CYCLIC OLEFIN COPOLYMER STRIP PROCESSING FOR FREEFORM FABRICATION OF MULTI-LAYERED MICROFLUIDIC SENSING SYSTEMS

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Abstract

Researchers have developed techniques for multi-layered fabrication of microfluidic chips which allow for increased scope of channel geometries and associated improved sensing capabilities. In these techniques, slits have been fabricated in thin layers of polymer or glass, typically of a couple of hundred micrometers thick. These layers are then bonded to each other using adhesives, hot embossing or a combination of bonding methods. This paper presents a new fast freeform methodology for 3D channel geometries to be fabricated in COC chips using laser and xurographic processing for slit formation and cyclohexane promoted bonding for multi-layer joining at room temperature.

Introduction

Microfluidics devices are widely used in research and in chemical, environmental and biotechnology sensing applications. A microfluidic device or chip can be a device of a few millimetres to a few square centimetres in size, integrating 3D micro and nano features. They can vary from single channel per chip layouts to much more complicated designs. They are fabricated to handle small quantities of fluids, have high sensitivity, and their function may incorporate several laboratory functions in a single chip [1]. Their development has introduced a positive transformation within chemical and biological research due to their rapid and high-throughput analysis and minimized consumption of sample and reagent [2]. Traditional methods of chip fabrication involve bonding two polymer or glass layers after engraving the desired design on one of the layer surfaces. Lithography, electron beam writing, photo-patterning and chemical etching are the most common engraving techniques used to fabricate microfluidic chips [3]. Thermal bonding is the most widely used and established method of bonding. Other bonding techniques include chemical treatment of surface, application of adhesive layer and laser exposure to the active bonding medium [4].

Fabrication and utilisation of multilayer microfluidic chips is an emerging area of work and has become a focus of the microfluidic research field in recent years [5]. This technique comprises the process of slit fabrication in thin layers of glass or polymers, typically of a couple of hundred micrometers maximum thick and then the bonding of these layers to form a 3D structure inside the microfluidic chip, see Figure 1.
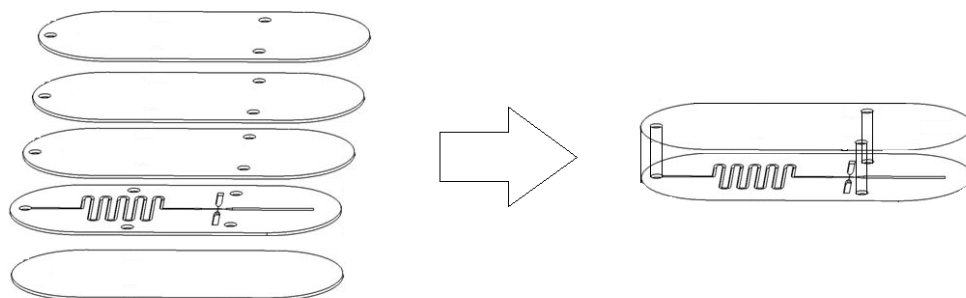
Figure 1 Schematic of the process of multi-layer microfluidic chip fabrication.

At the beginning of last decade the first attempts to fabricate multilayer chips, were made with Polydimethylsiloxane (PDMS), silicon, glass or a combination of two or more of these materials [6-11]. Since most of these works are focused in the fabrication of microfluidic devices for specific chemical or biological application, testing was limited to flow and chemical capabilities aspects. In more recent publications, up to eight-layer microfluidic chips of poly(methylmethacrylate) (PMMA) have been fabricated [5, 12]. Pressure tests, fluidic electrical resistance and mixing experiments, have been performed to assess the strength of the bonding as well as the electrical and chemical capabilities of the chips. All these publications used photolithography, wet-chemical and ion etching techniques to fabricate slits, except in some works where CO_2 laser was used to create features in PMMA [12].

Despite limited research with solid freeform techniques (SFF), it is easy to see that there is a high potential to develop 3D microfluidic devices using 3D SFF microfabrication methods. Bonding remains the most critical and inconsistent step in multilayer microfluidic chip fabrication [2]. SFF methods can overcome this problem; methods such as 3D printing circumvent traditional bonding techniques leading to microfluidic devices with high integrity and precise alignment of feature. In this work, a new fast freeform process of fabrication of multilayer Cyclic Olefin Copolymer (COC) microfluidic chip is presented.

