Electronic Supporting Information

Perfect polymer interlocking by spherical particles: capillary force shapes hierarchical composite undercuts

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Experimental

Materials

ZnO nanoparticles with a medium size of 100 nm were purchased from Sigma Aldrich (CAS number 1314-13-2). Zinc oxide tetrapods were obtained by employing the newly developed flame transport synthesis by Mishra et al. Victrex® PEEK 450G sheets of 5 mm thickness were purchased from RS Components GmbH and cut into small chips of 20 x 20 mm and about 2.5 mm thickness. PEEK has a melting point of 343 °C, has a decomposition onset temperature of 575 °C and a tensile strength of 98 MPa. For the blood contact test another PEEK was used (PEEK-OPTIMA, Invibio Inc., West Conshóhocken, USA) because of its medical approval. The two-component PDMS elastomer Sylgard 184 by Dow Corning consists of a basis polymer and a cross linker. The given mixing ratio in weight parts is 10:1 and the cured PDMS has a tensile strength of 6.7 MPa. For the contact angle measurements, the solution was thinned down in order to produce very thin layers of PDMS by drop casting and check for a homogenous coating. The thinner used for the silicone elastomer is Q7-9180 Silicone Fluid 1 CST also purchased from Dow Corning. The thinned PDMS had a m/m mixing ratio of 1:50 PDMS elastomer to thinning fluid.

Energy Dispersive X-ray Spectroscopy

The morphology of the surface both before and after coating with PDMS and pulling off have been investigated using a scanning electron microscope (SEM) Carl Zeiss (7 kV, 10 µA). The analysis of the composition of the surface sculptures have been carried out by energy-dispersive X-ray microanalysis (EDX) equipped to the SEM. Chemical analyses by EDX were performed with a Si/Li detector (Noran, Vantage System).

Sample preparation

For adhesion testing of the sculptured PEEK surface, three distinctly different treatments of the samples were applied. As a control untreated PEEK samples were cleaned and cut. To test the impact of a multiscale undercut formation two variations of the particle powder were considered. Firstly, only ZnO nanoparticles were used. Secondly, a treatment was done with a 2:1 weight ratio mixture of ZnO and Al microparticles to provide a second length scale as well as better heat conductivity.

Both powders were applied to the smooth PEEK surface and pressed to form a semi-solid layer of approximately 200 µm thickness. The thickness varied around 100 µm for each sample and depending on the thickness, the duration of the experiment was changed. This particle layer is heated to temperatures above the melting temperature of PEEK, depending on the thickness and the heat conductivity of the samples. PEEK is a very stable polymer and can easily withstand temperatures of 600 °C and above. The temperature is applied via a brass heat element with a diameter of 16 mm and thermal insulation to make manual handling feasible. For pure ZnO powder films temperatures of up to 600 °C were necessary to significantly melt the surface. Due to the heat conductivity of aluminum the temperature for structuring the Al-ZnO-system could be reduced to 450 °C. The heating process can take somewhere between 2-10 seconds, again depending on the thickness of the particle layer and its composition. The melting of the PEEK is clearly visible and was always used as an indicator for the end of the experiment. After sculpturing the remaining, non-embedded micro particles are brushed off with a standard cleaning brush under running water and dried at room temperature.

Adhesion Tests

The area used for the adhesion strength calculation was the overlap area between two PEEK platelets of a maximum size of 2 by 2 cm. Any PDMS which is not covered by PEEK on either side is not taken into consideration. The PEEK plates have then been pressed onto a hot aluminum rod, where they melt and form a strong bond to the rod's surface. The stamps have a length of 25 mm and steel cables attached at the back which have a thickness of 3 mm and eliminate tilting forces. These prepared samples are then structured with one of the sculpturing methods stated above. Before applying the PDMS on the structured surface, the two components are mixed together and degassed to remove all the air bubbles, which would reduce the tensile strength of the PDMS film and thus decrease the adhesion to the sculptured PEEK surface. After mixing and degassing both sides of the respectively sculptured samples were covered with a thin layer of prepolymer and pressed together. Kept in this state they were stored at 80°C for 24 hours to ensure complete polymerization of the PDMS. After the hardening of the PDMS the samples were cooled down to ambient temperature. For the mechanical testing a self-built tensile

testing machine has been used with a maximum force of 500 N. The pulling speed has been set to 0.1 mm/s and the samples have been pulled until fracture. The position over the measured force has been recorded and normalized on the least adhesive area between two samples.

