Lithographically fabricated SU8 composite structures for wettability control

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Abstract

SU8 is a negative resist which is widely used for the fabrication of micron scale lateral features over a wide range of heights using photolithographic methods. This has been extensively used as a method to produce surface structure to which hydrophobicity can be added and a model super-water repellent surface of achieved. However, such an approach requires at least two-steps and does not embed the desired properties as part of the structure itself or create multiple levels of topographical structure. In other applications, a variety of inclusions have previously been studied to tailor the properties of SU8. In this work we report an approach to, and results from, incorporating inclusions, in our case glass beads, of different wettabilities into the SU8 structures produced by photolithography. In particular, we focus on ridge structures expected to be of use in flow systems as drag reducing surfaces. We used scanning electron microscopy and profilometry to investigate how the inclusion of either hydrophobic or hydrophilic glass beads (sieve size of 20-30 μm) affects the definition of the structures formed and contact angle goniometry to define what effect such inclusions has on the wettability of the SU8 composite structure. It was found that the inclusion of hydrophobic glass beads in the SU8 resist resulted in poorly defined structures compared to both SU8 on its own and SU8 to which hydrophobic glass beads were added. In contrast, inclusion of hydrophilic glass beads resulted in a well-defined ridge structure with the majority of the beads located in the 'valleys'. Both EDX analysis and contact angle data indicated that the surface chemistry of the beads themselves (both the hydrophobic and hydrophilic beads) were masked by the SU8. Counter-intuitively, the inclusion of hydrophobic beads in the SU8 composite resin resulted in ridges with increased wettability, compared to SU8 ridges, as opposed to the inclusions of hydrophilic beads that resulted in surfaces with increased effective hydrophobicity .

Introduction

SU8 is a commonly used negative resist for the fabrication of sub-micron scale structures based on a novolak epoxy resin [1] and is capable of producing structures of high aspect ratios [2]. The versatility of SU8 is highlighted by the range of applications for which it can be used. For example sensors [3] and microlenses [4] have been fabricated out of SU8 as have templates for soft lithographic techniques [5, 6] and functional surfaces displaying properties such as superhydrophobicity [2]. The inclusion of particles in SU8 can be done to impart greater functionality on the final structure, an example of this being the inclusion of SiO_2 particles in an SU8 matrix to increase wear resistance [7]. Carbon nanotubes have also been used as inclusions within a SU8 matrix to make an inkjet-printable conductive composite [8] and SU8 / ZnO nanoparticle composites have been investigated as piezoelectric materials [9].

The aim of this work was to incorporate glass beads, of different wettability, within SU8 resin with the objective of fabricating hierarchical structures with designer wetting properties. In particular, the formation of hierarchical structures is integral to forming superhydrophobic surfaces [10]. The ridge type of structures on shark skin aid their drag reduction [11] and similar ridge type structures have suggested by Rothstein *et al.* [12, 13] as possible drag reducing artificial surfaces. Therefore, a subsidiary aim in this article is to introduce approach to forming ridge-type drag reducing SU8 structures. The effect of the hydrophobicity of the glass beads upon the morphology of lithographically defined ridge structures was investigated using scanning electron microscopy (SEM) and profilometry in order to see how the inclusions altered the morphology of photographically defined ridge structures compared to those fabricated from SU8 resist (with no inclusions). The wettability of such ridge structures was measured using contact angle analysis. This approach introduces a single step to a standard methodology in order to fabricate ridge structures with textured features.

Methodology

Fabrication

Chemical functionalisation of the inclusions

General purpose glass microspheres (20-30 μm sieve size), Whitehouse Scientific, UK) were immersed in 30 vol% HCl solution (Fisher Scientific, UK) for 24 hrs and then rinsed three times with fresh de-ionised (DI) water and dried at 80 °C for 3 hrs. This treatment renders the glass beads hydrophilic, as confirmed by a glass microscope slide treated in an identical manner to the glass beads displaying a water contact angle of ~0° [14]. The glass microspheres were then immersed in a 5 vol% solution of a waterproofing agent (Extreme Wash-In solution, Grangers, UK) in DI water for 48 hrs and then dried 80 °C for 3 hrs. This treatment renders the glass beads hydrophobic, as confirmed by a glass microscope slide, treated in an identical manner to the glass beads, displaying a water contact angle of ~ 117° [14].

