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Polymer-filled macroporous hydrogel for low friction

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ABSTRACT

This paper demonstrates that macroporous hydrogels, filled with mobile polymer chains, markedly reduce friction. We fabricate a macroporous hydrogel by freeze and thaw, soak the macroporous hydrogel in an aqueous solution of mobile polymer chains, and slide the polymer-filled macroporous hydrogel against glass. The polymer-filled macroporous hydrogel reduces friction compared to a neat hydrogel with or without mobile polymer chains, and to a macroporous hydrogel with water (no mobile polymer chains). Furthermore, the polymer-filled macroporous hydrogel maintains low friction after long-time sliding. The polymer-filled macroporous hydrogel mimics a division of labor between the pores and mobile polymers in a synovial joint. Both the mobile polymer chains and the macropores contribute to low friction.

Low-friction hydrogels are essential to many applications, including contact lenses [1], implants [2], medical devices [3], joint replacements [4,5], and artificial tissues [6,7]. The low-friction hydrogels protect biological tissues from damages during repetitive contact, deformation, and slide.

The development of low-friction hydrogels has long been inspired by a salient example in nature: the synovial joint [8]. In the synovial joint of an animal, the low friction depends on two characteristics—pores in the cartilage and synovial fluid [9–11]. The latter is an aqueous solution of long, mobile polymers, stored in the pores of the cartilage and in the joint cavity. The synovial fluid stabilizes a hydration layer, between the articular cartilages in contact, under normal and tangential forces [12,13].

Existing approaches to the development of low-friction hydrogels often mimic either the pores or the mobile polymer chains of the synovial joint, but rarely both. One approach lubricates the surface with an aqueous solution of mobile polymer chains [14–17]. This approach requires the materials to be immersed in the polymer solution, and is inapplicable in most applications. A second approach produces a polymer brush on the hydrogel surface [18,19]. The brush creates a hydration layer, but wears off after long-time sliding. A third approach makes all polymer chains in the hydrogel network capable of creating the hydration layer [20,21]. As old dangling chains wear off, new dangling chains generate from the hydrogel network. When the main chains of the hydrogel network or short side chains are used to generate dangling chains, the length of the dangling chains is comparable to the mesh size of the hydrogel. This approach leads to a conflict: a network of short chains is needed for high stiffness, but a network of long chains is needed to generate long dangling chains. A fourth approach makes porous hydrogels to lower friction, but the pores are not filled with mobile polymer chains [22,23]. In a fifth approach, mobile polymer chains are blended in a hydrogel, but the presence and importance of pores in the hydrogel have not been studied [24,25].

Here we design experiments to show that, like a synovial joint, a low-friction hydrogel requires both pores and mobile polymer chains (Fig. 1). In a polymer solution, a mobile chain can explore the space in the solution. In a polymer network, a mobile chain intertwines with the polymer network, but can still move through the mesh of the polymer network by the process of reptation [26]. To enable this mobility, we choose polymer chains that do not adhere to the polymer network of the hydrogel. To mimic the hydration lubrication mechanism of a synovial joint, the polymer chains are selected to carry charges to have strong interaction with surrounding water molecules [27,28]. We fabricate a macroporous hydrogel by freeze and thaw, soak the macropores hydrogel in an aqueous solution of mobile polymer chains, and characterize friction of the polymer-filled macroporous hydrogel against glass. The polymer-filled macroporous hydrogel reduces friction compared to a neat hydrogel with or without mobile polymer chains, and to a macroporous hydrogel with water (no mobile polymer chains). The polymer-filled macroporous hydrogel retains low friction after long-time sliding. Our experimental observations support the hypothesis that the combination of mobile polymer chains and macropores contribute to low friction.

