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Making Honeycomb Microcomposites by Soft Lithography[**]

By *Bing Xu*, *Francisco Arias*, and *George M. Whitesides*[*]

This paper reports the use of soft lithography to fabricate honeycomb microcomposites, and describes an initial, qualitative study of failure in these microstructures. A honeycomb composite consists of a honeycomb-shaped structure (the core) sandwiched between two sheets of high tensile material, such as organic polymer, paper, or aluminum (the face sheets).[1] Macroscopic honeycomb composites exhibit excellent mechanical strength and provide high strength-to-weight ratios: the honeycomb core offers structural support to the laminate layers, and its open structure contributes a low weight to the composite. To maximize the strength-to-weight ratio, cores usually have a high aspect ratio, and face sheets are thin compared to the thickness of the cores. For structures with a given weight, honeycomb composites provide high impact resistance, high fatigue resistance, tuned damping, and resilience.[1] The applications of honeycomb composites with macroscopic dimensions are broad, and include components of air and space vehicles (where low weight is required for structural components),[2] sports equipment, component of safety features of automobiles, heat exchangers, and seismic retrofits.[1]

Small structures of new types—microelectromechanical systems (MEMS), high performance components of disk drives, microrobots, and small air vehicles—are creating a need for small structures tuned in terms of moduli and vibrational damping that are as sophisticated as the highly developed composite macrostructures, but that involve features too small to be fabricated economically by the methods used historically for composites. The current method for fabricating honeycomb microstructures is anisotropic etching of Si.[3] This method is very successful for silicon, but has limitations—long processing time, cost—when applied to other materials.

The method described here for the fabrication of honeycomb microcomposites—soft lithography[4]—has a number of advantages: It can be applied directly to a wide range of materials, including polymers and ceramics (by sol-gel methods); it provides a route to complex metallic microstructures, when combined with electrochemistry; it supports the fabrication of high aspect ratio ($<$ 1:15) structures (which have, in the past, been accessible primarily by synchrotron-based LIGA (lithography, galvanoforming, and molding), an expensive process) when SU-8 (MicroChem Corp.), a negative photoresist for thick structures,[5] is used; and it also allows rapid turn-around when rapid prototyping[6,7]—a generally applicable technique, provided the feature sizes are > 20 μm—is used in the fabrication of test structures. Here we illustrate the fabrication of honeycomb microcomposites that are made of polymers or metals using soft lithography; extension of this procedure to other types of microcomposites is straightforward.

We constructed honeycomb microcomposites using the following design criteria: First, the face sheets should be thick enough ($>$ 20 % of the thickness of the composite) to withstand the stresses induced by plausible tensile loads. Second, the core should be thick enough and have sufficient shear modulus to prevent overall buckling. Third, the core cell should be sufficiently small to prevent intercell buckling. We used these general guidelines in the design of honeycomb microcomposite, although the structures reported here have not been optimized for any particular application.

Figure 1 illustrates the procedure used to fabricate honeycomb cores. We used rapid prototyping and photolithography to fabricate a honeycomb master made of thick (200–700 μm) negative photoresist (SU-8). This honeycomb pattern was designed using a personal computer and printed onto a transparent sheet with a commercially available, high-resolution printer. The resulting print was used for contact photolithography.[8] The masks can have line widths in the range of 25–150 μm; we used cell sizes in the range of 200–1000 μm. Photoresist layers with thickness from 200 to 700 μm were spin-coated on silicon wafers. We were able to obtain honeycomb grids with an aspect ratio of 1:15 and height up to ~700 μm with a single cycle of coating, exposure, and development.

We fabricated both polymeric and metallic honeycomb cores. For the polymeric honeycomb cores, we used two soft lithographic techniques—microtransfer molding (μTM)[9,10] and microembossing[11]—because they are compatible with a variety of polymers. We made stamps for the fabrication of polymeric honeycombs by casting and curing polydimethyl-

