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Reaction injection molding and direct covalent bonding of OSTE+ polymer microfluidic devices

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Abstract. In this article, we present OSTE+RIM, a novel reaction injection molding (RIM) process that combines the merits of off-stoichiometric thiol-ene epoxy (OSTE+) thermosetting polymers with the fabrication of high quality microstructured parts. The process relies on the dual polymerization reactions of OSTE+ polymers, where the first curing step is used in OSTE+RIM for molding intermediately polymerized parts with well-defined shapes and reactive surface chemistries. In the facile back-end processing, the replicated parts are directly and covalently bonded and become fully polymerized using the second curing step, generating complete microfluidic devices. To achieve unprecedented rapid processing, high replication fidelity and low residual stress, OSTE+RIM uniquely incorporates temperature stabilization and shrinkage compensation of the OSTE+ polymerization during molding. Two different OSTE+ formulations were characterized and used for the OSTE+RIM fabrication of optically transparent, warp-free and natively hydrophilic microscopy glass slide format microfluidic demonstrator devices, featuring a storage modulus of 2.3 GPa and tolerating pressures of at least 4 bars.

Introduction

Polymers form the most versatile class of materials for the fabrication of microfluidic devices due to their low material cost and the available structuring methods, allowing for both prototyping and mass manufacturing [1]. State-of-the-art polymeric microfluidic parts are predominantly fabricated by replication techniques, such as thermoforming, hot embossing, injection molding, reaction injection molding (RIM) and casting [2]. The first three techniques are developed for thermoplastic polymers, which constitute a solid pre-polymerized material that can be melted, reshaped and solidified during processing. Some of the common thermoplastic materials for microfluidic applications include cyclic olefin polymer (COP), cyclic olefin copolymer (COC), polymethylmethacrylate (PMMA), polycarbonate (PC) and polystyrene (PS) [3,4]. RIM and casting are optimized for thermosetting polymers, which are made of a liquid polymer precursor that is shaped and polymerized during processing. Poly(dimethylsiloxane) (PDMS) is by far the most popular thermosetting polymer for microfluidic applications [5], but also other materials such as polyurethane [6] are used.

Despite their broad range and variety, the aforementioned standard replication techniques and polymers suffer from an inherent and significant drawback: the fabricated parts have surfaces that are chemically non-reactive to themselves or to other common microdevice materials, thus precluding direct bonding. To build a complete and functional microfluidic device from two or more replicated microstructured parts, laborious and/or difficult to control back-end processes are required that depend on either modification of the polymer surface by techniques such as plasma bonding, thermal bonding or ultrasonic bonding, or on the addition of new material by chemical bonding or adhesive bonding [7,8]. A few techniques circumvent the necessity of such back-end processing by employing a two-step curing process during fabrication in which a polymer part is molded and only partially polymerized in the first step and then subsequently bonded to other parts and fully polymerized in the second step. Thermosets relying on dual polymerization reactions [9] are advantageous for device fabrication compared to thermosets based on single polymerization reactions [10,11] due to a well-defined and controlled partial reactive group conversion after the first curing step.

Recently, off-stoichiometric thiol-ene (OSTE) [12] and off-stoichiometric thiol-ene-epoxy (OSTE+) [9,13] thermosets were introduced as materials specifically designed to address the issues of back-end processing in

microdevice applications. A review of the capabilities of OSTE and OSTE+ polymers is given in [14]. OSTE+ polymers are formed by a dual polymerization system consisting of three monomers and two initiators. The polymer precursor reacts via two sequentially triggered polymerization reactions between the (1) allyl-thiol and (2) thiol-epoxide monomers [9], respectively, using energy in the form of heat or UV-light, depending on the selected initiators, see below:

The first reaction (1) generates an intermediately polymerized material consisting of a thiol-ene network with unreacted thiol functional groups and free monomers with epoxide functional groups. The second reaction (2) consumes the remaining unreacted functional groups and the material becomes completely polymerized and obtains its final material properties, exhibiting a native hydrophilic surface due to the formation of hydroxyl groups [15,16]. In the intermediate period between the two reactions, the unreacted thiol and epoxide groups are available for covalent surface reactions that can be used in back-end processing [9,13,17].

Previous fabrication processes for making OSTE+ microstructured parts using casting in molds made of polymer materials [13,16,18,19] suffer from two main drawbacks. Firstly, for certain mold designs and processing parameters, heat generated from the exothermic first polymerization reaction inadvertently accelerates the second polymerization reaction, which limits the reproducibility of the casting process and the subsequent bonding due to variations in the intermediate mechanical and chemical material properties of molded OSTE+ parts. Secondly, the shrinkage of the OSTE+ precursor during polymerization potentially leads to low replication fidelity of molded parts, with non-flat surfaces, warping and/or deformed microstructures as a result. Thus, to be able to exploit and take full advantage of the processing capabilities of OSTE+ polymers, a new fabrication method is needed that addresses the separation of the dual polymerization reactions and the shrinkage related issues during molding.

