DIRECT LITHOGRAPHY OF RUBBERRY OSTE+ POLYMER

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ABSTRACT
We present a Rubbery, Off-Stoichiometric Thiol-Ene-epoxy (OSTE+) polymer for direct lithography manufacturing, demonstrate its use in pneumatic pinch microvalves for lab-on-chip applications, test the lithography process achieving pillars of aspect-ratios (a.r.) 1:8, and characterize it’s surface as hydrophilic.

KEYWORDS: OSTE+, PDMS, lab-on-a-chip, microvalve

INTRODUCTION
OSTE+ is a polymer system developed specifically for lab-on-a-chip (LoC) applications. OSTE+ has the potential to bridge the gap between research prototypes and commercial prototypes [1-2] due to a number of attractive characteristics, including a fast turn around fabrication process, tunable surface properties and adhesive-free low temperature bonding to a large range of substrates, including itself [3-4].

Traditionally, PDMS has been used as the device material in labs-on-chip when elastomeric properties are needed [5] because of its rubbery properties and easy fabrication. However PDMS is severely limiting in many applications, due to its high gas permeability, sample absorption, need for plasma assisted bonding to glass and silicon, and non-suitability for direct lithography.

We recently presented the first rubbery OSTE+ polymer and manufactured devices by micromolding. The mechanical material properties are similar to those of PDMS but feature low gas permeability and low absorption of small molecules [6]. Here, we introduce the first rubbery OSTE+ formulation suitable for manufacturing with direct lithography

THEORY
The excellent OSTE+ properties for LoC stem from the presence of reactive thiol and epoxy surface groups at the polymer surface after the first cure, which allow for covalent adhesive-free bonding and surface modifications. However, lithography requires a developing step after the first cure, which risks to rinse away the surface epoxy monomers, hence, making the surface unreactive. To avoid non-functional surfaces after the first cure, parts of the epoxy and allyl monomers in the previously presented rubbery OSTE+ prepolymer mix [6] were exchanged by allyl glycidyl ether (AGE) (Table 1). The AGE monomer contains both an allyl and an epoxy group, where the allyl group links to the forming polymer during the first cure via a thiol-ene “click” reaction, ensuring covalently linked reactive epoxy surface groups after development. The Albipox 1000 epoxy monomers react with the free bulk and surface thiol and epoxy groups during the second cure, resulting in an inert surface.

### Table 1. Rubbery OSTE+ polymer recipe.

<table>
<thead>
<tr>
<th>Component</th>
<th>Allyl</th>
<th>Thiol</th>
<th>Epoxy</th>
<th>Allyl/Epoxy</th>
<th>Initiators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>Trimethylolpropane diallyl ether</td>
<td>Tris[2-{3-mercapto-propionyloxy}ethyl] isocyanurate</td>
<td>Albipox 1000</td>
<td>Allyl glycidyl ether (AGE)</td>
<td>1st: Irgacure184 2nd: DBN</td>
</tr>
<tr>
<td>Stoichiometric ratios</td>
<td>0.9</td>
<td>1.2</td>
<td>0.1</td>
<td>0.1 allyl &amp; 0.1 epoxy (0.05% &amp; 0.05% w/w)</td>
<td></td>
</tr>
</tbody>
</table>

EXPERIMENTAL

Rubbery OST E+ was prepared using Tris[2-(3mercapto-propionyl-oxy)ethyl]isocyanurate (Sigma-Aldrich), Trimethylolpropane diallyl ether (Sigma-Aldrich), Albipox 1000 (Evonik) and AGE (Sigma-Aldrich) at a stoichiometric ratio of 0.9:1.2:0.1:0.1 (allyl:thiol:epoxy:AGE), resulting in a total functional stoichiometric ratio of 1:1.2:0.2 (allyl:thiol:epoxy). Irgacure 184 (Sigma-Aldrich) and 1,5-Diazabiclo(4.3.0)non-5-ene (DBN, Sigma-Aldrich) were used as initiators.

Geometric test structures consisting of 250 µm diameter pillars and 250 µm and 500 µm wide trenches were manufactured in different heights (500, 1000, and 2000 µm) by lithography using a collimated near-UV mercury lamp (OAI, Milpitas) as seen in Figure 1.

Figure 1: Manufacturing of lithography test structures

A pneumatic pinch microvalve [5] was fabricated using only direct lithography for structuring and plasma/adhesive-free bonding of layers at 75°C for 2 hours under clamping as shown in Figure 2.

Figure 2: Manufacturing of microvalves. (A) Layer manufacturing using direct lithography UV curing. (B) Layer bonding using temperature accelerated curing.

The microvalve was tested by filling the liquid channel with a blue dye, pressurizing the control channel in increments of 50 kPa until the valve was characterized as closed, i.e. when a discontinuation of blue fluid in the flow channel direction could be observed.

The contact angle with water of the finished material was measured by the sessile drop method and averaging 5 different measurements.

RESULTS AND DISCUSSION

For the geometric test structures, the highest pillar a.r. achieved was 1:8 (Figure 3A). This is comparable to other rubbery pillars, specifically PDMS, for which a.r. of 1:6 was achieved from molding from a photolithography defined and etched Silicon mold [7], and lower than the a.r. of 1:20 which was achieved from a more complex double casting technique involving a casted and surface treated PDMS mold, in turn molded from a photolithography defined master mold [8]. For trenches and walls, a.r. of 1:4 were achieved for both 250 and 500 µm wide trenches, while a.r. of 1:8 failed due to capillary collapse in the development step (Figure 3B). The current a.r. limitation are likely caused by capillary collapse due to a non-optimized drying procedure after lithography and may be improved in future work.

The microvalve manufactured by direct lithography was observed to close between 100 and 150 kPa, (Figure 4A) which is comparable to PDMS microvalves of similar geometries [8].
The surface of this Rubbery OSTE+ was characterized as hydrophilic with a contact angle of 73° (Figure 4B), whereas PDMS is naturally hydrophobic with contact angles of 90°-110°.

Figure 3: Lithography test structures. (A) Pillars at a.r. of 1:4 (left) and 1:8 (right). (B) Walls and trenches of a.r. 1:2 and 1:4 (left) and 1:4 and 1:8 (right image).

Figure 4: (A) Valve testing. (B) Contact angle measurement.

CONCLUSION
We have presented a Rubbery OSTE+ compatible with direct lithography manufacturing. We have shown that it is possible to manufacture pillars with a.r. of at least 1:8 and trenches with a.r. of at least 1:4, and to manufacture functioning microvalves using only direct lithography. We characterized the surface of the material as naturally hydrophilic. Hence, Rubbery OSTE+ is turning out to be an interesting alternative to PDMS for a range of applications, especially where the unique features of OSTE+ are desired.

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REFERENCES

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