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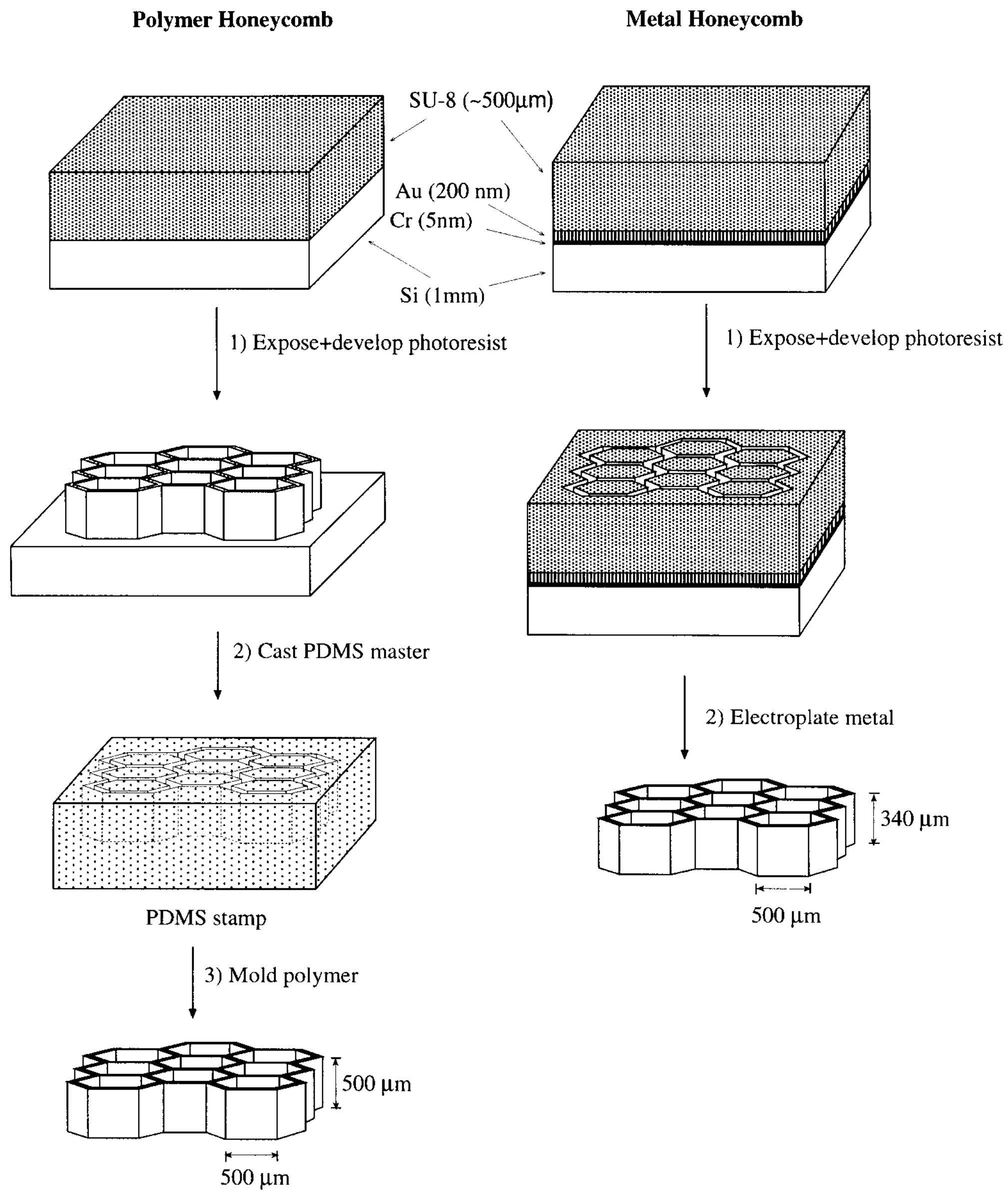

Fig. 1. Schematic representations of the processes employed to fabricate the honeycombs.

siloxane (PDMS) against patterned SU-8 photoresist. When the PDMS mold was used in μTM, we made its thickness < 5 mm to ensure its flexibility; flexibility is important for conformal contact between the stamp and the supporting substrate of the molds. A drop of liquid prepolymer (UV-curable polyurethane; NOA 73, Norland Products) was placed on the patterned surface of the mold, and the excess prepolymer was removed by scraping it away with a piece of flat PDMS. The filled mold was then placed in contact with a substrate (e.g., a glass slide). Exposure to UV light (Type 7825-34, Canrad-Hanovia 450 W medium-pressure, Hg vapor lamp) for 30 min cured the prepolymer. Figure 2a shows a polyurethane (PU) honeycomb made by using μTM.