Materials and methods

The COC was provided by Zeon Chemicals Europe Ltd, in the form of A4 sheets. COC compositions used in this work were ZF14 and ZF16. Layer thickness of 40µm, 100 µm and 188µm were processed into 3D structures. These materials were chosen as they are becoming increasingly popular due to their advantageous properties of high optical transmission, low refractive index, low water absorption and resistance against eluting chemicals such as methanol, ethanol, acetone and nitric acid [13].

Figure 2 presents the straight channel test design fabricated in this work. The chips were assembled from three layers. The chip dimensions were 40×20mm, the inlet and outlet ports were 1mm in diameter, while the channel length was 30mm.
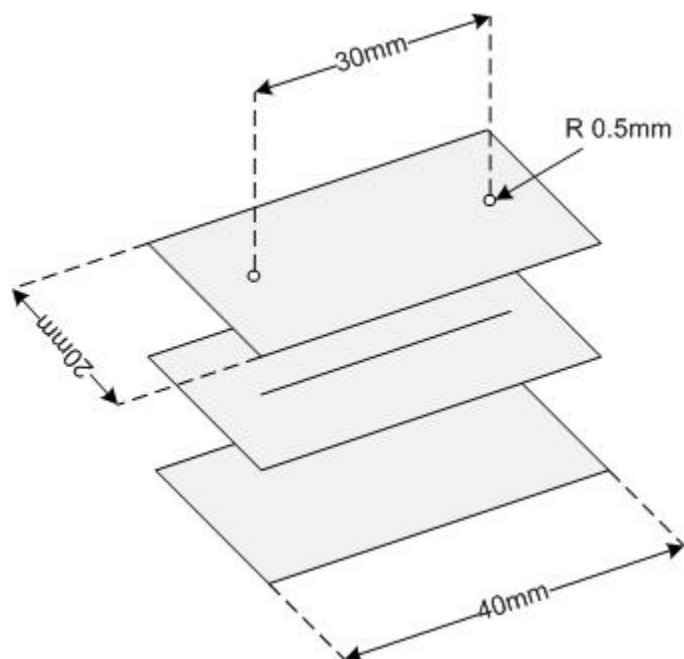
Figure 2 Schematic of the microfluidic chip single channel test design.

The main steps of fabrication of the microfluidic device in this work were the following:
- creating slits on the thin layers of COC
- exposing layers to Cyclohexane vapour
- aligning slits and applying pressure for determined time

The characterization and testing consisted in flow tests to analyse the applicability of the chips and tensile tests to measure the strength of the bonding.

Cyclohexane bonding

A bonding technique previous published was used in this work [2]. The COC layers were bonded by exposing them to cyclohexane vapour. The apparatus used included a hotplate, a number of clock glasses, an alignment jig and a pneumatic press. Before bonding, the COC was cleaned and rinsed with isopropanol and water, then dried with nitrogen. The protective polyethylene (PE) cover layer was removed using scalpel and tweezers, the sample were rinsed and dried once more before exposure to cyclohexane. Using the hotplate, the cyclohexane was heated to 70ºC to produce vapours within the chamber. Once there was a uniform vapour presence within the chamber the COC was exposed to the solvent by swapping the chamber cover with another that had the COC sample attached to its underside.

After exposure to the solvent the samples were placed in a pre-made alignment jig. Half of the surface area was covered with card to prevent bonding of the entire surface area. After pressing, the newly bonded samples were then exposed to UV light (2 J/cm_2, 260 nm) to increase bond strength. Nine sets of processing conditions for bonding were examined. These include three periods of vapour exposure (30, 40, and 50 seconds) and three periods for applied bonding pressure of 0.4 MPa (3, 4, and 5 minutes), see Figure 3. These nine treatment conditions were tested for bond strength, see Figure 4. The COC samples prepared for tensile testing were ZF14, 40×20mm and 40 μm thick.
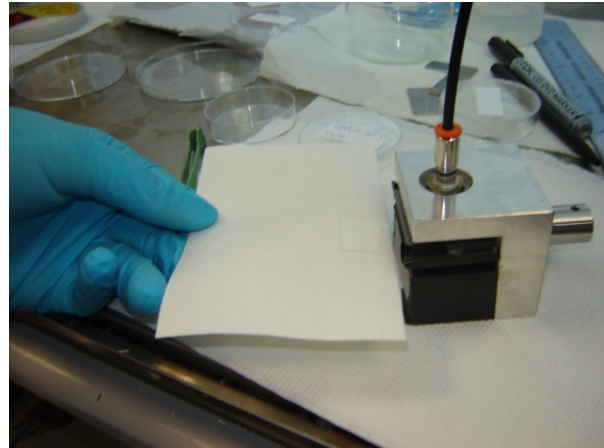
(a)   (b)

Figure 3 Pictures of (a) sample being exposed in clock glass and
(b) compression in the pneumatic rig at 4 bar.