Contact Angle Measurement

To qualify a homogenous coating with very thin layers of PDMS, Al-ZnO-structured samples were coated with only a very thin layer of PDMS by using two differently diluted solutions (one part by weight of curing agent has been mixed with 10 parts of base polymer and further diluted with 5 or 50 parts of thinning fluid respectively) A few droplets of this solution were put onto a sculptured PEEK sample, treated with a 1:1 mixture by weight parts of ZnO and Al. The samples P1-P8 were treated multiple times with the 1:50 PDMS/thinner fluid solution and the samples P9-P11 were treated with 1:5 PDMS/thinner fluid solution. Each treatment consisted of multiple coatings, increasing with the sample number and starting from 1 coating step again for the samples P9-P11. After each treatment the samples were stored in an oven at 80 °C. After the final treatment the sample rested for 24 hours in the oven at 80 °C. The samples P9-P11 showed a thick layer of PDMS after coating, whereas the samples P1-P8 showed no change in appearance after the treatment. The samples were then put into a self-built contact angle machine. A droplet of 50 µL was dispensed on the surface of the samples and multiple images were taken from the side and the angle at the interface between droplet and substrate was measured.

Blood Contact Tests Sample Preparation

For evaluation of the blood adhesion, two sample types have been fabricated. The first sample type is a BAS PEEK sample with a 2 mm thick PDMS coating. The coating also contained 5 w.-% tetrapodal zinc oxide produced by the previously introduced flame transport synthesis[24] to increase the stiffness of the PDMS layer. The top of the sample was covered by a glass slide, to ensure the smoothness of the resulting surface and put into a furnace for 24 h at 80 °C. The second sample was prepared using the previously mentioned silicone thinner in a thinning ratio of 1:50 by weights. The coating was applied by wetting the surface three times and letting it dry after each iteration for one hour at 80 °C.

The silicone was coated on the small medically approved PEEK plates. Before the blood contact tests, all samples were cleaned in an ultrasonic bath in acetone (Carl Roth GmbH + Co. KG, Karlsruhe, Germany), ethanol (70 % denatured, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and distilled water for 5 minutes each. The samples were fixed in a PTFE tank (4.5 cm diameter, 6 cm height, 95.4 cm^3).

The blood was stored in blood collection tubes with heparin (S-Monovette 4.9 ml, Lithium-Heparin, Sarstedt AG & Co. KG, Nümbrecht, Germany). Test medium was human blood, donated by healthy and drug free volunteers in the age of 27 to 55 years. 50 ml blood from one donor was filled into the tank and covered the samples. The tank was placed on a magnetic mixer (M22/1, Franz Morat GmbH & Co. KG, Eisenbach, Germany) with an integrated heating function to ensure a constant temperature of 37 ° C. For 5 minutes a mixing speed of 511 mm/s was adjusted to simulate normal blood flow condition in the aortic valve position. Afterwards the samples were rinsed in a standardized phosphate buffered saline solution (PBS-Lösung ohne CA 2+, MG 2+, Biochrom GmbH, Berlin, Germany). To fix the cells on the silicon, samples were put in a Monit-Graziadei-Solution (2 % glutaraldeyd, 0,6 % paraformaldehyde in 0,1 M cacodylat bufferer, ph 7.2, Institute for Anatomy, University of Lübeck, Germany). For analyzing the specimens with a scanning electron microscope (SEM) a thin gold layer was sputter-coated on the surface. Ten randomized visual fields were chosen from every sample (not including the fringe) of the SEM record. The pictures had a 1.200 x magnification and a size of 92 µm x 62 µm. The number of thrombocytes on each field was counted manually.

