Fabrication of durable haemophobic surfaces on cast acrylic sheets using UV laser micromachining

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A low-cost, high-speed micro-scale patterning procedure for generation of durable blood-repellent patterns on polymers using continuous wave (CW) ultra-violet (UV) laser with optical lens arrangement is demonstrated in this work. A laser engraver which can generate patterned structures in the range of 1–300 µm employing a 5 W, 445 nm CW UV laser with collimating lens arrangement was developed for this purpose. Subsequently, cell cast high impact acrylic sheets of 5 cm × 5 cm size were patterned to generate fishbone architecture like microstructures with central structure footprint 71.3 µm, peripheral structure footprint 29.8 µm and peripheral structure spacing of 77.8 µm. The patterned acrylic was evaluated for hydrophobicity and human blood-repellent nature using a contact angle goniometer. Hardness tests for checking durability of the patterned surfaces for various biomedical applications were conducted using a hardness tester. The tested Vickers hardness of the acrylic patterned sample was 17.41 HV which indicates durability of the fabricated patterns. Maximum static contact angle of 142.3° and minimum roll-off angle of 11.7° observed for blood on patterned acrylic confirm the haemophobic nature of the fabricated surfaces.

1. Introduction: Blood-repellent surfaces have gained significant research attention due to their diverse emerging applications ranging from surgical tools to biomedical implants [1, 2]. When a surgical tool, biomedical implant or clinical consumable come in contact with human blood, the interaction of the material with blood cells such as platelets, monocytes and so on leads to activation of coagulation and clot formation due to Vroman effect [3]. This poses serious concern in different situations as blood coagulation on surgical tool tips and clinical consumable can deter a surgeon from the normal operating procedure or may lead to inflammation and thrombosis in biomedical implants.

As blood-repellent surfaces can be promising in this regard, various researchers have attempted to fabricate blood-repellent surfaces. Four different methods namely decreasing effective area of surface, decreasing adhesion area of the surface, hydrodynamics to alter platelet adhesion and high curvature surfaces to restrict protein adhesion are used to generate blood-repellent surfaces [4]. All of these methods focus on inhibiting the adhesion/contact of platelets and protein to the surface in contact and is achieved in narrow spaces and hydrophobic surfaces.

Till date, blood-repellent patterned surfaces are developed on smaller areas due to cumbersome fabrication procedure, high fabrication costs and inability to generate perfectly repeatable patterns on larger areas [5, 6]. Furthermore, hardness of these generated surfaces using standard methods is not checked for their use in clinical consumables or implants.

2. Existing literature: Modification of the desired surfaces to render them blood repellent has been conducted using various methods such as atomic layer deposition assisted sacrificial etching [7], sand casting technique [8], oxidation and hydrothermal synthesis [9]. All of these proposed methods require dedicated instrument, cumbersome procedure and could be limited to lab-scale generation of patterned haemophobic surfaces over smaller areas (in range of few millimetres). To the best of our knowledge, the hardness of the existing blood-repellent patterned surfaces using standard hardness testing procedure in literature is not available.

In order to bridge the gaps in existing techniques for fabrication of blood-repellent hydrophobic surfaces, we propose an inexpensive method for high throughput, fast, large area fabrication of durable blood-repellent surfaces on cell cast high impact acrylic which could be used for various applications ranging from surgical consumables to biomedical implants. Furthermore, we also evaluate the hardness of the developed patterned surfaces to check the durability of the fabricated patterns for different applications.

3. Methodology: Microscale blood-repellent patterned hydrophobic surfaces were generated using an in-house developed computer numerical controlled based laser micromachining setup with a travel resolution of 100 nm along *X*, *Y* and *Z* axes. The sample to be machined was placed on the *X*–*Y* plane and a low-cost 445 nm continuous wave (CW) ultra-violet (UV) laser with a lens assembly to yield a focused beam with spot diameter 10 µm was attached to the *Z*-axis. An *X*–*Y* grid shaped trajectory was traversed by a cell cast high impact acrylic sample (Make: Chemcast, 2025 black) over 5 cm × 5 cm area such that fishbone architecture shaped microstructures with central structure footprint 71.37 µm, peripheral structure footprint 29.84 µm and peripheral structure spacing of 77.81 µm could be generated due to heat-affected zone. The laser power during laser micromachining was set to 0.5 W. The dimensions of the patterns were deduced after repetitive experiments and observations on variation of contact angle with pattern dimensions. The experimental setup for laser micromachining is shown in Fig. 1.

