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Toward Fabric-Based Flexible Microfluidic Devices: Pointed Surface Modification for pH Sensitive Liquid Transport

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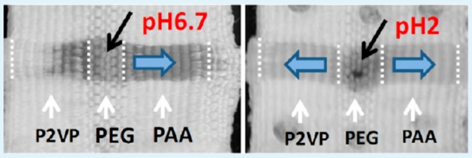

ABSTRACT: Microfluidic fiber channels with switchable water transport are fabricated in flexible textile PET/PP materials using a preprogrammed yarn-based fabric and a yarn-selective surface modification method. The developed robust and scalable fabrication method is based on the selective functionalization of the PET yarns with an epoxide-containing polymer that is then followed by grafting patterns of different pH-sensitive polymers PAA [poly(acrylic acid)] and P2VP [poly(2-vinyl pyridine)]. The selective functionalization of the fabric yields an array of amphiphilic channels that are constrained by hydrophobic PP boundaries. Aqueous solutions are transported in the amphiphilic channels by capillary forces where the direction of the liquid transport is defined by pH-response of the grafted polymers. The channels are fed with liquid through hydrophilic, pH insensitive PEG [polyethylene glycol] ports. The combination of the PAA and P2VP patterns in the amphiphilic channels is used to create pH-sensitive elements that redirect aqueous liquids toward PAA channels at pH > 4 and toward both PAA and P2VP channels at pH < 4. The system of pH-selective channels in the developed textile based microfluidic chip could find analytical applications and can be used for smart cloth.

KEYWORDS: *microfluidic devices, fabric, polymer grafting, wicking, yarn, thread*

INTRODUCTION

The development of economical, accurate, and user-friendly microfluidic devices has attracted great attention in the field of bioengineering, drug development, and medical diagnostics.[1,2] Indeed, microfluidic chips that are engineered to transport small volumes of fluids to a precise location, are extensively reported in literature.[1−7] Currently, lithographic techniques are regularly and successfully used to create microchannels in silicon, glass, and polymer substrates for the transport of liquids.[8−10] However, the complexity and the relatively high cost of lithographic manufacturing are continuous stimuli for the development of more economical and scalable approaches to the fabrication of microfluidic devices.[11−16] Specifically, fibrous materials, such as paper and threads (yarns), are under consideration for the capillarity-driven distribution of fluids without the utilization of external pumping devices.[17]

High wicking ability is the most prominent characteristic of paper-based microfluidic devices (μPADs).[18−25] Further advantages of paper-based devices are that paper is inexpensive, lightweight, biodegradable, broadly available, compatible with biological samples, and easy to functionalize.[26] On the other hand, paper wicks liquid isotropically, and to fabricate a microfluidic device, it is necessary to create flow channels using lines of hydrophobic polymers.[11,12] The micropatterns on paper have been fabricated with simplified lithography, plasma activation, and deposition of a hydrophobic polymer with an inject printer or pen.[18,21,22,27,28] To date, an analysis of blood type, pH value, and glucose and protein content in urine with μPADs has been successfully performed.[19,20,29]

Recently, threads/yarns have become alternative material for low-cost point-of-care (POC) diagnostics.[11−15,30] Many types of yarn, such as cotton,[15] nylon,[12] polyester,[31] silk,[14] and PVDF,[17] have been used to develop thread-based microfluidic devices (μTADs). Protein, nitrite, and ketone colorimetric assays, enzymatic colorimetric assay for glucose and alkaline phosphate detection, uric acid analysis, and antibody−antigen reaction have been performed with μTADs.[12,14,32] Numerous advantages of the yarn can be mentioned: flexibility, lightweight, one-dimension capillary flow, straightforwardness of chemical modification, possibility of large volumetric flow, and vast potential for mass production.[11,12,33] The potential for thread to control fluid direction and to be incorporated into complex microfluidic structures has been recently demonstrated. For example, Li et al.[32] tailored the wettability of cotton yarn with plasma oxidation and sewed the yarn into the polymer surface to fabricate μTAD. Reches et al.[12] demon-

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strated three different designs for the μTAD: woven array, branching design, and sewn array design. In addition, the wicking properties of nine different threads before and after plasma treatment were examined. It was also shown that thread knots can be employed as effective mixers, splitters, and locations for the detection zone.[12,13] The flow resistance of knots with different topologies has also been studied.[30] Bahandari et al.[14] utilized a conventional weaving technique to fabricate a fabric-based sensor. Specifically, silk yarns (with different wicking properties) were used to form strip-control units in fabric. Owens et al.[11] utilized hydrophobic polypropylene (PP) and hydrophilic poly(ethylene terephthalate) (PET) yarns to systematically engineer woven textile fabric to create amphiphilic microchannels with defined orientations and locations. As a result, the microfluidic coflow of immiscible liquids (water and dodecane) within the textile structures was demonstrated.

In general, either unmodified or premodified threads/yarns are used to obtain the thread-/yarn-based microfluidic prototype devices. To scale up the production of the devices, traditional textile machinery has to be used and various sizing agents should be applied to the yarns before the manufacturing. Therefore, an extensive cleaning procedure to remove sizing agents (after the fabric is made) is needed to expose the fiber surface. During the cleaning procedures, the surface properties of the unmodified and premodified fibers constituting the yarns will be changed and may not possess the necessary characteristics. One of the ways to overcome this limitation is to produce textile materials of necessary structure from unmodified yarns only that can be later locally modified using high-throughput (e.g., inkjet printing) techniques to target a specific application. To this end, we report here a methodology for pointed surface modification of model textile microfluidic devices to produce functional (pH sensitive, acidic, and basic reported here) yarn-based channels in the textile device.