The remainder of this paper first briefly introduces OSTE+RIM. Next, we describe the characterization of optical and mechanical properties for two OSTE+ formulations that are relevant for OSTE+RIM processing and microfluidic applications. In addition, we investigate proper mold properties required for a successful OSTE+RIM process. Thereafter, we describe the fabrication and evaluation of a microfluidic demonstrator device using an OSTE+RIM based manufacturing process. Finally, we discuss OSTE+RIM and its characteristics compared to previously presented polymer replication techniques for making microstructured OSTE+ parts and devices.

Introduction to OSTE+RIM based manufacturing

OSTE+RIM is a novel fabrication process based on reaction injection molding of OSTE+ polymers. The process consists of three consecutive steps: the injection of OSTE+ thermoset precursor into a mold; the first polymerization step of the precursor; and the subsequent demolding of the intermediately polymerized part.

Two unique features distinguish the OSTE+RIM process from casting: temperature stabilization and shrinkage compensation. Temperature stabilization during molding relies on that the heat generated from the first exothermic allyl-thiol polymerization reaction is conducted away from the polymerizing OSTE+ precursor in the mold cavity through the mold. Consequently, an unintentional acceleration of the second thiol-epoxide reaction is avoided and the dual polymerization reactions of OSTE+ are separated. Shrinkage compensation during molding relies on that the OSTE+ precursor, which mainly shrinks while being liquid and solidifies at a late stage of the first allyl-thiol polymerization [20], backfills into the mold cavity so that the molded part has a low total shrinkage. The separation of the polymerization reactions and the low shrinkage result in replicated microstructured parts that are characterized by their well-defined chemically reactive surface, available for facile subsequent back-end processing, and their low residual stress and high replication fidelity, respectively.

An OSTE+RIM mold design consists of a bottom part and a top part. At least one of the mold parts needs to be heat conductive to allow for the temperature stabilization. Current OSTE+ formulations use UV-light to trigger the first polymerization step. When using such formulations, at least one of the mold parts needs to be UV-transparent. Future OSTE+ formulations that exclusively use heat-triggered polymerization may not have the latter requirement. One or both mold inserts can feature mold cavities containing microstructures that are replicated during molding.

Figure 1. The plots show the storage modulus of **a)** OSTEMER 322 and **b)** OSTE+ 40 after the first polymerization of thiol-allyl (blue/bottom line) and the second polymerization of thiol-epoxide (red/top line). After the first cure the intermediately polymerized OSTE+ polymers are soft at room temperature, however, the second cure results in stiff and thermoplastic-like materials.

The OSTE+RIM process, which is described in detail in the below section “Fabrication of demonstrator devices”, begins with the assembly of the mold and is followed by the injection of the OSTE+ precursor into the mold cavity via an injection port while air escapes through a ventilation port. To initiate the first polymerization step, the OSTE+ precursor in the mold is exposed to UV-light. While the allyl-thiol reaction lasts, the generated heat is dissipated via the mold and the liquid OSTE+ precursor backfills into the mold from the injection and the ventilation ports to compensate for shrinkage. The mold is then opened and the replicated OSTE+ part is demolded. Unwanted polymer structures from the mold injection and ventilation channels are cut off and removed.

After OSTE+RIM, the replicated and intermediately polymerized OSTE+ part is available for back-end processing. In a typical process, the OSTE+ part is aligned to, and brought in contact with another part for direct covalent bonding. The stack is exposed to UV-light and/or heated in an oven to initiate and/or accelerate, depending on which OSTE+ formulation is being used, and complete the second thiol-epoxide polymerization to achieve a covalent bonding between the parts and to obtain the final material properties of the polymer.

Properties of OSTE+RIM polymers

In this section we introduce the OSTE+ polymer formulations used for demonstrating OSTE+RIM, as well as a characterization and discussion of their mechanical and optical properties.

To evaluate the potential of using OSTE+RIM for OSTE+ formulations with either a thermally or a UV-light initiated second cure, two different OSTE+ polymers were tested: the commercially available UV-thermally cured OSTEMER 322 (Mercene Labs, Sweden), and; a UV-UV cured OSTE+ 40 formulation. Detailed information about the two OSTE+ formulations is provided in Appendix.

Mechanical properties

The mechanical properties of intermediately and fully polymerized OSTEMER 322 and OSTE+ 40 were investigated. Samples were fabricated as described below in section “Fabrication of demonstrator devices” and analyzed using a dynamic mechanical and thermal analysis instrument (DMA Q800, PerkinElmer, USA). The analysis data, see figure 1, show how the OSTE+ polymers undergo significant changes in mechanical properties before and after the second curing step, transforming from being soft like PDMS [21] to being stiff like COC [22]. Specifically, OSTEMER 322 and OSTE+ 40 feature a final storage modulus of 2.3 GPa and 1.9 GPa at room temperature (RT) and a T_g (*i.e.* Tan delta peak) of 69 °C and 73 °C, respectively.

