UV-LIGHT STRUCTURED SILANIZATION FOR SELECTIVE BONDING AND FABRICATION OF PAPER-BASED MICROFLUIDIC CHANNELS

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ABSTRACT
We present UV-light induced silanization techniques that can be used for bonding stereolithographically structured microfluidic devices to polydimethylsiloxane (PDMS) as well as for structuring paper-based microfluidic devices. By using a printed lithography mask locally constrained silanization is achieved. This is beneficial for bonding microfluidic devices especially when the liquid to be transferred within the device should not react with chemical leftovers on the channel walls. Furthermore, the technique may enable the production of “hidden channels”. Using the silanization technique for structuring paper-based microfluidic devices we could reduce the fabrication time of such devices to less than ten minutes.

KEYWORDS: Bonding, Paper-Based Microfluidics, Silanization

INTRODUCTION
During the last years microstereolithography (µSTL) has become a promising alternative to classical microfabrication technologies. This technology enables fast fabrication of complex 3D structures [1]. However, the technique is limited to specific resins. Thus direct integration of flexible membranes is impossible. Membranes that are needed for the creation of microfluidic actuators, e.g., valves and pumps, need to be fitted subsequently. On behalf of leak-tight connection a bonding protocol is needed. However, in microfluidics bonding is usually a complicated process. Liquid adhesives tend to clog small microfluidic capillaries. For setting up stacked devices tailored methods, e.g., plasma-induced and corona-based bonding have been developed. However, these techniques are limited to glass and siloxane (such as PDMS) surfaces. In order to use these bonding techniques for other materials silanization techniques have been proposed [2]. These silanization techniques either apply heat to the samples or immerse them in liquid solvents. Both procedures damage most STL epoxy components. Besides, various admixtures added to the STL epoxy resins for designing the material properties not only influence the behavior of the bulk material but also greatly influence the surface chemistry, i.e., the type and amount of chemical groups that are available on the surface. Therefore, we developed two different silanization techniques (using (3-glycidoxypropyl)trimethoxysilane (GPTMS) [3] or dimethoxydimethylsilane (DMDMS), respectively, see Figs. 1 a/b). In combination these methods cover and thus allow bonding of nearly every commercially available STL epoxy to PDMS.

The second application of UV-light based silanization is the creation of paper-based microfluidic channel structures (Fig. 2c). Silane-based approaches previously demonstrated using the sol-gel based process [4] are time-consuming and require etching steps. Using photoinduced structured silanization processes, paper-based microfluidic devices can be fabricated within five minutes. DMDMS can be directly applied for both, structured bonding as well as fabricating paper-based microfluidic devices using lithography. GPTMS as a trifunctional silane is not suitable for the creation of locally confined silanization by means of lithography. By replacing GPTMS with the bifunctional (3-glycidoxypropyl)dimethoxyethylsilane (GPDMDS) we were able to create locally confined silanization for both, bonding and paper-based microfluidics.

THEORY
The various STL resins that are commercially available come with different surface properties. Thus the silane that is used to create a PDMS like surface needs to be chosen very carefully. As depicted...
in Fig. 1 we used two types of silanes, one equipped with oxirane rings (GPTMS or GPDMS) and one that contains two methoxy groups (DMDMS). During an acid attack which is induced by a photo acid generator (PAG) the silanes couple to the surface. At the same time the unreacted methoxy groups start to form a network, which has similar properties as a PDMS surface. For silanes containing 3 methoxy groups this network is strongly cross linked and has properties closest to that of PDMS. Bonds formed with this silane are very strong. However, the ability of the silane to crosslink inhibits effective light based structuring. Thus silanes with two functional groups need to be used for this purpose. Therefore, for paper-based microfluidics DMDMS is used. In addition this silane does not contain functional groups that would be able to react with the samples to be treated in the paper-based device.