Specifically, fabrication of model microfluidic textile chips woven from PP and PET fibers was studied in this work. PP fibers were used to form hydrophobic boundaries for the yarn microchannels made of PET. Next, the PET yarns were modified with a nanoscale layer of epoxy-containing polymer to introduce the epoxy reactive groups to the fiber surface. The modification did not affect the PP parts of the fabric, leaving them hydrophobic and nonreactive. As a result, generic reactive channels were obtained. Finally, the reactive channels were locally modified with polymers of dissimilar nature via the "grafting to" technique,[34] and fabric was obtained, possessing PET yarn-based channels having carboxylic (acidic) and pyridine (basic) surface functionalities within each channel. The dimensions of the modified area can be controlled via the volume of a droplet of a reactive polymer solution placed on a predetermined location on the fabric. We foresee that, using inkjet printing techniques, the method reported in this publication can be easily scaled-up and employed to mass produce yarn-based microfluidic devices.

■ EXPERIMENTAL SECTION

Materials. PET multifilament yarn (500/70 Denier-3Ztwist) was provided by Middleburg Yarn Processing Co Inc. PP multifilament yarn (100/40 Denier) was provided by Fiber Visions, Inc. and was twisted (4Z) with Saurer Allma Assembly Twisting Machines to achieve required mechanical properties for weaving. All chemical reagents (acetone, toluene, ethanol, methanol, methyl ethyl ketone (MEK), HCl, and NaOH) were purchased from Sigma Aldrich. In our experiments, we used freshly deionized (DI) water produced by Milli-Q (Millipore) deionizer. The pH value of the DI water, as measured by Sartorius Docu pH Meter, was 6.7 ± 0.1. The pH value was adjusted to a required level using HCl (for pH2) and NaOH (for pH 9).

Poly(glycidyl methacrylate) (PGMA) ($M_n \approx 80\,000$ g/mol) was synthesized by free radical polymerization of glycidyl methacrylate (Aldrich) and fluorescence labeled with a small amount of Rhodamine B (Alfa Aesar) according to the published procedure.[34] Polyacrylic acid (PAA) ($M_w \approx 100\,000$ g/mol, 35 wt % in H_2O) was purchased from VWR International. The polymer was precipitated in acetone and dried in a vacuum oven. Carboxy-terminated poly(2-vinyl pyridine) (P2VP-COOH) ($M_n \approx 53{,}000$ g/mol) was purchased from Polymer Source. Poly(ethylene oxide) (PEO) ($M_n \approx 1\,000\,000$ g/mol) was purchased from Sigma Aldrich. Poly(ethylene glycol) monomethyl ether ($M_n \approx 5000$ g/mol) obtained from Aldrich was modified by succinic anhydride (Aldrich) to obtain a carboxy end group derivative (PEG) according to the published procedure.[35] Acylation was carried out by refluxing with large excess (ca. 20) of succinic anhydride in tetrahydrofurane (THF). PEG was purified by multiple precipitations from THF solution in diethyl ether.

Instrumentation. Scanning electron microscopy (SEM) imaging of fabric was performed using a FESEM-Hitachi S4800. PET film deposition for model study was performed using a dip coater (Mayer Fientechnik D-3400). Ellipsometry measurements were taken using a COMPEL discrete polarization modulation automatic ellipsometer (InOmTech Inc.) at an incidence angle of 70° and the refractive index of the polymer layers was set to 1.5. Atomic force microscopy (AFM) was conducted with a Dimension 3100 microscope (Digital Instruments, Inc.). Silicon tips with spring constants of 50 N/m were used to scan the surfaces. All of the imaging was done at a scan rate of 1 Hz, employing the tapping mode. Static contact angle measurements were taken using a contact angle goniometer (Kruss, Model DSA10). Contact angle measurements were taken with the liquid of interest and a static time of 30 s before angle recording. Calculations of the contact angles were made using the ImageJ (NIH) software. Fluorescence microscopy was conducted with an SZXILL100 microscope (Olympus Optical Co. Ltd., Japan).

Silicon Wafer Model Substrates. Highly polished single-crystal silicon wafers (Semiconductor Processing Co.) were used as model flat substrates. Silicon wafer substrates were initially cleaned with deionized (DI) water in an ultrasonic bath for 30 min. The wafers were then placed in piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for approximately 1 h and rinsed several times with DI water. After rinsing, the substrates were dried under a stream of nitrogen in class 100 clean room conditions. To obtain thin polyester films, PET was dip coated on the clean silicon substrate from a (1 wt/vol %) 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solution. The specimens were placed in a vacuum oven at 140 °C for ~3 h to ensure a complete removal of the solvent and a crystallization of the polymer constituting the film. The PET film was then subjected to an alkali treatment (40% NaOH for 2 min at room temperature) to generate hydroxyl and carboxylate end groups. To avoid film delamination, alkali solution was placed dropwise in the middle of the film, avoiding the edges of the sample. The thicknesses of the dip-coated PET and hydrolyzed PET films, as measured by ellipsometry, were ~70 ± 1.0 nm and ~66 ± 1.0 nm, respectively.

The PGMA anchoring layer was deposited on the hydrolyzed PET substrate from a 0.5 wt/vol % PGMA-RhB solution in MEK by adsorption at 50 °C for 3 h. The unattached polymer was rinsed off with fresh MEK. Then, PAA (1 wt/vol % in methanol), P2VP-COOH (1 wt/vol % in THF), or PEG (1 wt/vol % in methanol) were deposited on the PGMA-RhB layer by drop casting followed by annealing at 120 °C for 1 h, 120 °C for 2 h, and 120 °C for 3 h, respectively. To avoid dewetting during the annealing, 0.1% of ultrahigh-molecular nonreactive PEO was added to the PEG solution.

Fabric Substrates. Woven fabrics were manufactured in Clemson laboratory using computer-controlled AVL 40 in., 24-harness Industrial Dobby Loom. To start with, one-component PET, PP and two-component PET/PP blended fabrics were manufactured. Then, model textile microfluidic chips (Figure 1) comprising both PET and PP yarns were fabricated. Fabric preparation and activation were accomplished according to the procedure published elsewhere.[36,37] To remove any finishes or contaminants, each fabric was rinsed sequentially with DI water, acetone, toluene, ethanol, and last once again with DI water. The clean fabrics were then treated with 40% sodium hydroxide solution (40/30/30 wt % NaOH/methanol/DI water; alcohol was added to improve wettability) for 2 min at room temperature. The fabrics were then rinsed with DI water until all the residues were removed and dried at 80 °C in an oven until constant mass was achieved.