We investigated residual stress originating from the injection and shrinkage of OSTE+RIM processed OSTEMER 322 single parts and bonded devices by examining anisotropy in polymer chain orientation using crossed polarized light. No characteristic flow-induced orientation of the polymer chains from the mold injection could be detected, which is in contrast to what is commonly found in injection molded thermoplastic parts. This can be attributed to the low molecular weight OSTE+ monomers having time to reorient prior to reaching the gel point during molding. Whereas minor local anisotropy was visible with the naked eye around microstructures, no anisotropy could be seen under a transmitted polarized light microscope (ORTHOLUX II-POL BK, Leitz, Germany), because gradients in polymer chain orientation were too small to be detectable under magnification.

Figure 2. Measured UV-light absorption spectra per mm thickness of material for **a)** OSTE+ 40 and OSTEMER 322, of which the samples have different second cures: 75 °C for 24 h; 110 °C for 15 min or; 150 °C for 5 min, respectively, and **b)** candidate mold materials. The dashed lines at 395 nm and 365 nm indicate common wavelengths for UV-light sources and UV-light sensitive initiators.

There were no visible differences between the molded parts and the bonded devices, indicating that the bonding did not introduce any significant stress at the bond interface of the devices. We conclude that residual stresses in OSTE+RIM are minimal.

Optical properties

The optical properties of fully polymerized OSTEMER 322 and OSTE+ 40 were analyzed. Three different samples of OSTEMER 322 and one sample of OSTE+40 were fabricated as reported in section “Fabrication of demonstrator devices”, with the exception that the second cure of the OSTEMER 322 was performed in an oven at 150 °C for 5 minutes, 110 °C for 15 minutes and 75 °C for 24 hours, respectively. After fabrication, the UV-light absorption was measured with a spectrophotometer (Cary 100 Bio UV-Vis Spectrophotometer, Agilent technologies, USA). OSTEmer 320-40 and OSTE+ 40 feature substantial absorption at wavelengths below 380 nm and 420 nm, respectively, but both materials are optically transparent at higher wavelengths, see figure 2a. Overall, the OSTE+ formulations have very similar absorption spectra, with the exception that OSTE+ 40 has a small peak centered at approximately 380 nm, most likely arising from remaining TPO-L photoinitiator. Interestingly, the UV-light absorption properties of OSTEMER 322 are very accurately reproduced despite the different curing parameters of the three samples. Compared to common thermoplastic polymers, the OSTE+ polymers have similar optical characteristics as polyethylene terephthalate (PET).

Summary

The investigation showed that the intermediate mechanical properties of molded OSTEMER 322 and OSTE+ 40 parts are soft, thus, suitable for easy demolding and with the ability to closely conform to most surfaces, including rough and non-flat parts, prior to bonding. The investigation also showed that after the OSTE+ materials are fully polymerized, *i.e.*, after back-end processing, the fabricated parts are stiff, providing mechanical robustness for practical work, and are optically transparent in the visible spectrum. Moreover, OSTE+RIM does not introduce any significant residual stress, neither in molded parts, nor in bonded devices.

Properties of OSTE+RIM molds

In this section we investigate the prerequisites for a successful molding during OSTE+RIM processing in terms of the optical and heat conductive properties of the mold materials. Specifically, we investigate the influence of the molding temperature on demolding, on the resulting mechanical properties of the molded OSTE+ parts and on the bonding capabilities in back-end processing. In addition, we evaluate methods to stabilize the temperature during the first step curing in OSTE+RIM.

Optical properties of mold materials

During molding, the OSTE+ precursor in the mold cavity is intermediately polymerized by exposure to UV-light. Parts of the mold therefore need to be optically transparent, preferably at 365 nm and/or 395 nm, which are

Figure 3. The *in-situ* molding temperatures of **a)** OSTEMER 322 and **b)** OSTE+ 40 during the exothermic thiol-allyl reaction of the first polymerization step in molds that have either high (Al) or low (PMMA) heat conductance. The dotted lines mark the maximum temperatures in each measurement and the differences between the lines are marked with arrows.

common wavelengths for UV-light triggered initiators. The optical properties of candidate mold materials were therefore investigated by measuring the UV-light absorption spectra with a Cary 100 spectrophotometer, see figure 2b. Glass, PET, COC and to a large extent also PMMA are transparent above 365 nm, making the materials optically suitable for OSTE+RIM. PC has a very limited use since it absorbs light up to a wavelength of 400 nm.

Temperature stabilization during molding

The impact of the heat generation from the first exothermic allyl-thiol polymerization reaction on the demolding, the mechanical properties of intermediately polymerized OSTE+ parts and the subsequent bonding capabilities were investigated. The OSTE+ precursors were intermediately polymerized in the mold, as reported in section “Fabrication of demonstrator devices”. The OSTE+ *in-situ* temperatures were monitored in real-time during molding using integrated thermocouple type K probes (T010.0.20.K.02000, Roth+CO. AG, Switzerland). The impact of temperature stabilization was evaluated by using two different mold materials: PMMA, which provided low heat conductance, and; Al, which provided high heat conductance. The molding was performed at room temperature, which was 28 °C at the time, or with active cooling of the molds using a Peltier element (PE-071-14-15-S, Laird Technologies, USA), providing an initial mold temperature of 20 °C. After molding, qualitative analyses of the demolding and the mechanical properties of the molded OSTE+ parts were made by physical touch and the parts were split in two pieces that were subsequently bonded to each other.