The patterned samples were subjected to study of surface morphology using field emission scanning electron microscopy (FESEM, Zeiss Sigma 300, Carl Zeiss make). The static contact angle and roll-off angle of DI water and blood sample collected from two healthy individuals with the patterned acrylic sample were measured using contact angle Goniometer employing static sessile drop method with mean volume of microdroplet as 4.11 µl. (Attension theta, Biolin scientific make). Each experiment was repeated for ten times and the mean of contact angle and roll-off angle was obtained. The hardness of the developed patterns

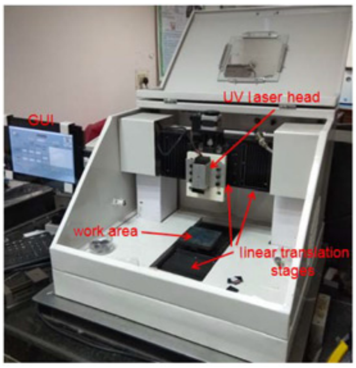

Fig. 1 *Experimental setup used for laser micromachining*

on acrylic was measured using hardness tester (Falcon 500, Make: Innovatest) with a loading of 1 kgf. The Vickers hardness test was conducted for five times at different locations on the pattern and mean of hardness was obtained.

4. Results and discussions: The FESEM images for the patterned acrylic blood-repellent surfaces are shown in Fig. 2.

The contact angle and roll-off angles of water and blood on smooth acrylic and patterned acrylic sample were tested for ten times using the goniometer. The mean of contact angle and

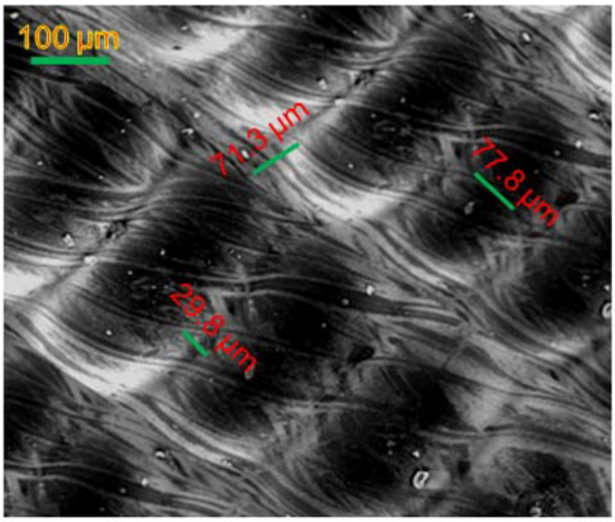

Fig. 2 *FESEM image of the developed patterned structures on acrylic using UV laser micromachining*

Table 1 Mean contact angle and roll-off angles found from the experiments

	DI water	Blood sample I	Blood sample II
contact angle on non-patterned surface (in degrees)	38.6	76.4	77.8
contact angle on patterned surface (in degrees)	100.2	140.1	142.3
roll-off angle on non-patterned surface (in degrees)	39.6	34.1	32.7
roll-off angle on patterned surface (in degrees)	19.4	13.9	11.7

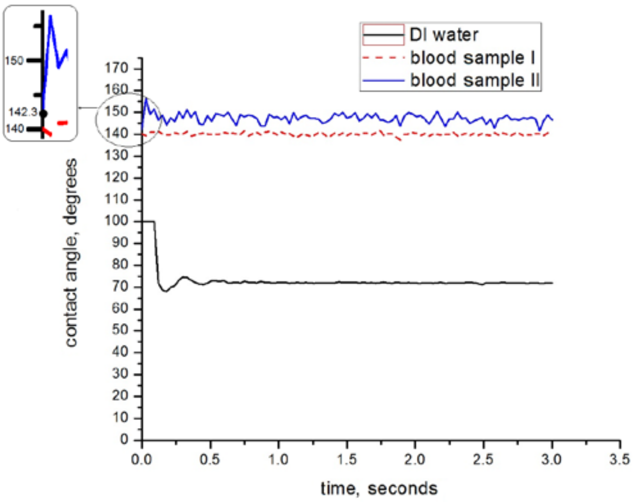

Fig. 3 *Variation of mean of contact angle for DI water, blood sample I and blood sample II on patterned surface with time for the ten set of experiments conducted*

roll-off angle from the ten experiments at the instant the droplet falls on the surface are summarised in Table 1.

The variation in mean contact angle with time after the droplet falls on the surface during contact angle measurement for the ten sets of experiments is shown in Fig. 3. For blood samples I and II, the contact angles remain nearly equal to 140.1° and 142.3° and do not vary significantly with time. For DI water the contact angle initially at the start of experiment was 100.2°, however it reduces to 67.5° in 0.18 s after start of the measurement process.

The mean Vickers hardness of the patterned acrylic sample was 17.41 HV as measured using hardness tester.