Preparation of SU8 structures

Firstly the SU8 composite was made by stirring either hydrophilic or hydrophobic glass beads (1.05 g) into SU8-50 (2.42 g, MicroChem) by stirring them vigorously, by hand, in a 30ml glass vial for 10 minutes to yield a composite solution consisting of 30wt% glass beads. The vial, containing the composite, was then placed in a vacuum desiccator which was then evacuated for ~1hr to remove air bubbles from the SU8 / particle composite solution.

To prepare the structured SU8 (or SU8 composite) surfaces a glass microscope slide was cleaned by immersion in a 20% aqueous solution of Decon 90 (Decon) for 8 minutes and rinsed in distilled water before being immersed in distilled water in a sonic bath for 8 minutes then rinsed with isopropyl alcohol and dried with $N_{2(g)}$. The clean glass microscope slide was then immersed in a 2 vol% solution of 3-aminopropyltriethoxysilane (≥98%, Sigma Aldrich) in acetone for 1 minute then rinsed with acetone and dried with $N_{2(g)}$.

A few drops of SU8 (or SU8 composite) solution was applied to the glass microscope slide and spin coated using a WS-650S spin coater (Laurell Technologies Corporation, USA) at a speed of 500rpm for 10s then at 2000rpm for 30s. The coated microscope slide was then placed on a hot plate, set at 65°C, for 30 min, the temperature was then increased to 95°C and held for 30 min before the microscope slide was removed and allowed to cool to room temperature.

The sample was then exposed to UV light (λ = 365 nm) for 15 s through a photomask (J D Photomasks, UK) situated in a mask aligner (Süss MicroTec MJB4). The pattern on the photomask was an array of 100μm thick lines which were 100μm apart which would yield a ridge-like morphology upon exposure to UV light and subsequent development.

After exposure to UV light the sample was placed on a hotplate and held at 65°C for 30 min before being developed by immersion in EC solvent (Dow Chemical Company) for 20min. The sample was then rinsed with isopropyl alcohol and rinsed using $N_{2(g)}$. This process yielded ridge structures with heights of 59 ± 7 μm (SU8 with no beads), 32 ± 7 μm (SU8/hydrophilic bead composite) and 38 ± 13 μm (SU8 / hydrophobic bead composite).

In order to establish the effect of both the ridge structure and bead inclusions upon the wettability of SU8 an unpatterned SU8 sample, with no glass bead inclusions, was prepared by using the same protocol as described above except that the exposure to UV radiation was not performed in the presence of a photomask. This yielded a surface which exhibited a water contact angle of 77.3 ± 1.1° which is in good agreement with the literature [2], [15] and provided a control to firstly determine the effect of the ridged structure on the wettability of SU8 and then the effect that the inclusion of the glass beads within the SU8 has on the ridged structure.

Characterisation

Contact angle

Contact angle analysis (transverse and parallel to ridges where present) was carried out on hydrophobic and hydrophilic glass microscope slides and on fixed hydrophobic glass beads using a DSA 10 contact angle meter (Krüss, Hamburg, Germany) and analysed using DSA software (Krüss). The (observed) static contact angle (θ) was measured by placing a water droplet (15 μl) on a surface. The volume of the droplet was then increased and decreased to measure the advancing (θ_A) and receding (θ_R) contact angles, which are the contact angles at which the solid-liquid-vapour contact line just begins to advance and recede, respectively.

SEM

To prepare the sample for observation under the scanning electron microscope (SEM) it was placed in a sputter coater (K575X - Peltier cooled, Emitech) and was exposed to Ti (1 cycle, 60s duration exposure at 150mA) and then to Au (1 cycle, duration of 240s at 85mA). These settings gave film thicknesses of ~20nm and ~100nm for Ti and Au respectively. Micrographs of the samples were obtained using a JSM-840A scanning electron microscope (JEOL, Japan) using a tungsten filament as an electron source which was operated at 20 kV. Image capture and EDX analysis were captured using INCA software.

Profilometry

Surface profilometry was carried out using a Dektak 6M stylus profilometry (Veeco, country). Two scans, of 1.5 mm in length, were performed on different areas of each sample.

