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Direct additive manufacturing of hydrophobic microstructures using soft polymer

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Abstract

Soft polymers are essential for medical applications where biomimicking of soft biological structures is needed. The performance of these soft polymers can be boosted by incorporating hydrophobic re-entrant structures using 3D printing. However, the direct additive manufacturing via Digital Light Processing (DLP) of such structures using commercially available biocompatible soft polymers without photoabsorbers has not yet been explored. In this study, hydrophobic surfaces with re-entrant structures in the form of walls were 3D printed in a bottom-up DLP printer using a commercially available biocompatible polymer with shore hardness A90. These structures were printed in vertical orientation with respect to the building plate. Due to the adhesion of each printed layer to the vat membrane, bent structures were observed on the sides of the sample which allowed the partial intrusion of the water below the overhang. Even with this, the structures were able to prevent the full wetting of water into the structure. Anisotropic wetting was observed with water static contact angles reaching in the range of 144-149° and 112-115° for a 10 µL droplet as examined on different sides.

Soft polymer, Hydrophobic micr ostructures, Additive manufacturing

1. Introduction

Additive manufacturing of soft polymers is increasingly gaining interest because of its potential application in the healthcare industry [1]. With the trend in the research gearing towards improving the resolution of 3D printing technologies, it is foreseen that superior surface properties can be achieved through surface functionalization by directly printing micro/nano structures. Among the surface functionality that poses high significance to the medical industry is hydrophobicity. This further provides self-cleaning [2], and anti-fouling properties [3] that are essential for medical devices. Among the most favorable surface morphologies found in nature for liquid repellency is the overhanging structures in springtail cuticle [4].

Printing re-entrant structure using a commercially available resin is challenging because of the resin's relatively high depth of curing unless it is incorporated with additional photoabsorbers [5]. These photoabsorbers enhance the z-axis resolution of the resin. In the medical device industry though, the addition of chemicals can lead to more paperwork in compliance with the industry's strict regulatory requirements. This study then aims to explore 3D printing of re-entrant microstructure using commercially available biocompatible soft polymers in a common bottom-up DLP setup without the addition of a photoabsorber.

2. Methodology

2.1. Materials

A commercially available biocompatible resin FotoTec®DLP.flex Shore A90 (Dreve Otoplastik GmbH, Germany) was used in this study.

2.2 3D printing

The re-entrant surface microstructures in the form of walls were designed and modelled as shown in Figure 1 using SolidWorks 2021 Computer-Aided Design (CAD) software (SolidWorks Corp., USA). This was then sliced using the in-house developed AMLab software [6]. The model was positioned such that the re-entrant wall structure is perpendicular to the building plate as shown in Figure 2. The samples were printed using the in-house built vat photopolymerization setup with 0.5x lens and 1 neutral density filter [6], [7]. These were printed using 50 µm layer height, exposure time of 15 s, light amplitude of 50 in the slicer which is equivalent to 4.9 mW/cm^2 irradiance, build plate feed rate of 300 mm/min, and build plate repositioning distance of 5 mm. The biocompatible resin was used as received.

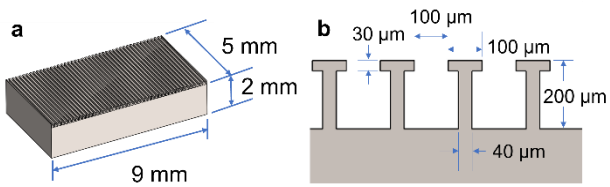

Figure 1. a) CAD model of the part with surface structure and b) detailed drawing of the re-entrant structures with dimensions.

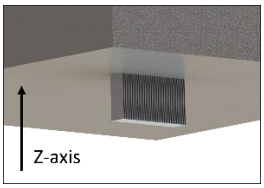

Figure 2. The part is oriented on the building plate such that the re-entrant structures are on the sides. The building plate moves in the z-direction during printing.

2.3 Characterization

The static contact angles were measured using a contact angle goniometer (Ramé-Hart Instrument Co.). A volume of 10 µL of deionized (DI) water was used. Contact angles as seen parallel and perpendicular to the walls were both measured. The microstructures were examined using Olympus LEXT Infinite Laser Microscope.

