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Production of microreactor systems by additive manufacturing technology

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Abstract

Microreactor systems are reactors with three-dimensional structures which are under a millimeter in size. They are commonly fabricated by wet and dry etching, precision machining, laser treatment, blasting and lithographic techniques. Additive manufacturing technologies have been overlooked in this area. This paper presents a part of research related to fabrication of microstructured reactors (microreactors and millireactors) by using two additive manufacturing technologies (fused filament fabrication and stereolithography). One example of static mixer used in a millireactor and one reactor designed for uniform droplet production are also presented.

Keywords: *microreactor, millireactors, additive manufacturing, fused filament fabrication, static mixers*

1. Introduction

Compared to conventional reactors, microreactor systems are significantly smaller in size. Microreactor systems are generally described as reactors with three-dimensional structures, the inner dimensions of which are under a millimeter in size, but usually between 10 and 100 micrometers [1-3]. Also, sometimes they are divided according to the dimensions of the internal structural units into nanoreactors (1 nm to 100 nm), microreactors (100 nm to 1 mm) and millireactors (1 mm to 10 mm) [4].

When conducting reactions in such small systems that are several orders of magnitude smaller than conventional reactors, the diffusion path is very short, resulting in intense mass and energy transfer, causing numerous positive effects such as higher conversions and fewer byproducts.

Microreactors are most commonly made by wet and dry etching, precision machining, laser treatment, blasting and lithographic techniques. Additive manufacturing (3D printing) technologies have, up till few years ago, been overlooked in this area due to a perceived limitation of resolution. Additive manufacturing technologies, especially fused filament fabrication printers, have become widely available, enabling rapid and easy prototyping and small-scale production of prototypes and objects. By using additive manufacturing technologies, the whole manufacturing process, from microreactor design in a CAD (computer-aided design) program (Fig. 1) to design and usage, can take only a few hours and microreactors with different microchannel geometries can be easily and quickly manufactured and studied. The paper will describe part of research related to microstructured reactors fabrication and design of static mixers, but also how chemical compatibility of materials was studied.

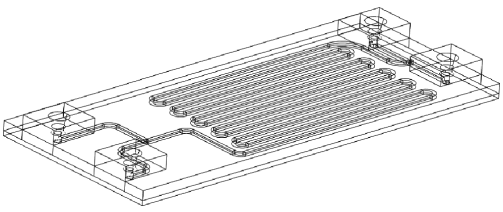

Fig 1. CAD model of the microreactor

2. Manufacturing of microreactors

The Zortrax M200 printer and the Z-Glass transparent material were used to manufacture microreactors by fused filament fabrication technology. The resulting microreactors were not completely transparent. It was found that with the maximum fill settings in the model preparation program, the fill was incomplete, leaving the air between layers, causing a loss of transparency. In addition, incomplete filling causes leakage in microreactors, i.e. liquid spills in the mass of microreactor (Fig. 2).

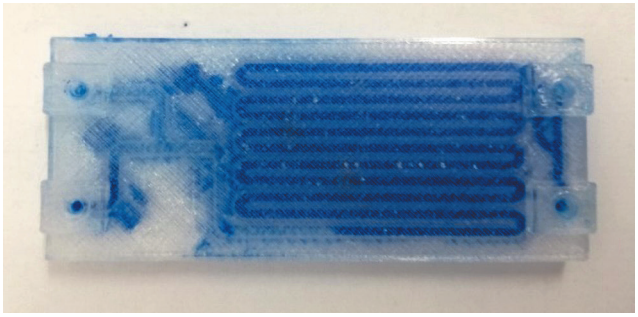

Fig 2. Microreactor manufactured on Zortrax M200 printer, visible penetration of blue colored fluid into microreactor mass between the layers