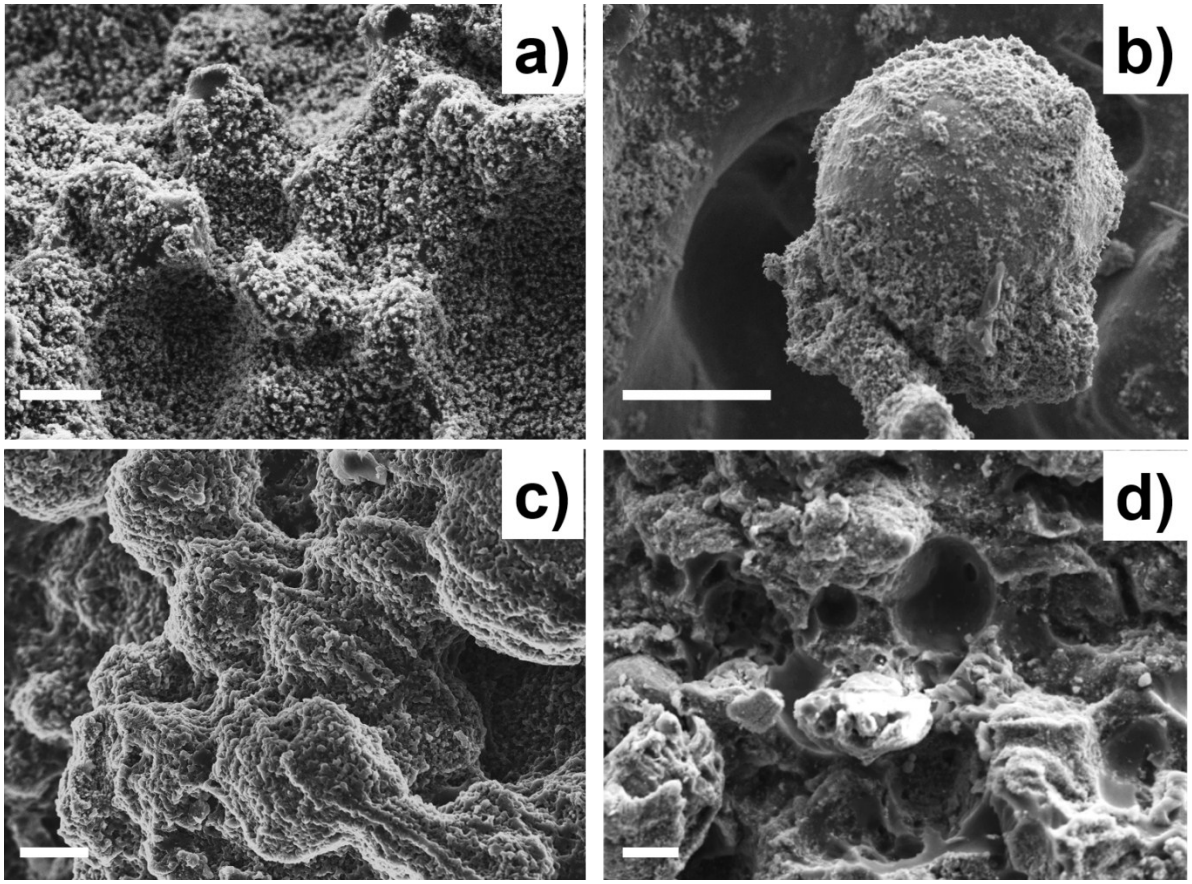

Figure S1 SEM images of various structured surfaces. Simple structures surface with ZnO nanoparticles is shown in a), b) shows a complex undercut structure made from Al and ZnO, c) and d) show the negatives of the samples seen a) and b) after the detachment experiment. The roughness of both samples can be clearly seen.