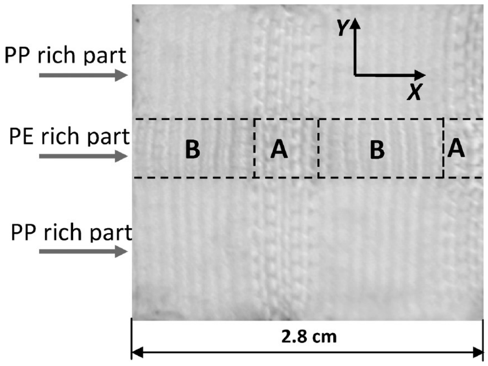

Figure 1. Model textile microfluidic chip where PET-rich stripes are embedded in PP hydrophobic fabric. PET rich part A: Fabric with two-directional positioning of the PET yarns. Section A does not contain any PP threads. PET rich part B: Fabric where PET yarns are positioned in the *X* direction only. Perpendicular (*Y*) fibers in the section B are made of PP.

The alkali-treated fabrics were soaked in a 0.5 wt/vol % PGMA-RhB solution in MEK and vacuum was applied several times to allow polymer solution to penetrate into the yarns of the fabrics. The fabrics were left immersed in the PGMA solution for 3 h at 50 °C. After treating with PGMA, the fabrics were washed several times with MEK and dried until constant mass was obtained. PEG, P2VP-COOH, and PAA were then sequentially grafted to the PET yarns in the PET/PP assembly. This was accomplished by sequentially depositing ~30 μL of each solution dropwise via a micropipet in a specified location for each polymer to create demanded patterns made of different grafted polymers. Annealing each polymer layer was conducted for 1 h at 120 °C prior to depositing the next polymer. The samples were not rinsed to remove unattached polymers until the grafting of all polymers was completed. At the end of the grafting, the samples were rinsed several times with methanol to remove any ungrafted polymers.

■ RESULTS AND DISCUSSION

Model Textile Microfluidic Chip. Model textile microfluidic chips comprised of a fabric possessing a weave pattern where PET-rich stripes were embedded in the PP hydrophobic fabric (Figure 1). The chips were cut of the larger piece of fabric produced using a dobby loom. In this fabric structure, the PP fibers were used to form hydrophobic boundaries for the yarn microchannels made of PET. PET rich part of the chip contained two structural sections (marked A and B in Figure 1). The section A is the fabric with two-directional positioning of the PET yarns. This section does not contain any PP threads. An aqueous liquid placed on A should readily propagate without preferential path in both perpendicular (*Y*) and parallel (*X*) directions until it reaches PP rich part of the textile chip. The section B is the fabric where PET yarns are positioned in the *X* direction only. Perpendicular (*Y*) fibers in the structure are made of PP. Therefore, an aqueous liquid will move preferentially into *X* direction. In fact, when water was placed on the different sections of the chip we observed isotropic (*X*-*Y*) and anisotropic (*X*-direction) propagation of the liquid placed on A and B, respectively. It is important to highlight that movement of water into the PP rich part of the chip was not observed.

In the textile chip, element B is envisioned as a logical element where a liquid possessing a certain characteristics is propagating, while movement of another liquid can be arrested. In this work we targeted to control the movement of an aqueous system based on its pH. To create pH sensitive elements nanoscale layers of pH sensitive polymers were grafted to the yarns in the sections B. Section A is envisioned as a distribution center in the textile microfluidic chip. Liquid placed there is propagating isotropically and, therefore, all yarns in the sections B are supplied with a liquid of interest. To modify fibers in the section B a pH insensitive polymers were employed.

Surface Modification of PET Fibers with an Epoxy-Containing Polymer. Developing a procedure for the surface modification of PET fibers within the PET/PP fabric with a reactive epoxy-containing polymer was the first key step in our study. We selected a PGMA that contained an epoxy group in every repeating unit for the modification of the fiber surface. The polymer was demonstrated to be an effective macromolecular anchoring layer for grafting polymers to inorganic and polymeric surfaces using the “grafting to” and “grafting from” approaches.[34,36,38−40] This method of surface modification was previously used in our laboratory to successfully modify fibrous polymer materials.[37,41−44]

In our initial experiments, fabric consisting of only PET yarn was used. Specifically, to modify the PET threads in the fabric, PGMA macromolecules were adsorbed on the fiber surface from a 0.5% solution in MEK. The chemisorption of the polymer chains was achieved via the reaction between the epoxy groups in the macromolecules and the carboxyl/hydroxyl groups on the fiber surface.[45] Prior to the adsorption, we treated the PET fabric with NaOH solution for 2 min to increase the concentration of the reactive carboxyl groups on the surface. This procedure is an accepted surface hydrolysis method that is commonly employed to increase the reactivity of a polyester fabric.[46] In the model experiment, conducted for the thin PET film deposited on a silicon wafer, we estimated by ellipsometric measurements that only about 3−4 nm of the film (and therefore the fiber) is removed during the treatment. As a result, the water contact angle for the film changed from 65° to 35°, indicating the formation of a significant number of polar (carboxyl and hydroxyl) groups on the PET surface. AFM imaging of the model sample demonstrated that there was, in fact, no significant change in the morphology of the PET film after treatment with NaOH (Figure 2a−2d). Likewise, the SEM study confirmed that the PET fibers were intact after the 2 min exposure to the alkali solution (Figure 3a).