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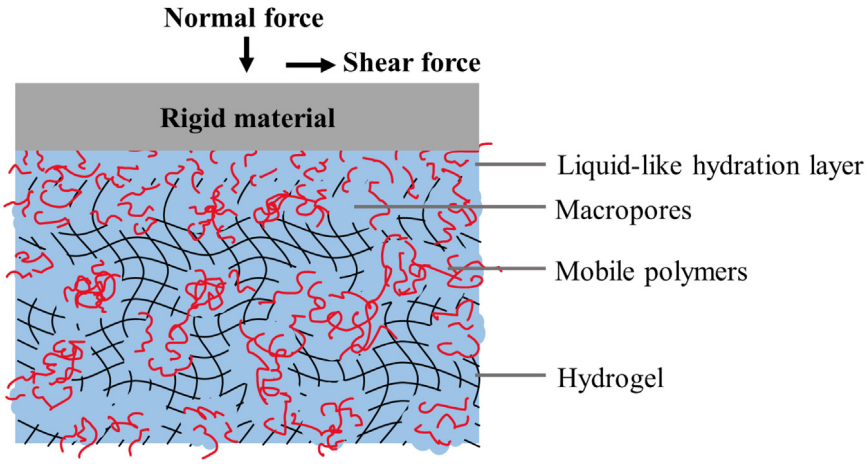

Fig. 1. A polymer-filled macroporous hydrogel reduces friction against a rigid material under normal and shear forces. Between the hydrogel and the rigid material, the mobile polymers stabilize a liquid-like hydration layer. The macropores store mobile polymers and may play a role to maintain long-term low friction.

We fabricate a polymer-filled macroporous hydrogel as follows (Fig. 2). We pour deionized water into a glass mold, and add 135.2 g of monomer acrylamide (AAM, sigma-aldrich, A8887) for each liter of water. We then add each of the other ingredients with a weight ratio relative to AAM: 0.0006 of the crosslinker N, N′-methylenebisacrylamide (MBAA, sigma-aldrich, M7279), 0.0025 of the crosslink accelerator tetramethylethylenediamine (TEMED, sigma-aldrich, T7024), and 0.007 of initiator ammonium persulfate (APS, sigma-aldrich, A9164). The resulting precursor is an aqueous solution of small molecules. We cure the precursor in a freezer with temperature held at −20 °C for 12 h [29]. Ice crystals grow in the precursor solution and expel the reactants into the surrounding space, where monomers link into polymer chains, and polymer chains crosslink into a polymer network. Upon thaw in the ambient condition, the ice crystals melt, and a system of connected macropores form in the hydrogel. The size of the pores (black areas) is around 50 μm, observed through optical microscope (Fig. 2f). Although we do not check the connectivity of the pores, according to the synthesis method described in the literature [29], these pores are indeed interconnected. We then soak the macroporous hydrogel in an aqueous solution of a species of mobile polymer chains for about 12 h. The initial size of the as-prepared macroporous hydrogels is 2 cm × 2 cm × 0.3 cm. This size becomes 3 cm × 3 cm × 0.5 cm after soaking for two hours and does not change after 12 h. At this state, the polymer chains fill all the pores in the same concentration and also some of them diffuse into the hydrogel. Therefore, we regard soaking macroporous hydrogels any time beyond two hours as the equilibrium condition. Water content changes before and after soaking, all as-prepared hydrogels have a water content of ∼88 wt%. After soaking, the hydrogel swells, and the water content becomes ∼96 wt%. It is known that the water molecules in the hydration layer are firmly attached to the charges they surround and cannot be easily squeezed out under compression but still maintain fluidity in response to shear, thus giving rise to hydration lubrication and reduced friction [27,28]. Therefore, we select two species of polyelectrolytes: a polyanion (alginate, FMC Corporation, G0311401), a polycation (chitosan, Carbosynth, OC289001499; Polysciences, Inc., 21161; Sigma-aldrich, 419419), and a nonelectrolyte (polyacrylamide, Sigma-aldrich, 92560; 738743; 749222) is also included as a control.

We begin the study using alginate-filled macroporous hydrogels (1 wt% alginate with Mw ∼170–240 kDa). For comparison, we prepare water-filled macroporous hydrogel, neat PAAM hydrogels (no macropores) using the same precursor but cure at room temperature for 12 h, and neat hydrogels containing alginate chains (no macropores) by adding 1 wt% alginate into the same precursor and then curing the mixture at room temperature for 12 h.