Tensile testing

Tensile testing of the bonded samples was performed using a Hounsfield H20K-W tensile testing machine. The rate of extension was maintained at 2.5mm/min. The samples were placed in the jaws of the machine as shown in Figure 4. The initial distance between the jaws was set at 20mm for each test; the force versus extension data were recorded for each test. These were then used to calculate the stress and percentage strain experienced at the bond surface.
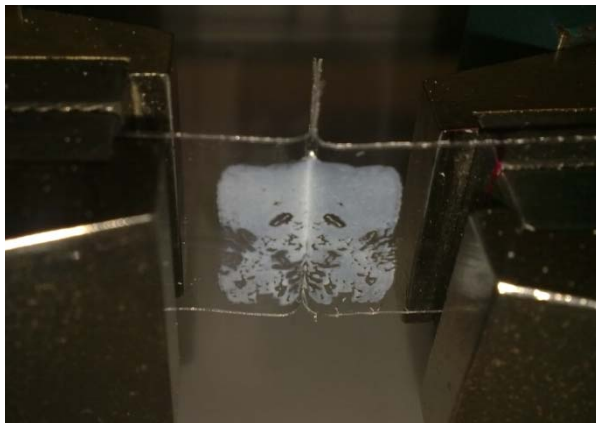
(a)   (b)

Figure 4 Picture of the (a) start of a tensile test of the bond strength
and (b) a sample tested to failure.

Microfluidic chip fabrication

The same procedure for tensile test sample bonding was used to bond the test microfluidic chips. To reduce the risk of damaging the more delicate middle layer, the top and bottom layers were simultaneously exposed to the cyclohexane vapour. After exposure the layers were assembled using the same jig as previously stated. Once aligned the chip was pressed by hand to push any possible air pockets out of the bonded areas and then placed in the pneumatic press. After pressing, the newly bonded samples were then exposed to UV light.

Slit fabrication

The feature on the chip layers were produced by two methods, CO_2 laser ablation and razor writing. These methods were chosen as they require little initialization, with easy reproducibility and the can produce multiple layers within one set up. The chips were assembled from three layers, as shown in Figure 2. The chip dimensions were designed as 40×20mm, the inlet and outlet ports were 1mm in diameter, while the channel length was 30mm.

Laser processing

A 10.2µm wavelength continuous CO_2 laser, GEM-100L, was used with the chip layout imported from an AutoCAD design. The laser processing was optimised to reduce excessive burning of the material. It was found that a cutting speed of 2mm/s and a power output of 7 W produced the most defined channels. A constant flow of compressed air was maintained on the cutting surface during ablation which improved the channels smoothness by cooling the molten polymer quickly. The channel widths produced using this method were on average 180µm. A polyethylene cover on the COC film was removed after laser ablation to reduce contamination and scratching of the material. It was found that placing the COC film with the PE cover facing up during laser cutting made removing the cover from the cut layers much easier, cutting with the PE facing downwards made the removal of the cover difficult and also lead to fibres of PE becoming trapped in the burring from cutting. The time taken to produce nine layers, which corresponds to three assembled chips, was 15 minutes. The microfluidic chips produced by laser ablation were made from ZF14 with film thickness of 100µm.

Razor writing

The razor writing or xurographic method was much less time consuming. The Graphtec Craft ROBO Pro, which has a specified mechanical positioning resolution of 5µm, was used to cut the individual layers for the multilayer chips. It was possible to populate a much larger area with chip layers as the plotter was capable of carrying film sizes of up to A3, when compared to the limited 150 by 115 mm area possible in the laser ablation machine. The chip patterns were again imported from AutoCAD, this was the same as used for laser ablation. An A4 sheet of the Zeonor ZF16 with a thickness of 188µm was cut into 30 layers (providing material for 10 assembled chips); the total cutting time required was approximately 5 minutes. The A4 sheet of COC was first attached to an A3 adhesive carrier sheet, it is important to place the COC with its PE protective cover facing downwards as this prevents PE fibres and debris from attaching to the blade, which would reduce the accuracy of the cut. With the rotary style of cutting relatively little heat was introduced during the cutting avoiding the burring potential present in laser ablation. The depth of the cutter can be varied if thicker material would need to be cut, however different cutters are also required for the cutting of certain materials. The blade used in this work (CB09UA) was suitable for cutting material of thicknesses up to 250µm. The cutting speed at which the plotter operated was 20mm/s.