We studied the deposition of the PGMA layer by adsorption from the MEK solution on the model PET film treated with NaOH. The reactive layer can, indeed, be deposited on the PET surface using this method. The thickness of the layer (2.9 nm) for the model PET film deposited on silicon wafer was determined using ellipsometry. The surface coverage (Γ), the PGMA chain density (Σ), and the surface concentration of the epoxy groups present on the surface of the functionalized PET film (epoxy groups/nm^2 = ΣN, where N is the degree of PGMA polymerization, $N \approx 560$) were estimated as described elsewhere.[47] Γ = 3.1 mg/m^2, Σ = 0.024 chain/nm^2, and the

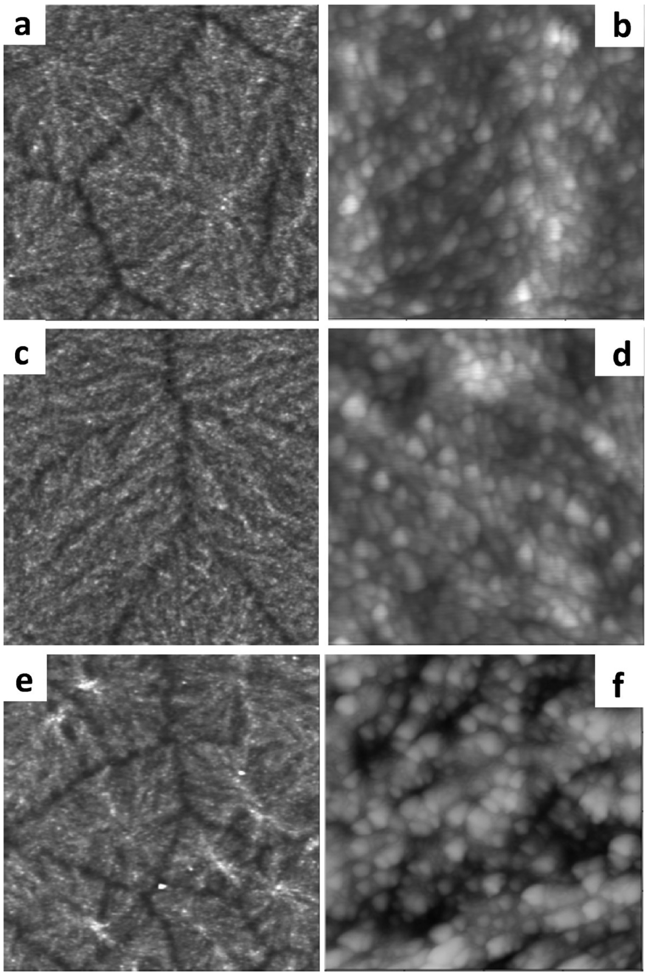

Figure 2. Topographical AFM images of the PET film deposited on silicon wafer (a, b) before treatment with NaOH, (c, d) after treatment with NaOH, and (e, f) after subsequent PGMA adsorption. Vertical scale: 20 nm. Image size: (a, c, e) 10 × 10 and (b, d, f) 1 × 1 μm.

surface concentration of the epoxy groups (≈13 groups/nm^2) were obtained. This data suggests that, by the deposition of minute amounts of PGMA onto the surface, a significant number of reactive groups were anchored to the PET surface. The modification of the model substrate with a nanoscale PGMA layer did not significantly alter the surface morphology of the PET film (Figure 2e and 2f). A change in the water contact angle from 35° to 53° upon deposition of the PGMA layer also confirmed deposition of the epoxy polymer on the surface.

The surface modification approach used to treat the model PET film was applied to the one-component PET, PP, and PET/PP blended fabrics. A SEM study demonstrated that the PET fibers were undamaged after the modification procedure (Figure 3a and 3b). Macromolecules labeled with Rhodamine B were used to confirm homogeneous deposition of the PGMA chains on the fiber surface. Fluorescent microscopy of the textile material treated with fluorescent tagged PGMA showed that the fibers in the PET yarn were evenly covered with the reactive polymer (Figure 3c and 3d), and that when the surface modification method was applied to the PP yarns, no fluorescent signal was observed. This latter result indicated that PP fibers were not covered with the PGMA adsorbed layer, and demonstrates that this treatment method can be used to selectively modify fibers in the PET/PP blended fabric. In fact, when the PET/PP fabric was subjected to the PGMA solution, only PET fibers were modified with the reactive polymer, as evidenced by fluorescent microscopy (Figure 3d). This point surface modification can create hydrophilic and reactive PET yarn channels within hydrophobic and inert PP threads. Water contact angle measurements conducted for the PET/PP blended fabric confirmed the point modification of the textile structure. Figure 4a and 4b shows the high contact angle of a water droplet deposited onto the PP yarns and the absorption of a water droplet when deposited onto the PET yarns.

Modification of PET Yarns in Textile Chip with Polymer Grafting. The PP/PET textile microfluidic chip was treated with NaOH and modified with PGMA. The modification did not affect the PP parts of the fabric, leaving them hydrophobic and nonreactive, thus resulting in generic reactive stripes constituted from PET yarns. To affect the wetting behavior and functionality of the stripes, they were locally modified with polymers of dissimilar nature. The grafting was conducted using the "grafting to" technique, by which end-functionalized polymer molecules reacted with complementary functional groups located on the surface to form tethered chains.[34] For our experiments, we selected three different polymers possessing carboxyl groups capable of reacting with the epoxide groups of the PGMA: PAA, P2VP-COOH, and carboxyl-terminated PEG. The polymers were selected based on pH sensitivity of their surface energies and water sorption characteristics. Surface energy and water sorption differences established by the treatments were used to control the movement of the aqueous liquid along the PET stripes.