We characterize friction using a rheometer (HR-3, TA Instruments). A sample of the hydrogel (3 cm × 3 cm × 0.5 cm) is adhered to a polyester sheet (McMaster-Carr, 8567K22) using a commercial glue (Elmer's Original Crazy Super Glue). We then fix the polyester sheet on a steel substrate using a double-sided adhesive tape (3M Scotch). We bring a diameter of 20 mm glass plate (attached on the geometry by using double-side tape) in contact with the hydrogel under a normal force W, and then rotate the glass plate with an angular velocity ω (Fig. 3a). This experimental setup is convenient to operate, but leads to inhomogeneous sliding velocity. Following a common practice, we calculate the friction force F by [30]

$$F = \frac{4T}{3R},$$

where T is the torque measured by the rheometer and R is the radius of the contact area. The frictional coefficient μ can be generally written as $\mu = \mathrm{F/W}^{\alpha}$, where the scaling exponent α is in the range of 0–1.0, depending on the properties of hydrogels themselves and the sliding materials, e.g., the chemical structure, charge density, water content, crosslink density of hydrogels, as well as surface properties of opposing substrates [8,30]. Here, we do not explore how the chemical structure of the hydrogel determines the value of α, and we simply choose $\alpha = 1$ for all hydrogels. The frictional coefficient is calculated by [30]

$$\mu = \frac{F}{W} = \frac{4T}{3RW}.$$

The pressure is calculated by $W/\pi R^2$.

At a fixed angular velocity of 0.1 rad/s, the frictional coefficient of the alginate-filled macroporous hydrogel decreases from 0.139 to 0.008 when the pressure increases by three orders of magnitude (Fig. 3b). The frictional coefficient is inversely proportional to the normal pressure. At a same angular velocity, as the normal pressure increases, the frictional coefficient decreases. The frictional coefficients of the alginate-filled macroporous hydrogel are about one order of magnitude lower than those of the neat hydrogel and the water-filled macroporous hydrogel at various pressure levels.

We also measure the frictional coefficient at various angular velocities and at a fixed pressure of ∼7.5 × 10^4 Pa (Fig. 3c). In the range of 0.1–10 rad/s, the frictional coefficients of the

