GENERATION OF COMPLEX EMULSIONS USING MONOLITHIC, DUAL-MATERIAL 3D-PRINTED MICROFLUIDIC DEVICES

Jin Li[1], Pantelitsa Dimitriou[1], Oliver Castell[2] and David Barrow[1]

[1]*School of Engineering, Cardiff University, United Kingdom*

[2]*School of Pharmacy and Pharmaceutical Science, Cardiff University, United Kingdom*

ABSTRACT

Forming high-order, water/oil, multiple emulsions often depends upon the juxtaposition of hydrophilic and hydrophobic ducts within a fluidic circuit. This frequently requires post-fabrication surface modifications, and the manual assembly of discrete fluidic parts. Here, we demonstrate a 3D printing approach to fabricate monolithic, integrated, microfluidic devices, from both hydrophobic and hydrophilic polymers, in one step. These integrated fluidic devices are used to produce highly compartmentalized emulsions, as liquid droplet templates, for the creation of programmable artificial cell as a novel biotechnology application.

KEYWORDS: multiple emulsions, dual-material 3D printing, 3D-printed microfluidics, hydrophilic manifolds

INTRODUCTION

Complex emulsion droplets, incorporating compartmentalised (bio)chemical reagents presents the prospect of programmable, miniaturised reactors, which have a wide range of applications in our daily life, such as in food, cosmetics, drug delivery and clinical therapy [1]. Microfluidics enables a precise capability to regulate the emulsification process, producing uniform droplets with encapsulated reagents. The types of droplet formed, (i.e. water droplets in oil (w/o) and vice versa), are determined by the wettability of the droplet forming structures (e.g. ducts). To generate multiple emulsion droplets (e.g. w/o/w or o/w/o), it typically requires juxtaposed, contrasting surface energies within fluidic manifolds. However, as most fluidic substrate materials are insufficiently hydrophilic, post processing (e.g. chemical or plasma treatments) is usually required for glass capillaries and PDMS chips, before being integrated with other fluidic parts. Such multiple steps, especially through manual fabrication processing, may give rise to performance variations between different parts, and could reduce the repeatability of devices to form droplets of complex morphology.

In our previous work, we developed a one-step, dual-material, fabrication process for fluidic devices with fused filament 3D printing [2]. These devices were composed of hydrophobic polylactic acid (PLA) channels and hydrophilic polyvinyl alcohol (PVA) channels, and were used to form Janus water/oil/alginate capsules as the chassis of polarised, emulsion-based artificial cells. However, the water-soluble PVA, limits the lifetime of these devices. Here, we report the fabrication of dual-material microfluidic devices, printed from Nylon and PLA filaments. Nylon is naturally hydrophilic and the printed device has a much longer useable lifetime, than does PVA. By patterning the Nylon and PLA channels, triple and quadruple emulsion droplets were produced with multiple encapsulants and controllable compartmentalisation. Such printed devices and droplets could be a new platform to produce programmable artificial cells for material and biotechnology applications, as described on our website.

EXPERIMENTAL

All the chemicals were purchased from Sigma-Aldrich and used as received. The dual-material 3D-printed microfluidic devices were printed with an Ultimaker 3, fused filament printer, using Ultimaker brand transparent Nylon filament and transparent PLA filament. Fluid precursors were loaded in 15 mL centrifuge tubes (Falcon), and injected to microfluidic devices via PTFE tubing (SUPELCO) using pressures pumps (ELVEFLOW). Images were taken with a measuring microscope (Nikon MM800) and a high speed camera (MegaSpeed), and analysed with Fiji software. More detail can be found in our previous work [2].

RESULTS AND DISCUSSION

Using microfluidics, the formation of oil droplets in continuous water flow, is considered more challenging than the opposite case, due to the oil phase normally having a lower interfacial tension than water. Figure 1 shows the formation of oil droplets in a continuous water phase within a hydrophilic, 3D-printed Nylon microfluidic device. The inlet flow rates are 5ml/hour and 50ml/hour, for the oil phase and the water phase, respectively. The mean diameter of the oil droplets is 0.18mm with a 0.0103 polydispersity (<0.1 is considered as monodisperse sample). The polydispersity of oil droplets can be improved with precise temperature and viscosity control [3].

