

NANORIM: SUB-MICRON STRUCTURING WITH REACTION INJECTION MOLDING

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ABSTRACT

We report “nanoRIM”, the first reaction injection molding (RIM) replication method for thermosets with demonstrated feature sizes down to 250 nm. NanoRIM constitutes the first scalable manufacturing method for thermoset polymers that allows combining large ($> \text{cm}$) and small ($< \mu\text{m}$) lateral feature sizes with varying replica thickness in the same device. We demonstrate nanoRIM for manufacturing replica in off-stoichiometry thiol-ene (OSTE) thermoset.

INTRODUCTION

Downscaling feature sizes through cost-effective and commercially scalable fabrication methods has been a research focus since the emergence of micro/nanofabrication. While diverse high-tech cleanroom processing techniques have evolved during the recent decades, these multi-step and costly fabrication methods are limited to applications in the field of semiconductors and optoelectronic that require high-precision and low-defect end products [1, 2]. Nevertheless, there is a growing demand for low-cost and high throughput polymer chip production in different areas. The medical diagnostics market, as a case in point, exemplifies the apparent need for inexpensive materials and commercially adaptable fabrication techniques capable of chip production for fast and efficient sample analysis or pathogen detection. Such devices, embedded with structures of macro to sub-micron feature sizes, act as an enabler for diagnostic tests on portable and disposable plastic chips.

Reaction injection molding (RIM) of polymer parts in microfabrication was introduced in the 1980s. However, the commercialisation of this platform has been hindered due to monomer mixing difficulties, high shrinkage rates of ca. 20%, and long cycle times of up to several hours (thermal curing) [3, 4]. As the logical alternative, micro-injection molding (μIM) has dominated the market, notwithstanding the fact that this method demands very sophisticated equipment able to handle high clamp, injection and packing pressures ($> 100 \text{ MPa}$) and temperatures above 150°C , which in turn requires complicated variotherm systems to deal with the viscous plastic melts [5–7]. These μIM machineries have shown micro/nanofabrication capabilities down to 25 nm with aspect ratios of two [8]; nevertheless, they cannot process thermoset polymers such as PDMS or the more recent off stoichiometry thiol-enes (OSTE), a novel class of superior materials in micro/nanofluidic chip manufacturing [9]. To date, the smallest structures realized in thiol-ene microfluidic chips fabricated via RIM has been approximately 150 μm [10], which calls for a serious downscaling improvement to address the mass production of cm/mm size components which contain $\mu\text{m}/\text{nm}$ features.

This work presents the first RIM of OSTE with submicron feature size, which is $a > 2$ orders of magnitude reduction in size compared to the previous work. Moreover, we demonstrate replication of cm-sized thermoset replicas that contain nm-scale features.

METHODS AND FABRICATION

Materials

OSTE thermoset is the polymer of choice for the NanoRIM platform, owing to its delayed gelation, low shrinkage, low viscosity of the precursor and also the rapid UV polymerization offered by this click-chemistry system. These offer unique features for polymer device manufacturing, along with several other advantages such as the potential for tunable mechanical properties, low temperature bonding and in-situ surface energy patterning.

OSTE precursor was prepared by using two monomers and a photo initiator: Pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, Sigma-Aldrich, Germany); triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TATATO, Mercene Labs, Sweden); and 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184, Sigma-Aldrich, Germany). The mixing ratio, with regards to the number of functional groups in each monomer, was designed to yield a polymer with 40% of thiol group excess. The blend was stirred (SpeedMixerTM DAC 150.1 FVZ) prior to injection.

Mold-insert fabrication

To produce the mold insert for the NanoRIM process, a millimeter size fused silica chip was patterned through e-beam lithography. Reactive ion etching (RIE- Oxford Plasmalab 100) was used to fabricate high resolution and high aspect-ratio features (figure 1.a). The patterns cover a diverse range of micro/nanostructures, including cubical and cylindrical wells and KTH logos with lateral size variations in aspect ratios up to 5. The mold structures are intentionally devised to be blind holes and trenches with no intrinsic air vents, rendering the most complicated filling situation. To provide an anti-sticking layer and facilitate the demolding process, the chip was spin coated (3000 rpm- 45 sec) with silane (Dynasylan-F 8263, Evonik, Germany) and baked for 12 minutes. The chip was then carefully embedded inside a micromachined PMMA part, thus forming a transparent mold insert with mm to sub- μm features.

