Tunability of Liquid-Infused Silicone Materials for Biointerfaces

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Abstract
The ability to control the properties of bio-inspired liquid-infused surfaces is of interest for a wide range of applications. Liquid layers created using oil-infused polydimethylsiloxane (PDMS) elastomers offer a potentially simple way of accomplishing this goal through the adjustment of parameters such as curing agent ratio and oil viscosity. In this work, we examine how tuning these compositional parameters affects the properties of the infused polymer, including infusion dynamics, stiffness, longevity in the face of continuous liquid overlayer removal, and resistance to bacterial adhesion. We find that curing agent concentration appears to have the greatest impact on the functionality of the system, with a lower base to curing agent ratio resulting in both increased longevity and improved resistance to adhesion by Escherichia coli. We further demonstrate how these findings may be exploited to introduce patterned wettability to the surface of the infused polymers for controlling the spatial arrangement of bacteria, as well as derive experimentally based models to predict diffusivity of the oil into the polymer. These results demonstrate a new degree of control over immobilized liquid layers and will facilitate their use in future applications.

Key Words
Infused polymers, anti-adhesion, fouling-release, bacteria, SLIPS
I. INTRODUCTION

Tunable materials can dramatically increase our capacity to engineer more targeted solutions to specific problems, enabling new technologies and industries.\textsuperscript{1–4} Heightened control of a material’s performance, whether over bulk properties or spatially controlled functionalities, can be more easily achieved with materials that possess a wide range of properties that may be manipulated through either their manufacturing or environmental conditions. Polydimethylsiloxane (PDMS) elastomers are a material widely known for broad tunability. Adjusting the ratios of PDMS curing agent to base during fabrication has been used to control stiffness in studies of cell mechanobiology\textsuperscript{2,5} and cell differentiation,\textsuperscript{6} in some cases even independent of surface roughness and energy.\textsuperscript{2} The stiffness of PDMS has also been shown to affect bacterial attachment and antibiotic susceptibility.\textsuperscript{7} Furthermore, the modification of PDMS surface chemistry via plasma treatment has been used to promote increased protein deposition\textsuperscript{8} and specific adhesion of hydrophilic polymers.\textsuperscript{9}

More recently, slippery surfaces produced by infusing siloxane polymers with compatible oils have garnered attention as optically transparent fouling release materials with the ability to self-heal.\textsuperscript{10–14} The performance of these systems is based on immobilizing a surface layer of oil to provide overall slipperiness, and on the replenishment of that surface layer via effusion of the oil from the polymer bulk\textsuperscript{10,15–17} or reservoirs therein.\textsuperscript{11,13} Infused polymer systems have been demonstrated to be effective against bacterial biofilm adhesion both under static\textsuperscript{11} and flow conditions,\textsuperscript{10,17} as well as against marine fouling organisms,\textsuperscript{18,19} and recently have also been shown to work as a substrate for the growth and release of cell sheets.\textsuperscript{16} However, the use of oil infusion
as a tunable parameter to achieve more precise control over the material properties of these systems has not yet been examined.

Here, we explore how two key tunable parameters, curing agent concentration of the PDMS gel and viscosity of the infusing silicone oil, affect the stiffness, longevity, and bacterial resistance of the oil-infused PDMS system. We derive an experimentally-based theoretical model to describe the equilibrium swelling of the infused polymer and predict final composition arising from various combinations of curing agent concentration and infusing oil viscosity. We then develop a further model to extract oil diffusivity from our systems. We examine the tunability of relevant properties, including the elastic modulus, overlayer longevity, and resistance to bacterial adhesion, and show how these can be leveraged to achieve controlled interfacial adhesion through plasma-induced patterning of surface wettability. We anticipate that the sharing of this information will enable the rational design of infused PDMS, and bring this promising technology closer to practical application in fields such as tissue engineering, cell mechanobiology, surface-directed microfluidics, and diagnostics.

