

SUPERIOR DRY BONDING OF OFF-STOICHIOMETRY THIOL-ENE EPOXY (OSTE(+)) POLYMERS FOR HETEROGENEOUS MATERIAL LABS-ON-CHIP

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ABSTRACT

We demonstrate biocompatible bonding to a multitude of LoC substrates using OSTE(+), a novel polymer formulation with a unique dual cure system developed specifically for microfluidic applications. OSTE(+) allows for soft lithography microstructuring, strong biocompatible dry bonding to almost any substrate during LoC manufacturing, while simultaneously mimicking the mechanical properties found in thermoplastic polymers, hence allowing for true prototyping of commercial LoCs. In this work, we describe the simple micropatterning process, curing mechanisms and show leak-free dry bonding to nine different substrate materials. Uniquely, strong bonding is achieved to COC, the thermoplastic of choice for microfluidics, which opens up the possibility of hybrid thermoplastic/OSTE(+) LoCs. In this work, we demonstrate bonding to nine different untreated substrates at 37°C and room temperature to demonstrate good bonding properties even at lower temperature. We also show the high resilience of the epoxy bond by immersing an aluminum substrate with a bonded OSTE(+) layer into boiling water while simultaneously subjecting the assembly to pressurized air.

KEYWORDS

Off-stoichiometry thiol-ene, OSTE, OSTE(+), soft lithography, bonding, COC, microfluidics, microfabrication

INTRODUCTION

The most commonly used materials for microfluidics, i.e. PDMS and thermoplastics, suffer from cumbersome and often ineffective bonding processes, especially when packaging biofunctionalized surfaces, which makes LoC assembly difficult and costly [1,2]. To overcome this deficiency, a novel bonding technology must be effective for many types of substrates, provide strong bonds, overcome the demanding operating conditions, especially in the low temperature bonding regime, while simultaneously allowing for biocompatible bonding conditions.

Previously, we introduced a family of off-stoichiometry thiol-ene (OSTE) polymers, specifically developed to overcome material and surface related limitations in labs-on-chip [3]. Whereas bonding characteristics are excellent to pre-functionalized substrates [4] or gold [5], OSTE still requires active surface coatings on the substrate for the thiol to form covalent bonds. To overcome this limitation, we have recently introduced off-stoichiometry thiol-ene epoxy, OSTE(+) [6] demonstrating bonding thin porous silicon on OSTE(+) polymeric chip without any surface modification prior to bonding at 70°C. OSTE(+) is a polymer formulation with a unique dual cure system developed specifically for microfluidic applications (Figure 1), which allows for microstructuring via soft lithography, photopatterning and machining, while simultaneously mimicking the mechanical properties found in thermoplastic polymers, hence allowing for true prototyping of commercial LoCs. In this work, we investigate bonding of OSTE(+) to different substrate materials.

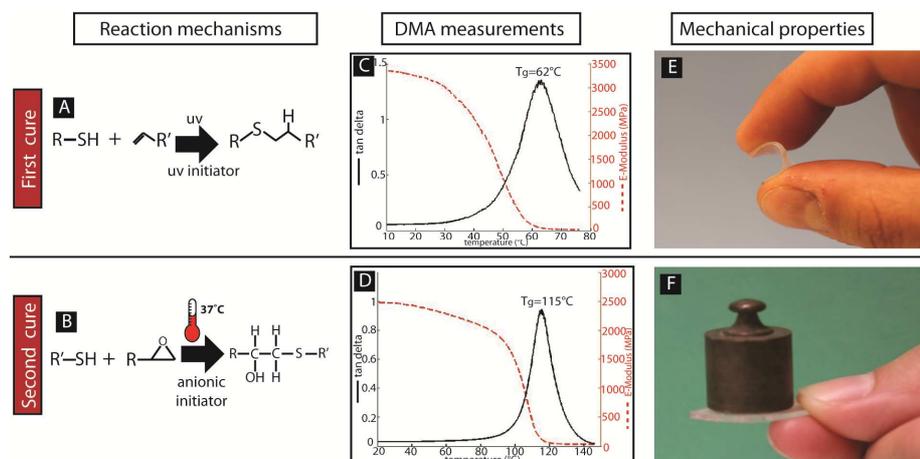


Figure 1: (A) and (B) The reaction mechanisms for the dual cure ternary monomers. (C) DMA measurement after UV cure and (D) DMA measurement after thermal cure for OSTE(+) TGIC with high Tg suitable for PCR applications. (E) The mechanical properties after first UV cure, the OSTE(+) is very soft and compliant (F) after thermal cure, the OSTE(+) has the same modulus as engineering thermoplastics.