Microtransfer molding works only with liquid prepolymers. In order to apply soft lithography to thermoplastic polymers, we used microembossing, with the PDMS stamp as a pattern transfer element. Figure 2b shows a honeycomb in polyvinylidene difluoride (PVDF), made by using microembossing. The PDMS stamps and PVDF pellets (Aldrich, M_w = 180 000) were heated above 250 °C, compressed using pressure (8×10^4 Pa), and then cooled to room temperature. After cooling, separation of the PVDF and the PDMS stamp yielded honeycomb structures with a thin layer (90 μm) of PVDF that served as the facing sheet layer.

Since the SU-8 photoresist becomes a cross-linked epoxy polymer after exposure, it is also possible to make polymeric microstructures or microdevices directly from SU-8. Figure 2c shows an epoxy honeycomb made of SU-8. Initially, we used NaOH (15 %, aqueous) or HF solution to release the honeycomb structures from a silicon wafer. Such processes are time-consuming and require caustic chemicals. Thus, we have developed an alternative process to create a freestanding honeycomb core using PDMS as a sacrificial layer: First, a film of PDMS (5–10 μm) was spin-coated on a silicon wafer and cured at 80 °C. Second, SU-8 photoresist was spin-coated on top of the PDMS film. Third, the SU-8 was exposed and developed in propylene glycol methyl ether acetate (PMEGA), and the honeycomb structure was peeled off the silicon wafer (which is reusable). Finally, immersion of the epoxy/PDMS bilayers in tetrabutylammonium fluoride (TBAF) solution (1.0 M in THF) for 10 min dissolved the PDMS backing and yielded a freestanding honeycomb structure. The combination of SU-8 and rapid prototyping has the advantage that many types of structural designs for microcomposites, especially complicated ones, can be tested simply and rapidly. Figures 2d and 2e show two variations of

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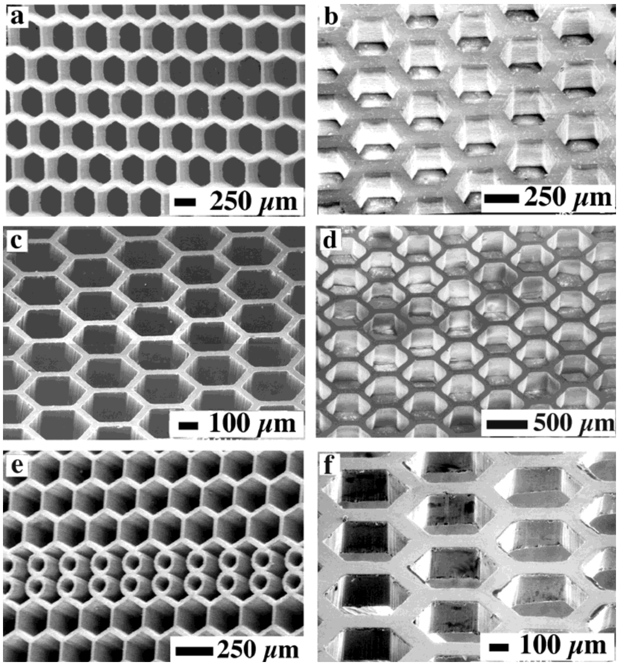

Fig. 2. SEM images of honeycombs. a) PU honeycombs with line width of 50 μm and height of 222 μm. b) PVDF honeycombs with line width of 118 μm and height of 400 μm. c) Epoxy honeycombs with line width of 61 μm and height of 660 μm. d) PVDF honeycombs with curved cell walls, line width 110 μm, height 430 μm. e) Epoxy honeycombs connected by circles, with line width of 50 μm and height of 300 μm. f) Nickel honeycombs made by electroplating, with line width of 110 μ and height of 280 μm.

honeycomb structures made by rapid prototyping. We believe that it will be possible to tune the properties of the honeycombs by the incorporation of structures with different and appropriate geometry.