The results showed that the two OSTE+ polymer formulations had different temperature profiles during the first curing step of the allyl-thiol polymerization, see figure 3. The initiation of the reaction generated a rapid temperature increase in OSTEMER 322 (fig. 3a), whereas it was generally slower in OSTE+ 40 (fig. 3b). The molds with active cooling maintained lower temperatures throughout the molding compared to molds of the same material but in the absence of active cooling. The Al mold maintained lower temperatures throughout the molding compared to the PMMA mold. Particularly, the temperature rose 13-17 °C in the Al mold in absence of cooling whereas it rose 25-27 °C in the cooled PMMA mold, in which also a higher maximum temperature was measured. The OSTE+ parts that were molded in the Al mold were repeatedly soft and very similar to each other to the touch, in line with the results reported in figure 1. The parts could be easily demolded and bonded strongly to them selves. The OSTE+ parts that were molded in the PMMA mold reached higher temperatures during polymerization, particularly in the absence of active cooling where the maximum temperatures were up to 61 °C. The parts were more difficult to demold or, as experienced in preliminary tests, became directly bonded to the mold. In addition, the parts were significantly stiffer and provided only a weak or no bond to other substrates.

Summary

The results indicate that when the temperature is stabilized in the mold during the first allyl-thiol polymerization reaction, acceleration of the second thiol-epoxide polymerization reaction is avoided and the replicated OSTE+ parts repeatedly attain similar mechanical properties, are easily demolded and can be successfully bonded. Hence, it is crucial to conduct the generated heat away from the polymer to the mold, which must be actively cooled or, more importantly, be made from a material with high heat conductance. We chose to use Al as the material for the

bottom part of the mold due to its high heat conductance and excellent machining properties. In addition, we selected PET and glass materials for the top part of the mold due to their high UV-light transparency.

Fabrication of demonstrator devices

This section reports on the experimental evaluation of the OSTE+RIM process and the back-end processing, by fabrication and testing of microstructured OSTE+ parts that are bonded to form complete microfluidic OSTE+ devices.

Mold design and fabrication

The bottom mold parts were made of 5 mm thick Al (alloy 6082-T) and milled using 2 mm fishtail end mills (MF208-0200-0510-M, InGraph Poland) in a circuit board plotter (Protomat S62, LPKF, Germany). All sidewalls in the mold cavities were perpendicular to the bottom surface with no tapering. To generate parts for building a complete microfluidic OSTE+ device, we made two different bottom mold parts, each accommodating two mold cavities and thus generating a batch of two replicated OSTE+ parts per mold cycle, see figure 4. The two cavities in the mold to the left in the figure were used for making a 75.5 mm x 25.5 mm and 600 μm thick microfluidic layer, including 300 μm deep and 200 μm -1 mm wide channels, 2-5 mm wide chambers and 1 mm diameter through-hole microfluidic interconnects, and a matching 300 μm thick cover. The two cavities in the mold to the right in the figure were used for making 3 mm high 4x1 and 3x1 fluidic tube connector arrays that were 20.0 mm x 5.0 mm and 15.0 mm x 5.0 mm, respectively, matching the design of the vertical interconnects in the microfluidic layer. The tube connector arrays included 1 mm diameter pillars for the physical alignment of fluidic gaskets that were placed in the mold before starting the OSTE+RIM process. Both molds included an injection port, a ventilation port and an interconnection channel between the two mold cavities, allowing for mold filling of both cavities with OSTE+ precursor in a single sequence. The injection ports had a diameter of 4 mm to ensure that standard syringes with Luer Slip interfaces could be pressed in with a leak-tight fit. Importantly for OSTE+RIM, the injection and ventilation ports also acted as reservoirs for backfilling of OSTE+ precursor during molding and accommodated enough volume to compensate for the shrinkage. The fabricated molds were not polished before use, thus, milling patterns in the mold cavities were present during molding. Cleaning of the molds from polymer residues was done either by sonication in acetone and thereafter in isopropanol, by exposure to low pressure O_2 plasma (Femto version A, Diener Electronic GmbH + Co. KG, Germany) or by rinsing in Microposit remover 1165 (DOW Chemical Company, USA).

The top part of the mold consisted of an unstructured PET release liner with a fluoropolymer coating (ScotchPak 9775 Release Liner, 3M, USA) that was placed above the mold cavity, and that also acted as a carrier for the demolded OSTE+ part in the back-end processing, and a glass plate (Photronics Inc., USA) on top that mechanically supported the liner during molding. The materials were selected for their high UV-transparency, the suitable temporary adhesion of PET liner on OSTE+ and the flat and mechanically rigid properties of glass. Both the release liner and the glass plate were cut to match the size of the Al bottom parts of the mold.

OSTE+RIM – fabrication of parts

The fabrication of OSTE+ microfluidic demonstrator devices using OSTE+RIM and direct covalent bonding was performed according to the fabrication scheme illustrated in figure 5. The mold layout and the mold cavity designs that we used are illustrated in figure 5 a and b, respectively. Before starting the OSTE+RIM process, the molds for the tube connector arrays were prepared by placing silicone tube stubs, later functioning as fluidic gaskets for external tubing in the final microfluidic device, on the 1 mm alignment pillars in the mold cavities.

