (figure 3) with a velocity of 50 mm s^{-1}. Each time the actual coordinate matches one of the pre-programmed valve coordinates, a dispensing is triggered by the software. This procedure is repeated a defined number of times 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 1 min.

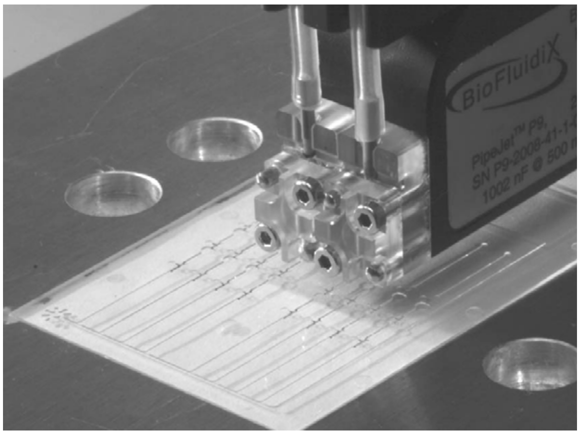

Figure 3. Patterning procedure of the RNA amplification chip. The nL-dispenser is moved in parallel over the valve structures and a dispensing is triggered during movement.

Table 3. Summary of the solutions used in the experiments (please refer to table 2) and the estimated valve surface coverage.

Valve no	Solution no	Estimated surface coverage (nL mm^{-2})
1	1, 3, 5	150
2	1, 3, 5	150
3	1, 3, 5	200

Table 3 summarizes the estimated surface coverage as well as the coating solutions for valves 1–3 (refer to figure 2). Note that more material is applied to the valves surfaces in comparison to the substrates used for the contact angle measurements. This can be explained by the non-uniform valve coating due to wicking of the coating solution after dispensing, i.e. a higher amount is dispensed into the restrictions to ensure superhydrophobicity for the Teflon-CB coating (refer to table 1).

Further, for the Teflon-CB coating, solution 5 is used which requires more dispenses than the highest concentrated solution. However, when using the latter for coating the smallest structures (width w = 50 μm), Teflon-CB coated filaments have been observed in the restrictions in some cases. This originates from an increase in solid concentration due to evaporation. To reduce the risk of valve clogging, the lower concentrated solution has thus been used for the hydrophobic patterning.

3.3. Burst pressure measurements

For determining the burst pressure, each channel is individually connected to the measurement setup, primed with deionized water and sealed (figure 4). Then, valve B is closed and valve A is opened. The syringe pump is now used to create a defined underpressure. If the hydrophobic valve breaks, a pressure drop is detected by the pressure sensor. The burst pressure corresponds to the pressure level prior to the pressure drop.

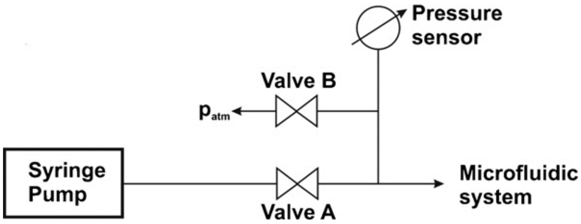

Figure 4. Schematic for measuring the burst pressure featuring switching valves, a pressure sensor and a syringe pump.

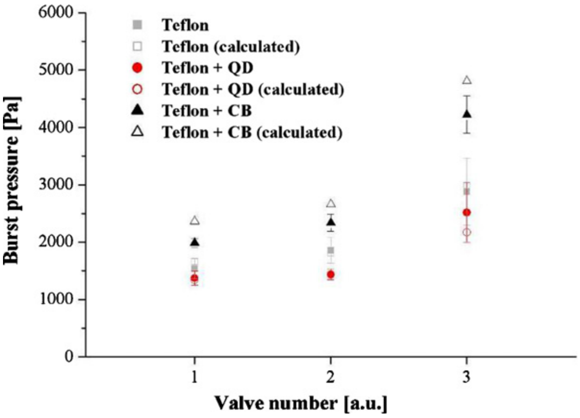

Figure 5. Measured and calculated burst pressures of the three valves for the three different coatings. Each average pressure and *CV* value represents data from ~15 valves. The highest burst pressures and the best reproducibilities (mean *CV* = 6.1%) are achieved with the Teflon-CB coating. The higher mean *CV* of 14.5% for the solely Teflon coating can be explained by the inability to do an on-site quality control.

The measured burst pressures for valves patterned using optimized parameters are summarized in figure 5. The parameters have been acquired by visually inspecting Teflon-CB-coated valves and varying the single droplet volume, number of droplets, time between dispenses as well as spot position. It can be seen that with the Teflon-CB coating, the highest burst pressures as well as the best reproducibility (coefficient of variation *CV* < 4% for valve 1, *CV* < 7% for valve 2 and *CV* < 8% for valve 3, respectively) can be achieved (mean *CV* = 6.1%).

The deviation of the theoretical values (calculated by modifying the Young–Laplace equation according to [29]) could indicate that the radius of curvature of the meniscus is limited for this geometry. The liquid plug is deformed prior to valve burst and the meniscus could get in contact with the restriction walls prematurely when it is pulled inside the restriction. Thus, a coating featuring a contact angle greater than 140° does not further increase the burst pressure of the presented valves.

The higher *CV*s for the Teflon (*CV* < 12% for valve 1, *CV* < 13% for valve 2 and *CV* < 21% for valve 3, respectively, mean *CV* = 14.5%) reflect the inability to do an on-site quality control. Depending on the maturity of the chip processing, the spotting coordinates or number of droplets may have to be changed to compensate for variations in, e.g., the hydrophilic coating. This can prove to be quite difficult if no visual feedback is possible.

For the Teflon-QD, the higher *CV*s (*CV* < 9% for valve 1, *CV* < 9% for valve 2 and *CV* < 23% for valve 3, respectively) can be explained by the difficult handling of the liquid due to its very fast evaporation. This impacts on the accuracy of dispensing and increases the risk of clogging the dispenser nozzle. A very mature spotting process is therefore required to effectively apply this solution. Also, the burst pressures are lower due to the reduced contact angle. Thus, only in cases where solely a fluorescent dye can be accepted as a method for quality control, Teflon-QD is recommended as coating while Teflon-CB is the clear favorite in all other cases.

3.4. Biocompatibility of Teflon-CB

Teflon-CB as coating has also been tested in respect to biocompatibility. To this end, standard PCR strips were coated with Teflon-CB (solution 5) covering small and large surface areas within microcentrifuge tubes (Eppendorf). The Teflon-CB solution was applied to the tubes in 1 μL droplets while three different tests were performed. The coated strips were subsequently used to perform NASBA reactions based on the PreTect$^{\text{TM}}$ HPV-Proofer kit (NorChip AS) to evaluate whether the Teflon/carbon black surface would inhibit the enzymatic reaction. A positive control for HPV 16 was used as sample material. Each tube contained a reaction mixture of 20 μL. All tubes with positive control amplified. Thus, it is assumed that for large reaction volumes, the Teflon/carbon black surface does not inhibit the enzymatic reaction.

4. 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 good adhesion of the coating. If applied on passive valve structures, it can largely increase the burst pressures of the valves. Third, the biocompatibility of the material should allow for the application in a wide range of lab-on-a-chip-based assays.

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

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