For some applications, we wished to have metal honeycombs, since metals have high Youngs modulus (and can therefore withstand high tensile loads) and high thermal/oxidation stability. To fabricate metallic honeycomb cores, the photoresist (SU-8) was patterned, using the mask generated from rapid prototyping, on a thin film of gold (200 nm thick) supported on a silicon wafer. Nickel or copper was electroplated on the exposed gold. Maintaining a low current density (10 mA/cm^2) ensured a smooth texture to the electroplated nickel, but required long deposition times. For the nickel honeycomb core shown in Figure 2f, a small circulation pump in the electroplating bath decreased the influence of mass transport on the kinetics of electroplating. This structure, with a height of ~340 μm and area of 50 cm^2, still required 90 h in the electroplating bath. The long electroplating time and the low current density are also necessary for obtaining nickel with good mechanical properties. We used a similar process and time to make copper honeycomb cores with height of ~300 μm.

After the successful fabrication of honeycomb cores, we made the microcomposites by bonding the honeycomb core and the face sheets with adhesives. We prepared the final polymeric honeycomb composites (Fig. 3b) by gluing an epoxy polymer honeycomb core (made from cross-linked SU-8) to PVDF face sheets (made by pressing PVDF pellets). We used epoxy (S-208, Devcon Consumer Products) as an adhesive (with thickness ~5 μm). This process should be applicable to a wide range of polymeric materials.

For nickel microcomposites, we used a layer of solder (Pb/Sn = 80/20, m.p. ~350 °C) to connect the face sheets and core. A 25 μm thick layer of solder was electroplated[12] on the nickel face sheets (25 μm, Alfa). This process required 50 min at a current density of 10 mA/cm^2. Under an inert atmosphere, the nickel honeycomb core and nickel face sheets were heated in contact with one another (pressure 8×10^4 Pa) at 320 °C for 1 h. Figure 3a shows the nickel honeycomb composite obtained in this process. We also used a liquid bonding process to fabricate copper microcomposites: a thin layer of tin (~4 μm) was electroplated on the copper face sheets (25 μm, Alfa) at 10 mA/cm^2 for 10 min, and heated with a copper honeycomb core at 300 °C in an oven. The resulting Cu/Sn alloy acted as the bonding layer.

These examples demonstrate the fabrication of polymeric and metallic microcomposites, with cell size in the range of 100s of μm to mm. Electroplating, combined with soft lithography, provides procedures that generate metallic microstructures conveniently, although with the current disadvantage of long electroplating time for structures with height > 300 μm. The rapid prototyping procedure[6,7] is suitable for the design and test of prototype microcomposites since it is an excellent pattern-generating tool, it is compatible with the required sizes of the structures, and it can very easily vary the cell size and shape to tune properties. The application of PDMS to microembossing provides a versatile tool for the fabrication of thermoplastic materials.

We have also initiated qualitative study on modes of the failure of these honeycomb microstructures. The epoxy honeycomb structures were chosen for bending tests: Figure 4 shows a schematic representation of bending tests, and summarizes representative results. The honeycomb plates were supported on both ends, and a force was applied in the middle of the structures (over an area of ~20 mm^2). A honeycomb core with l = 20 mm, w = 14 mm, h = 0.6 mm broke when the force (130 g) was 1.6×10^3 times larger than the weight of the honeycomb (81 mg). The corresponding microcomposite (l = 20 mm, w = 12 mm, h = 0.8 mm, and PVDF as face sheets), broke when the force (2.1 kg) was 8.8×10^3 times larger than the weight (238 mg) of the microcomposite. With 125 μm polymethylmethacrylate (PMMA) as the face sheets, the composites (l = 20 mm, w = 13 mm, h = 0.85 mm, 165 mg) broke when the applied force (1.9 kg) was 1.2×10^4 times over the weight of the composite. In the latter experiment, the honeycomb composite first slightly deformed, then adhesion began to fail, the face sheet debonded partially from honeycomb core, and the core then broke at the region bearing the force. This result reinforces the fact that bonding is critical to achieving a high strength-to-weight ratio. Although these tests are qualitative, they suggest that honeycomb microcomposites, made using soft lithography, are promising materials for applications in mi-