Results and discussion

The effect of the hydrophobicity of glass bead inclusions on the structure of photolithographically defined SU8 structures was investigated with a view to the formation of hierarchical structures. Figure 2 shows SEM images of photolithographically defined structures made from both SU8 resist and composite resists consisting of SU8 mixed with either hydrophobic or hydrophilic glass beads (20 - 30 μm in diameter). The processing conditions for all three resists were the same allowing the only variable to be the nature of the inclusions. Ridges fabricated from SU8 resist exhibit well defined, straight sided structures (Figure 2a). However, the use of SU8 with hydrophobic inclusions lead to structures that are poorly defined (Figure 2b) with some of the beads migrating to the air-resist interface and, in some cases, the beads detaching from the resist which is evident by the dimples in the ridges as seen in figure 2bi. The migration of the hydrophobic bead inclusions to the air-resist interface can also be explained by the observation that a droplet of SU8 forms a contact angle of ~95° on a glass microscope slide that had been modified in the same manner as the glass beads. By changing the hydrophobicity of the inclusions there is a marked difference in the SU8 structures fabricated by photolithography as is demonstrated by comparing figures 2b and 2c. The inclusion of hydrophilic glass beads in the SU8 composite resist (Figure 2c) results in much more well defined and smoother structures compared to those fabricated from hydrophobic bead resists (Figure 2b). The hydrophilic beads appear to be less aggregated at the air-resist interface (i.e. the tops of the ridges) than the hydrophobic beads and this suggests that they are more easily dispersed throughout the composite resist after the initial mixing process. This is consistent with the observation of a droplet of SU8 exhibiting a contact angle of ~51° on a clean, glass microscope slide. Profilometry investigations found that the width of the 'valleys' between ridges was 89 ± 2 μm for SU8 with no inclusions which was similar to that of structures formed using SU8 / hydrophilic bead composite (86 ± 2μm) but the difference was striking when compared to structures formed from SU8 / hydrophobic bead composite (80 ± 15 μm). The profilometry results back up the SEM images in shows that the inclusion of hydrophobic beads in the SU8 / bead composite has a deleterious effect on the structures formed by the photolithography process compared to the inclusion of hydrophilic beads.

The ridges formed from the SU8 / hydrophilic bead composite resist also shows two levels of roughness with the tops of the ridges being almost featureless and the bottom of the 'valleys' exhibiting a rough surface due to the particulate aggregation. EDX analysis was used to analyse the (near) surface chemistry of the SU8 / SU8 composite ridges (Table 1). The ratios of silicon to carbon of ridges made from SU8 / hydrophilic bead composite (Si/C = 0.19) was similar to that of ridges made form SU8 / hydrophobic bead composite (Si/C = 0.23) which, in turn, was much higher than that of ridges made from SU8 with no inclusions (Si/C = 0.02); this observation confirms the presence of glass beads. However, the Si/C ratios of the composites were lower than that of hydrophilic and hydrophobic beads (Si/C ratios = 0.93 and 0.64 respectively) which suggests that the beads are embedded within the SU8 composite rather than at the surface. Therefore, it can be assumed that the surface chemistry of all ridge structures are the same and that all glass beads are coated in, at least, a thin layer of SU8.

Table 2 shows the static, advancing and receding water contact angles of photolithographically defined ridge structures fabricated from both SU8 and SU8-bead composite structures and figure 3 depicts the static angles on flat SU8 and that on the ridge structures. The incorporation of hydrophobic glass beads into the SU8 matrix appears to increase the wettability of the ridges whilst the incorporation of hydrophilic beads increases the water contact angles observed on the SU8 structures, both perpendicular and parallel to the ridges. This rather counter-intuitive observation can be explained by considering the topography of the structures. In comparison to flat, unpatterned SU8, the poorly defined SU8-hydrophobic bead composite ridges offer only a slight increase of roughness, whilst the SU8 ridges (single level roughness) and SU8/hydrophilic bead ridges (dual level roughness) lead to well defined structures of increased roughess. As the roughness increases from SU8/hydrophobic bead to SU8 ridges (no inclusions) to SU8/hydrophilic ridges the increase of contact angle is more pronounced when compared to that of flat SU8 (θ_{static} = 77.3 ± 1.1°). This observation, in conjunction with the EDX data discussed earlier, indicates that the beads near the composite surface are coated by a thin SU8 layer which masks their hydrophilicity.

Such amplification of intrinsic hydrophobicity by hierarchical surface structure [16] underpins the design of superhydrophobic surfaces [10]. Relatively large contact angle hysteresis was observed for ridge structures fabricated from both SU8 ($\Delta\theta$ = 44.4°± 11.0° and 35.4°± 7.8° perpendicular to and parallel to the direction of the ridges, respectively) and SU8-hydrophilic inclusion composite materials ($\Delta\theta$ = 38.0°± 19.4° and 45.8°± 21.7°, perpendicular to and parallel to the direction of the ridges respectively). The variability of the contact angle hysteresis appears to increase upon the addition of hydrophilic inclusions within the SU8 resist which suggests that a water droplet exists in a (partial) Wenzel state on the ridge structure.