NanoRIM set-up

The NanoRIM set-up, illustrated in figure 1, consists of multiple parts: 1) a movable aluminum part ($30 \times 30 \times 3 \text{ mm}^3$) with a through hole to pass the UV light that acts as a carrier to mount the mold insert; 2) a mold body that accommo-

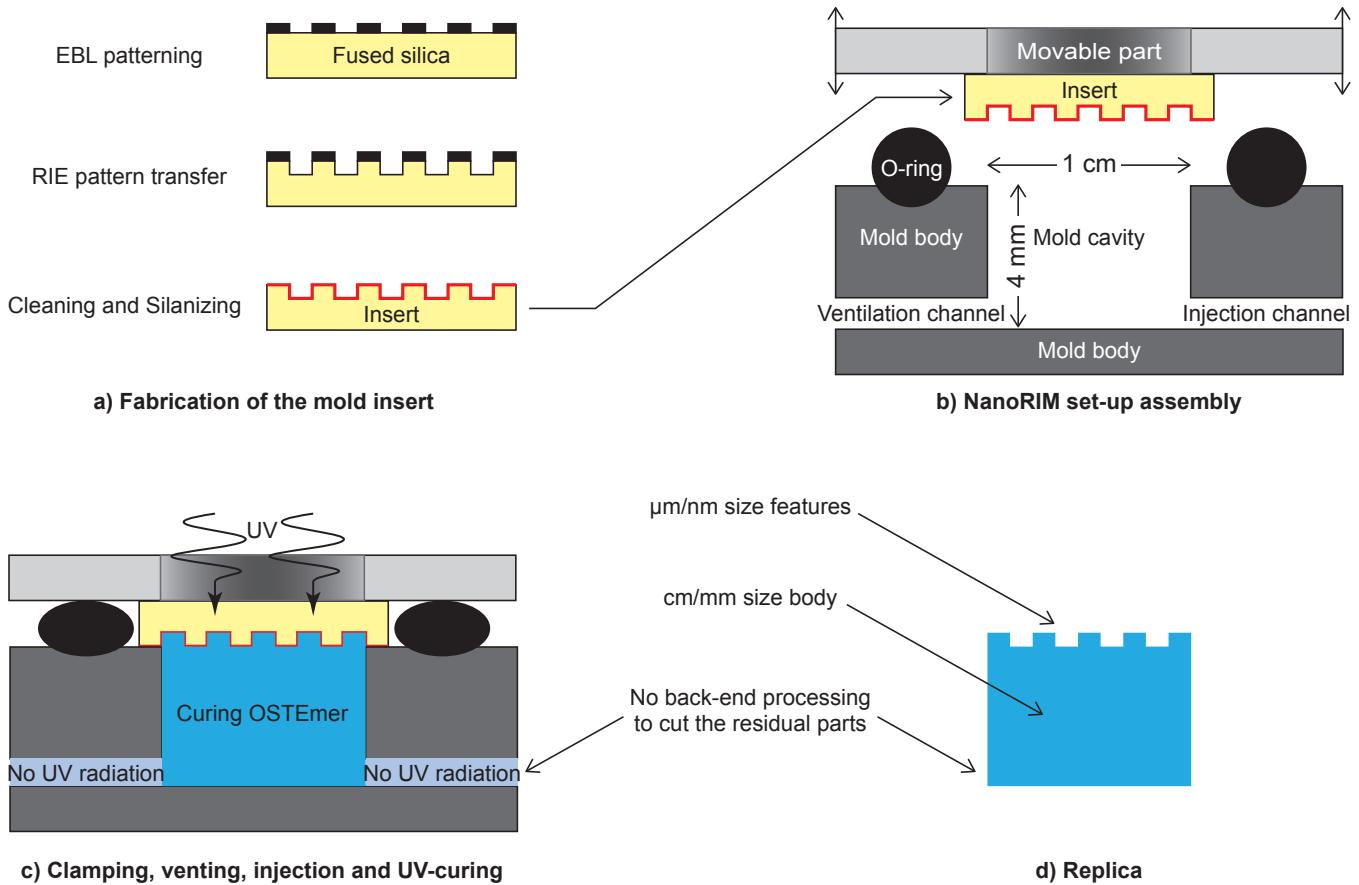


Figure 1: NanoRIM set-up and process flow

dates a cm-sized cavity and the injection and ventilation channels of 2 mm diameter; 3) an O-ring mounted on the interface between the movable part and body part that facilitates the vacuum sealing. Injection and ventilation channels are connected to the injection source and an in-house vacuum (20 mbar) through Mini luer connectors (microfluidic ChipShop, Germany), silicone tubes (I.D.: 1.5mm, O.D.: 3mm) (VWR, Belgium) and pinch valves.

NanoRIM-fabrication of replica

The mold insert was mounted on the movable part (figure 1.b) with patterns facing down to the mold cavity. The mold parts were then aligned and clamped together.

Prior to the precursor injection, the vacuum was applied inside the mold cavity and the tubes. Afterwards, the precursor was injected inside the cavity by a standard syringe with Luer slip interface. The set-up was then detached from the silicone tubes and exposed to UV light (12 mWcm^{-2}) (OAI, Milpitas, USA) for 2 seconds (figure 1.c). Thereafter, the movable part was separated from the mold body and the replica, adhered to the insert, was removed from the mold cavity. The replica was then separated manually from the mold insert (figure 1.d).

RESULT AND DISCUSSION

Figure 2 shows photographs and SEM images of a replicated part. The polymer replica of $> 1\text{cm}$ diameter and $\sim 5\text{mm}$ thickness contains different geometrical structures with a diverse range of lateral and vertical feature sizes. The cm-sized part is illustrated in figure 2a. Figure 2.b shows an overview of structures with step heights of 420 and 140 μm . A closer view of micro/submicron features replicated from the fused silica chip is shown in figure 2.c. NanoRIM offers an excellent replication fidelity both for micro- and nanostructures. This has been confirmed by very homogeneous filling profile over a $50 \times 50 \mu\text{m}$ sized structure (figure 2.d), where the nanoroughness on the roof is replicated from the same roughness of the mold. This also reveals an excellent capability to replicate hierarchical $\mu\text{-nm}$ structures. The polymer shows an outstanding capability in filling the nanocavities despite applying mild vacuum and using no packing pressure. The bird-view over an array of pillars of 850 nm in diameter illustrates the mold filling ratio of $> 95\%$ (figure 2.e). The replicated pillars, with an aspect ratio of > 4 , show nearly the same aspect ratio of the mold. Despite non-optimized demolding, features with lateral size down to 250 nm were replicated (KTH logo in figure 2.f).