II. MATERIALS AND METHODS

A. PDMS Sample Preparation

PDMS (Dow Sylgard 184 polydimethylsiloxane) was prepared by mixing elastomer base and curing agent at ratios of 5:1, 10:1, and 20:1. Samples were mixed and deaerated in a planetary centrifugal mixer (Thinky Mixer ARE-310) at 2000 rpm for 1 min followed by 2200 rpm for 1 min. Samples for all experiments other than the overlayer stripping/CAH tests were poured into plastic molds, degassed for at least 45 minutes, then cured at 70°C. After at least 48h of curing,
samples were removed from their mold and infused by submersion in silicone oil (Gelest) at 25°C until equilibrium mass was reached. For individual experiments, all samples were run in parallel to permit comparison.

To obtain absorption profiles, 20 x 20 x 5 mm PDMS squares undergoing infusion were removed from the silicone oil bath periodically over a 100-hour time period. The samples were held vertically for 30 s to allow excess oil to drain off the surface, then weighed on an analytical balance. The percent mass increase was calculated by $\Delta m = \frac{m}{m_0} - 1$, where $m$ is the mass at time $t$ and $m_0$ is the initial mass.

B. Equilibrium Oil Fraction Modeling

We presumed that the ability of cured PDMS to swell by absorbing the oil is determined by two factors: 1) the entropy of mixing the oil and cured polymer, which is positive and favorable due to an increase in the system’s randomness, and 2) the reduction in network entropy of the expanding polymer network, which is unfavorable due to a decrease in the number of possible network conformations.\textsuperscript{29} Given the highly matched chemical composition of the silicone oil and PDMS, it is reasonable to assume that there is no substantial enthalpic change during infusion of the PDMS network with a chemically very similar oil. Taking from classical statistical theory of elastomer deformation and Flory-Huggins solution theory,\textsuperscript{30} we derive an equation to describe the equilibrium swelling of our PDMS-silicone oil system:

It is known that the shear modulus ($G$) of a polymer is given by

$$G = \frac{\rho RT}{M_c} \quad \text{(Eq. 1)}$$
where \( \rho \) is the polymer’s mass density, \( R \) is the ideal gas constant, \( T \) is temperature, and \( M_c \) is the number-average molecular weight of the chain between crosslinks.\(^{31,32} \) Assuming an equilibrium state of swelling, Equation 1 may be applied to the Flory-Rehner equation:

\[
\ln(1 - \phi_1) + \phi_1 + \chi \phi_1^2 + \frac{\rho_1 V_2}{M_c} \phi_1^{1/3} = 0 \quad (\text{Eq. 2})
\]

where \( \phi_1 \) is the volume fraction of polymer, \( \chi \) is the Flory-Huggins polymer-solvent interaction parameter, \( \rho_1 \) is the polymer density, and \( V_2 \) is the molar volume of solvent (in our case, silicone oil). Given the high degree of chemical matching between the system’s components, the \( \chi \) term may be neglected (\( \chi \approx 0 \)). Furthermore, knowing that the volume fraction of oil \( \phi_2 \) is equal to \( 1 - \phi_1 \), and \( V_2 \) is the quotient of the oil’s molecular weight \( M_2 \) and its density \( \rho_2 \), the equilibrium volume fraction of oil in infused PDMS (\( \phi_2 \)) can be implicitly written as

\[
\frac{\ln(\phi_2^{1/3}) + \phi_2 - 1}{(1 - \phi_2)^{1/3}} = \frac{1}{RT} \frac{G M_2}{\rho_2} \quad (\text{Eq. 3}).
\]

where \( \phi_2 \) is the volume fraction of oil, \( R \) is the ideal gas constant, \( T \) is temperature, \( G \) the shear modulus of the cured and dry PDMS network, \( \rho_2 \) the oil’s density, and \( M_2 \) its molecular weight.