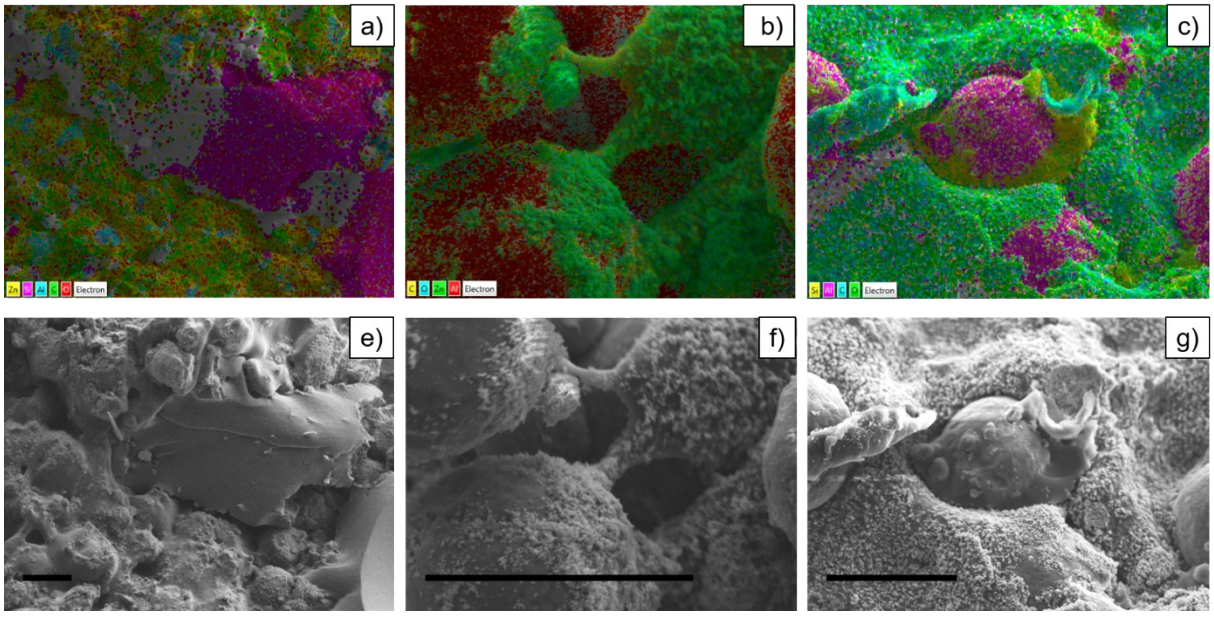

Figure S2 a) and e) show the EDX elemental map and the corresponding SEM image of a complex structured surface with cohesively failed PDMS. b) and f) show PEEK flowed through a dense network of ZnO particles and embed Al micro particles. c) and g) show an Al particle with cohesively failed PDMS around it. The scale bar is 50 µm