Next, hydrophobic PLA and hydrophilic Nylon, were used to print dual-material devices, so that the fluidic circuit is patterned with both hydrophobic and hydrophilic channels to form multiple water/oil emulsions in a stepwise mechanism. For example, figure 2 shows a PLA/Nylon device, where fluidic channels have hydrophobic-hydrophilic-hydrophobic wettability, which allows the formation of w/o/w/o emulsions.

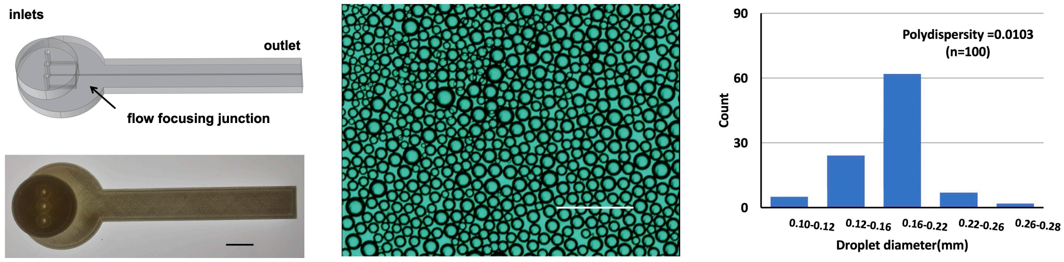

Figure 1. Left, a sample of a 3D-printed Nylon chip. Mid & right, formed oil droplets in water phase and their size distribution. Scale bars denote 1mm.

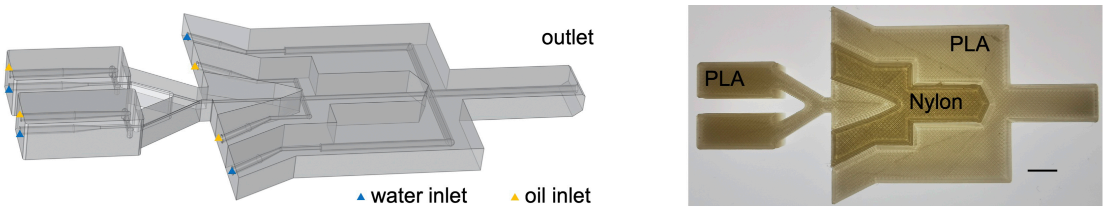

Figure 2. A sample of PLA/Nylon 3D-printed device with multiple inlets for producing high-order emulsions. Scale bar denote 1mm.

Using this 3D printing approach, one can prototype fluidic manifolds with customised fluid architectures for the formation of complex emulsions. Figure 3 shows the collection of emulsions from the printed device outlet, showing the capability to control the morphologies of multiple emulsions, such as containing various encapsulants.

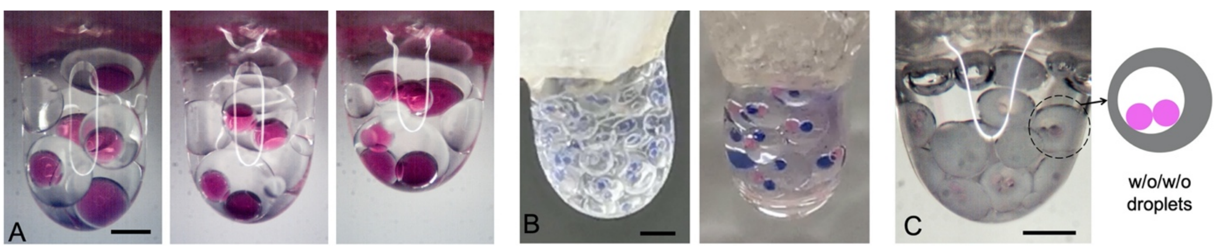

Figure 3. Formed triple w/o/w emulsion droplets with control of encapsulated droplet numbers (A) and types (B). Image C indicates the generation of w/o/w/o quadruple emulsion droplets. Scale bars denote 500um.

CONCLUSION

In summary, we report the one-step fabrication of dual-material, 3D-printed fluidic devices. These devices were patterned with the hydrophilic Nylon and the hydrophobic PLA fluidic circuit, to produce multiple emulsion droplets with various encapsulants. Future work will focus on the spatial organisations of the encapsulated droplets as programable sequences for the creations of more complex and functional artificial cells.

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CONTACT

Dr. J. Li, e-mail: LiJ40@cardiff.ac.uk, Pr. D. Barrow, e-mail: Barrow@cardiff.ac.uk .