Flow testing

The microfluidic chips fabricated were subjected to flow tests. Droplets of red-diluted water were deposited on one of the inlets of the chip and vacuum pressure applied on the outlet. Zeonor ZF16, required a longer period of exposure to cyclohexane vapour (60 and 75 s compared to 30 and 40 for ZF14; 50 s was not used for ZF14 in these tests). This can be explained by the different glass transition temperature of the two materials. The duration of pneumatic exposure was maintained at 5 min for all samples. Additional bonding strength through 2W UV exposure was applied to some samples.

Results and Discussion

Bonding strength testing

Figure 5, 6, and 7 show the tensile test results for the cyclohexane exposure times of 30, 40 and 50 seconds respectively. Table 1 summarizes the numerical results collected from graphs in Figures 5, 6, and 7.
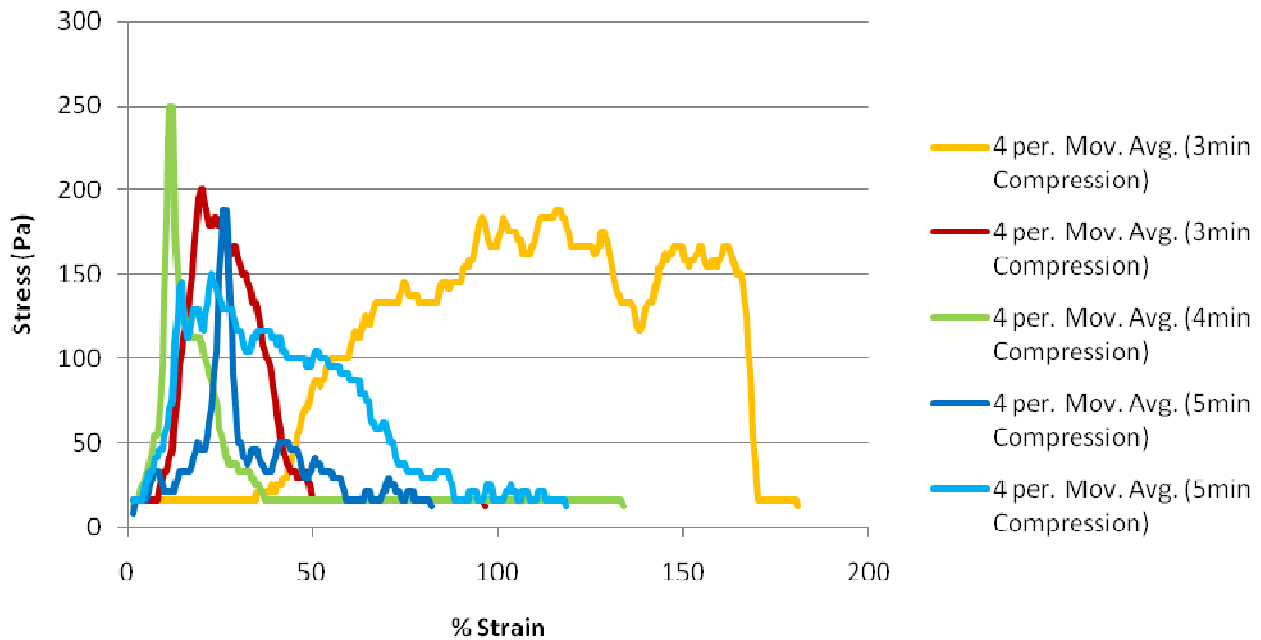