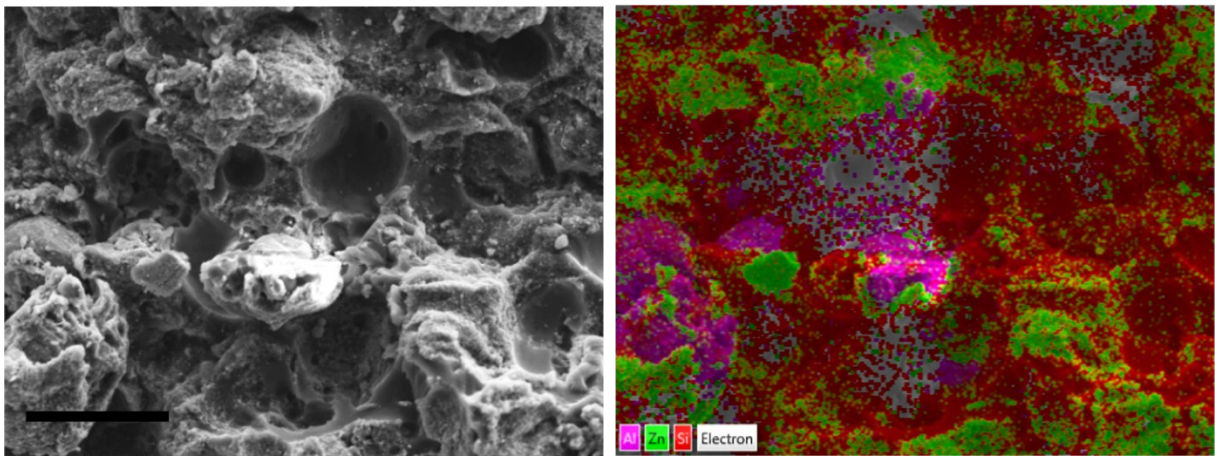

Figure S3 SEM image and EDX elemental map of a PDMS surface after detachment from a complex structured PEEK surface. Cohesively failed, flat PDMS parts can be seen as well as Al and ZnO particles detached from the PEEK.

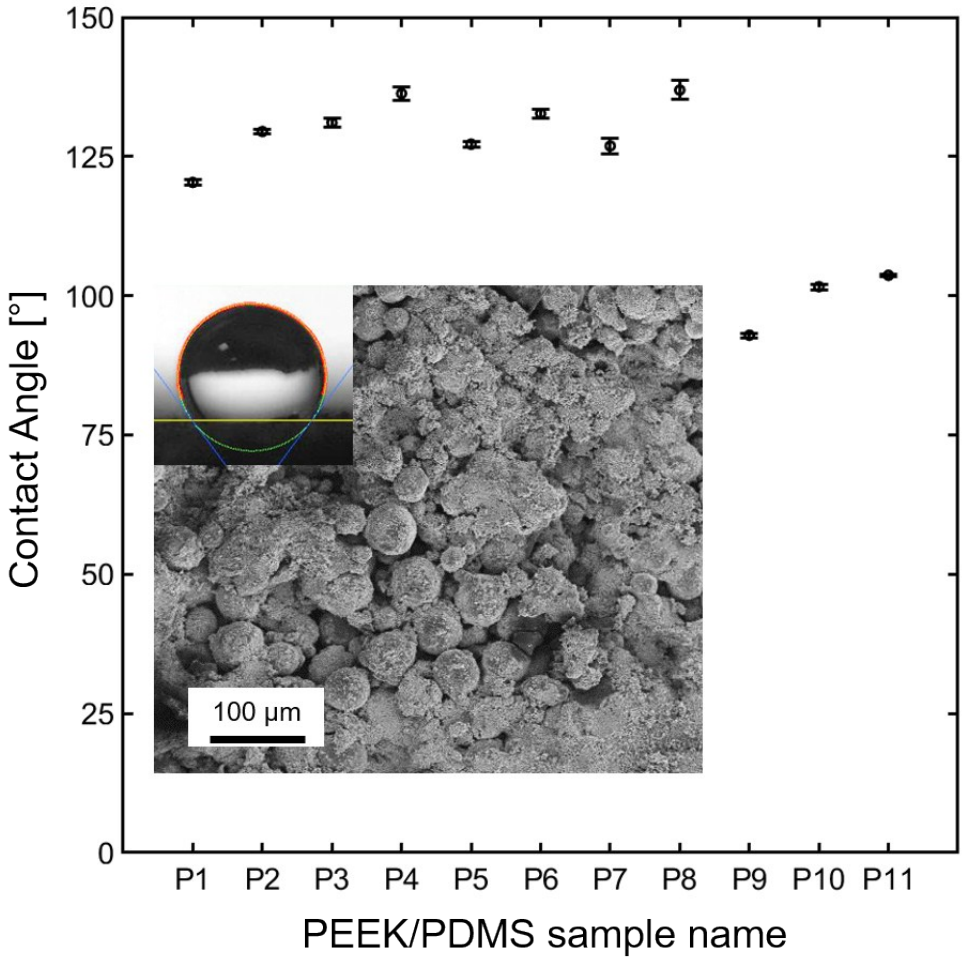

Figure S4: The contact angle in dependency of the thickness of the PDMS coating is shown. The inset shows the surface of a hierarchically structured sample and an exemplary image of a contact angle measurement on the coated surfaces.