Among the polymers selected, PEG is soluble in most liquid media, including water of different pH and ionic strength, ethanol, toluene, hexane, and many others. PAA chains (pK = 4.5−4.7) demonstrate significant variations in the interaction with water as a function of pH:[48] (a) At low pH values, they are practically not swollen in water; (b) at high pH values, PAA macromolecules are significantly swollen in an aqueous environment. P2VP chains are not soluble in water at pH > 4 due to a hydrophobic backbone. P2VP macromolecules, however, can be protonated and dissolved in an acidic aqueous solution. In general, P2VP demonstrates the properties of a weak polyelectrolyte. The polymer is soluble at pH < 4 because of the protonated charged pyridine nitrogen when electrostatic repulsion overcomes the short-range hydrophobic attraction in the backbone of the polymer chain. Conformation of the P2VP chain is sensitive to the pH and ionic strength of aqueous solutions.[49,50]

Initially, we grafted the polymers to the model substrate, PGMA-modified PET film deposited on a silicon wafer. This reference experiment was conducted to estimate the thickness of the polymer layer that can be attached to the surface of PET fibers in the fabric structure, as well as to measure the wettability of the fibers. Table 1 shows the parameters of the grafted layers. The thickness of the layers was 7−11 nm. AFM images showed that the surface morphology of the PET films was altered by the grafting (compare Figures 2 and 5). The grafted layers evenly covered the PET surface on micro- and nanoscale levels. As reported previously in similar experiments, the PEG-grafted layers (Figure 5e and 5f) formed crystalline structures on the surface.[51−53]

The modification with polymer grafting significantly changed the wettability of the PET surface with water of different pH

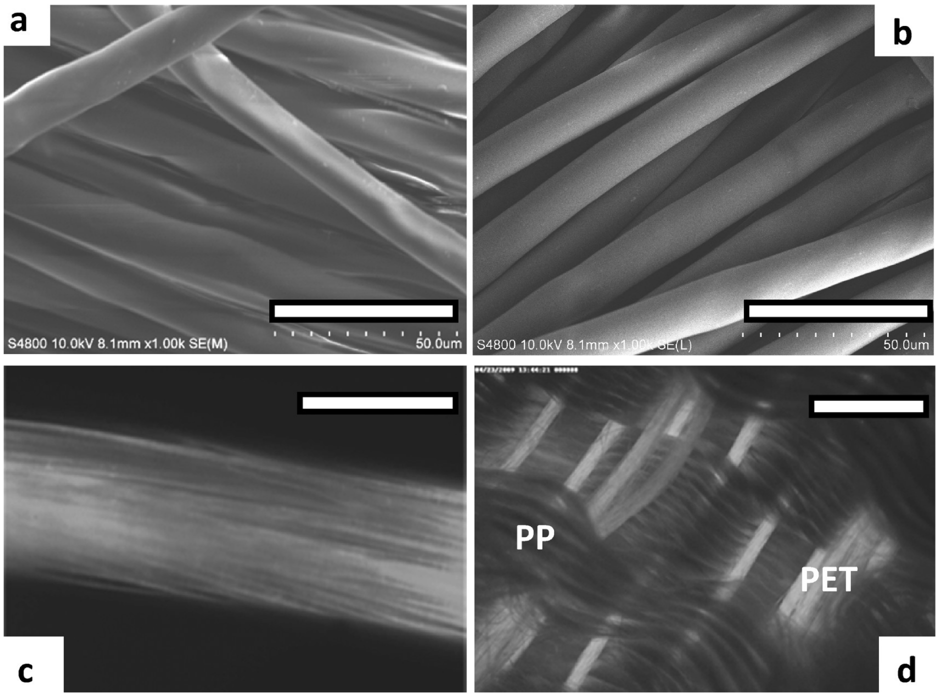

Figure 3. SEM images of the one-component PET fabric after (a) treatment with NaOH and (b) subsequent PGMA adsorption. Fluorescent microscope images for PET yarns in PET(c) and PET/PP blended (d) fabric. Scale bar are (a, b) 50 μm, (c) 500 μm, and (d) 3000 μm (3 mm).

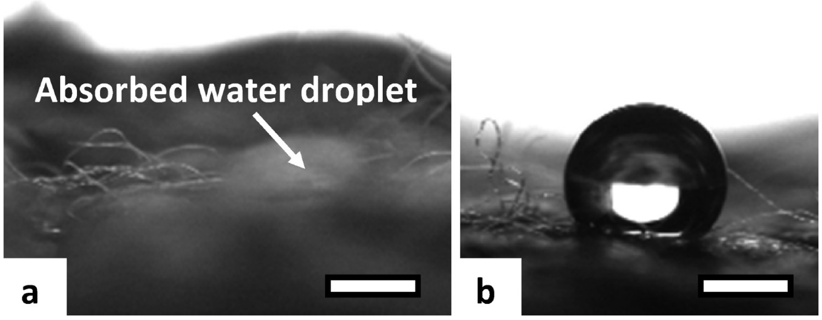

Figure 4. Photographs of water droplet (pH 6.7) deposited on the yarns constituting PET/PP two component fabric (presented in Figure 3d) modified with PGMA layer. (a) Absorbed droplet deposited on the PET yarns. (b) Droplet deposited on the PP yarns. Scale bar is (a, b) 1 mm.

Table 1. Parameters of Model PET Film and Deposited Layers

substrate	thickness (nm)	grafting density (chains/nm^2)
PET film	69.0 ± 1	
PET film treated with NaOH	65.5 ± 1	
PGMA-RhB layer	2.9 ± 0.3	0.01
PEG layer	6.7 ± 0.8	0.89
PAA layer	7.3 ± 1.2	0.05
P2VP layer	11.0 ± 0.9	0.15

values (Table 2). PAA-grafted layers demonstrated high wettability at pH 6.7 and 9. At pH 2, where the majority of the carboxyl groups are protonated, the contact angle increased to 30.5° from 17° (pH 6.7). The P2VP grafted layers showed even more significant changes in wettability as a function of pH. At pH 2, the P2VP chains are protonated and water-soluble. This explains the low water contact angle of 14° that was observed for the PET surface modified with P2VP grafting. Higher contact angles (46° for pH 6.7 and 57° for pH 9) were observed for the P2VP layers. The wettability of PEG-grafted layers was not significantly affected by changes in pH.

The wettability measurements for the grafted films indicated that by grafting PAA and P2VP to the different parts of the textile chip, it should be possible to regulate the transport of water based on the pH value of the aqueous system. Therefore, we modified two adjacent sections B of the PET rich stripes (Figure 1) in the textile structure with P2VP and PAA grafting conducted at the same conditions as were used for the model PET films (Figure 5). The part A connecting the modified fragments was grafted with PEG (Figure 6). By grafting PEG, we obtained a pH-insensitive port for the deposition of a water droplet possessing the pH of interest. We tested wettability of the grafted area with water of pH2, pH6.7, and pH9 and found that the grafted areas were wetted by water of different pHs and, therefore, are capable to transport an aqueous liquid. Wettability of PP rich part of the chip was not altered during the grafting procedures (Figure 6a and c).