OFF-STOICHIOMETRY THIOL-ENE EPOXY, OSTE(+)

Here, we introduce two new polymer formulations: 1) OSTE(+) TGIC, which consists of thiol (Pentaerythritol tetrakis (2-mercaptoacetate)), allyl (triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione) and epoxy (Tris(2,3-epoxypropyl) isocyanurate) monomers at a stoichiometric ratio of 1/1.4/0.4; and 2) OSTE(+) BADGE, where the epoxy in 1) is changed for BisphenolA diglycidylether (BADGE) at a stoichiometric ratio of 1/1.8/0.8. In the dual cure process employed, the thiol and allyl react readily via an alternating radical copolymerization initiated via Lucirin TPO (BASF) and 400nm UV-light (Fig. 1A), while the thiol and epoxy react readily at slightly elevated temperatures (37°C) via an alternating anionic polymerization mechanism initiated by a strong base (DBN: 1,5-diazabicyclo[4.3.0]non-5-ene), see Fig. 1B.

FABRICATION

We fabricated demonstrators with 30 μm wide microfluidic channels in OSTE(+) BADGE materials by soft lithography on PDMS molds (Fig. 2). The structures were UV cured (365 nm, 2 minutes at 6 mW/cm²) and the polymerized OSTE(+) was demolded.

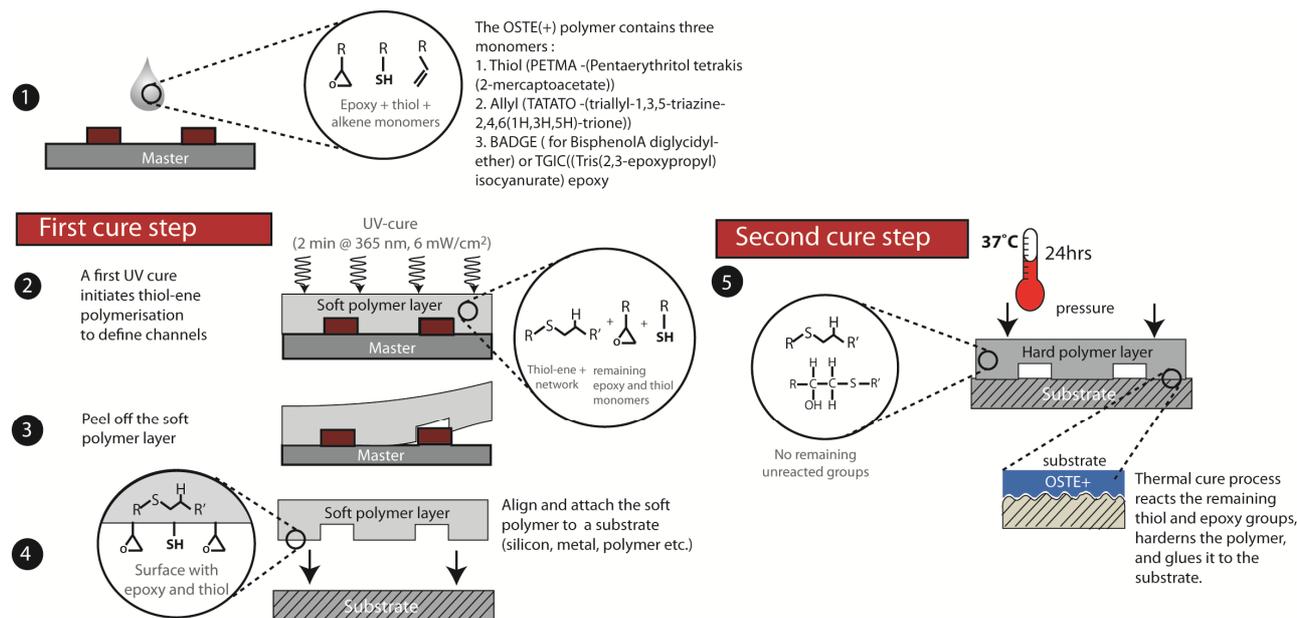


Figure 2: The fabrication steps for the fluidic devices

After this first cure, a first and second batch of OSTE(+) structures were dry bonded by simply contacting them to native surfaces (which has been cleaned with isopropanol) of Si, glass, BCB, PDMS, Al and Cu (first batch) and Cyclic Olefin Copolymer (COC) 6017 from Topas, COC with 100 nm evaporated TiO₂ coating and COC with KMPR 1025 resist coating (second batch). The PDMS (1:30 Sylgard 184) was bonded at room temperature to OSTE(+) via thiol-vinylsiloxane UV-initiated curing at 254nm. The structures were thereafter left for the second cure to take place: 2 hours at room temperature for batch 1, and 24 hours at 37°C for batch 2.

