Supporting Information

Biomimetic Soft Polymer Microstructures and Piezoresistive Graphene MEMS Sensors using Sacrificial Metal 3D Printing

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Effect of acidic treatment on swelling and surface texture of PDMS

Step IV of the processing methodology described in the paper consists of ultrasonic acidic etching of the 3D-printed metallic mold to release the cured PDMS structure. Experiments were conducted to ensure the compatibility of the acidic solvent with PDMS. Three PDMS samples (10 mm × 10 mm × 3.5 mm) were ultrasonically agitated in the acidic solvent (5 wt. % $FeCl_3$, 20 wt. % HCl, balance H_2O) for 4 hours at a temperature of around at 50 °C after which they were rinsed in water and air-dried. To investigate any potential swelling of PDMS in the acidic solvent, the samples were weighed on a scale (least count 10^{-4} g) before and after the acidic treatment. No detectable weight change was observed after 4 hours of acidic immersion in any of the three tested samples, indicating that the acidic etching did not cause any swelling of the PDMS sample. This was consistent with the findings of Lee et al. (Ref. [52] in the main paper) who also reported the compatibility of PDMS in hydrochloric acid. Further, scanning electron microscopy (Philips ESEM-XL30) was conducted on the PDMS surface to investigate any surface degradation. As shown in Fig. S1, the acidic treatment did not cause any significant damage to the surface. Moreover, to the naked eye, the PDMS samples maintained their characteristic transparency even after the treatment.

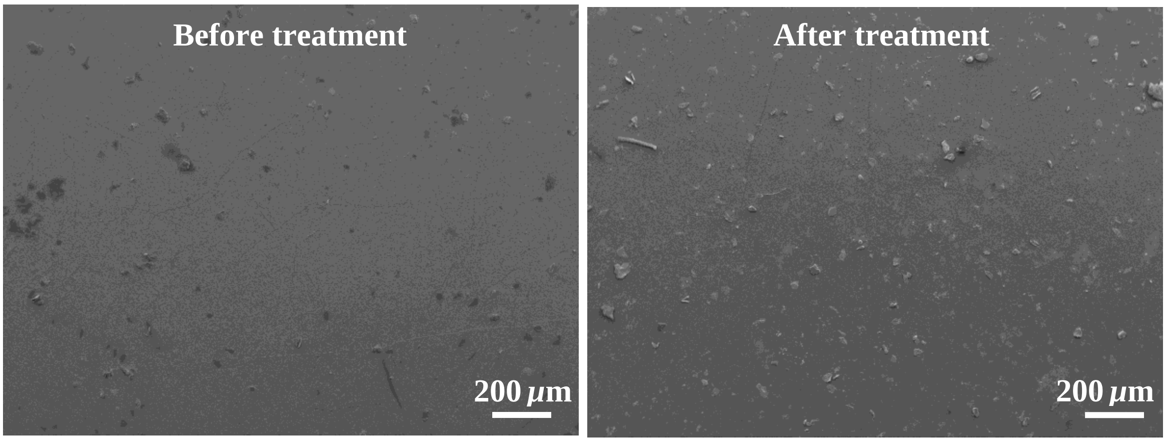

Figure S1. Effect of acidic immersion on PDMS surface (SEM images, 50× magnification).

Effect of acidic treatment on the mechanical properties of PDMS

To investigate the effect of the acidic treatment on the mechanical properties of PDMS, two types of mechanical tests were conducted on treated and untreated samples. The acidic treatment was the same as that described in Section S1.

Uniaxial tensile test

Uniaxial tensile tests were performed using a micromechanical tester (Kammrath & Weiss GmBH). The dog bone-shaped PDMS tensile samples, 11.5 mm in gauge length and 3.5 mm × 3.5 mm in cross-section, were casted out of a 3D-printed mold and strained at a rate of 0.17 %/s till a strain of 80%. The tests were performed on three untreated samples and three treated samples. A representative stress-strain curve from the tensile test is shown in Fig. S2a.