C. Diffusion Modeling

The swelling of PDMS in oil is modeled by linear poroelasticity.\(^{33-35} \) The change of the sample thickness over time derived from the model was used to fit to the experimental results to obtain diffusivity. The governing equations of the swelling problem can be described as follows:

The displacement of the solid matrix is a field variable \( u_i(x_1, x_2, x_3, t) \). In the linear region, the strain is defined as
\[ \varepsilon_{ij} = \frac{1}{2} \left( \frac{\delta u_i}{\delta x_j} + \frac{\delta u_j}{\delta x_i} \right). \text{ (Eq. 4)} \]

The mechanical equilibrium requires that

\[ \frac{\partial \sigma_{ij}}{\partial x_j} = 0. \text{ (Eq. 5)} \]

The volume change is assumed to be entirely due to the change of solvent concentration \( C \), that is

\[ \varepsilon_{kk} = \Omega (C - C_0). \text{ (Eq. 6)} \]

where \( \Omega \) is the volume of a single solvent molecule.

Let \( J_i \) be the flux of solvent molecules (e.g. the number of silicone oil molecules passing through a unit area per unit time). The conservation of molecules indicates that

\[ \frac{\partial C}{\partial t} + \frac{\partial J_k}{\partial x_k} = 0 \text{ (Eq. 7)} \]

Darcy’s law is adopted as the kinetic model:

\[ J_i = -\left( \frac{k}{\eta \Omega^2} \right) \frac{\partial \mu}{\partial x_i} \text{ (Eq. 8)} \]

where \( k \) is the permeability of the PDMS network, \( \eta \) is the dynamic viscosity of the oil, and \( \mu \) is the chemical potential.

For isotropic material, the constitutive relation is

\[ \sigma_{ij} = 2G_s' (\varepsilon_{ij} + \frac{\nu'}{1-2\nu'} \varepsilon_{kk} \delta_{ij}) - \frac{\mu-\mu_0}{\Omega} \delta_{ij} \text{ (Eq. 9)} \]

where \( G_s' \) is the shear modulus of the swollen PDMS system, and \( \nu' \) is the drained Poisson’s ratio.
Combining equations (5), (7), (8), (9), we derive a diffusion equation in terms of solvent concentration:

\[
\frac{\partial C}{\partial t} = D \nabla^2 C, \quad (\text{Eq. 10})
\]

where \( D \) is the diffusivity, which is related to permeability \( k \), swollen shear modulus \( G_s' \), viscosity \( \eta \) and drained Poisson’s ratio \( \nu' \) as

\[
D = \frac{2(1-\nu')G_s'k}{(1-2\nu')\eta}. \quad (\text{Eq. 11})
\]

The numerical simulation was carried out by using ABAQUS (ABAQUS, Inc.). The Soils solver was applied. The PDMS samples before infusion were set as the reference state, with zero internal stress and zero chemical potential. The initial thickness of the sample is \( H \). Submerging the PDMS sample into the silicone oil instantly changes the sample’s surrounding chemical potential to a non-zero constant value \( \mu \). The chemical potential difference drives silicone oil to diffuse into the PDMS matrix until the chemical potential inside the sample equilibrates with that of its environment, thus the sample thickness increases over time although no additional stress is applied on the sample throughout the process. The chemical potential boundary value \( \mu \) can be analytically calculated using the final thickness increase and known mechanical parameters from nanoindentation tests via the theory of linear poroelasticity. Notice that as the PDMS fully swells, the stress in the system is zero, and equation (9) gives

\[
\bar{\mu} = \frac{2(1+\nu')G_s'\Delta(\infty)}{(1-2\nu')H}. \quad (\text{Eq. 12})
\]

where \( \Delta(\infty) \) is the change of sample thickness and its value is obtained from experiment. In Supplementary Figure 1, the fitting curves of thickness increase over time are plotted together with the experimental data.
D. Measurement of Elastic Modulus

The elastic moduli of fully infused 20 x 20 x 5mm PDMS squares were determined using an Agilent Nano Indenter G200 with a 100 μm diameter diamond flat punch. During each test, the flat punch contacted the surface of the sample and oscillated at 180 Hz to determine the dynamic moduli of the samples. The storage and loss modulus were determined by the integrated software at four points on each sample, then used to calculate the elastic modulus. The storage modulus was also used with Equation 1 to estimate the number-average molar mass of the polymer chains between crosslinks (Mc).

