

UV/Ozone Surface Treatment for Bonding of Elastomeric COC-Based Microfluidic Devices [†]

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Abstract: Reliable bonding of microstructured polymer parts is one of the major challenges in industrial fabrication of microfluidic devices. In the present work, the effects of a UV/ozone surface activation on the bonding process were investigated for the combination of a commonly used thermoplastic cyclic olefin copolymer (COC) with an elastomeric COC (eCOC) as a new thermoplastic elastomer material. Bonding was studied using two-component injection molded parts of COC and eCOC, together with microfluidic COC chips. Surface activation and bonding process parameters were optimized and bond strengths were characterized by the wedge test method. The results showed that strong bonding of this polymer materials combination can be achieved at temperatures significantly below the bulk glass transition temperature of COC.

Keywords: polymer microfluidics; thermocompression bonding; surface modification; microfluidic valves; cyclic olefin copolymers

1. Introduction

Over the last decades microfluidic devices became more and more popular in life sciences and medical technology [1]. This is based on advantages such as low sample and reagent volumes, fast analysis times, and small size of the devices; potentially making them suitable for point-of-care applications. In the beginning of microfluidics, devices were made of glass or silicon. Nevertheless, they are not suitable for most applications, due to high costs of these materials and the manufacturing processes. Currently, thermoplastic polymers are the most promising materials, showing good optical and chemical properties and allowing for low cost, industrial manufacturing by microinjection molding. The bonding process is one of the key issues in fabrication of thermoplastic microfluidic devices. In particular, for microvalves and other actuators, requiring the combination of elastomeric and rigid polymer materials, reliable bonding is a major challenge. Several different thermocompression bonding methods with additional surface activation by e.g., solvents, plasma, UV, corona etc. have been described [2]. Here, bonding of a new materials combination, consisting of microfluidic COC parts with a novel thermoplastic elastomer material (elastomeric COC) is reported.

2. Materials and Methods

Surface modification and bonding experiments were carried out using injection molded polymer chips (75 mm × 25 mm microscope slide format) with several doormat type microvalve structures. The microfluidic base plates, containing the microchannel structures (typically 200 μm × 100 μm), were molded in COC (Topas® 8007S-04, Topas Advanced Polymers, Frankfurt/Main, Germany). Membrane plates for valve actuation, consisting of rigid COC (Topas® 8007S-04) support structures and flexible eCOC (Topas® Elastomer E-140, Topas Advanced Polymers, Germany) membranes, were fabricated by two-component injection molding. The eCOC surfaces were bonded to the microfluidic COC base plates. Thermocompression bonding of these devices was facilitated by UV/ozone surface activation. An U-shaped, ozone-generating, low-pressure mercury lamp (Heraeus Holding GmbH, Germany) with emission wavelengths of 185 nm and 254 nm, was used as UV and ozone source respectively. The surfaces of the microfluidic base and membrane plate were exposed to UV radiation between 0 and 20 min in ambient air. Chemical surface properties were characterized by water contact angle measurements (using a dataphysics OCA instrument) and attenuated total reflection infrared (ATR-IR) spectroscopy (using a Bruker Tensor spectrometer with a Ge crystal ATR unit). The devices were bonded using a conventional hot press, applying an air pressure of 2 bar. The bonding temperature was varied between 60 °C and 80 °C in steps of 5 °C. The pressure holding time was varied between 5 and 10 min. Bond strengths were characterized by the so-called wedge test. There, a blade of known thickness is inserted between the bonded substrates and the crack propagation length L is measured. The bond strength γ is calculated using the Maszara model [3] given by,

$$\gamma = \frac{3t_b^2 E_1 t_{s1}^3 E_2 t_{s2}^3}{16 L^4 (E_1 t_{s1}^3 E_2 t_{s2}^3)} \quad (1)$$

where E is the Young's modulus of the two different materials, t_s and t_b is the thickness of the substrate and the blade. Statistical analysis was performed using RStudio and MATLAB® (The MathWorks, Inc.).