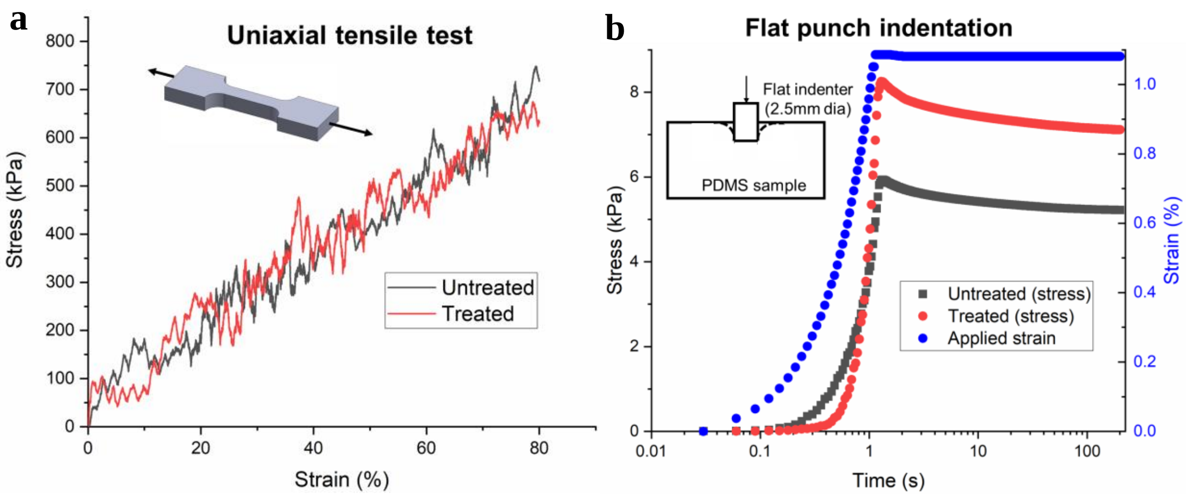

Figure S2. Effect of acidic treatment on mechanical properties: a) uniaxial tensile test, and b) flat punch indentation test to calculate stress relaxation modulus.

Stress relaxation tests using flat punch indentation

Rectangular PDMS blocks (10 mm × 10 mm × 3.5 mm) were subjected to flat punch indentation tests using a cylindrical steel rod (2.5 mm diameter). In contrast to the uniaxial tensile tests, the flat punch indentation test allowed us to probe the surface properties of the PDMS samples for low strains (~ 1%). The custom-built low load compression testing (LLCT) apparatus (Sharma et al. 2011, doi: 10.1016/j.exer.2011.08.009) enabled us to control the indentation depth and measure the resulting compression force. The indentation strain (defined as the ratio of the indentation depth to the sample thickness) was set to 1.08% (~ 350 µm) and was maintained at this value for 200 seconds during which the PDMS sample displayed stress relaxation behavior owing to its viscoelasticity. The Young's relaxation modulus was monitored and compared at the end of 200 seconds for the treated and untreated samples, with five stress relaxation tests performed per sample. A sample stress-strain curve from the stress relaxation test is shown in Fig. S2b.

Results

As shown in Table S1, the Young's modulus measured by the tensile test was more or less identical for both the untreated and treated samples. On the other hand, the relaxation modulus (at the end of 200 seconds) measured in the flat punch test increased by 34% (from 480±47 kPa to 645±150 kPa) after the acidic treatment, indicating that the acidic treatment enhanced the surface hardness of the PDMS samples without affecting the bulk properties. It must be noted that for the sensing application proposed in our paper, the bulk properties of PDMS were more important than the surface properties, since the sensing elements (i.e. graphene piezoresistors) were located inside the sensing structures. We thus conclude that the acidic treatment did not cause any mechanical deterioration of the PDMS samples.

Table S1. Effect of acidic treatment on mechanical properties (bulk and surface)

	Before acidic treatment	After acidic treatment
Young's modulus (tensile test)	862±55 kPa	849±26 kPa
Stress relaxation modulus (flat punch indentation)	480±47 kPa	645±150 kPa

Printing multi-material structures using the proposed method

The processing methodology (Fig. 1 in the main text) can, in general, be extended to the fabrication of multi-material polymeric microstructures with different properties (e.g. density, Young's modulus, etc.) in different locations as illustrated for a representative case in Fig. S1 below. The mold is designed and 3D-printed to fabricate an array of three thin pillars (aspect ratio = 50) with a thick base for handling the structure. Each pillar cavity is filled with a different polymer and degassed sequentially. Curing can be conducted after filling polymer 3 or separately after each individual filling step, depending upon whether the curing recipes for polymers 1-3 are similar or different. After polymers 1-3 are cured, the base is filled with a different polymer and cured. Finally, the metal mold is etched away to obtain the multi-material polymeric microstructure comprising four different polymers. This method can be used to develop structures in castable polymers such as PDMS, hydrogels, liquid crystals, polymethylmethacrylate (PMMA), and various types of silicone-based polymers such as polydimethylsiloxane (PDMS).