Figure 4. A photograph of two types of fabricated bottom Al mold parts for OSTE+RIM. The left mold was used for making the microfluidics (bottom cavity) and the cover (top cavity) parts in and the right mold was used to fabricate the fluidic tube connector arrays. The arrows indicate the fluidic structures that match the tube connector arrays and the inset shows a magnification of engravings in the fluidic structures in the mold cavity.

Molds

OSTE+RIM - 1st polymerization step

Back-end processing - 2nd polymerization step

Figure 5. Schematic illustration of the mold layout **a)**, the mold cavity designs **b)** and the process scheme for making microstructured OSTE+ parts using OSTE+RIM **c)-h)** and for making complete microfluidic devices through bonding of OSTE+ parts in the back-end processing **i)-m).**

The OSTE+RIM process began with the assembly of the mold by clamping the Al-PET-glass stack and was followed by the injection of the OSTE+ precursor into the mold cavity by a syringe that was fitted into the injection port (fig. 5 c). To initiate the first polymerization step, the OSTE+ precursor in the mold was exposed to UV-light (fig. 1d). Parts based on OSTEMER 322 were exposed to unfiltered and collimated UV-light (14 mWcm^{-2}) by a 365 nm near-UV short arc mercury lamp (OAI, Milpitas, USA) for 60 s or by a 1 W (5 mWcm^{-2}) 365 nm LED array for 30 s (Phoseon, USA). Parts based on the OSTE+ 40 precursor were exposed to filtered (optical high-pass filter transmitting $\geq 400 \text{ nm}$, Schott AG, Germany) and collimated UV-light (14 mWcm^{-2}) for 110 s by the OAI mercury lamp. While the allyl-thiol reaction lasted, the generated heat was dissipated away via the Al mold part and the liquid OSTE+ precursor backfilled into the mold cavity from the injection and ventilation ports to compensate for shrinkage. The mold was then opened and the glass lid removed (fig. 5e). The release liner was lifted up in a continuous motion from one side of the mold to the other, releasing the intermediately polymerized and temporarily laminated OSTE+ part, which adhered more strongly to the liner than to the insert. When releasing the OSTE+ tube connector arrays from the mold, the silicone tube stubs were transferred from the mold to the OSTE+ replica in which they had become physically integrated. Thereafter, the liner was used as a carrier, allowing for handling of the released OSTE+ part without the need to directly contact the part surface and thus eliminating the risk of contaminating the surface and its unreacted functional groups. Unwanted polymer structures from the mold injection and ventilation channels were cut off and removed (fig. 5f). The OSTE+RIM process was repeated using both types of molds (fig. 5g), generating all parts needed to build a complete microfluidic device in the assembly and bonding steps of the back-end process (fig. 5h).

Direct covalent bonding – fabrication of devices

In the back-end processing, here demonstrated by direct covalent bonding, the intermediately polymerized microfluidic OSTE+ part was manually aligned to, and brought in direct contact with, the unstructured cover using the release liners as carriers (fig. 5i). If needed, pressure was applied locally by hand to evacuate trapped air between the two parts. The assembled OSTE+ parts covered by the release liners were then sandwiched between a flat metal plate and a glass plate to avoid deformation of the final device due to resting on an uneven surface while hardening during the second polymerization step (fig. 5j). The thiol-epoxide reaction was initiated by heating the fabricated and stacked OSTEMER 322 parts in an oven at 110°C for 15 minutes. The OSTE+ 40 parts were exposed to the unfiltered and collimated UV-light (14 mWcm^{-2}) for 100 s. Thereafter, the manufactured OSTE+ 40 device was left in room temperature over night or heated in an oven at 75°C for 2 h to accelerate and complete the polymerization process to achieve a covalent bonding between the parts, and to obtain the final material properties of the polymer.

After full polymerization, the adhesion between the OSTE+ polymer and the release liners weakened and the liners could be easily lifted off from the device (fig. 5k). The molded and intermediately polymerized tube connector arrays were assembled and bonded to the microfluidic parts of either formulation, similarly as described above (fig. 5l). After complete polymerization, the liners of the tube connector arrays were removed and the fabrication of the OSTE+ microfluidic device was finished (fig. 5m).

Fabrication of test structures for replication accuracy and shrinkage evaluation

The surface roughness of the machined Al, and consequently of the replicated OSTE+ microfluidic parts, were too large to allow for an accurate comparison of the size and shape of fluidic structures in the mold and replica. Therefore, a dedicated Si mold insert was fabricated by deep reactive ion etching (DRIE) to form $150 \mu\text{m}$ wide and $45 \mu\text{m}$ high ridges, and thereafter thermally oxidized to achieve a $1 \mu\text{m}$ thick smooth oxide surface. The Si mold insert was attached to the bottom of an unstructured Al mold cavity, which was used for the molding of an OSTEMER 322 replication test part using OSTE+RIM. After molding, the OSTE+ part was demolded and fully polymerized.