Figure 5 Tensile test results for 30 second cyclohexane exposure
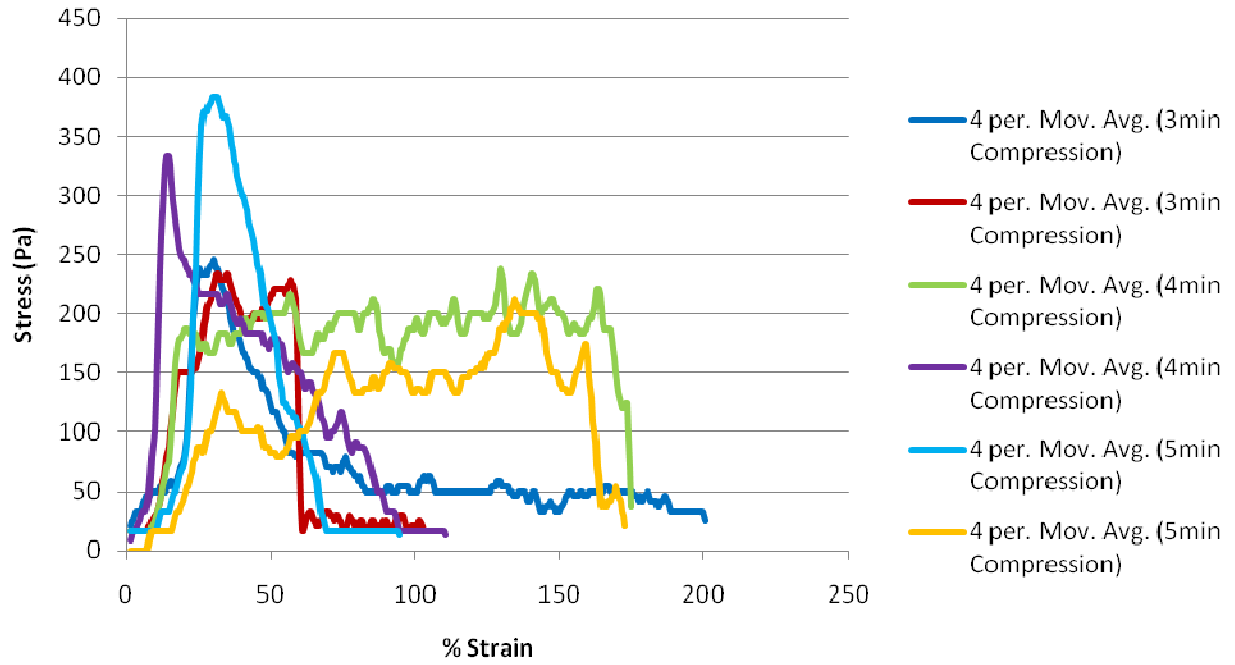and compression times of 3, 4, and 5 minutes.

Figure 6 Tensile test results for 40 second cyclohexane exposure
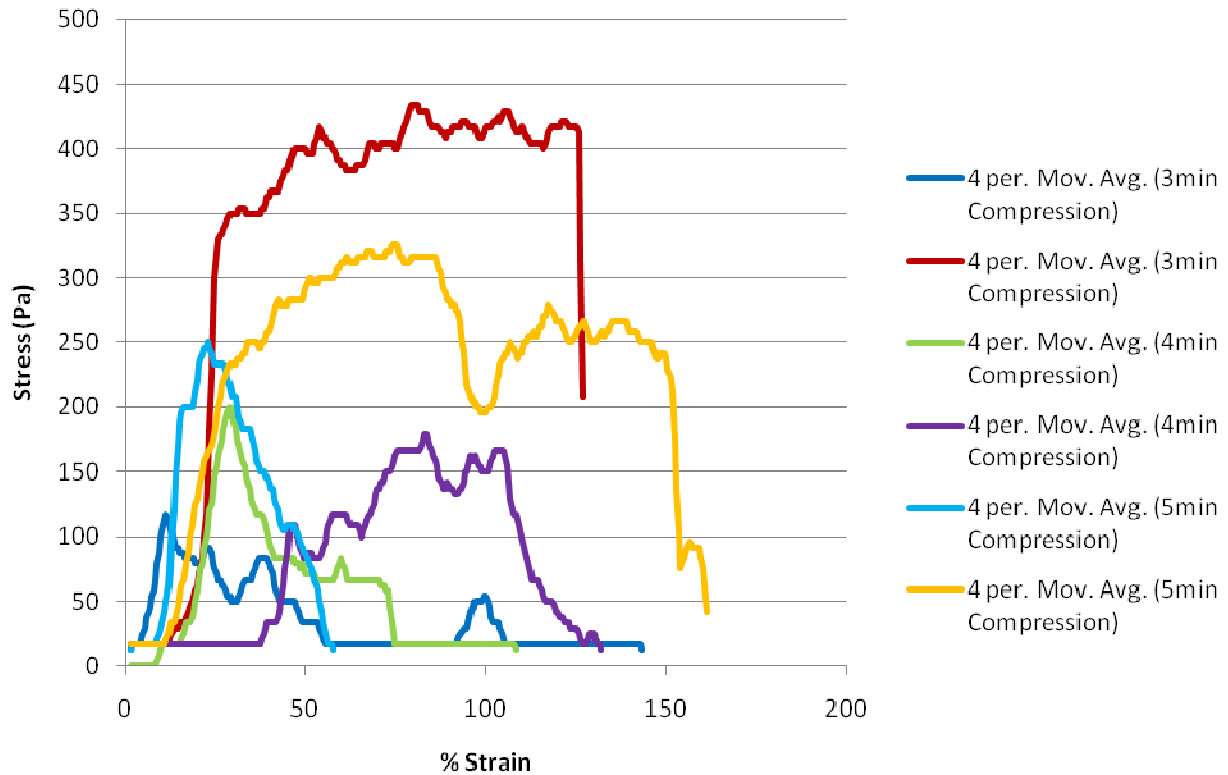and compression times of 3, 4, and 5 minutes.