E. Continuous Liquid Layer Removal and Contact Angle Hysteresis Measurements

Samples for liquid overlayer removal and CAH were prepared by dipping clean glass slides into uncured, degassed PDMS, then cured vertically and infused following the methods described in Section IIA. The final thickness of the coating on the slides was ~1mm, well above the value which in previous works has been shown to affect parameters such as the force required to remove an ice cylinder from a PDMS surface. Once infused, samples were placed on a custom-built dipping machine that would immerse them in a beaker continuously overflowing with clean water for 45 s, then retract and suspend them in air for 45 s. This process was repeated, with the samples periodically removed from the setup to measure CAH using a force tensiometer (Krüss) in a Wilhelmy Plate dynamic contact angle measurement setup. In these measurements, the water reservoir was thoroughly rinsed between each measurement to avoid cross-contamination of oil.

F. Surface Liquid Replenishment
Square petri dishes (6 x 6 cm) were filled with 45g of PDMS, degassed, and cured as described in Section IIA. Six samples measuring 1.5cm x 3cm were cut from each plate, and infused in 10cSt silicone oil until completely saturated. Samples were then wiped with a lint-free cloth in order to remove excess silicone oil and lightly scratch the PDMS surface. The replenishment of the sample overlayers was then observed under a Zeiss AX10 microscope at 10x magnification. Using the microscope’s programmable moving base, time-lapse photos were taken of each sample at 5-10 locations of similar scratch density in fifteen-minute intervals for 24-48 h. The series of photos were analyzed with MATLAB by first converting them to gray scale using the canned MATLAB function rgb2gray. Once in gray scale, the program used the canny edge detection filter with a 0.03 threshold to detect the scratches on the surface of the PDMS. These scratches were modeled as white pixels on a black background. The disappearance of scratches was assumed to relate to the replenishment of the liquid overlayer on the PDMS surface. This change in the surface oil layer was tracked by the percent change in white pixels across the series of pictures, with the very first photo in each series considered 0% replenished.

G. Bacterial Attachment

Stocks of Escherichia coli strain J96 (ATCC 25922) were incubated overnight at 37°C in LB Miller Broth and kept continuously shaking in an orbital shaker until a density of approximately $10^8$ cells/mL was reached. Stocks were used to inoculate 6-well plates containing a 20 x 10 x 5 mm PDMS sample in 7 mL of tryptic soy broth with 1.5% NaCl in each well. The PDMS samples were sterilized by autoclaving for 20 min at 121°C, which has been previously shown to not degrade or damage the material. An inoculation ratio of 1:100 stock to medium was used. Immediately
following inoculation, all samples were incubated at 37ºC. To simulate dynamic growth conditions during this period, samples were kept shaking at 100 rpm on an orbital shaker. After 48 h, samples were removed from culture, dipped in PBS to remove planktonic organisms, and placed in a test tube containing 10 mL PBS. The test tubes containing the samples were then vortexed for 90 s and sonicated for 180 s to remove adherent bacteria. The PBS containing bacteria colonies was then serially diluted, plated, and counted to obtain CFU counts. Counts from the infused PDMS samples were normalized to counts from non-infused PDMS samples of the same base to curing agent ratio.

H. Plasma Treatment and Patterning

For investigations of the effects of plasma treatment, non-infused PDMS samples were placed in an oxygen plasma etching chamber for 5 min at a power of 250 W and oxygen gas flow of 15 sccm. Patterns were produced by placing a steel mask over the sample prior to plasma treatment. After removal from the plasma chamber, samples were immediately immersed in silicone oil for infusion as described in Section IIA. Samples were then incubated in a nutrient broth solution containing *E. coli* as described in Section IIG under static rather than shaking conditions.