Evaluation of demonstrator devices

OSTEMER 322 and OSTE+ 40 parts with mechanical and optical properties reported in figure 1 and 2a, respectively, were successfully and repeatedly molded using OSTE+RIM. The OSTE+ parts remained similarly soft to the touch for several hours after molding and did not become significantly stiffer until several days later, matching the shelf-life of the precursor and indicating a controlled and successful separation of the two polymerization reactions during molding. No deterioration of the Al or Si molds was observed after multiple

Figure 6. Photographs showing **a)** the Al mold cavity with engravings and surface and edge roughness originating from the milling, **b)** an OSTEMER 322 part with surface structures and roughness replicated from the Al mold cavity, **c)** two different OSTE+ polymer microfluidic devices: the top left one made of OSTE+ 40; and the lower right one made of OSTEMER 322, **d)** the Si mold insert with a ridge structure, **e)** the fully polymerized OSTEMER 322 replicated test part with a corresponding channel structure, and **f)** a magnification of a corner in the OSTE+ replicated test part.

molding and cleaning rounds, which is explained by the soft mechanical properties of the partially polymerized OSTE+ polymer.

Replication fidelity

Visual inspection of the OSTE+ parts using microscopy imaging showed accurate replication of the molded structures with no apparent loss of details, including the surface roughness and jagged edges originating from the milling of the Al mold parts, see figure 6 a and b. The replication accuracy and shrinkage of the molded OSTE+ parts were estimated by comparing the size of specific structures, such as the dimensions of complete parts, channels, open through hole interconnects and engravings, in the Al inserts and in the fabricated parts by microscopy inspection using the software of a camera equipped stereomicroscope (M205 C, LEICA AG, Germany). Given a 1 % estimated tolerance of measured distances by the microscope software, no shrinkage was observed. Thus, the linear shrinkage of the produced OSTE+ microfluidic parts was not exceeding 1%.

The replication accuracy and shrinkage were further investigated by comparing tactile surface metrology investigations of the Si mold insert and the corresponding replication test part. The Si insert and the OSTE+ replication test part were diced and their cross-sections were imaged under a microscope, see figure 6 d and e. The ridge of the Si mold insert and the corresponding channel of the replication test part were measured using a stylus profiler (KLA-Tencor P-15, Milpitas, USA) and optical microscopy. First, based on the profilometer data, we identified the flattest region on the bottom of the etched Si Mold, and the corresponding regions on the replication test part. We used the profilometer software to determine the surface roughness in that region. Thereafter we determined the height difference between this flattest etched region and the non-etched region for the Si-mold, and for the corresponding regions on the replication test part. Finally, optical microscopy was used to measure the width of the features. The resulting measurement data is shown in table 1.

The measurement error on a single stylus profilometer measurement is $0.25\ \mu\text{m}$, according to the device manual. Whereas optical microscopy has a theoretical resolution limit of approximately $290\ \text{nm}$ ($\lambda = 550\ \text{nm}$, $NA_{\text{air}} = 0.95$), the total error resulting from placing a scale bar on a microscopy picture is estimated at $1\ \mu\text{m}$ due to imprecision in determining the exact edge position. Measuring corresponding height positions on the mold and the replica is only possible to within a certain accuracy, and the difference in position will lead to a difference in height

Table 1. Surface metrology data of the channel microstructure in the Si mold insert and in the fully polymerized OSTE+ replication test part.

	Surface roughness (nm)		Height (μm)		Width (μm)	
	Si mold	OSTE+ replica	Si mold	OSTE+ replica	Si mold	OSTE+ replica
Stylus profilometry	170 p-p	70 p-p	46.5 ± 0.39	46.0 ± 0.36	n.a.	n.a.
Optical microscopy	n.a.	n.a.	44.6 ± 1.4	45.1 ± 1.4	149.8 ± 1.4	150.6 ± 1.4

in the same magnitude order as the surface roughness. The total error in the (differential) height and width measurements in table 1 was determined as the quadratic average of these error sources.

Bond quality

The molded OSTEMER 322 and OSTE+ 40 parts were successfully bonded, without exception, to form complete devices, see figure 6c. Upon visual inspection, the surface roughness on the OSTE+ parts became invisible after bonding where contact was made whereas it was still visible in the cavities of microfluidic channels and chambers, indicating a conformal contact between the bonded parts. After bonding, the OSTEMER 322 and OSTE+ 40 parts could not be manually delaminated, even when using a scalpel. The burst pressure was tested on each type of device by closing all but one inlet port and then connecting external tubing inserted into the open inlet with a compressed air source. The differential pressure at room temperature between atmosphere and the devices, which were submerged in water for easy visual detection of leaking air bubbles, was measured in real-time using a computer controlled pressure sensor setup as the pressure was increased. At approximately 4 bars of differential pressure, the tubing that was connected to the open inlets popped out, whereas no sign of bursting or delamination of the bonded OSTE+ parts were visible in any device. The test showed that the OSTE+RIM fabricated devices, including the tube connectors, withstood operating pressures far exceeding typical conditions in microfluidic applications.