Figure 7 Tensile test results for 50 second cyclohexane exposure
and compression times of 3, 4, and 5 minutes.

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Table 1 Young's Moduli (E) and ultimate tensile strengths (UTS)
recorded from the tensile test results.

| Compression Duration (min) | Exposure Duration (sec) | | | | | |
| | 30 | | 40 | | 50 | |
	E (Pa)	UTS (Pa)	E (Pa)	UTS (Pa)	E (Pa)	UTS (Pa)
3	2.344	200	12.381	250	13.333	116.65
3	19.609	200	10	233.325	35.294	433.325
4	44.446	283.325	14.668	250	14.104	200
4	-	-	33.334	350	3.704	183.325
5	25.642	200	21.569	383.325	14.584	250
5	9.524	150	6.141	216.65	12.381	333.325

It can be seen from the results of the tensile test that an increased exposure time to the cyclohexane vapour related to an increase in the ultimate tensile strength of the bonding. The increased exposure time allowed greater penetration of the cyclohexane vapour into the bulk material, allowing improved activation and cross linking of polymer chains. There is however a disadvantage to overly long exposure time as the material softens, increasing the likelihood of blocking channels during bonding. Saturation of the COC with cyclohexane will cause rapid softening and to some extent degradation of the material. It was noticed that a transfer of some COC material occurred on equipment that was used to handle the material when the exposure time exceeded 50 seconds. A confidence interval was constructed to compare the UTS achieved from different solvent exposure durations. At 90% confidence, the UTS for the chips bonded at 30 seconds solvent exposure were significantly less strong than chips bonded at 40 and 50 second exposure times. No significant difference was noted between bond strengths for chips bonded with 40 and 50 s exposure times.

Tearing of a couple of the COC films occurred during tensile testing. As the bonding in areas around the edges of the samples was consistently poorer than internal bonding, this could cause these couple of thinner material samples to fail at the interface between bonded and non-bonded regions. The bonding process, including UV cross linking, likely strengthens the material, while the compression causes it to become denser. The alignment of the samples during bonding, as well as during testing may also explain the tearing phenomenon experienced. Incorrectly aligned sample, when under tension in the manner in which it was performed, can produce a small torque/twist of the material, causing the tensile force to concentrate at a corner of the bonded area instead of it being perpendicular to it.

By comparing the stress strain charts it can be seen that an increased exposure time results in an increase in the bonds tensile strength, however the same cannot be said for increased compression duration. The stress strain curves also demonstrate the variability of the bonding strength across the length of the bond area. The best example of this is seen in Figure 7 where the samples have been exposed for 50 seconds. The red and yellow curves, which relate to a 3 and 5 minute compression duration, are not smooth in nature. The stress increased and decreased as strain was increased. This would most likely have been caused by the variation in bond quality, and the presence of voids caused by air pockets and foreign particles.