Conclusions

The effect of glass bead inclusions of differing wettability in SU8 resist on the morphology of resultant lithographically defined structures has been investigated by the use of SEM and profilometry. It was found that the inclusion of hydrophobic beads lead to poorly defined structured, compared to SU8 with no inclusions, whereas the inclusion of hydrophilic beads in the resist beads leads to well defined structures with the beads providing texture at the bottom of the 'valleys'. When compared to ridges formed from SU8 the hydrophobic bead composite decreased the water contact angle and the inclusion of hydrophilic beads actually increased the contact angle. This suggests that the glass beads are covered by SU8 and the beads provide the wettability control by their contribution to the topography of the ridges, rather than surface chemistry. However, the hydrophilic bead composite ridge structures have more variable contact angle hysteresis, which we believe may result from the size and spherical shape of the particular inclusions we used and that more beads are located at the (sub)surface of the ridges in comparison to ridges formed from SU8-hydrophobic bead composite. The SU8-hydrophobic bead composite material may provide the basis of the development of superhydrophobic structures. The ridge structures, formed by the SU8/hydrophilic bead composite photoresist, consist of a high bead concentration in the 'valleys'. This could provide interesting structures on which to cast PDMS to use for either microcontact printing, for the formation of 'speckled' chemical patterns, or in microfluidics, by providing a facile way of introducing hierarchical structures of PDMS ridges.

Acknowledgments

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References

[1] A. del Campo, C. Greiner, SU-8: a photoresist for high-aspect-ratio and 3D submicron lithography, J. Micromech. Microeng. 17 (2007) R81–R95.

[2] N.J. Shirtcliffe, S. Aqil, C. Evans, G. McHale, M.I. Newton, C.C. Perry, P. Roach, The use of high aspect ratio photoresist (SU8) for super-hydrophobic pattern prototypes, J. Micromech. Microeng. 14 (2004) 1384-1389.

[3] C.V.B. Reddy, M.A. Khaderbad, S. Gandhi, M. Kandpal, S. Patil, K.N. Chetty, K.G. Rajulu, P.C.K. Chary, M. Ravikanth, V.R. Rao, Piezoresistive SU-8 Cantilever With Fe(III) Porphyrin Coating for CO Sensing, IEEE Trans. Nanotechnol. 11 (2012) 701- 706.

[4] H.C. Wei and G.D.J. Su, Fabrication of a transparent and self-assembled microlens array using hydrophilic effect and electric field pulling, J. Micromech. Microeng. 22 (2012) 025007.

[5] Y. Xia and G.M. Whitesides, Soft Lithography, Annu. Rev. Mater. Sci. 28 (1998) 153-184.

[6] S. Diegoli,, C.A.E. Hamlett, S.J Leigh, P.M. Mendes, J.A Preece, Engineering nanostructures at surfaces using nanolithography, Proc. Inst. Mech. Eng. G J. Aerosp. Eng. 221 (2007) 589-629.

[7] S. Jiguet, M. Judelewicz, S. Mischler, H. Hofmann, A. Bertsch, P. Renaud, SU-8 nanocomposite coatings with improved tribological performance for MEMS, Surf. Coat. Technol. 201 (2006) 2289-2295.

[8] M. Mionić, K. Pataky, R. Gaal, A. Magrez, J. Brugger, L. Forró, Carbon nanotubes–SU8 composite for flexible conductive inkjet printable applications, J. Mater. Chem. 22 (2012) 14030-14034.

[9] K. Prashanthi, M. Naresh, V. Seena, T. Thundat, V. Ramgopal Rao, A Novel Photoplastic Piezoelectric Nanocomposite for MEMS Applications, J. Microelectromech. Syst. 21 (2012) 259-261.

[10] P. Roach, N.J. Shirtcliffe and M.I. Newton, Progress in superhydrophobic surface development, Soft Matter, 4 (2008) 224-240.

[11] D. W. Bechert and M. Bartenwerfer, The viscous flow on surfaces with longitudinal ribs, J. Fluid Mech. 206 (1989) 105-129.