Device characterization

The microfluidic OSTE+ devices were filled with differently colored dyed water through tubing inserted into the open inlets of the connector arrays and then inspected optically, see figure 7. No cracks, voids or leakage were observed along the channel edges (fig. 7a-c), even after hours of use. The fabricated devices were stiff, providing good robustness for manual handling and fluidic use despite the only 0.9 mm overall device thickness (fig. 7d). Moreover, the OSTE+ microfluidic devices were straight with flat surfaces and no warping, indicating little residual stress from the polymerization and bonding (fig. 7e). The contact angle of DI water on the surface of an OSTEMER 322 device was measured to 67 ° using an optical tensiometer (Theta, Biolin Scientific Holding AB, Sweden), confirming the native hydrophilicity of the OSTE+ surface. In figure 7f, the microfluidic part and the cover were made of OSTE+ 40 and the tube connectors were made of OSTEMER 322, demonstrating excellent heterogeneous bonding performance between different OSTE+ polymer formulations. All devices featured high optical transparency, however, the samples based on OSTE+ 40 had a slight yellow tint (not clearly visible in the photographs), possibly due to the small absorption peak that extends up to 420 nm, while those based on OSTEMER 322 were perfectly clear.

Discussion

Compared to previously reported work based on casting for making microstructured parts from OSTE+, particularly using PDMS molds, OSTE+RIM has two significant advantages.

One advantage is the temperature stabilization during molding through cooling via the mold insert to maintain a low polymerization temperature throughout the molding process and hence, separation of the dual polymerization reactions of OSTE+. Specifically, by using Al mold inserts with high heat conductance it is possible to repeatedly generate intermediately polymerized and soft OSTE+ parts with storage moduli as low as 3.2 MPa that last for several days. Subsequently, when accelerating the second polymerization reaction and completing the polymerization the parts become stiff and achieve a final storage modulus of up to 2.3 GPa. Without active acceleration, the devices only reach complete polymerization after being stored for several days. The temperature stabilization also allows for a strong and irreversible bonding between two molded and intermediately polymerized OSTE+ parts, tolerating at least 4 bars of differential pressure, due to the conservation of the surface reactive thiol and epoxide groups during molding. Moreover, the temperature stabilization was shown to be important to repeatedly achieve a successful demolding. Another advantage of using the temperature stabilized process of OSTE+RIM is that UV-light sources with higher power can be used, thus reducing the exposure time. With OSTEMER 322, we demonstrated a 30 s UV-light exposure using LED-lights during molding to fabricate a microfluidic part and a cover part in a single batch, which molding time is close to the cycle-times of industrial injection molding and at least twice as fast than what has been previously reported for producing a single OSTE+ part with casting using PDMS molds [13,16]. In this work, we fabricated a complete microfluidic OSTE+ device, including molding of OSTE+ parts and bonding in the back-end processing, in less than 20 minutes.

Figure 7. Photographs of fabricated OSTE+ polymer microfluidic demonstrator devices filled with aqueous color dye. **a)** An OSTERMER 322 device with top view magnifications of microfluidic features in **b)-c)** and side views in **d)-e)**. **f)** An OSTE+ 40 device with an alternative fluidic design and with integrated OSTERMER322-40 tube connectors (tubing removed in the photograph).

Another advantage of OSTE+RIM is the shrinkage compensation through backfilling of the liquid OSTE+ precursor into the mold cavity during the shrinkage of the first allyl-thiol polymerization reaction. The backfilling minimizes internal stresses and thereby enables excellent replication fidelity of the molded OSTE+ part. Whereas many commonly used polymers undergo shrinkage during polymerization/cooling, *i.e.* post-solidification of the polymer, which potentially leads to high residual stresses, warping and low replication fidelity [3], OSTE+ mainly shrinks during its first polymerization step while still being liquid, *i.e.* pre-solidification of the polymer, and thus, no or only little shrinkage induced residual stress is generated. In thermoplastic injection molding, the amount of shrinkage can vary locally due to inhomogeneous cooling from variations in the thickness of the mold cavity. In OSTE+RIM, the UV polymerization-induced shrinkage is expected to be homogenous throughout the mold cavity, independent of variations in thickness of the mold cavity. Local flow restrictions in narrow parts of the mold cavity could potentially limit the refilling of polymer precursor, however, this could not be observed in our measurements. The second polymerization reaction of OSTE+ induces negligible shrinkage [23] leading to very little residual stress in the finished device. Indeed, measurement data in table 1 indicate that geometrical differences between mold and replica are below the relative measurement error of 0.84% and 0.93%, for height and width, respectively. The low shrinkage is further supported by the cross-sectional images shown in fig. 6 d-e, where the replicated OSTE+ part is visually identical to the Si mold, including sharp 90 ° corners. The absolute replication error, being in the range 0.5-0.8 μm , is of similar magnitude order as the precision in SU8 processing or DRIE typically used for high-precision microfluidic molds. We conclude that stress-related issues, such as warping and non-flat surfaces, are insignificant and OSTE+RIM is well-suited for high-precision replication.