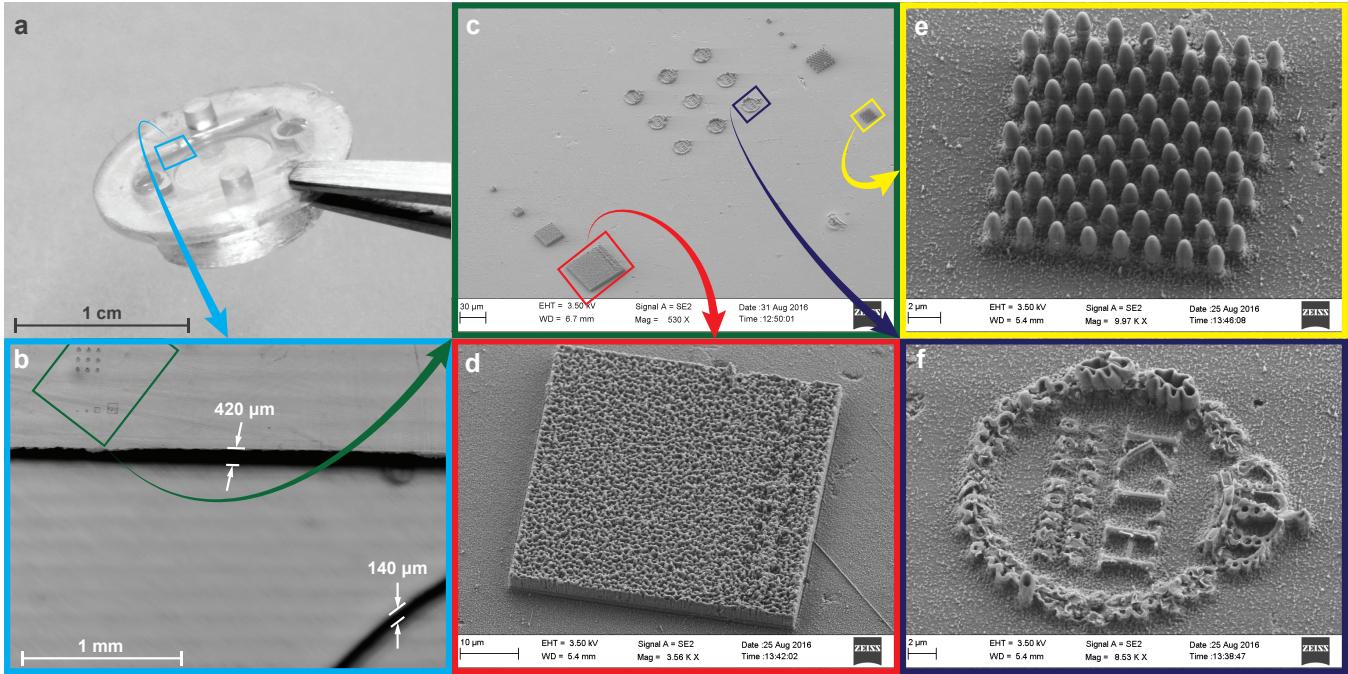


Figure 2: a) a cm-sized replica with micron-submicron structures; b) overview of μm /sub- μm structures; c) several surface features of $250 \text{ nm} < \text{size} < 50 \mu\text{m}$; d) a $50 \times 50 \mu\text{m}$ sized cubical structure; e) an array of pillars ($D=850 \text{ nm}$); f) KTH logo with replicated features down to 250 nm .

Table 1: Comparison of microstructuring methods for thermosets and thermoplastics devices with sub-micrometer precision

	THERMOSETS		THERMOPLASTICS
	NanoRIM of OSTE	Casting	μIM
Example materials	OSTE	PDMS, acrylates	PMMA, COC
Geometry	Demonstrated minimum lateral feature size	250 nm $< \text{nm}$, e.g. molecular imprinting (MIP)	25 nm [8]
	Aspect ratio of features	medium, limited by demolding	low, limited by mold filling
			medium, limited by cycle time and demolding
	Filling ratio	potentially high	limited
			limited by viscosity
Manufacturing	Typical cycle time for submicron features	< 1 min (2 s curing; currently limited by non-optimised demolding)	PDMS slow, acrylates fast
	Equipment and operation cost	potentially low	low
	Suitability for scalable manufacturing	potentially	single part processing
			μIM machines have limited shot volume suitable only for micro-replicas [11]

For features $< 250\text{nm}$, the mold is properly filled, but plug-defectivity is observed due to non-vertical demolding. The nanoRIM platform can be benchmarked with the state of the art polymer replication methods (table 1). Compared to micro-injection molding (μIM) of thermoplastics, NanoRIM of OSTE thermoset entails much less demanding operational condition such as functioning at room temperature, mild cavity vacuum conditions (20mbar), low clamp force, very low external injection pressure, zero packing pressure and low cycle-time for fabrication of full devices.

Nanoimprint lithography (UV-NIL) and direct photostructuring are two major fabrication techniques utilizing thermosetting polymers. Nonetheless, NIL and photostructuring are both limited in the replica thickness, (too) expensive for large-scale manufacturing and cannot provide full devices. Casting allows freedom in lateral feature design, but is not suitable for large scale manufacturing due to shrinkage, variability and low throughput [12]. NanoRIM, on the other hand, imposes no limit on replica geometries in terms of lateral and vertical dimensions. The low-shrinkage and short cycle-time of the polymerization also render material adaptability for commercial application.

CONCLUSIONS

The nanoRIM process enables rapid, reliable, high resolution and high fidelity replication of polymer structures through a simple and cost-effective fabrication method. The platform not only offers a facile and straightforward technique for off-cleanroom chip prototyping in laboratory scale, but also possesses the suitability for scalable production. These along with the freedom of structure design and diverse range of sizes provide a potential new path in polymer device manufacturing.

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