[12] J. Ou, B. Perot and J. P. Rothstein, Laminar drag reduction in microchannels using ultrahydrophobic surfaces. Phys. Fluids 16 (2004) 4635-4643.

[13] R. J. Daniello, N. E.Waterhouse, J. P. Rothstein, Drag reduction in turbulent flows over superhydrophobic surfaces, Phys. Fluids 21 (2009) 085103.

[14] C.A.E. Hamlett, S. Atherton, N.J. Shirtcliffe, G. McHale, S. Ahn, S.H. Doerr, R. Bryant, M.I. Newton, Transitions of water-drop impact behaviour on hydrophobic and hydrophilic particles, Euro. J. Soil Sci. 64 (2013) 324-333.

[15] Z. Gao, D.B. Henthorn,. C.-S. Kim, Enhanced wettability of SU-8 photoresist through a photogratfing procedure for bioanalytical device applications, J. Micromech. Microeng. 18 (2008) 450131-450137.

[16] N.J. Shirtcliffe, G. McHale, M.I. Newton, G. Chabrol, C.C. Perry, Dual-Scale Roughness Produces Unusually Water-Repellent Surfaces , Adv. Mater. 16 (2004) 1929-1932.

Figures

Figure 1: Schematic of structure formation

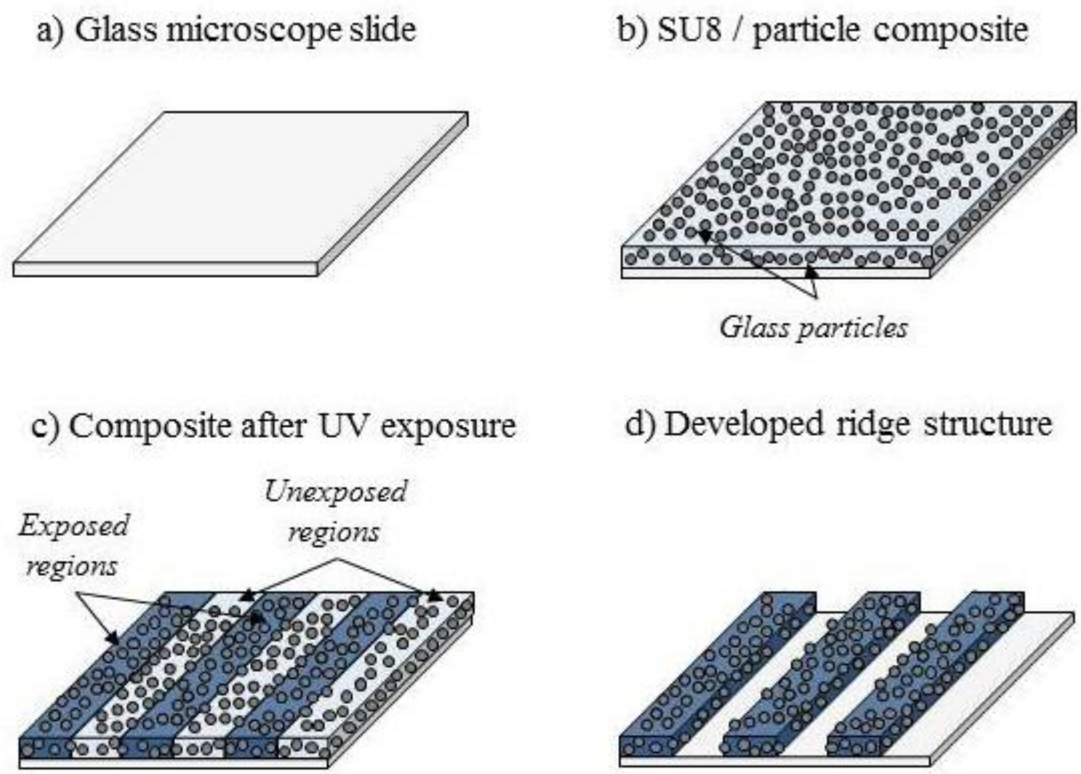

Figure 2: SEM images of SU8 structures with a) hydrophilic and b) hydrophobic bead inclusions.