![Figure 1: Matching the silanes and the epoxy surfaces that can be found on µSTL epoxy resins. a) For surfaces that provide a lot of oxirane rings a silane which itself offers an oxirane ring structure is used. b) DMDMS can couple to hydroxyl groups which are provided as connection points by other µSTL resins again creating a pseudo-PDMS layer.](image)

**EXPERIMENTAL**

![Figure 2: Setups for bond strength testing. a) Setup for testing hydrolytic stability. Microfluidic chips consisting of an epoxy resin were bonded using one of the techniques described. b) Sample for determining the bond strength via tensile testing. A sample consists of two epoxy test specimens which are both bonded to the same membrane. c) Whatman filter with UV-light structured channels.](image)

For bonding the silane mixture (either GPTMS with 2.9 vol% triarylsulphonium hexafluoroantimonate (TASHFA) or GPDMS with 2.54 vol% TASHFA or DMDMS with 9.6 vol% TASHFA and 17.7 vol% bidistilled water) is thinly dispersed on the surface. The coated sample is then covered with a mask and exposed to UV-light (Ultra Vialux UV-Strahler, purchased from Osram, Germany) for 5 min. The sample is cleaned from uncured silane using 2-propanol. The coated epoxy and the PDMS to be bonded are activated using a corona discharger for 10 s. The substrates are then put together and left under light pressure for at least 25 min. The hole bonding process can be carried out in half an hour. For structuring paper-based microfluidic devices a Whatman 1 filter was soaked with the DMDMS solution. Then the paper was covered with a mask and put under UV-light for 5 min. After this time the paper was washed with 2-propanol and dried at room temperature. Effective structuring of paper-based devices was proven using dyed water (see Fig. 2c).

The hydrolytic stability of the bonds was demonstrated using microfluidic chips that were fabricated out of STL epoxy resins. These chips were bonded to a PDMS membrane and probed with dyed water at a flow rate of 275 l/min (see Fig. 2a). Tensile testing for determining the maximum bond strength was carried out according to DIN EN 15870:2009 using a commercially available tensile testing system (type INSTRON 4505 Universal Testing System) equipped with a 1 kN load.
cell. The samples (see Fig. 2b) for tensile testing were fabricated in-house. Both the GPTMS and the GPDMS technique were tested on Accura 60, a commonly used STL resin. The DMDMS technique was demonstrated on DELO Katiobond 4552, a UV-curable glue. However, we also used this technique for bonding microfluidic chips made of commercially available STL resins, e.g., Watershed XC 11122.

RESULTS AND DISCUSSION

During hydrolytic stability testing the membrane of the sample bonded with GPTMS ruptured after 46.5 h. The DMDMS bond failed after 53.5 h. Both failures were caused by the deformation of the epoxy material which tends to swell in water. Longer product life should be achieved by using STL resins which do not swell in water. Results of tensile testing can be found in Table 1. As depicted the bond strengths of the bonding strategies demonstrated within this paper can compete with those reported in literature for PDMS/PDMS bonds. The high variation between maximum and minimum bond strength is known to be a characteristic of corona based bonding [5]. It can also be seen that silanes with two methoxy groups lead to lower bond strengths. Thus they should primarily be used for structured silanization where the others are not suitable.

Table 1. Results of tensile testing compared with bond strengths reported in literature for PDMS/PDMS bonds produced with a corona discharger.

<table>
<thead>
<tr>
<th></th>
<th>PDMS/PDMS</th>
<th>GPTMS bond</th>
<th>GPDMS bond</th>
<th>DMDMS bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>290 kPa [5]</td>
<td>356.9 kPa</td>
<td>39.6 kPa</td>
<td>150.4 kPa</td>
</tr>
<tr>
<td>Maximum</td>
<td>380 kPa [5]</td>
<td>686.5 kPa</td>
<td>64.4 kPa</td>
<td>273.2 kPa</td>
</tr>
<tr>
<td>Minimum</td>
<td>227 kPa [5]</td>
<td>156.8 kPa</td>
<td>24.6 kPa</td>
<td>43.4 kPa</td>
</tr>
</tbody>
</table>

CONCLUSION

We demonstrated that UV-light based silanization is an efficient technology for both bonding microfluidic chips and structuring paper-based devices. We demonstrated hydrolytic stability of the bonds for more than 40 hours. Tensile testing revealed that the bond strength achieved using the new technology can compete with those reported in literature for PDMS/PDMS bonds.

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