

RAPID FABRICATION OF OSTE+ MICROFLUIDIC DEVICES WITH LITHOGRAPHICALLY DEFINED HYDROPHOBIC/ HYDROPHILIC PATTERNS AND BIOCOMPATIBLE CHIP SEALING

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ABSTRACT

Here we present an uncomplicated and robust method for rapid prototyping of microfluidic devices featuring: 1) lithographically defined, permanently surface modified hydrophilic and hydrophobic regions with contact angles varying from 18° to 118°, in which all four channel walls are surface modified in a single step using polymer chain grafting; 2) polymer chains grafted from open surfaces before bonding, making this method suitable for batch fabrication; 3) biomolecule-compatible, room temperature, dry, homogeneous chip-sealing, in which native as well as hydrophobic/hydrophilic modified OSTE+ surfaces allow for epoxy-epoxy and thiol-epoxy covalent bonding, hence greatly simplifying alignment and dramatically increasing device yields. We demonstrate the method with a functional microfluidic device. This represents a complete, simplified and robust method for batch-manufacturing compatible prototyping of microfluidic devices with tunable mechanical and surface properties.

KEYWORDS: Microfluidics, Lithography, Hydrophilic, Hydrophobic, Surface modification, Dry bonding, OSTE+, Thiol-ene, Thiol-ene-epoxy, Microdevice.

INTRODUCTION

The control of surface energy within microchannels is essential for microfluidic flow manipulation [1,2]. Combining a surface modification process acting on all four walls in a rectangular channel with retained bonding capabilities remains a challenge. Current protocols for surface modification of microchannels include surface activation by plasma and/or silanization [3] and chemical reactions on the surface, e.g. polymer grafting [4], followed by bonding using adhesives. However, the resulting surface properties are often short-lived and/or unevenly distributed in deep microchannels. Moreover, surface modification in closed microchannels as demonstrated in [5] (e.g. using grafting after channel bonding) is not compatible with batch manufacturing. We previously demonstrated thiol-ene (OSTE) polymer based techniques and their surface hydrophilic/hydrophobic patterning [6]. Such techniques invariably consist of two *different OSTE materials* (allyl-excess-OSTE and thiol-excess-OSTE layers) and, hence, *different surface modification chemistries* are necessary, i.e. rendering homogeneous modification of all channel surfaces in a single step difficult to achieve [7]. We recently introduced a dual-cure off-stoichiometry thiol-ene-epoxy (OSTE+) material, whose epoxy reactive surface allows unassisted room-temperature bonding to a large range of other surfaces, including itself [8].

In this study, we present the first lithographically defined permanent surface modification method, allowing surface patterning on open homogeneous microdevices layers and subsequent dry layer bonding, which leads to a simplified fabrication process and potentially increased manufacturing throughput.

THEORY

Dual-cure OSTE+ polymers feature temporally separated thiol-ene and thiol-epoxy polymerization processes by using two different initiation mechanisms. A first, rapid and long wavelength photo-initiated thiol-ene polymerization step leaves excess thiols and unreacted allyl glycidyl ether (AGE) epoxide groups unreacted. These thiols and epoxies are present also at the surface of the material, where they can be used for surface modification and/or direct bonding during a second, slower, short wavelength, anionically initiated, polymerization step.

The surface hydrophobic/hydrophilic patterning takes place after the first polymerization step by applying a toluene solution on the polymer surface that contains benzophenone (BP) initiator, AGE and fluorinated (for hydrophobic surfaces) or hydroxylated methacrylate (for hydrophilic surfaces). UV exposure of this solution creates active thiyl radicals through reactions between thiols (on the polymer surface) and BP (inside surface patterning solution). Methacrylate or AGE monomers react with the created thiyl radicals and polymers rapidly form in a chain-wise copolymerization grafting process. Hydrophobic regions are defined by first using a solution containing fluorocarbon methacrylate, and hydrophilic regions are defined thereafter by using a solution containing hydroxyl methacrylate.

The surface modified layers are bonded together by contacting and short wavelength UV-light exposure. The latter leads, in an anionic polymerization step, on one hand to the reaction between remaining thiols and epoxide groups in the bulk material, hence stiffening the bulk material, and on the other hand to a reaction between thiols and epoxide groups in the grafted chains on the surface, hence bonding the layers.

EXPERIMENTAL

A) Layer and channel structuring:

A microfluidic three layer device was fabricated in a process which combines UV-curing, photolithography, and molding using OSTE+ polymer. The OSTE+ pre-polymer was a mix of pentaerythritol tetrakis (3-mercaptopropionate)