EVALUATION

Burst pressure measurement were performed: 1) under boiling water (100 °C) on an OSTE(+) TGIC – Al bonded sample; and 2) at ambient conditions on an OSTE(+) BADGE – COC bonded sample (Fig. 3). Both samples had a 15 mm diameter, were 1 mm thick and contained a 2 mm diameter hole on which a ramping pressure was applied. Both tests revealed a bond burst pressure in excess of 3 bars. To test the bond quality, all channels were capillarilly filled with dyed water and were found to be leak tight (Fig. 4).

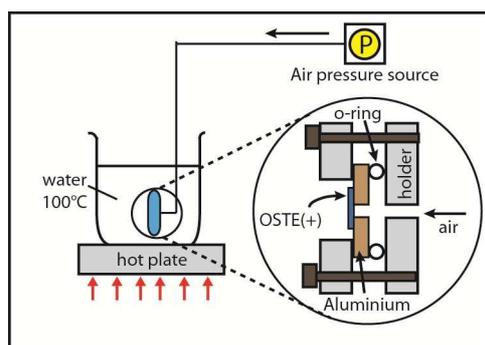


Figure 3: The experimental set up for the burst pressure of OSTE(+) at 100°C

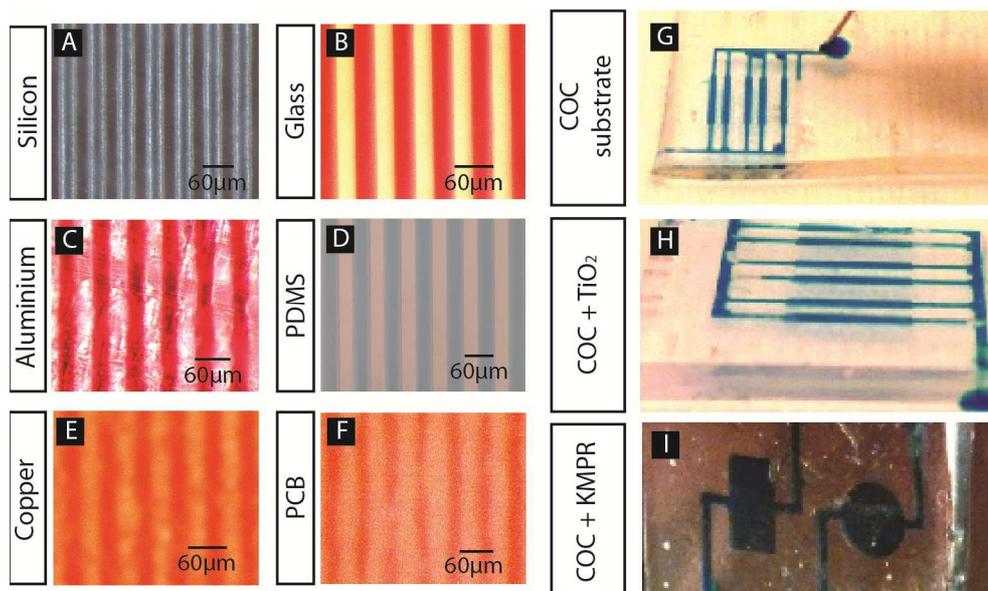


Figure 4: Batch 1 - Leakage tests using different substrates with OSTE(+) polymer channel width of 30µm. (A) Si, (B) Glass, (C) Al, (D) PDMS with 30% excess, (E) Cu and (F) PCB. Batch 2 - (G) Leakage tests using COC as the substrate. Bonding condition was at 37°C and cured for 24 hours. (H) COC and TiO₂ and (I) COC and KMPR 1025.

CONCLUSIONS

We demonstrate a novel OSTE(+) polymer which effectively bonds to nine dissimilar types of substrates, requires no surface treatment prior to the bonding at room temperature, features high T_g , and achieves good bonding strength to at least 100°C. Uniquely, strong bonding is achieved to COC, the thermoplastic of choice for microfluidics, which opens up the possibility of hybrid thermoplastic/OSTE(+) LoCs.

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