I. Quantification of Biofilm Coverage

Biofilm coverage was analyzed by staining samples via a 10-minute incubation in a 0.1% (w/v) solution of crystal violet (CV) in deionized, distilled water. This was followed by gentle rinsing in deionized, distilled water to remove excess stain, air-drying, and photography with a Canon EOS Rebel T4i camera (Melville, NY). Images of patterned biofilm were taken with a Zeiss LSM 710 confocal microscope in brightfield mode. Image analysis was performed as following using MATLAB (Mathworks, MA, USA). Photographs taken of the CV-stained samples were cropped
to the region of interest (i.e. to substrate edges) and converted from RGB color model to HSV (hue, saturation, value). Cropped images (n = 3) were binarized based on an interval defined in hue/saturation/value and the biofilm coverage was defined as percentage of the binarized biofilm over the whole image area. In this process, any purple color, whether from bacterial cells, biofilm polymers, or protein was counted as part of the surface coverage and quantified.

J. Statistics

One-way analysis of variance (ANOVA) with Tukey post-hoc tests (IBM SPSS Statistics 23) were used to test for significant differences among the samples. Comparison of CFU counts were conducted after using square root data transformation. In all cases, a P-value of less than or equal to 0.05 was considered significant.

III. RESULTS AND DISCUSSION

A. Characterization and Modeling of Infusion

In the 2-part Sylgard 184 PDMS mix used in this work, both the base and the curing agent contain vinyl-terminated siloxane oligomers. In addition, the curing agent contains a network-forming siloxane oligomer with silicon-hydride bonds, which in presence of a platinum-based catalyst undergoes hydrosilylation to form the PDMS elastomer. Varying the ratio of base to curing agent results in changes in the network structure and can be used to alter the matrix properties. To quantify how these changes to the matrix, as well as the viscosity of the infusing oil, could be used to tune parameters surrounding the initial fabrication of the system, PDMS samples with elastomer base-to-curing agent ratios of 5:1, 10:1, and 20:1 by weight were submerged in polydimethylsiloxane oils (trimethylsiloxy-terminated) with viscosities of 3, 10, and 20 cSt (see Supplementary Table 1 for corresponding molecular weights and densities). It has
previously been demonstrated that curing temperature can play a large role in network formation
and final surface properties,\textsuperscript{37} therefore all samples were prepared and cured simultaneously at
70°C.\textsuperscript{28} The samples were periodically weighed over time during the infusion process, with the
result shown in Figure 1A. For oil viscosity, the results show that infusion with more viscous
silicone oil results in a smaller increase in mass (%): for the 10:1 mixing ratio, infusion 3, 10, and
20 cSt oils resulted in mass increases of 92 ± 0.5%, 70 ± 1.1%, and 52 ± 1.0%, respectively. This
is in agreement with previous studies on the infusion of PDMS solids by PDMS liquids, which
show a decrease in the equilibrium concentration of PDMS liquid as a function of the molar mass
of the penetrant,\textsuperscript{41} and may indicate differences in the equilibrium constants of the systems. The
difference in equilibrium mass could also be seen as an overall increase in percent area of the
samples (Supplementary Fig. 2), with 10:1 square samples exhibiting a side length increase of
~25% when infused with 3 cSt oil, ~20% with 10 cSt oil, and ~15% with 20 cSt oil.

For curing agent concentration, the data show that samples made with a 20:1 mixing ratio
exhibits lower infusion rates than samples made with 10:1 and 5:1 ratios. In 10:1 and 5:1 samples
infused with 3cSt oil, maximum mass increase is reached after 24 h while for 20:1, it is reached
after 48 h. Furthermore, samples with a 20:1 mixing ratio have a greater total oil uptake than 10:1
and 5:1 samples. When infused with 10 cSt oil, 20:1 samples show an equilibrium mass increase
of 143 ± 1.7%, while 10:1 increase by 70 ± 1.1% and 5:1 samples 63 ± 0.5%. These differences
may be explained by the average molecular weight of the polymer chains between the crosslinks
(M\textsubscript{c}),\textsuperscript{30,31} a possibility which will be explored in greater depth in the following section. The result
is also similar to observations made for PDMS swelling in chloroform, which showed a ~44%
increase for 5:1 PDMS, a 48% increase for 10:1 PDMS, and a 62% increase for 20:1 PDMS.\textsuperscript{42}
should be noted that the PDMS used in these studies, Sylgard 184, is a proprietary mixture. Therefore, a full in-depth analysis of the chemistry behind the differences in oil uptake is beyond the scope of this work; nevertheless, using these results, the final dimensions and oil content of the infused PDMS system may be tuned through the careful selection of both curing agent ratio and oil viscosity.