3. Results and Discussion

3.1. Polymer Surface Activation

Pristine and UV/ozone treated COC and eCOC surfaces were characterized by contact angle measurements using drops of deionized water in order to identify changes in wettability and surface energy. Figure 1a shows the mean contact angle values ($N = 9$ for the COC base plate, $N = 3$ for eCOC membrane plate) for different exposure times. For both materials, the contact angles decreased strongly within the first ten minutes of UV/ozone exposure. Quite hydrophilic polymer surfaces with contact angles around 40° were obtained and no significant further decrease was found for longer exposure times. Interestingly, the results show that contact angles measured on the eCOC surfaces were always a few degrees lower compared to the rigid COC material. Chemical surface analysis by ATR-IR spectroscopy shows a new absorbance band around 1744 cm⁻¹ (see Figure 1b) for both polymer material types. This band can be assigned to carbonyl functional groups stemming from oxidation processes at the polymer surface and it continuously increases with exposure time. These surface characteristics and the levelling behavior of wettability after approximately 10 min UV exposure are in good agreement with previous reports on UV/ozone treatment of COC [4–6]. Based on these results, an UV/ozone treatment time of 10 min was selected for the subsequent bonding experiments.

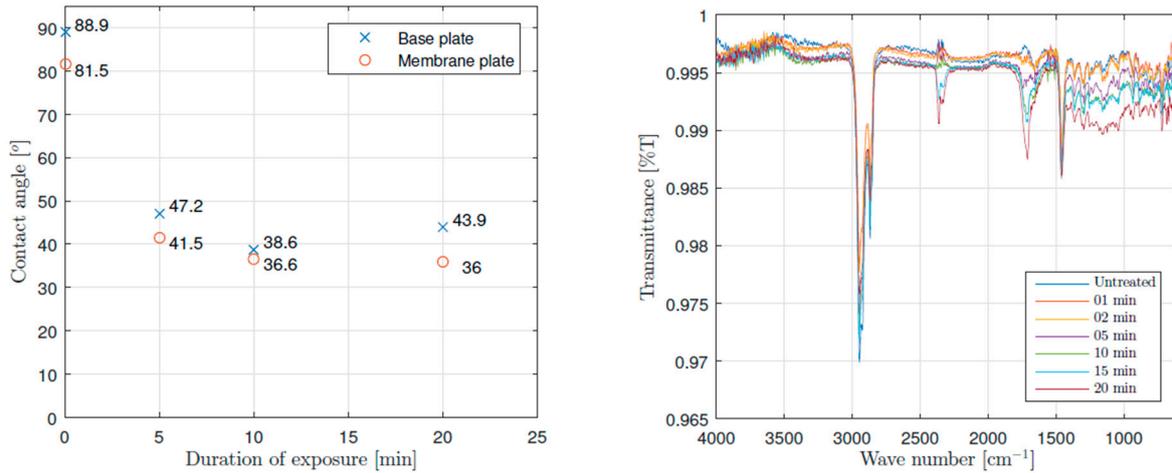


Figure 1. (a) Water contact angles for base (COC) and membrane plate (eCOC), and (b) ATR-IR spectra of COC for different UV/ozone exposure times.

3.2. Thermocompression Bonding

Thermocompression bonding was investigated systematically by variation of temperature and pressure holding time. In order to avoid clogging or deforming of channels, the glass transition temperature of the COC ($T_g = 78 \text{ }^\circ\text{C}$) was set as the upper limit of bonding temperatures. Figure 2 shows the difference of bond strengths for 0 and 10 min of UV/ozone exposure for different bonding temperatures. The statistical investigation showed normal distributed data for temperatures $>65 \text{ }^\circ\text{C}$. Significantly higher bond strengths were obtained for UV/ozone modified polymer surfaces also for temperatures well below the bulk T_g of the COC material. This can be explained by improved interdiffusion of polymer chains at the COC/eCOC interface, as previously reported for UV/ozone assisted bonding of two identical COC surfaces [4,5]. Results of different pressure holding times are summarized in Table 1. As expected, it can be seen that the bond strength increases also with temperature and pressure holding time.