OSTE+RIM also addresses other fabrication issues related to casting of OSTE+. Firstly, when OSTE+ is molded using a casting process, air bubbles risk to become trapped in the polymer precursor when it is being poured into the mold cavity and when a lid is subsequently added to close the mold. In OSTE+RIM, the low viscosity of the polymer precursor allows for easy mold filling into the closed OSTE+RIM mold through the injection port of the mold, thus significantly reducing the risk of introducing and trapping air bubbles during mold filling. The ventilation port of the mold could potentially be used for connecting vacuum to the mold during mold

filling to further reduce the risk of trapping air, however, this was not required for our mold designs. Secondly, whereas casting suffers from squeeze-film formation during molding, eliminating the possibility of making open holes in the replicated part, it is possible with OSTE+RIM to fabricate through-hole openings such as fluidic interconnects, as shown in the fabricated OSTE+ device.

The demonstrated variant of OSTE+RIM is limited by the incorporation of the release liner. The liner eliminates the possibility to have structures in the top part of the mold cavity, which would be possible if the liner would be replaced with a patterned COC or glass lid [24]. However, the compromise of using the liner enables a very easy-to-use fabrication scheme where the replicated OSTE+ parts, laminated to the liners, never need to be directly handled during processing.

In contrast to all other polymer replication techniques for microfluidic applications that we know of, OSTE+RIM generates replicated polymer parts that express surface reactive groups available for facile back-end processing, such as direct covalent bonding, resulting in devices with native hydrophilic surfaces. This is achieved with a user and laboratory friendly process that includes a minimal number of processing steps and methods, circumventing the necessity of traditional laborious and difficult-to-control back-end processes. Compared to the dual step curing processes demonstrated using the single polymerization reactions, OSTE+RIM enables a controlled intermediate stop of the polymerization by relying on two separate polymerization reactions, potentially allowing for higher reproducibility. OSTE+RIM is similar to industrial-like reaction injection molding techniques and is promising for both research applications and industrial manufacturing of microstructured devices, and therefore has the potential to bridge the critical lab-to-fab gap [25] in the field of microfluidics.

Conclusions and summary

In this article, we have presented and demonstrated OSTE+RIM, a novel fabrication method based on reaction injection molding of OSTE+ thermoset polymers for making OSTE+ polymer microstructured parts that can be directly bonded by covalent reactions. The method is unique by offering a molding technique that repeatedly generates microstructured polymer parts with low residual stress, high replication fidelity and reactive surface chemistries available for subsequent and facile back-end processing. It was shown that microscopy glass slide format OSTE+ microfluidic devices with hydrophilic surfaces were successfully molded, covalently bonded and tested with no leakage, no warping, stiff mechanical end properties and high optical transparency using two different OSTE+ formulations. The main novelties of the work are the temperature stabilized dual step OSTE+ polymerization in combination with a reaction injection molding technique, ensuring the separation of the two polymerization reactions during molding, and the shrinkage compensation during molding by backfilling of polymer precursor into the mold, making the unique shrinkage behavior of OSTE+ a strong advantage in OSTE+RIM for making high quality microstructured parts.

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Appendix

OSTEMER 322

The UV-light and heat cured thermoset OSTEMER 322 was supplied as a two-part mixture, including a UV-light sensitive initiator for the first thiol-allyl reaction and a heat sensitive initiator for the second thiol-epoxide reaction. As its name suggests, OSTEMER 322 has a 40% off-stoichiometric ratio between allyl and thiol functional groups. Before injection into the mold, the two parts were mixed in a 1:0.87 ratio by stirring, vortexing and degassing in an exicator connected to a vacuum pump to form the polymer precursor. The second reaction between the thiol and epoxide functional groups starts immediately upon mixing but at a negligibly slow pace in room temperature and is accelerated first when heated.

OSTE+ 40

The dual UV-cured thermoset OSTE+ 40 was based on three monomers: pentaerythritol tetrakis (3-mercaptopropionate) (PETMP); triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TATATO); and bisphenol A diglycidyl ether (BADGE) (all three from Sigma-Aldrich, Germany). In addition, the polymer precursor also contained two UV-light sensitive initiators: ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L) for the first thiol-allyl reaction; and a pre-commercial anionic photolatent curing agent for the second thiol-epoxide reaction (both from BASF, Germany). The name OSTE+ 40 refers to that PETMP and TATATO were mixed in a 40% off-stoichiometric ratio of thiol over allyl groups. BADGE was mixed in a stoichiometric ratio between the epoxides and the remaining thiol groups. Hence, the mixing ratio of the monomers was 1.05 of PETMP, 1 of TATATO and 0.6 of BADGE. To prepare the OSTE+ 40 precursor, TATATO was split into 1/3 and 2/3 portions. 0.5 wt% of the anionic curing agent was added to the 1/3 portion (blend 1) of TATATO and the other portion was mixed with the PETMP and BADGE monomers (blend 2). Blend 1 was heated in an oven at 75 °C for 30 minutes to enhance the dissolution of the anionic curing agent and then mixed with blend 2 when cooled down. To form the final polymer precursor, 0.5 wt% of the TPO-L initiator was added to the mixture and stirred thoroughly, followed by degassing in an exicator connected to a vacuum pump.