Transport of Water in the Model Textile Chip. The fluid wicking kinetics can be described in a first approximation by the Lucas–Washburn equation:[54,55]

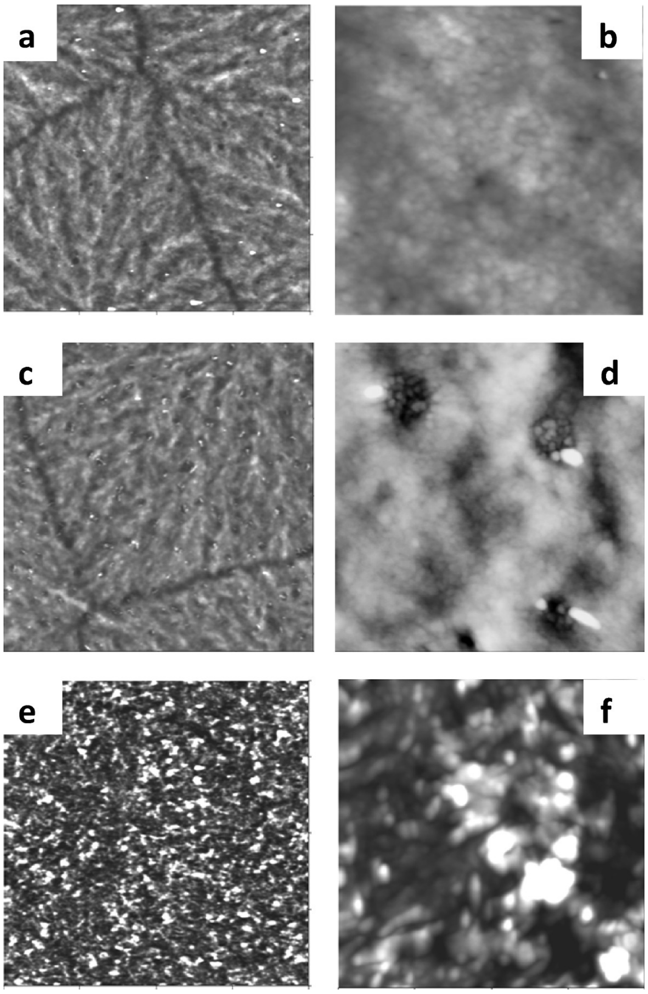

Figure 5. Topographical AFM images of the PET film modified with PGMA layer and grafted with P2VP (a,b) PAA, (c,d) and PEG (e,f). Vertical scale: 20 nm. Image size: (a,c,e) 10 × 10 and (b,d,f) 1 × 1 μm.

Table 2. Contact Angles for Substrates

substrate	contact angle, degree pH 6.7 contact angle	 pH 9 contact angle	 pH 2 contact angle
PET film	64.7 ± 0.8		
PET film treated with NaOH	35.0 ± 2.7		
PGMA-RhB layer	53.5 ± 0.6		
PEG layer	53.0 ± 1.4	46.3 ± 3	56.2 ± 1.1
PAA layer	16.9 ± 1.7	8.5 ± 0.7	30.5 ± 0.7
P2VP layer	46.3 ± 2.5	57.4 ± 1.3	14.0 ± 0.4

$$L = \sqrt{\frac{2kP_c}{\mu\varepsilon}t} \qquad (1)$$

where L is the length of wet part of the fabric as a function of time t, k is the fabric permeability, ε is its porosity, and μ is the viscosity. Modeling the fibrous material as a bundle of capillaries, the capillary pressure can be estimated as $P_c \approx 4\gamma \cos \theta/D$,[56] where γ is the interfacial tension of the liquid/air pair; D is the characteristic pore diameter; and θ is the contact angle that the liquid meniscus forms with the pore wall. Using this scaling relation, one can see that the dependence of the wicking kinetics on the contact angle is as follows $L \propto (\cos \theta t)^{1/2}$.

According to eq 1, the movement of a liquid in the textile structure is proportional to the square root of cos θ. The square root values of cos θ with the values of θ from Table 2 are as follows $\sqrt{\cos \theta} = 0.99$ (PAA, pH 9), 0.985 (P2VP, pH 2), 0.97 (PAA, pH 7), and 0.93 (PAA, pH 2). The square root values of cos θ for P2VP at pH 7 and P2VP at pH 9 are $\sqrt{\cos \theta} = 0.83$ and 0.73, respectively. Having these materials with different contact angles, we investigated whether these small differences in the materials wettability is sufficient to direct the transport of an aqueous solutions in a certain direction.

The first experiments were conducted with water of pH 9. At this pH the difference between wettability of the sections A modified with P2VP and PAA is the largest (Table 2). In the experiment 5 μL droplets were placed in a sequential manner on the section B of the textile chip modified with PEG grafted layer (Figure 7). The water from the first drop readily filled the section A and started movement into the section B of the chip modified with PAA grafting. The liquid practically did not penetrate into the PP rich part of the chip and section modified with P2VP grafted chains. As more droplets were added the liquid continues to move into the PAA section until the section is full. After that the liquid started to penetrate into the P2VP section of the chip (Figure 6a and 7). When the experiment was conducted for the water of pH 6.7 the same results as for pH 9 were obtained (Figure 6b). For liquid with pH 2, however, when the droplets were deposited on the PEG port, the liquid moved into both P2VP and PAA directions (Figure 6c).

Therefore, fabric sections modified with P2VP and PAA demonstrate significantly different kinetics of fluid penetration for water with higher pH values. In essence the grafted P2VP layers serve as a pH sensitive element which allows the directed movement of micro amounts of water into prescribed direction. It is important that in all cases the liquid deposited on the PEG port was confined within the PET-rich stripes and was not transported into PP-rich parts of the fabric structure. The obtained results demonstrate that with pointed surface modification, it is possible to regulate the transport of microamounts of water through the textile chip.

