Norland optical adhesive (NOA81) microchannels
with adjustable surface properties and
high chemical resistance against IR-transparent organic solvents

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Abstract

The optical adhesive NOA81 (Norland Products Inc.) is a promising UV-curable material for low-cost microfluidic applications. We demonstrated that its surface energy can be adjusted by different surface treatments or by mixing an additive in the uncured bulk polymer, which is a serious asset to the development of microfluidic systems. The surfaces were characterized by dynamic contact angle measurements and the chemical resistance of NOA81 microchannels was tested by flowing organic solvents therein. The control over the surface energy and the chemical resistance of the polymer was demonstrated by successful oil-in-water and water-in-oil droplet generation.

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1. Introduction

IR-laser spectroscopy is a powerful and label-free technique for gas and liquid sensing. We are developing an integrated IR-sensing platform for liquids and will use microfluidics for sample pretreatment and transportation. To increase the sensitivity for molecule detection in aqueous solutions, the analyte is transferred by liquid-liquid extraction from the IR-light absorbing aqueous phase to an IR-transparent organic phase. The most common device for a liquid-liquid extraction is the microfluidic H-filter [1] (shown in Fig. 1). The simulation in Fig. 2 illustrates such an extraction of cocaine from non-Newtonian saliva into water. To enhance the mass transport of the analyte from the aqueous to the organic phase, we increase the interface between both liquids by droplet generation. For this particular application it is of crucial importance to control the surface properties of microfluidic channels. The material itself has to show chemical resistance against IR-transparent organic solvents and it should not swell upon contact with liquids, as it is observed for samples made of PDMS, the most common polymeric material for rapid prototyping of microfluidic channels [2].

2. Materials and Methods

2.1. UV-curable glue NOA81

Microfluidic channels are often fabricated by silicon or glass bulk micromachining, which is expensive, relatively complex and time consuming. In recent years, polymers like polydimethylsiloxane (PDMS) or SU-8 photo-epoxy have become popular...
for microfluidic applications due to their high flexibility, ease of fabrication and high reproducibility by rapid prototyping methods [3]. The UV-curable adhesive NOA81 is a promising liquid photo-polymer for low-cost microfluidic chip production. Different molding based fabrication methods for NOA81 are already presented for microfluidic applications [4, 5]. Compared to PDMS, the most widely spread polymeric material for microfluidic channels, NOA81 has better chemical resistance to organic solvents, is impermeable to air and water vapor, is less prone to swelling upon contact with fluids, and surface treatments (for example oxygen plasma) are more stable [2]. NOA81 is absorbing in the IR-range, perfectly transparent in the visible range, and is also suitable for fluorescence detection based applications.

2.2. Fabrication process of all-polymer microfluidic channels

For the chemical compatibility tests we fabricated microfluidic channels by a simple rapid prototyping technique, similar to [4, 5]. Fig. 3 shows the two phase fabrication process: First in the cleanroom a layer of SU-8 on a glass substrate was structured in the shape of the microfluidic channels by common photolithography (Fig. 3A). The master was then taken out of the cleanroom and PDMS (Sylgard 184, Dow Corning, USA) was molded onto it (Fig. 3B). In the second phase NOA81 was casted and then cured under the UV-lamp on the structured PDMS master. In parallel also a thin film of NOA81 was cured, sandwiched between two PDMS sheets (Fig. 3C). Both parts were put together on a glass substrate forming the all-polymer microfluidic channels. Permanent bonding was achieved either by O2-plasma treatment for hydrophilic channels (Fig. 3D) or by further UV-curing after bonding for hydrophobic channels.

3. Results and Discussion

3.1. Study of the wetting behavior of water on differently treated NOA81 surfaces

To evaluate the surface energy of cured NOA81 surfaces, wettability measurements using water droplets were performed as shown in Fig. 4A. Without any modification, NOA81 was slightly hydrophilic and showed an advancing contact angle of...
Fig. 4. Dynamic wetting behavior analysis on different NOA81 surfaces: (A) Measurement of the advancing ($\theta_a$) and receding ($\theta_r$) contact angle on both sides of a water droplet on a surface of NOA81 with 1wt% of APTES in its bulk. (B) Comparison of the wetting behavior of differently treated NOA81 surfaces. As additive APTES was mixed in the uncured polymer.

$\theta_a=80\pm3^\circ$ and a receding contact angle of $\theta_r=20\pm3^\circ$. After O$_2$-plasma treatment the surface showed perfect wettability, but this effect faded with time. On the other hand, a subsequent exposure to fluoro-silane ($C_8H_4Cl_3F_13Si$) vapor turned the surface hydrophobic ($\theta_a=113\pm3^\circ$, $\theta_r=61\pm3^\circ$). This surface modification was stable (at least for 40 days). Following the concept developed in [6], we added 1wt% of APTES ($H_2N(CH_2)\_3Si(O\_2C\_2H_5)$) to uncured NOA81. By changing the bulk with this method, we achieved the same stable (at least for 40 days) hydrophobicity as with the fluoro-silanisation (see Fig. 4(B)). This bulk modification allows easy control over the wetting behavior of parts hidden deep in microfluidic systems, which is hard to achieve by other silanisation techniques.

3.2. Chemical resistance to IR-transparent organic solvents

For the chemical compatibility tests IR-transparent organic solvents were perfused in the all-polymer microfluidic channels made of NOA81 (see Fig. 5) at a rate of 1µl/min. Our samples resisted against n-pentane, n-hexane, cyclo-hexane, and n-heptane. For more than 5 hours no effect was observed under the microscope; neither swelling, nor delamination at the bonding site, as it appeared immediately after exposure to chloroform.

3.3. Oil-in-water and water-in-oil droplet generation

Microfluidic flow focusing devices were fabricated as described in Fig. 3 to demonstrate the chemical resistance and the wettability control of NOA81 surfaces by oil-in-water and water-in-oil droplet generation (see Fig. 6).
Fig. 6: (A) Oil-in-water droplet generation: Ethylacetate droplets generated in saliva (colored with amaranth) in a hydrophilic microfluidic channel. (B) Water-in-oil droplet generation: Saliva (colored with amaranth) droplets generated in ethylacetate in a hydrophobic microfluidic channel.

To produce oil droplets in an aqueous environment, hydrophilic (O₂-plasma treatment) microchannels are used. First they were filled completely with the aqueous solvent and then the organic solvent was added through the channel located in the middle. By adjusting the ratio of the flow rates of the aqueous to the organic solvent, the droplet sizes can be varied.

For water-in-oil droplet generation the opposite is valid, and hydrophobic channels are needed. The hydrophobicity of NOA81 surfaces is established by mixing small amounts of APTES in the uncured polymer.

4. Conclusion

This paper presented successful wettability control of polymerized NOA81 surfaces (at least for 40 days). We also showed that NOA81 is resistant to different IR-transparent organic solvents and does not swell upon contact with liquids like PDMS does. Both results were validated by water-in-oil and oil-in-water droplet generation.

Future work will include a study of cocaine extraction from aqueous phase to IR-transparent organic solvents using droplet generators for increasing passive diffusion of analytes between the different phases. This microfluidic device is part of the NanoTera project IRSENS, which goal is to build an integrated optofluidic system for cocaine detection by IR-spectroscopy.

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