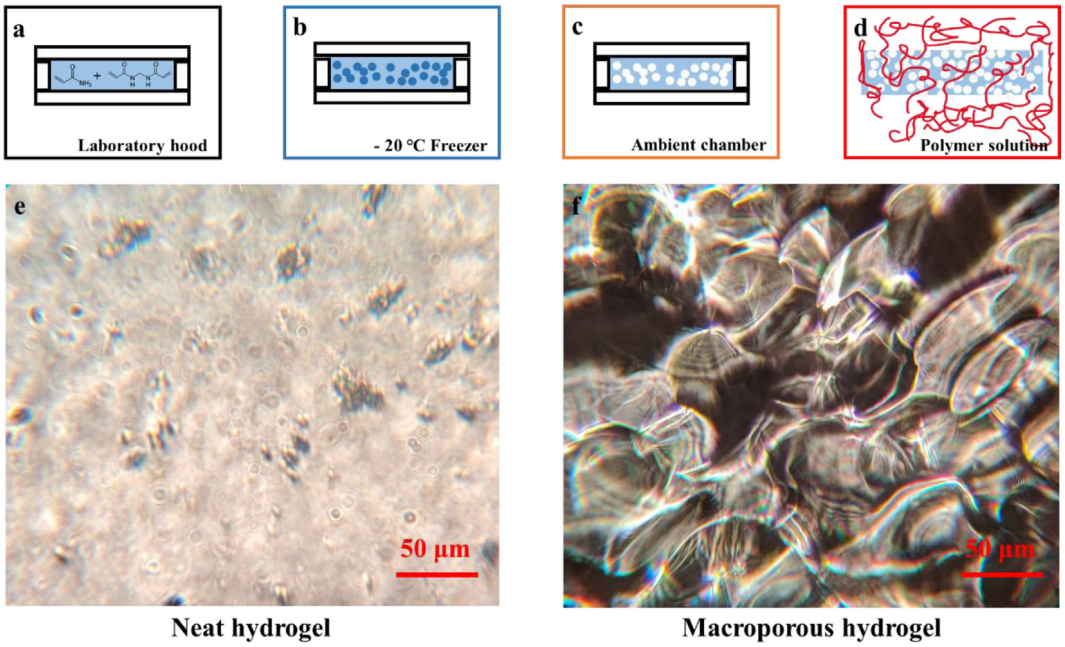

Fig. 2. Fabrication of the polymer-filled macroporous hydrogel. (a) Precursor of the hydrogel is an aqueous solution of small molecules, and is prepared in a glass mold. (b) The precursor is cured in a freezer for 12 h at −20 °C. Ice crystals grow in the precursor and expel the reactants, so that the polymer network of the hydrogel forms outside the ice crystals. (c) The hydrogel is thawed in the ambient. The ice crystals melt, and the hydrogel forms a system of connected macropores. (d) The macroporous hydrogel is soaked in an aqueous solution of mobile polymers, so that the mobile polymer chains permeate throughout the macropores and the network in the hydrogel. (e) Optical microscopic image (Olympus IX-71) of a neat hydrogel prepared using the same precursor by cured for 12 h at room temperature; (f) Optical microscopic image (Olympus IX-71) of a macroporous hydrogel.

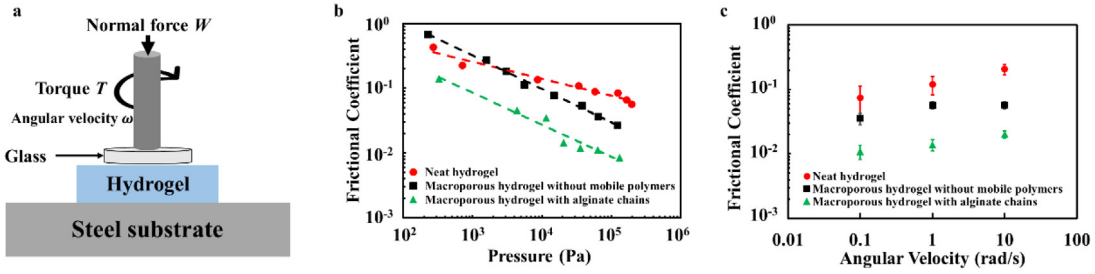

Fig. 3. Friction test. (a) Schematic of the setup. (b) Frictional coefficient as a function of pressure for three kinds of samples. Angular velocity is fixed at 0.1 rad/s. (c) Frictional coefficient as a function of angular velocity for three kinds of samples. Pressure is fixed at $\sim 7.5 \times 10^4$ Pa. Sample size = 2. In each sample, data are collected as the mean value of 5 friction measurements.

alginate-filled macroporous hydrogel are on the order of 0.01, lower than those of the neat hydrogel with no macropores by one order of magnitude, and are about half of those of the water-filled macroporous hydrogel. Because the viscosity of alginate solution (1 wt%) is almost constant in the testing range of 0.1–10 rad/s [31]. At a same normal pressure, a higher angular velocity gives a higher shear force, which leads to a higher frictional coefficient.

These experimental results confirm the significance of the mobile polymer chains in lowering friction. Our data are consistent with the following picture. The alginate chains are long, mobile, hydrophilic, and negatively charged. Consequently, the alginate chains stabilize the surrounding water molecules and form a liquid-like hydration layer, at the hydrogel/glass interface, under the normal and tangential forces. The liquid-like hydration layer lowers the friction.

We further test the significance of the macropores in maintaining the low friction after long-time sliding (Fig. 4). We prepare six kinds of samples: neat hydrogel, neat hydrogel with mobile alginate chains, macroporous hydrogel filled with water and macroporous hydrogel filled with mobile alginate, chitosan, or PAAM chains. All samples are fully equilibrated in either pure water or in aqueous solutions of the polymer chains before the friction test. To prevent dehydration during the long-term tests, we add water or polymer solution to the peripheral surface of hydrogels, but not the top surface where friction test is performed. The results show that the alginate-filled macroporous hydrogel has the lowest frictional coefficients at all time. Its surface is smooth with a little scratch after 6 hour-test (the bottom inset in Fig. 4). By contrast, the neat hydrogel has a high frictional coefficient. The observation of large fluctuation of frictional coefficient with time is probably due to the gradual damages of the hydrogel surface. At the time between 2.5 and 3.5 h, the hydrogel surface is severely damaged, and the friction coefficient increased markedly (the top inset in Fig. 4). The alginate-filled neat hydrogel has a similar frictional coefficient to that of the alginate-filled macroporous hydrogel during the first half hour, but its frictional coefficient gradually increases and reaches the same value as those of the neat hydrogel without alginate. The macroporous hydrogel filled with water has highest frictional coefficient. Those observations show that both the alginate-filled neat hydrogel and the alginate-filled macroporous hydrogel may have the similar liquid-like hydration layers in the beginning and thus have a comparable low friction. As the sliding continues, the porous structure of hydrogels may play roles to maintain the low