By properly selecting the design parameters, microreactors that do not leak and are transparent have been successfully manufactured. This was achieved primarily due to the complete filling of the mass around the microchannels and very good adhesion between polymer layers. Settings which had to be tweaked were the speed of fabrication, and the nozzle temperature which had to be slightly above the recommended temperature in order to achieve a better adhesion of the layers that will not leak. It is also important that the substrate is completely aligned with the nozzle, i.e. that there is no variation in the distance between the nozzle and the substrate when creating a single layer. The proper distance of the nozzle from the substrate at the beginning of construction is also important. If the nozzle is too close to the substrate, the buildup of the following layers will cause excess material to build up, which can clog the duct. If the nozzle is

too far from the substrate, there will be insufficient material and no good contact between the polymer lines and the layers will occur, causing poor transparency and leakage inside the microreactor. It has been observed that microreactor transparency is a good indicator of whether the resulting microreactor will leak. If the microreactors are transparent and do not have visible lines of polymeric material they will not leak (Fig. 3). Fig. 3 to 5 show 3D-printed microreactors, Fig. 5 shows a microreactor channels with diameter 0.49 mm.

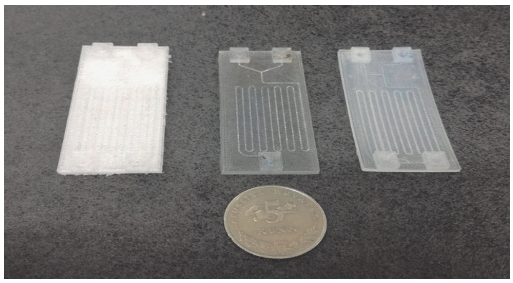

Fig 3. Comparison of microreactor transparency; a) Microreactor made of Z-Glass material on a Zortrax M200 printer, b) Microreactor made of Z-Glass material on a home-made printer, c) Microreactor made of Tough material on a home-made printer

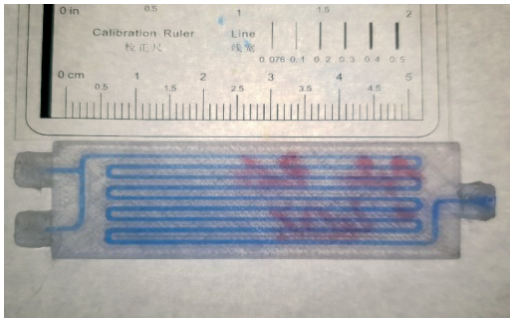

Fig 4. Manufactured microreactor and reference scale for determining microchannel width

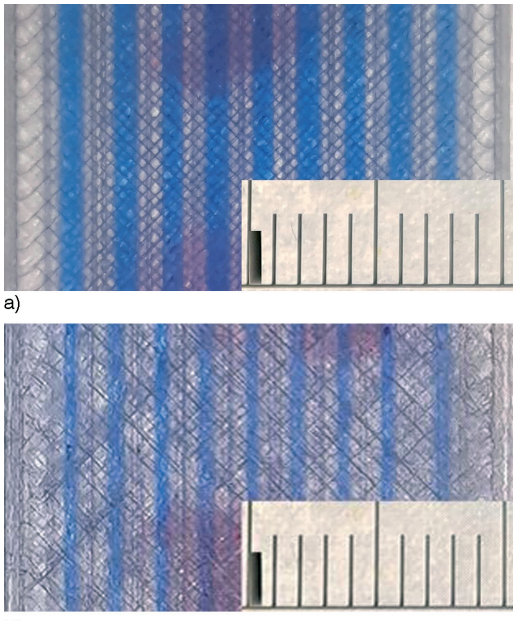

Fig 5. Measuring the channel width of a 3D-printed microreactor, diameter is a) 0.86 mm and b) 0.49 mm (scale is 10 mm).

3. Chemical compatibility of filaments

Transparent filaments of various polymers are commercially available that can be used to make microreactors. Chemical compatibility of filaments in contact with reactants and synthesis products is an important property that must be tested before using the material and fabricating the microreactor. Otherwise, dissolution, swelling, chemical reaction, or loss of material transparency may occur during the reaction. Chemical resistance of polymer materials is commonly tested with the swelling test. In this test, polymer material is immersed in different solvents during defined period. Before the test, material sample is weighted, to define its mass before exposure to solvents. During the test, material sample is weighted several times and those values are compared with initial mass of the sample [5, 6].