**Figure 1.** (A) Mass increase over time of 5:1, 10:1, and 20:1 PDMS exposed to excess 3, 10, or 20 cSt silicone oil. Error bars are present on all data points and represent standard deviation for $n = 3$. (B) Equilibrium oil volume fractions in infused PDMS samples with varying curing agent concentration.
concentration and oil viscosity. The black curve shows the theoretical prediction (Eq. 1), while the squares indicate experimental data points. Data points for 30:1 samples are included to further validate the model.

Figure 1b shows a universal curve for determining the equilibrium volume fraction of oil, calculated through applying the Flory-Rehner equation\textsuperscript{30} to the system through Equation 3. Plotting the theoretical model against the experimental measurements showed good agreement between the two, with a decrease in oil viscosity and/or increase in curing agent mixing ratio leading to a higher equilibrium volume fraction of oil. Some deviation from the theoretical curve is observed for samples with low curing agent mixing ratios, with the 5:1 samples showing equilibrium oil volume fractions similar to samples mixed at 10:1. This echoes the results seen in Figure 1a, where the 5:1 and 10:1 samples showed similar equilibrium mass increases. The data suggest that the equilibrium volume fraction of oil thus depends only on the shear modulus of the cured and dry PDMS network (G), the molecular weight of the oil (M\textsubscript{2}), and the density of the oil (\(\rho_2\)). It is important to note that G and M\textsubscript{2} dominate over \(\rho_2\), as the density of the silicone oil does not change as dramatically as its molecular weight with increasing viscosity (Supplementary Table 1).

As a final measure of the infusion properties of our system, we used experimental data on the change in thickness of the samples, as they were infused, to derive the effective diffusion coefficient (diffusivity) of silicone oil molecules in the PDMS matrix based on poroelasticity theory.\textsuperscript{33–35} Exploring diffusivity of oil in our system is important in understanding the immobilized liquid layers’ longevity, environmental impact,\textsuperscript{29,43,44} and potential in facilitating the controlled release of selected chemicals such as drugs or target molecules.\textsuperscript{45} As silicone oil infuses
into the polymer matrix, the thickness of a PDMS sample increases and over time reaches an equilibrium value. The rate is related to the diffusivity of silicone oil in the polymer matrix. The value of diffusivity is obtained by comparing experimental data with our simulation. This numerical simulation is based on linear poroelasticity and was conducted using the finite element software ABAQUS. The details of the model and simulation are presented in Section IIC. Each infusion experiment was simulated individually based on the size and geometry of the sample. The material parameters in linear poroelasticity include shear modulus of the swollen polymer $G_s'$, which was obtained from nanoindentation testing of non-infused samples, the drained Poisson’s ratio $\nu'$, which is taken to be 0.35 from literature, and diffusivity $D$, which is to be determined. A series of diffusivity values were put into the simulation, and the calculated increase of thickness over time ($\Delta t$) was compared to the experimental results to extract the best-fitting diffusivity value $D$. The results of diffusivity $D$ for PDMS systems with different mixing ratios and silicone oil viscosities are listed in Table 1. These results are comparable to those reported by Dangla et al., who extracted a diffusion constant of $1 \times 10^{-11}$ m$^2$/s for 100cSt silicone oil moving through Sylgard 184 mixed at a 10:1 base to curing agent ratio, although lower likely due to the fact that a higher viscosity oil was used in that study.

### Table 1. Extracted values of diffusivity ($10^{-10}$ m$^2$/s) of silicone oils of different viscosities through PDMS at mixing ratios of 5:1, 10:1, and 20:1.