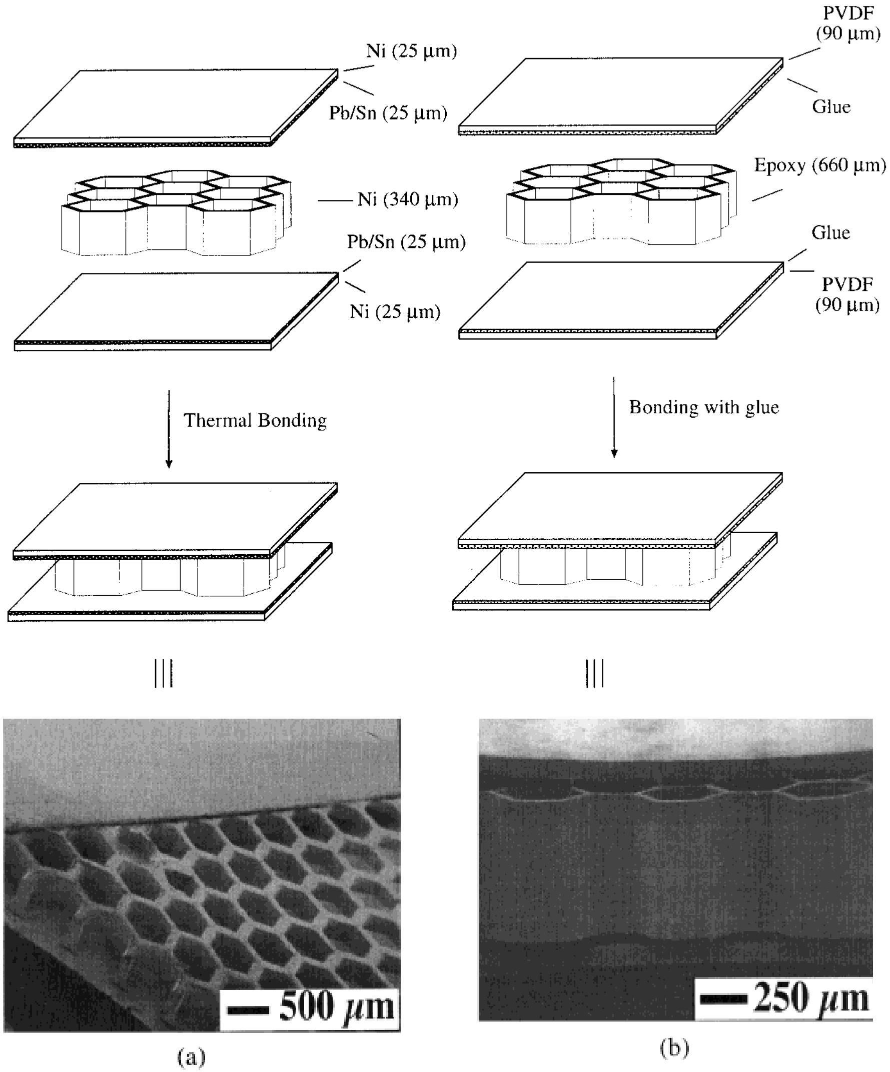

Fig. 3. Preparation and SEM images of honeycomb microcomposites. a) Ni/PbSn/Ni/PbSn/Ni honeycomb composite, top view. b) PVDF/epoxy/PVDF honeycomb composite, side view.

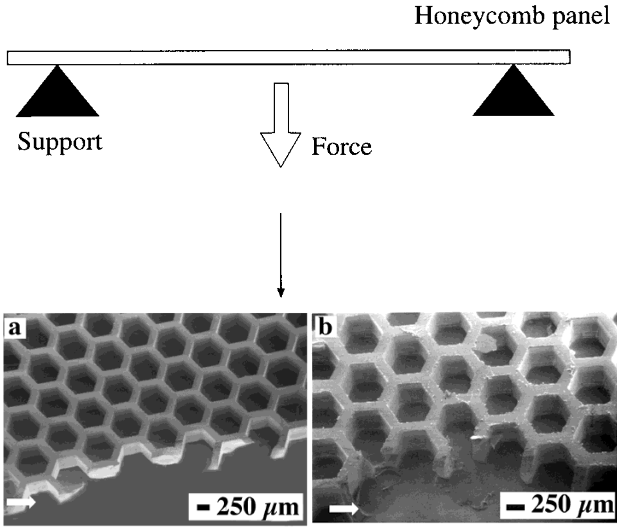

Fig. 4. Set-up for bending test and the results: a) The broken edge of a honeycomb core (there was no face sheet when the force was applied). b) The broken edge of a honeycomb core (there were face sheets when force was applied). The arrows indicate the approximate line of fracture.

crodevices when a high ratio of strength to weight is needed. We are currently extending soft lithography to other types of microcomposites and performing detailed mechanical studies on those microcomposites.

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