Swelling test was performed with four transparent polymer materials (Z-Glass, Tough, ABS-T and PLA) that can be used for microreactor manufacturing. Six different solvents were used. Redistilled water, ethanol and acetone were chosen as standard solvents that are commonly used for various applications. To test their compatibility with filaments, biodiesel, sunflower oil and a mixture of methanol and potas-

Table 1. Results of swelling test [7, 8]

Filament	Solvent	Mass increase after		Comment
		3 h [%]	6 h [%]	
PLA	water	0.4	0.4	/
	ethanol	0.4	1.3	/
	acetone	/	/	dissolved
	biodiesel	0.6	0.5	/
	sunflower oil	-0.1	-0.1	/
	methanol + KOH	/	/	dissolved
ABS-T	water	0.6	0.6	/
	ethanol	1.1	2.2	/
	acetone	/	/	dissolved
	biodiesel	21.1	30.3	lost transparency
	sunflower oil	-0.2	0.0	/
	methanol + KOH	7.3	9.8	lost transparency
Tough	water	0.0	0.0	/
	ethanol	0.0	0.0	/
	acetone	0.6	1.9	/
	biodiesel	6.6	9.9	/
	sunflower oil	0.6	0.4	/
	methanol + KOH	0.5	0.5	/
Z-Glass	water	0.0	0.0	/
	ethanol	0.0	0.0	/
	acetone	19.9	19.9	lost transparency
	biodiesel	1.1	1.4	/
	sunflower oil	-0.2	1.0	/
	methanol + KOH	/	/	dissolved

sium hydroxide (KOH) were used as specific product and reactants during biodiesel synthesis. Mass concentration of KOH in methanol was 36,12 g/L. Used biodiesel was produced via batch reaction and it was not purified. For the test, pieces of filaments (about 3 cm in length) were weighted and placed in vials with solvents. During the test with biodiesel synthesis components, vials were kept in a laboratory water bath at the temperature of 60 °C. The swelling test with redistilled water, ethanol and acetone was conducted under room conditions. Material samples were dried and weighted after 3 and 6 hours of immersion in all of the tested solvents. The mass values of the samples thus obtained were used for calculation of mass increase during the test. Results of the performed swelling test are shown in Table 1.

4. Effect of surface treatment on droplet formation in microreactors

Microreactors are increasingly used, and the main reasons for this are the small volumes of reagent consumed during the reaction and the rate of reaction carried out within the microreactor. In addition, reactions within liquid droplets are being increasingly investigated today, for which microreactors are also being tested. In order to carry out and control the reaction and to ensure reproducibility of the results it is necessary to obtain droplets of uniform size and shape.

The formation of droplets depends on the instability of the liquids and their surface tension. In passive microfluidic systems, the introduction of one immiscible fluid (dispersed phase) into another (continuous phase) leads to droplet formation by displacement, dripping, erupting or flowing

All these methods, except extrusion, are the result of capillary instability. Capillary instability is the effort of a fluid to minimize surface tension. The formation of droplets within a microreactor can be influenced by the introduction of force (electrical, magnetic or centrifugal) or by changing the material properties or the flow rate within the microreactor [9].

One of the key factors defining droplet shape is the channel geometry. In our study, the formation of droplets in channels perpendicular to each other was examined. For reactors with channel diameters of 1 mm to 2 mm, different flow rates were used (oil : water; in µL/min): 1000 : 100: 1000 : 200: 1000 : 400; 1000 : 500 for the reference sample, and additionaly 500 : 100, 500 : 500 and 500 : 50 for reactors with hydrophobized channels. Our research has shown that the size, shape and stability of droplet production is influenced by channel size, surface pretreatment (hydrophobization), and fluid flow rate.

Fig. 6a shows the flow instability in the untreated channel, while by treatment of the channels with a hydrophobic agent the flow becomes stable with the droplets in the outlet channel being regular. From all of the above, it is concluded that the treatment of the channels with hydrophobic treatment in some channels increases the number of droplets that become more regular (uniform in size). In some, however, it reduces the number of droplets, which become elongated. Flow rate also significantly affects the appearance and number of droplets in the channels.