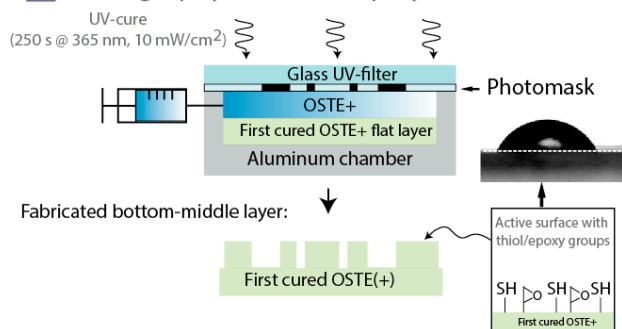
(PETMP, Mercene Labs, Sweden), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO, Mercene Labs, Sweden) and 1-allyloxy-2,3-epoxypropane, allyl 2,3-epoxypropyl ether (AGE, Sigma-Aldrich, Sweden) with 20% thiol excess by mixing allyl:thiol:epoxy in a functional group molar ratio of 1:1.2:0.2. Also, photoinitiator Lucirin TPO-L (BASF GmbH, Germany) and a photo-latent base (BASF GmbH, Germany) were added as 0.5 wt% and 1 wt%, respectively. The individual device layers were fabricated in the following steps (Fig 1-i):

1) To fabricate the non-structured bottom layer, OSTE+ pre-polymer was injected into a 1 mm thick, glass slide sized, aluminum mold with a glass cover clamped on top. The first photopolymerization was performed by placing a colloiddally colored 400 nm high-pass glass filter (Long pass GG400, Schott, Germany) on top of the mold followed by exposure to a collimated near-UV lamp (OAI, Milpitas, USA) for 250 s (@ 365 nm, 10 mW/cm²). 2) The middle layer, containing a photolithographically defined microchannel pattern, was fabricated on top of the bottom layer. A plastic foil photomask was placed between the glass cover and the mold. UV exposure was performed for 250 s @ 365 nm, 10 mW/cm². The unpolymerized area was removed by rinsing with acetone (Sunchem AB, Sweden). The excess thiols remaining on the surfaces of the microchannel walls could later be used for the hydrophobic/hydrophilic surface patterning. 3) The top layer was fabricated exactly as the bottom layer. Through holes were manually punched as in- and out- lets after the initial polymerization when the material was still rubbery.

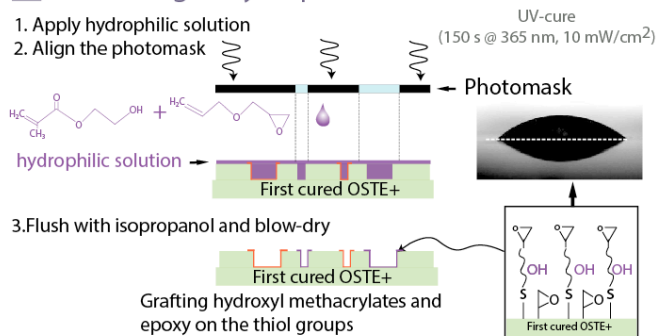
B) Hydrophobic/hydrophilic lithographically surface patterning process (Fig 1-ii,iii):

The surface patterning process was performed by applying the appropriate surface modification solution on the open polymer surface areas of the combined bottom-middle layer and of the top-layer, separately. The toluene solution contained 5% w/w of either fluorinated (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate, (Sigma-adrich, Sweden) or hydroxylated methacrylate (2-Hydroxyethyl methacrylate, Sigma-adrich, Sweden) as hydrophobic or hydrophilic surface patterning solution, respectively. To each solution an equimolar concentration of allyl glycidyl ether with 0.05% w/w benzophenone (BP, Sigma-Aldrich, Sweden) initiator was added. Due to the UV light attenuation of BP, a 150 μm spacer was placed between the photo mask and the polymer surface to control the solution thickness to create a more even UV-exposure profile in the channel. The surface patterning was initiated by collimated UV exposure (150 s @ 365 nm, 10 mW/cm²) in transparent areas of the mask. In this step, hydrophilic patterning is preferably conducted after the hydrophobic grafting to achieve optimal surface patterning results, for the reason that the former hydrophobic coated area can repel the infiltration of the subsequent hydrophilic solution. Both hydrophobic and hydrophilic patterning processes are followed by isopropanol (Sunchem AB, Sweden) washing for 30 s and drying in a nitrogen gas stream.