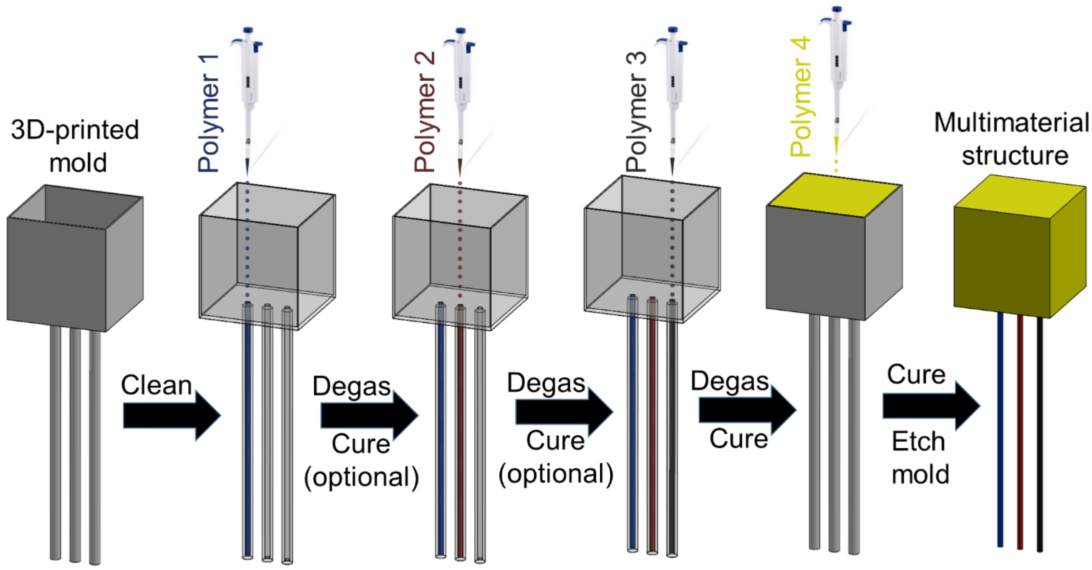

Figure S3. Multi-material polymer structure fabrication workflow.

Calibration of mini shaker dipole

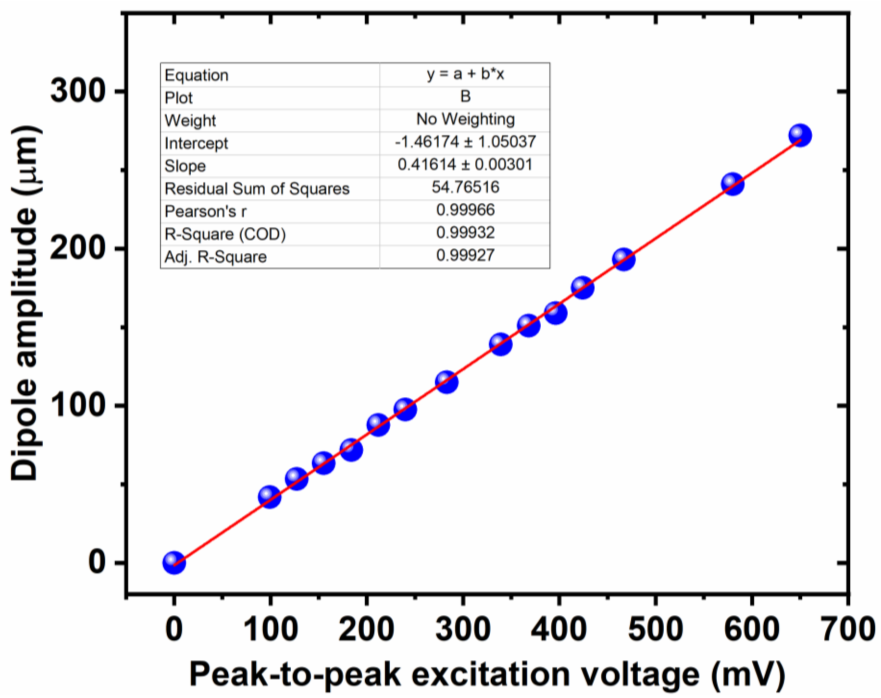

Figure S4. Calibration data of the mini shaker dipole setup using laser doppler vibrometry at a gain of 10 dB and an oscillating frequency of 35 Hz.