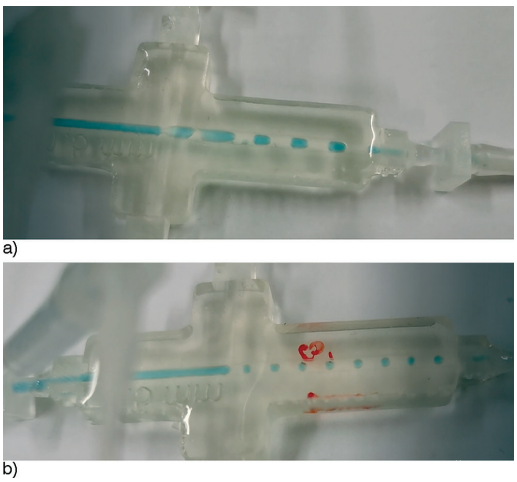

Fig. 6. Comparison of the number and shape of the droplets inside the channels (diameter of inlet 1.5 mm, outlet 2.0 mm), a) without treatment, b) treated with hydrophobic agent. Measured at flows: oil 1000 µL/min; water: 400 µL/min [10]

5. Addition of static mixers to millireactors

The idea of moving from batch to continuous processes is gaining interest in the industry since they allow for economical production and the inflow of larger quantities of input currents. Continuous production reduces energy consumption and waste production compared to the equivalent amount of product produced by the batch method. As many of these processes rely on good mixing and heat transfer, static mixers are being increasingly incorporated into process systems [11, 12]. Since mixing directly affects the efficiency of the process and the amount of released by-products, it is very important to characterize mixing in industrial processes for economic and environmental reasons. Static mixers, due to a series of fixed elements, redistribute fluid flow in directions transverse to the main flow. With this mixing method, mass transfer is occurring by convection rather than diffusion [13-16].

In our study [17], the effect of static mixers on the reaction conversion was examined. Fenton oxidation of organic pollutants (dye Reactive Blue 182) was studied. Millireactors with static mixers were fabricated by stereolithography (one of the additive manufacturing technologies). The millireactor used as a benchmark was a simple tubular millireactor, with 2 mm circular diameter. Several types of static mixers were designed and tested. The geometry of the millireactor with static mixers shown on Fig. 7 was in the form of a cylinder inside the cylinder with the inlet and outlet on opposite sides, which resulted in centrifugal mixing of the fluid. The flow rates used were between 100 µL/min and 2600 µL/min.

The values of Reynolds' numbers calculated for the tubular millireactor suggest laminar flow for all used flow rates. During the reaction, the laminar flow was clearly visible at all lower flow rates, while at higher flow rates,

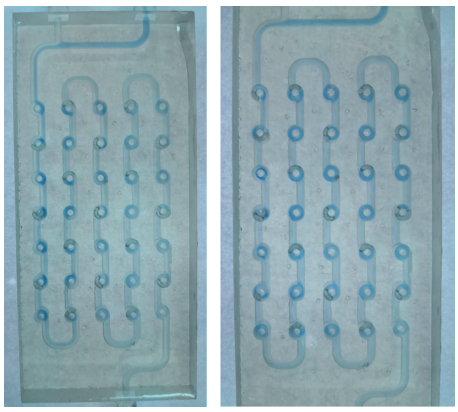

Fig. 7. Comparison of millireactors with centrifugal mixing while using low flow rates (200 μL/min, left picture) and high flow rates (2600 μL/min, right picture). Stronger mixing at the contact point of two reactant currents is noticeable on the right picture showing higher flow rate.

strong mixing at the contact point of two reactant currents was visible as shown in Fig. 7.

6. Conclusions

We have demonstrated the usefulness, feasibility and flexibility of additive manufacturing in the fabrication of microreactor systems. Within the timespan of one or two days, a microreactor geometry tailored to a specific reaction can be designed, manufactured, and used to perform chemical reaction. Due to the time and cost-effectiveness of this type of fabrication technique, it is possible to study several materials engineering and chemical engineering problems at the same time.

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