■ CONCLUSIONS

In conclusion, an effective method for pointed surface modification of a PET/PP textile material to produce yarn-based channels having different functionalities in the fabric was developed. Specifically, the PET yarns were selectively modified with an epoxide-containing polymer to obtain generic reactive channels. The modification did not affect the PP parts of the fabric, leaving them hydrophobic and nonreactive. To affect the wetting behavior and the functionality of the channels, they can be further locally modified with different pH-sensitive polymers. The dimensions of the modified area (patterns) can be adjusted by controlling the volume and placement of the droplet of a reactive polymer solution on the fabric. Stimuli-responsive properties of the channel coatings are used to regulate pH-triggered transport of liquids in the textile. We foresee that the textile with stimuli-responsive channels could find a number of intriguing applications for lab-on-chip analytical devices including devices built into apparel with smart functions. We expect that the developed method can be easily scaled- up and employed for the mass production of the yarn-based microfluidic devices.

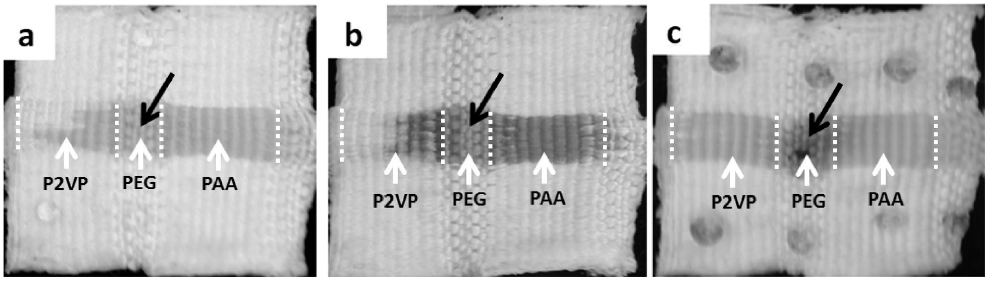

Figure 6. Movement of water in the microfluidic textile chips: (a) pH9, (b) pH 6.7, and (c) pH 2. Black arrow shows the place where droplet of water was deposited. White arrows and dashed lines indicating the part of the PET rich stripe modified with different polymers. (a) and (c) shows droplets of the aqueous solution placed on the PP rich parts of the textile chip.

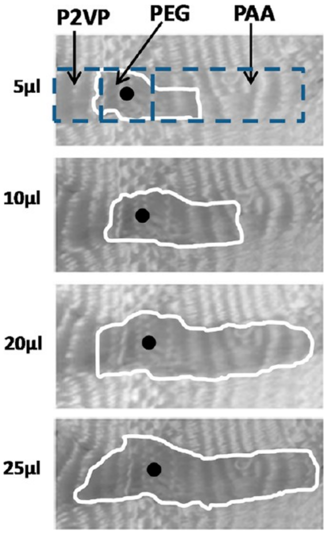

Figure 7. Movement of water (pH 9) in the textile chip as a function of water amount placed on the section (A) grafted with PEG. Black dot shows the location of the droplet placement. White line indicates border of the water propagation.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) McDonald, J. C.; Whitesides, G. M. *Acc. Chem. Res.* **2002**, *35*, 491–499.
(2) Klank, H.; Kutter, J. P.; Geschke, O. *Lab Chip* **2002**, *2*, 242–246.
(3) Becker, H.; Locascio, L. E. *Talanta* **2002**, *56*, 267–287.
(4) Tarn, M. D.; Pamme, N. *Expert Rev. Mol. Diagn.* **2011**, *11*, 711–720.
(5) Tentori, A. M.; Herr, A. E. *J. Micromech. Microeng.* **2011**, 21.
(6) Trietsch, S. J.; Hankemeier, T.; van der Linden, H. J. *Chemom. Intell. Lab. Syst.* **2011**, *108*, 64–75.
(7) Hansen, C. L.; Skordalakes, E.; Berger, J. M.; Quake, S. R. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 16531–16536.
(8) McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M. *Electrophoresis* **2000**, *21*, 27–40.
(9) Becker, H.; Gärtner, C. *Anal. Bioanal. Chem.* **2008**, *390*, 89–111.
(10) Beebe, D. J.; Mensing, G. A.; Walker, G. M. *Annu. Rev. Biomed. Eng* **2002**, *4*, 261–286.
(11) Owens, T. L.; Leisen, J.; Beckham, H. W.; Breedveld, V. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3796–3803.
(12) Reches, M.; Mirica, K. A.; Dasgupta, R.; Dickey, M. D.; Butte, M. J.; Whitesides, G. M. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1722–1728.
(13) Safavieh, R.; Zhou, G. Z.; Juncker, D. *Lab Chip* **2011**, *11*, 2618–2624.
(14) Bhandari, P.; Narahari, T.; Dendukuri, D. *Lab Chip* **2011**, *11*, 2493–2499.
(15) Li, X.; Tian, J.; Shen, W. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1–6.
(16) Ionov, L.; Houbenov, N.; Sidorenko, A.; Stamm, M.; Minko, S. *Adv. Funct. Mater.* **2006**, *16*, 1153–1160.
(17) Tsai, C. C.; Mikes, P.; Andrukh, T.; White, E.; Monaenkova, D.; Burtovyy, O.; Burtovyy, R.; Rubin, B.; Lukas, D.; Luzinov, I.; Owens, J. R.; Kornev, K. G. *Nanoscale* **2011**, *3*, 4685–4695.
(18) Martinez, A. W.; Phillips, S. T.; Wiley, B. J.; Gupta, M.; Whitesides, G. M. *Lab Chip* **2008**, *8*, 2146–2150.
(19) Khan, M. S.; Thouas, G.; Shen, W.; Whyte, G.; Garnier, G. *Anal. Chem.* **2010**, *82*, 4158–4164.
(20) Martinez, A. W.; Phillips, S. T.; Butte, M. J.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1318–1320.
(21) Abe, K.; Suzuki, K.; Citterio, D. *Anal. Chem.* **2008**, *80*, 6928–6934.
(22) Li, X.; Tian, J.; Nguyen, T.; Shen, W. *Anal. Chem.* **2008**, *80*, 9131–9134.
(23) Martinez, A. W.; Phillips, S. T.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 19606–11.
(24) Callegari, G.; Tyomkin, I.; Kornev, K. G.; Neimark, A. V.; Hsieh, Y. L. *J. Colloid Interface Sci.* **2011**, *353*, 290–293.
(25) Monaenkova, D.; Andrukh, T.; Kornev, K. G. *Soft Matter* **2012**, *8* (17), 4725–4730.
(26) Martinez, A. W.; Phillips, S. T.; Whitesides, G. M.; Carrilho, E. *Anal. Chem.* **2009**, *82*, 3–10.
(27) Bruzewicz, D. A.; Reches, M.; Whitesides, G. M. *Anal. Chem.* **2008**, *80*, 3387–3392.
(28) Minko, S., Luzinov, I.; Motornov, M., Sheparovych, R., Lupitskyy, R.; Liu, Y.; and Klep, V., Coatings via self-assembly of smart nanoparticles. In *Smart Coatings II*, ACS Symposium Series *1002*; Provder, T., Baghdachi, J., Eds.; American Chemical Society: Washington DC, 2009; Chapter 7, pp 145–157.
(29) Fang, X.; Chen, H.; Jiang, X.; Kong, J. *Anal. Chem.* **2011**, *83*, 3596–3599.
(30) Safavieh, R.; Mirzaei, M.; Qasaimeh, M. A.; Juncker, D. Presented at the Thirteenth International Conference on Miniaturized Systems for Chemistry and Life Sciences, Jeju, Korea, 2009.
(31) Ballerini, D. R.; Li, X.; Shen, W. *Biomicrofluidics* **2011**, *5*, 014105-1–014105-12.