3. Results and Discussion

Figure 3 shows the actual 3D-printed re-entrant structures. The structure's height is intended to be relatively high to gain more volume of entrapped air between these structures, thus preventing liquid intrusion into the base of the structure and making it more hydrophobic. However, with this height, the features printed near the edges of the sample bend with the structure's top pointing toward the sample's center. The same observations were also seen on the sample with spacings 150 and 200 µm. This can be due to the effect of adhesion to the vat membrane that is greatly affecting a flexible polymer. The edges of the sample experience a higher degree of stretching first compared to the center during the detachment from the membrane.

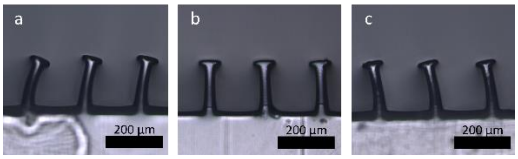

Figure 3. Images of the printed re-entrant structures taken near the right edge (a), middle (b), and left edge (c) of the sample.

The top topography of the structure was also assessed using laser microscope and the result is demonstrated in Figure 4. Lines seen are the stair-case effect due to layer-by-layer printing. Even though the resin is soft, it did not demonstrate cracks or pits on the layers of the prints.

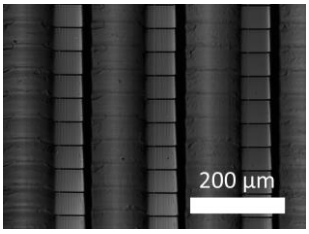

Figure 4. Surface structure as seen on the top of the sample.

The re-entrant structure revealed different wetting behavior as seen on different views (front and side) illustrated in Figure 5. The edges of the re-entrant structures as seen in the front view successfully pins the spread of the droplet resulting in a higher contact angle compared to the side view where there is no feature that can stop the water from spreading.

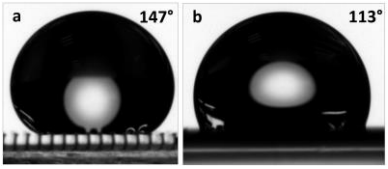

Figure 5. Anisotropic contact angles as seen on the front (a) and side view (b).

The effect of bent structures resulted in wetting beyond the re-entrant feature at the top of the structure. The bending caused a new overhang angle on the left side of the walls as seen in Figure 6 which tends to promote wetting more than what was originally designed.

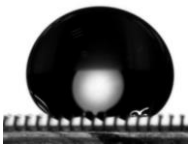

Figure 6. Partial water intrusion due to bent structures.

The static contact angles at the edge and middle part of the sample showed only minimal difference between the two (Figure 7). Even though there was partial wetting observed on the features near the edges, this was small to cause only a slight difference with the features at the middle part.

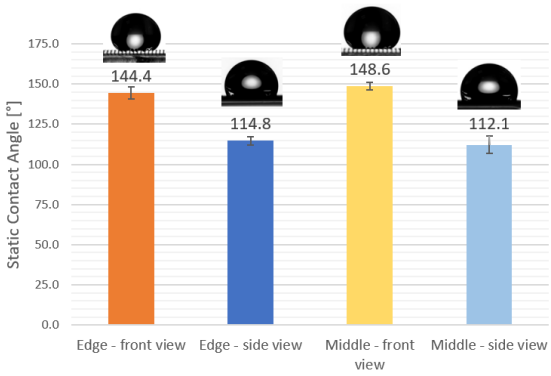

Figure 7. Static contact angles as seen on the front and side views for the features located near the edges and in the middle of the sample.

4. Conclusion

This study served as a preliminary investigation on 3D printing re-entrant structures using commercially available biocompatible soft polymer in a bottom-up DLP printer where soft polymer printing is challenging. Due to the flexibility of the resin and the adhesion of each printed layer to the membrane, bending structures were seen and were found prominent near the edges. This caused partial wetting into the structure. Even with this, the re-entrant wall structure designed here exhibited anisotropic hydrophobic wetting with optimal static contact angles ranging from 144-149° and 112-115° as seen on the front and side views, respectively. Optimization of this re-entrant structure can be further explored to enhance its mechanical stability.

Acknowledgement

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