Following could be inferred from the experiments and experimental results: (i) due to anisotropic nature of the cast acrylic sheets, the generated fishbone architecture has varying footprints along horizontal and vertical directions (Fig. 2). This property is phenomenal in inducing the haemophobic nature of the generated patterns when machined at constant laser power. (ii) Fishbone architecture based patterns with different central, peripheral and gap lengths within 100 µm can render a surface haemophobic as demonstrated in this work. The footprint of the fabricated patterns in micron scale is well appreciated in industry as it is simple, cost effective and fast to fabricate patterns in micron footprint as opposed to nanometer scale patterns. (iii) The maximum static contact angle and minimum roll-off angle of blood on the fabricated patterned surface were 142.3° and 11.7°, respectively, when tested with samples from two different healthy individuals which shows haemophobic nature of the fabricated patterns. The contact angle of the patterned surfaces with water was 100.2° which facilitates the use of such patterned structures for haemophilic applications rather than hydrophobic applications. The difference in contact angles of blood and water could be due to varying physics of wetting. In case of water, homogenous wetting regime on the patterns is generated in concurrence with the Wenzel model. It could be observed in Fig. 3 that the contact angle of water on patterned acrylic falls drastically after 0.18 s which signifies a transition from Cassie to Wenzel state. In case of blood due to its colloidal nature and presence of various blood cells, air pockets remain trapped between the blood and the patterns. Hence in case of blood, the interface physics relies on the Cassie-Baxter model. Furthermore, as the pattern footprints were in the range of the blood cell dimensions, transition from Cassie-Baxter to Wenzel regime does not occur as

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seen in Fig. 3. (iv) The mean Vickers hardness of the patterned sample was 17.41 HV which shows the patterns are extremely durable and prone to wear and tear. This justifies the use of the patterned structures in biomedical applications.

5. Conclusion: In this research, a fast, low-cost, economic procedure for generation of UV laser micromachined durable large area micropatterns is demonstrated which finds applications in haemophobic surfaces. The anisotropy of the work material is dexterously explored to generate fishbone architecture shaped patterns with maximum contact angle and minimum roll-off angle with blood of 142.3° and 11.7°, respectively, facilitating the patterned surface for their use in various haemophilic applications. As compared to deposition-based patterning methods available in literature used to fabricate lab-scale haemophobic surfaces over smaller areas, the proposed method is capable of generating highly durable patterns over larger areas. The proposed method and the fabricated patterns thus has relevance in clinical and biomedical sector and has promising future for the fabrication of blood-repellent clinical consumables, implants and so on.

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7 References

[1] Ding Y., Leng Y., Huang N., ET AL.: 'Effects of microtopographic patterns on platelet adhesion and activation on titanium oxide surfaces', *J. Biomed. Mater. Res., A*, 2013, **101A**, pp. 622–632

[2] Moradi S., Hadjesfandiari N., Toosi S., ET AL.: 'Effect of extreme wettability on platelet adhesion on metallic implants: from superhydrophilicity to superhydrophobicity', *ACS Appl. Mater. Interfaces*, 2016, **8**, pp. 17631–17641

[3] Jaffer I., Fredenburgh J., Hirsh J., ET AL.: 'Medical device induced thrombosis: what causes it and how can we prevent it?', *J. Thromb. Haemost.*, 2015, **13**, pp. S72–S81

[4] Jokinen V., Kankuri E., Hoshian S., ET AL.: 'Superhydrophobic blood repellent surfaces', *Adv. Mater.*, 2018, **30**, pp. 1–10, DOI: 10.1002/adma.201705104

[5] Davis A., Surdo S., Caputo G., ET AL.: 'Environmentally benign production of stretchable and robust superhydrophobic silicone monoliths', *ACS Appl. Mater. Interfaces*, 2018, **10**, pp. 2907–2917

[6] Darband G., Aliofkhazraei M., Khorsand S., ET AL.: 'Science and engineering of superhydrophobic surfaces: review of corrosion resistance, chemical and mechanical stability', *Arabian J. Chem.*, 2018, early access, DOI: 1 0.1016/j.arabjc.2018.01.013

[7] Hoshian S., Kankuri E., Ras R., ET AL.: 'Water and blood repellent flexible tubes', *Sci. Rep.*, 2017, **7**, pp. 1–8, DOI: 10.1038/s41598-017-16369-3

[8] Li Z., Nguyen B., Cheng Y., ET AL.: 'Durable, flexible, superhydrophobic and blood-repelling surfaces for use in medical blood pumps', *J. Mater. Chem. B*, 2018, **6**, pp. 6225–6233

[9] Movafaghi S., Leszczak V., Wang W., ET AL.: 'Hemocompatibility of superhemophobic titania surfaces', *Adv. Healthcare Mater.*, 2017, **6**, pp. 1–6, DOI: 10.1002/adhm.201600717