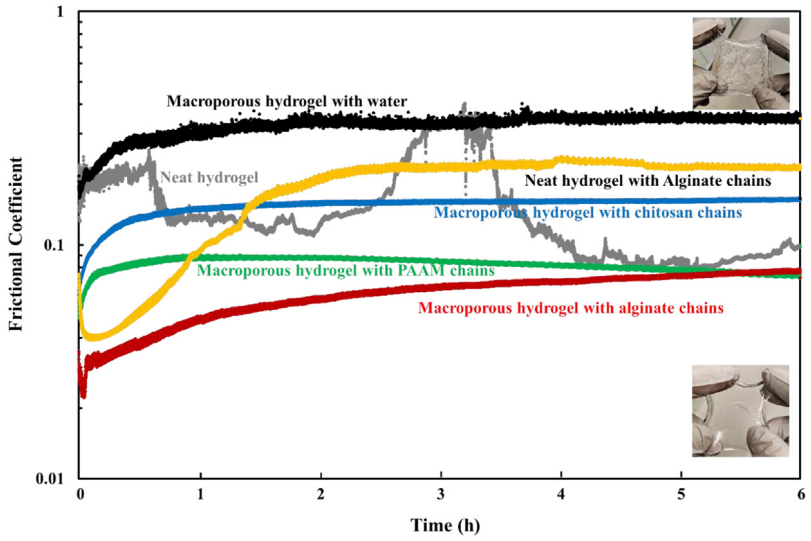

Fig. 4. Frictional coefficients of six kinds of samples over long-time sliding. All samples slide against a glass plate at a pressure of $\sim 3 \times 10^3$ Pa and an angular velocity of 1 rad/s. After sliding for 6 h, the neat hydrogel without mobile chains is severely damaged (top inset), but the polymer-filled macroporous hydrogels (with alginate chains) remains nearly intact (bottom inset). alginate: 1 wt%, Mw ~170–240 kDa; chitosan: 1 wt%, Mw > 375 kDa; PAAM: 1wt%, Mw ~5000 kDa.