Integration of MEMS force sensor into electric shaver head

The MEMS force sensor was integrated into the Philips 9000 series electric shaver head between the three rotary cutters. The sensor was electrically connected to copper tapes (Fig. S3) via conductive silver epoxy (EPOTEK H20E, Epoxy Technology Inc., USA) and was affixed to the base by dispensing polymer glue that also acted as insulation between the conductive electrodes. Finally, the circumference of the dome was lined with a thin layer of PDMS to make the sensor waterproof. The sensor electronics did not impede the operation of the shaver cutters. The ends of the copper tapes were subsequently connected to a resistance measurement circuit, either a Wheatstone bridge or a digital multimeter (Keysight U2741A) to monitor the sensor resistance in real time during shaving.

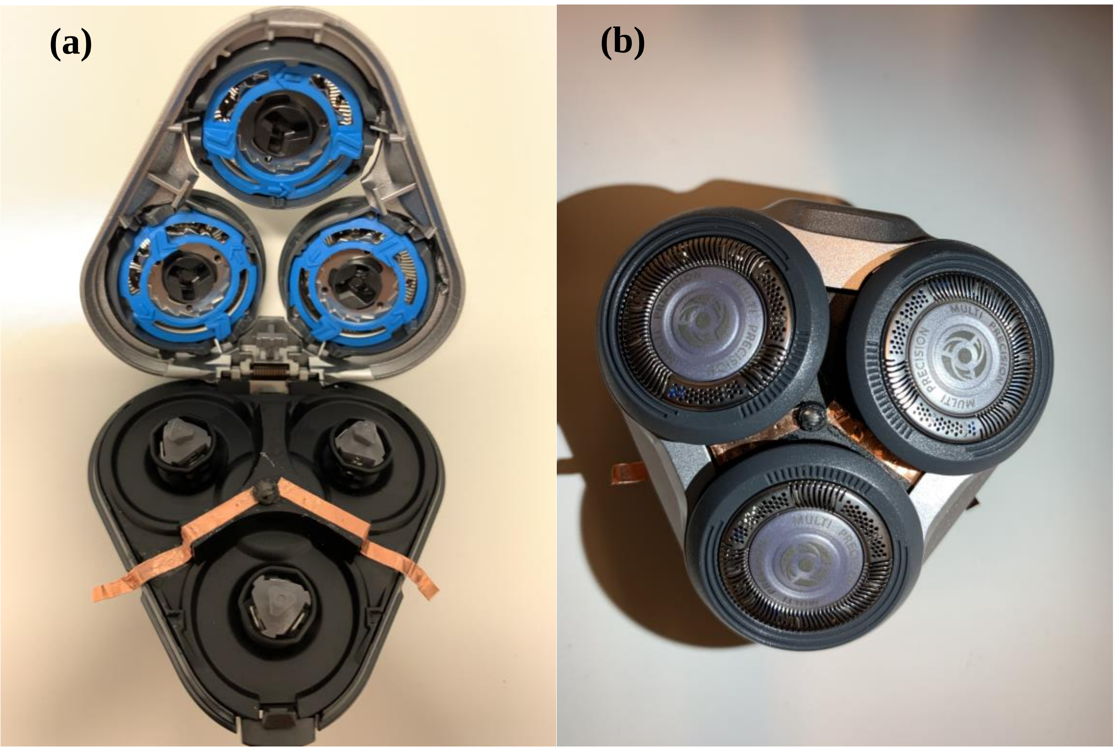

Figure S5. Integration of MEMS force sensor into Philips 9000 series shaver head. (a) Shaver cap opened for setting up sensor circuitry and bonding sensor to the shaver head. (b) Shaver cap closed for normal operation with ends of copper tapes sticking out for connection to Wheatstone bridge circuit.