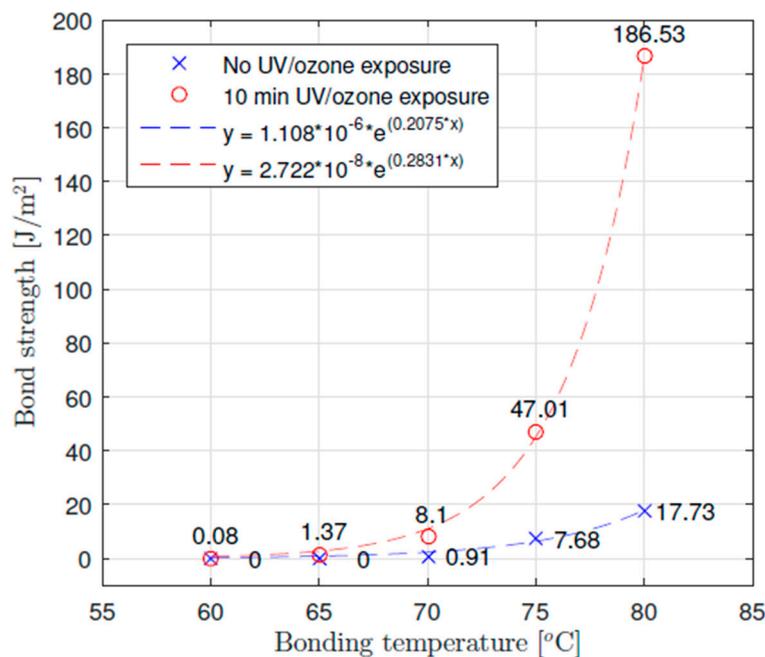


Figure 2. Bond strength (Median, N = 10) results of the wedge test for 0 and 10 minutes of UV/ozone exposure. (pressure holding time was 5 min). The dotted lines represent an exponential fit.

Table 1. Bond strength in J/m² (Median, N = 10) for different bonding temperatures and pressure holding times.

Bonding Temperature	Pressure Holding Time	
	5 min	10 min
60	0.076	0.951
65	1.37	5.11
70	8.10	11.7
75	47.0	37.5
80	186	445

3.3. Application for Microfluidic Valves

In order to demonstrate its practical value, the UV/ozone bonding process was applied to bonding microfluidic chips having several doormat type microvalve structures. The devices were found to be leakproof and could be pneumatically actuated. Hence, the UV/ozone activated bonding of rigid and elastomeric COC parts allowed manufacturing of microfluidic valves (Figure 3).

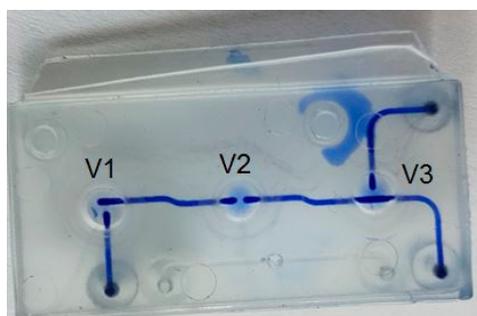


Figure 3. Doormat type microfluidic valves prepared by UV/ozone assisted bonding of injection molded COC and eCOC based microfluidic chips.

4. Conclusions

Process parameters for UV/ozone surface treatment and subsequent thermocompression bonding (e.g., temperature, time and pressure) were optimized with respect to bond strength and preservation of the channel geometries. The results demonstrate that the surface activation leads to a reduction of the necessary bonding temperature. It is well known that bonding of different COC grades often is more difficult than for identical polymer materials [7]. Nevertheless, after parameter optimization, the microfluidic COC chips could be strongly bonded with a new eCOC polymer. Furthermore, the eCOC layer could be used as membrane in microfluidic valves.

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Conflicts of Interest: The authors declare no conflict of interest.

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