(32) Li, X.; Tian, J.; Shen, W. *ACS Appl. Mater. Interfaces* **2009**, *2*, 1−6.
(33) Nilghaz, A.; Wicaksono, D. H. B.; Gustiono, D.; Abdul Majid, F. A.; Supriyanto, E.; Abdul Kadir, M. R. *Lab Chip* **2012**, *12*, 209−218.
(34) Zdyrko, B.; Luzinov, I. *Macromol. Rapid Commun.* **2011**, *32*, 859−869.
(35) Zdyrko, B.; Klep, V.; Li, X. W.; Kang, Q.; Minko, S.; Wen, X. J.; Luzinov, I. *Mater. Sci. Eng., C* **2009**, *29*, 680−684.
(36) Ramaratnam, K.; Tsyalkovsky, V.; Klep, V.; Luzinov, I. *Chem. Commun.* **2007**, 4510−4512.
(37) Ramaratnam, K.; Iyer, S. K.; Kinnan, M. K.; Chumanov, G.; Brown, P.; Luzinov, I. *AATCC Rev.* **2008**, *8*, 42−48.
(38) Tsyalkovsky, V.; Klep, V.; Ramaratnam, K.; Lupitskyy, R.; Minko, S.; Luzinov, I. *Chem. Mater.* **2008**, *20*, 317−325.
(39) Samadi, A.; Husson, S. M.; Liu, Y.; Luzinov, I.; Kilbey, S. M. *Macromol. Rapid Commun.* **2005**, *26*, 1829−1834.
(40) Liu, Y.; Klep, V.; Zdyrko, B.; Luzinov, I. *Langmuir* **2005**, *21*, 11806−11813.
(41) Burtovyy, O.; Klep, V.; Chen, H. C.; Hu, R. K.; Lin, C. C.; Luzinov, I. *J. Macromol. Sci., Part B: Phys.* **2007**, *46*, 137−154.
(42) Luzinov, I. Nanofabrication of thin polymer films. In *Nanofibers and Nanotechnology in Textiles*; Brown, P. J., Stevens, K, Eds.; Woodhead Publishing, Ltd.: Boca Raton, FL, 2007.
(43) Pittman, J. J.; Klep, V.; Luzinov, I.; Marcus, R. K. *Anal. Methods* **2010**, *2*, 461−469.
(44) Reukov, V.; Vertegel, A.; Burtovyy, O.; Kornev, K.; Luzinov, I.; Miller, P. *Mater. Sci. Eng., C* **2009**, 669−73.
(45) Kothe, M.; Muller, M.; Simon, F.; Komber, H.; Jacobasch, H. J.; Adler, H. J. *Colloids Surf., A* **1999**, *154*, 75−85.
(46) Hsieh, Y. L.; Miller, A.; Thompson, J. *Text. Res. J.* **1996**, *66*, 1−10.
(47) Iyer, K. S.; Luzinov, I. *Macromolecules* **2004**, *37*, 9538−9545.
(48) Currie, E. P. K.; Sieval, A. B.; Fleer, G. J.; Cohen Stuart, M. A. *Langmuir* **2000**, *16*, 8324−8333.
(49) Roiter, Y.; Minko, S. *J. Am. Chem. Soc.* **2005**, *127*, 15688−15689.
(50) Roiter, Y.; Trotsenko, O.; Tokarev, V.; Minko, S. *J. Am. Chem. Soc.* **2010**, *132*, 13660−13662.
(51) Zdyrko, B.; Klep, V.; Luzinov, I. *Langmuir* **2003**, *19*, 10179−10187.
(52) Zdyrko, B.; Varshney, S. K.; Luzinov, I. *Langmuir* **2004**, *20*, 6727−6735.
(53) Ionov, L.; Zdyrko, B.; Sidorenko, A.; Minko, S.; Klep, V.; Luzinov, I.; Stamm, M. *Macromol. Rapid Commun.* **2004**, *25*, 360−365.
(54) Lucas, R. *Kolloid Z.* **1918**, *23*, 15−22.
(55) Washburn, E. W. *Phys. Rev.* **1921**, *17*, 273−283.
(56) Scheidegger, A. E. *The Physics of Flow through Porous Media*, 3rd ed.; University of Toronto: Toronto, 1974.