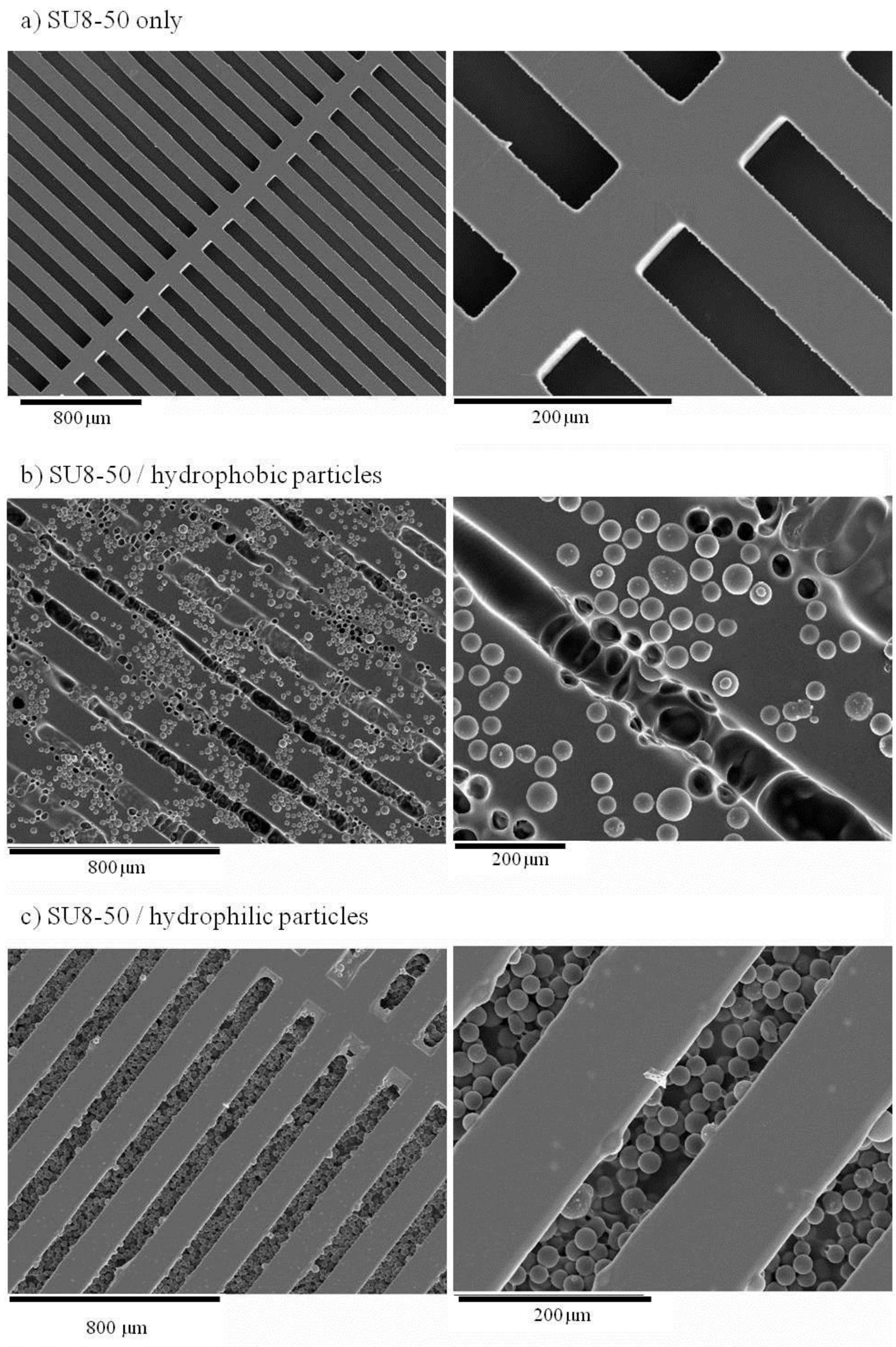

Figure 3: Images of water droplets on SU8 composite structures

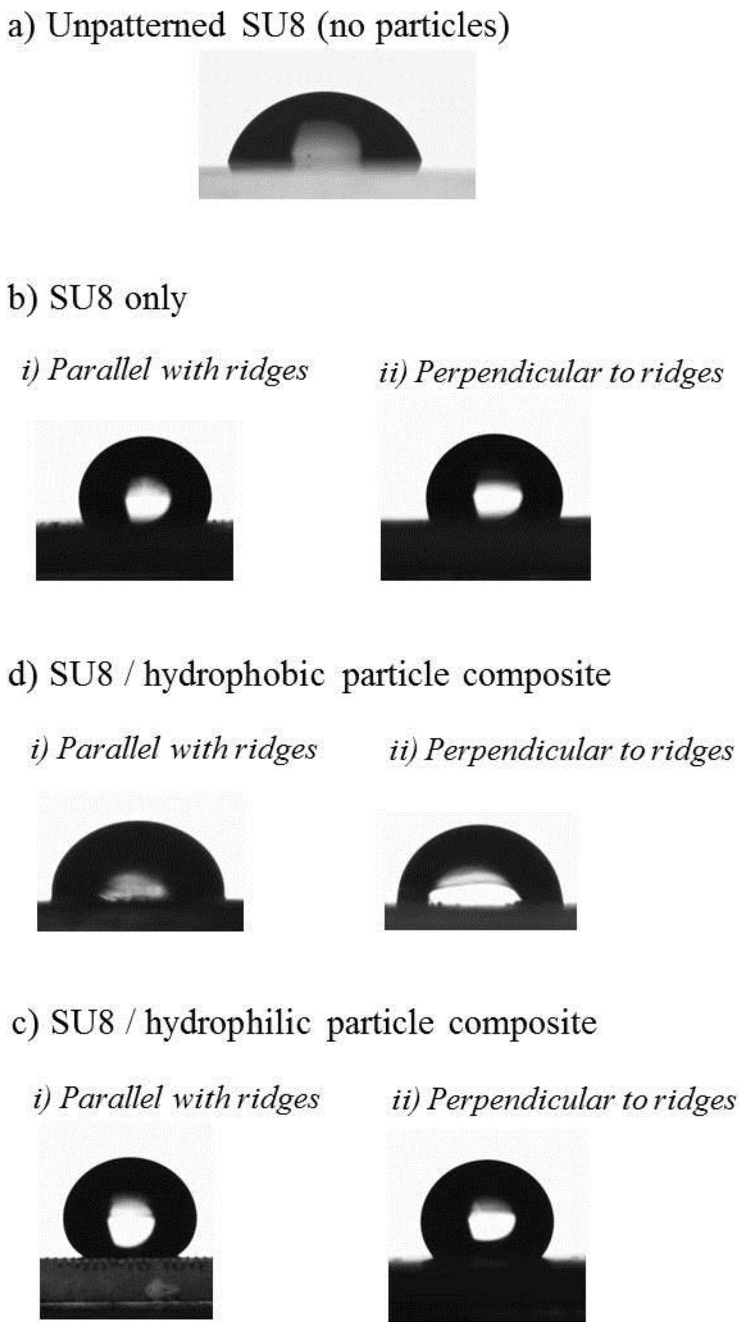

Table 1: EDX analysis of glass beads and lithographically defined ridges of SU8 and SU8 composites

Sample	**Atomic %**							**Si / C**
	Si	*O*	*Ca*	*Fe*	*Cl*	*C*	*Br*	**ratio**
Hydrophilic particles	16.34	52.75	10.15	0.53	0.03	17.62	2.56	0.93
Hydrophobic particles	19.54	46.20	2.90	0.60	0.02	30.41	0.30	0.64
SU8 ridges	1.16	27.44	2.43	2.43	0.14	66.26	0.31	0.02
SU8 / hydrophilic bead ridges	10.77	22.88	3.45	5.29	0.01	55.92	1.66	0.19
SU8 / hydrophobic bead ridges	10.90	32.34	4.93	2.41	0.10	47.57	1.72	0.23

Table 2: Contact angle data of ridge structures fabricated from SU8 and SU8 / bead composite resists

	θ	θ_A	θ_R	$\Delta\theta$
SU8 ridges				
Perpendicular to ridges	102.2°± 3.0°	115.8°± 5.9°	71.4°± 11.6°	44.4°± 11.0°
Parallel to ridges	111.6°± 5.6°	123.4°± 6.9°	88.1°± 4.4°	35.4°± 7.8°
SU8/hydrophobic beads				
Perpendicular to ridges	87.9°± 3.0°	90.9°± 5.6°	36.6°± 3.8°	54.3°± 4.8°
Parallel to ridges	92.0°± 2.5°	95.5°± 3.1°	39.0°± 11.2°	56.4°± 9.5°
SU8 / hydrophilic beads				
Perpendicular to ridges	130.0°± 8.8°	136.5°± 6.3°	98.5°± 20.4°	38.0°± 19.4°
Parallel to ridges	135.2°± 7.4°	140.1°± 9.3°	94.3°± 24.9°	45.8°± 21.7°