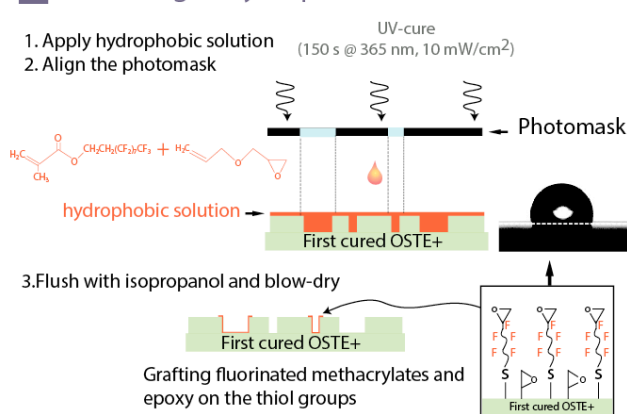
i Lithography of OSTE(+) polymer



iii Patterning of hydrophilic area



ii Patterning of hydrophobic area



iv Room Temperature dry bonding

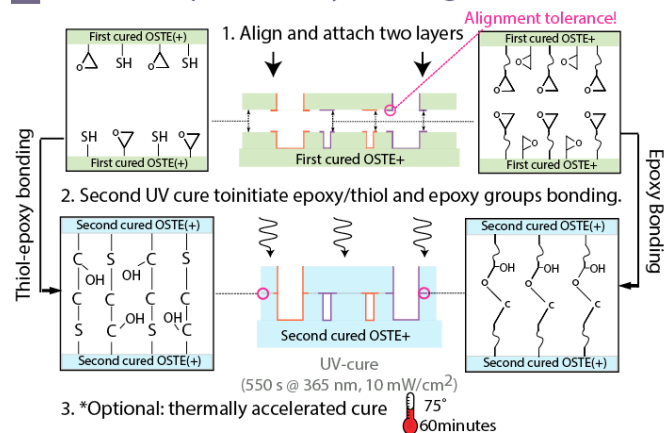


Fig 1: The fabrication of surface patterning OSTE+ polymer microfluidic devices.

C) Biocompatible chip-sealing (Fig 1-iv):

The surface-modified device layers are aligned and bonded via the second (low wavelength) cure step (550 s exposure under UV-light). A thermal treatment at 75 °C for 1 h was performed to accelerate the second polymerization step.

D) contact angle measurement:

To test surface modification efficacy, flat OSTE+ layers were fabricated using Step 1 described in part A and surface patterned as described in part B. The macroscopic contact angles were measured using a Theta optical tensiometer (Attension, Biolin Scientific, Sweden) equipped with a high resolution camera and micropipette dispensing 4 μ L DI water/droplet, and the droplet profiles were subsequently evaluated by CAM2008 (KSV Instruments-Nima, Finland).

E) Bonding strength evaluation:

A blister test was performed using a pair of bonded OSTE+ surface modified layers (detailed set-up described previously in [9]).

RESULTS AND DISCUSSION

Contact angle results (Fig 1-i,ii,iii, Fig 4): The contact angles of the hydrophilic, native and hydrophobic modified surfaces were measured as $24\pm 6^\circ$, $69\pm 3^\circ$ and $116\pm 2^\circ$, respectively. Accelerated aging in an 80 °C oven for 24 hours indicated room temperature surface stability for at least for three months.

Bond strength evaluation: The bond strength between two grafted OSTE+ layers was observed to withstand an air pressure of 5.5 ± 0.2 bar (maximum in the used set-up) in a blister test. This exceeded the strongest observed bonding strength achieved using OSTE+ without surface modification.

Microfluidic functionality results (Fig 3): Two microfluidic demonstrators with modified hydrophobic and hydrophilic zones showed controlled fluidic behavior where hydrophilic channel regions rapidly capillary filled with dyed water whereas hydrophobic regions remained dry.

A highlighted novelty of this work in comparison with to previous PDMS study is shown in Fig 2.

Material	PDMS	OSTE+
Native surface energy	Hydrophobic	Hydrophilic [7]
Surface modification method	Plasma treatment	UV-grafting
Durability	30min	>3 months*
Modified surface	Hydrophilic but not stable	Contact angle from 18° to 118°
Native surfaces bonding	Not possible	5 ± 0.2 bar
Modified surface bonding	Good	5.5 ± 0.2 bar

NOVELTY!

Accelerated aging, 24h@80°C in oven. Further shelf life testing ongoing.

Fig 2: Comparison of polymers used in microfluidic prototyping



Fig 4: Hydrophilic and hydrophobic surface patterning on one single chip.

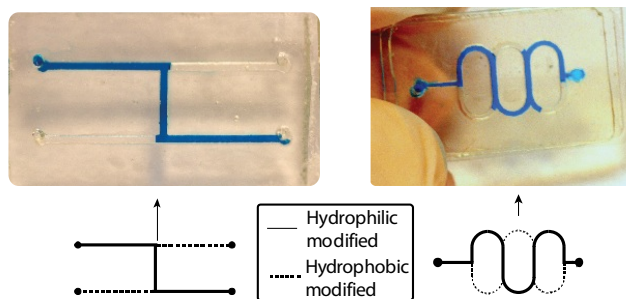


Fig 3: Surface patterned OSTE+ polymer microfluidic channels filled by dyed water. Solid lines on the left indicate hydrophilic patterned areas, and the dotted lines indicate hydrophobic patterned areas.

CONCLUSION

In this study, we demonstrate a complete and rapid prototyping of OSTE+ microfluidic device fabrication process, which combines lithography, molding, and permanent surface patterning. The surface wetting properties of OSTE+ polymers can be modified (contact angle from 18° to 118° , >3 months by accelerated aging) in an uncomplicated manner followed by robust bonding (withstanding 5.5 ± 0.5 bar, the maximum of our equipment). This integrated microfluidic device fabrication of OSTE+ method shows a promising, versatile, and application-friendly approach for microfluidic device manufacturing.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support by Barncancerfonden, Sweden. And we also express our gratitude to Mercene Labs AB for providing the OSTE+ polymers.

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