Slit formation

The repeatability of the laser ablation and blade cutting methods of rapid prototyping are well documented [14]. In this application the surface finish of the material is critical to a device's success. Edge burrs which can hamper proper bonding, can be caused on the underside of the film during laser ablation. For the fabrication of multilayer chips from polymer films the blade cutter is a more economical and time effective method, while eliminating the burring caused by laser ablation. The plotter itself is no larger than a typical desktop ink jet printer, with a similar user interface. However it is limited to polymer films of thickness of 250μm or less. Laser ablation has a greater flexibility in the materials (such as glass) and thickness that can be used for chip fabrication. Some ablation was performed on glass using the CO_2 laser, with varying degrees of success. In order to perforate the glass the lasers power must be of sufficient intense, however rapid increase in temperature can lead to cracking of the material by thermal shock.
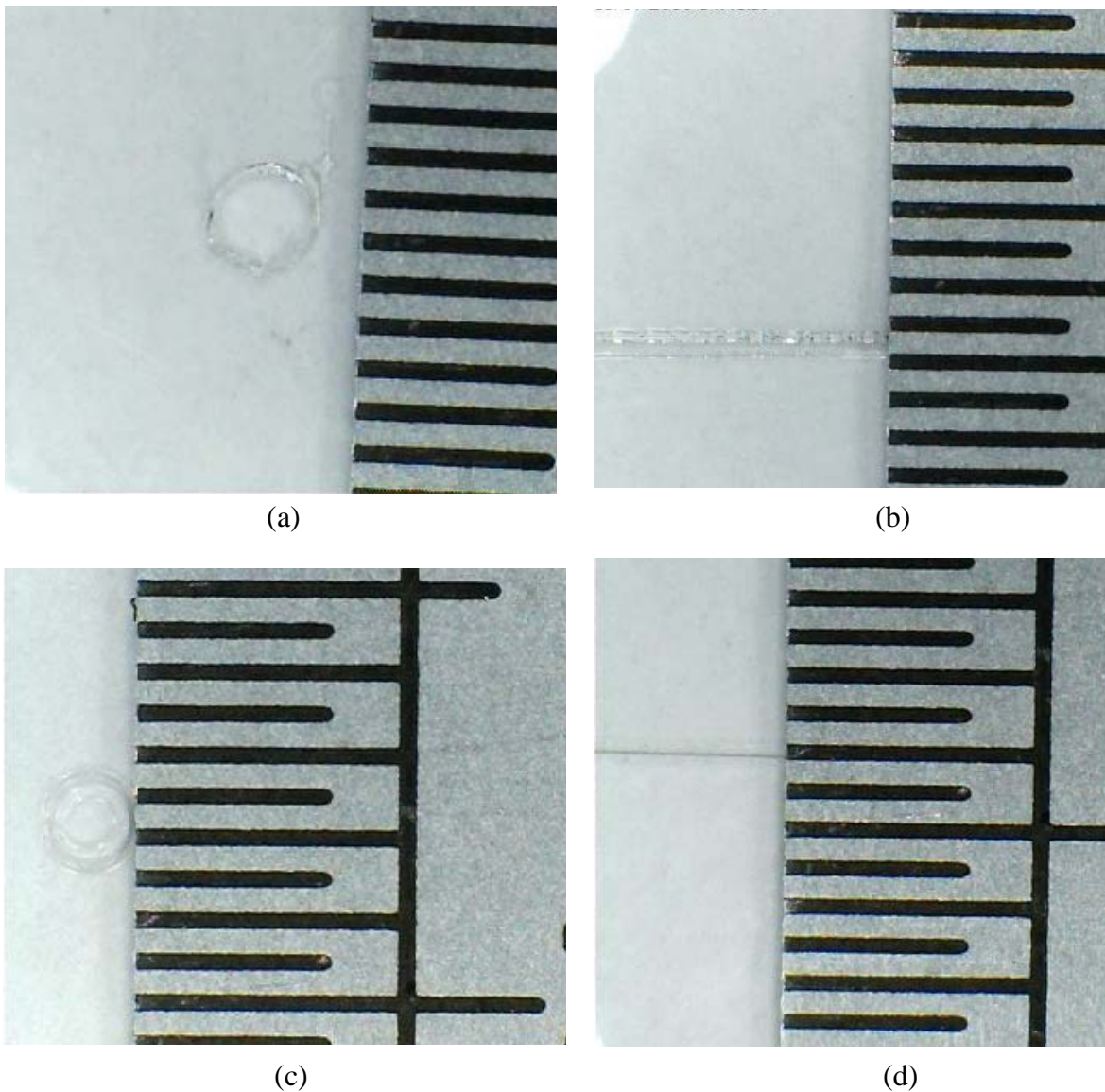
(a)

(b)

(c)

(d)

Figure 6 Pictures of (a) 1 mm diameter laser cut inlet, (b) 180μm width laser cut channel, (c) 0.7 mm diameter blade cut hole, and (d) 50 μm blade cut channel.