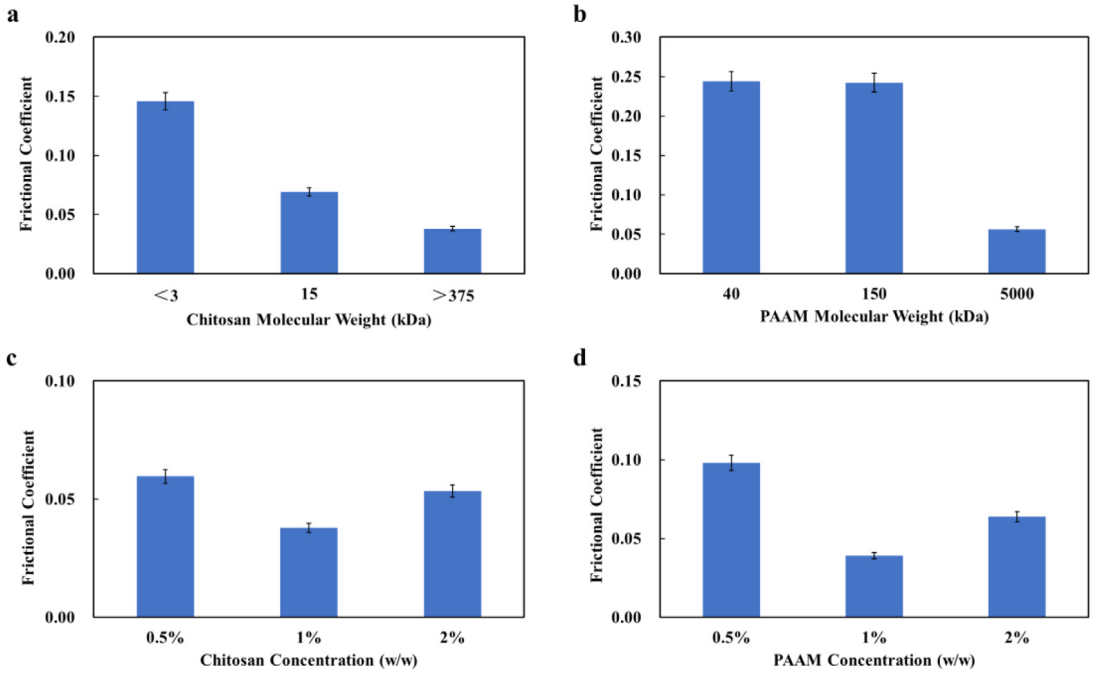

Fig. 5. Friction is affected by the length and concentration of the mobile polymers. The frictional coefficients of macroporous hydrogels filled with mobile chains of (a) chitosan and (b) polyacrylamide of various molecular weights. The concentration of the mobile polymers is fixed at 1 wt%. The frictional coefficients of macroporous hydrogels filled with mobile of (c) chitosan and (d) polyacrylamide of various concentrations. Chitosan: >375 kDa. PAAM: ~5000 kDa. All samples slide against a glass plate at a pressure of $\sim 3 \times 10^3$ Pa and an angular velocity of 1 rad/s. Sample size = 3. In each sample, data are collected as the mean value of 30 friction measurements.

friction, although the mechanism is unclear at the time of writing. For the water-filled macroporous hydrogel, because of the lack of polymer chains, the hydration layer is less stable, which leads to a high friction.

Among the polymer-filled macroporous hydrogels (alginate: 1 wt%, molecular weight ~170–240 kDa; chitosan: 1 wt%, molecular weight > 375 kDa; PAAM: 1 wt%, molecular weight ~5000 kDa), the alginate-filled macroporous hydrogel has the lowest frictional coefficient, and the chitosan-filled hydrogel has the highest frictional coefficient (Fig. 4). The difference may be attributed to the difference in chemistry. Alginate is a polyanion, chitosan a polycation, and PAAM a neutral polymer. Also recall that the glass surface bears hydroxyl ions, and is in effect a polyanion. In water, two surfaces of polyanions have negative fixed charges, and positive mobile ions. The latter forms an entropic cloud that causes the two polyanions to repel each other. This entropic repulsion stabilizes the liquid-like hydration layer. By contrast, a polyanion and a polycation may attract each other, setting mobile cations and mobile anions free in water. This repulsive–adsorptive effect has been well discussed in the literature [8]. In this case, the entropic cloud of the mobile ions promotes adhesion and increases friction. Such correlations

between chemistry and friction have long been studied in the literature [32–34], and are not studied further in this work.

We also investigate the effects of the length and the concentration of mobile chitosan and PAAM on friction (Fig. 5). (Alginate is available to us in only one molecular weight, and is not used in this set of experiments.) With a concentration of 1 wt% polymer, the frictional coefficient of both PAAM and chitosan can decrease many times as molecular weight increases. When polymers with high molecular weight are used, by varying the concentration, both chitosan and PAAM chains show lowest frictional coefficients at concentration of 1 wt%. These results are consistent with the picture of liquid-like hydration layer at the hydrogel-glass interface. When the length or the concentration of the mobile polymer chains is too small, a robust liquid-like hydration layer cannot be established, and the friction is high. When the concentration of the mobile polymer chains is too high, the mobile polymers are entangled and may further tether to the hydrogel network, increasing the drag during sliding due to polymer chain disentanglement and thus the friction is also high.

In summary, we have shown that a polymer-filled macroporous hydrogel reduces friction. The frictional coefficient is one order of magnitude lower than that of the neat hydrogel in a wide range of normal pressure and angular velocity. The low friction is maintained after continuous sliding over a long time. Our experimental data support the hypothesis that both pores and mobile polymers are significant for a hydrogel to maintain low friction under long-time sliding. In the synovial joint of an animal, the synovial fluid is stored in the joint cavity. Such a fluid reservoir may be inconvenient in many applications. In designing a low-friction hydrogel, one may store mobile polymer chains in the hydrogel. In addition to function as a reservoir and a conduit for mobile polymer chains, the hydrogel also needs to sustain cyclic load and adhere to a substrate. Such multifunctional requirements will likely lead to designs of architected materials, and will benefit from advances in fatigue-resistant and adhesive hydrogels [35–37]. It is hoped that polymer-filled macroporous hydrogels will be developed for broad applications in engineering and medicine.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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