Flow testing

Quality of the bond was tested during the fluid flow tests. Chips with more voids or foreign material were noticeably less leak resistant. This could be attributed to the burring and the excess material around the edges of each layer as produced by laser ablation. This however does not explain the poor bonding of the chips produced using the blade plotter. The most likely explanation for this is the time taken in alignment and the method of alignment itself. After exposure to the cyclohexane vapour the bottom layer of COC was removed from the clock glass, placed in the alignment jig, the middle layer was placed on top followed by the top layer. In order to complete the chip the inlet and outlet holes must be correctly aligned with the channel, all three layers must then be removed and pressed by hand to remove air pockets trapped in the bonded area. In the time taken to align all three layers and remove them from the press the cyclohexane is continuously diffusing further into the material and evaporating from the surface The process itself also introduced unwanted COC particles into the bonding area, while the bonding surfaces can be damaged by over stressing the tacky COC, creating large particles which in turn cause large air pockets.

After bonding, the microfluidic chips were tested to investigate flow through the channels and to assess leakage between the layers. Figure 9 shows a representative selection of the chips produced. Figures 9 (a) and (b) show the same chip before and after a coloured dye was applied. The inlet and outlet holes and the channel can be seen in Figure 9 (a), as well as the bonded areas. The non-complete sealing of the channel is highlighted in Figure 9 (b) after dye was applied to one of the holes and leakage occurred immediately without the need to apply a vacuum. Some flow was directed through the channel after the vacuum was applied. Similarly, Figure 9 (c) shows poor bonding surrounding the channel, this was as a result of the burring caused by laser processing. When a vacuum was applied to this chip little or no flow was seen within the channel, it instead flowed around it. There is better overall bonding displayed in the chip in Figure 9 (d). This shows the most successful attempt at multilayer chip fabrication and assembly. As can be seen the dye filled the entire channel. This was accomplished with the need for a vacuum pump, due to capillary attraction. After a period of time the solution began to leak into the area surrounding the channel. This does however demonstrate that multilayer microfluidic devices can indeed be fabricated using COC films and cyclohexane vapour assisted bonding. This last channel was fabricated at a much higher compression pressure.

Conclusions

From this investigation it was found that the optimum duration for exposure of COC to cyclohexane vapour was 40 seconds. This gave a good bond UTS but also maintains more of the materials integrity during bonding, reducing the chance of blocking the channel as compared to 50 second exposure time. Alignment of the layers is of utmost importance to the performance of fabricated microfluidic chips. To achieve this, automating the procedure should be considered which would reduce over stressing/damaging of the material and the infiltration of the bond area with foreign objects. With improve alignment, and reduced handling time, comes improved bond quality. By reducing the time taken to align the layers and place them for pressing, more cyclohexane will still be present on the materials surface, increasing the effectiveness of the process. To continue to improve the performance of the COC multilayer chip the blade cutter and laser process need to be used to prepare the individual layers as they have great potential to be even faster and provide more effective methods of multi-layer freeform fabrication.
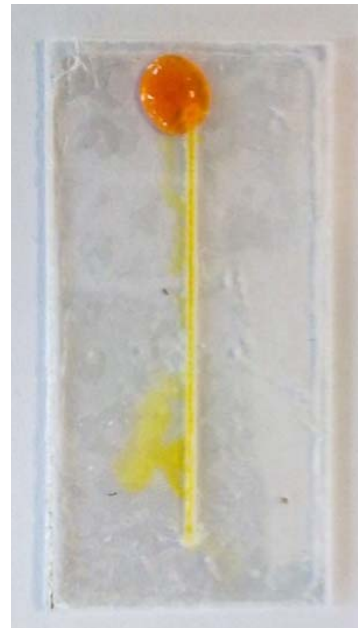
(a)   (b)

(c)   (d)

Figure 7 Pictures of microfluidic chip sample (a) before flow test, (b and c) after flow test with leaking and (d) after successful flow test.

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