<table>
<thead>
<tr>
<th>Viscosity (cSt)</th>
<th>Mixing Ratio (base:curing agent)</th>
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<tbody>
<tr>
<td></td>
<td>5:1</td>
</tr>
<tr>
<td>3</td>
<td>1.9±0.4</td>
</tr>
<tr>
<td>10</td>
<td>0.73±0.23</td>
</tr>
<tr>
<td>20</td>
<td>0.65±0.31</td>
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</table>
The maximum value of diffusivity is observed at the ratio of 10:1 for all oil viscosities tested. According to poroelasticity theory and Darcy’s law, the diffusivity value is linearly proportional to network shear modulus and permeability (see Section IIC). As the crosslink density increases, the network stiffness increases but permeability decreases. As a result, the diffusivity value exhibits an uptrend first and then a downtrend. Nevertheless, this model will be useful in formulating recommendations for more specific applications of the infused polymer system where controlled diffusion is required, such as in drug release, membrane filtration, or providing insight into the environmental impact of these materials.

B. Mechanical properties

To better understand how our system can be tuned, we explored changes in the elastic modulus (E) as a function of curing agent content and infusing oil viscosity. The tunability of the stiffness of unmodified PDMS has been used for many applications, including controlling stem cell differentiation, reducing the attachment of fouling organisms, and studying cell mechanobiology. We used nanoindentation to measure E of 5:1, 10:1, and 20:1 PDMS samples infused with 3, 5, 10, and 20 cSt silicone oil (Fig. 2). The data in Figure 2a show that the elastic modulus of the non-infused controls decreases with decreasing curing agent concentration and ranges from 2.7 (± 0.07) to 2.1 (± 0.09) to 0.9 (± 0.01) MPa for 5:1, 10:1, and 20:1 PDMS, values that are within the range of previous studies on PDMS. Infusion lowers E across all PDMS ratios, appearing to have the least effect on 5:1 PDMS. When infused with 10cSt silicone oil, E values dropped to 2.5 (± 0.06), 1.5 (± 0.05), and 0.37 (± 0.01) MPa: a 7%, 29%, and 59% drop for 5:1, 10:1, and 20:1 samples, respectively. In contrast, the elastic modulus of 5:1 PDMS infused with 20cSt oil was 11% less than 5:1 PDMS infused with 3cSt: 10:1 PDMS in 20cSt oil was 7%
less than in 3cSt oil; and 20:1 PDMS in 20cSt oil was 33% more than in 3cSt oil. Of these, however, only the change in the 5:1 samples from 3 to 20 cSt oil were significantly different (P < 0.05). These data suggest that the changes in elastic modulus in oil-infused PDMS are predominantly dependent on the base to curing agent ratio, and only to a lesser extent the viscosity of oil. Furthermore, the data display the wide range of moduli that can still be achieved in an oil-infused PDMS system (roughly 2.6 MPa to 0.3 MPa), showing the high degree to which the elastic modulus of an infused system can be tuned by manipulating only the PDMS mixing ratio. Furthermore, the fact that, for a given base to curing agent ratio, E appears to be minimally affected by oil viscosity may prove useful for tailoring overlayer replenishment rates without compromising desired mechanical properties.

**Figure 2.** (A) Elastic moduli of 5:1, 10:1, and 20:1 PDMS after infusion with oils of varying viscosities, with non-infused controls. Error bars represent standard deviation for n=3 independent
experiments. (B) Number-averaged molecular weight of the polymer chains between crosslinks (M_c) in unmodified PDMS as a function of base to curing agent mixing ratio.

The storage modulus (G’) obtained from the nanoindentation data can be used to calculate the number-average weight of the polymer chains between the crosslinks (M_c) using Equation 1.\textsuperscript{32,55} As shown in Figure 2B, this yields values of 2.8 (± 0.14), 3.7 (± 0.33), and 8.9 (± 0.12) kg/mol for the non-infused 5:1, 10:1, and 20:1 samples, respectively. A greater chain length between crosslinks in the 20:1 samples could permit more expansion of the matrix and uptake of the infusing oil,\textsuperscript{41} explaining the difference in equilibrium oil volume after infusion between the 20:1 and 10:1/5:1 samples shown in Figure 1A.

C. Liquid layer longevity

In most practical applications of infused polymers, the longevity of the lubricated system may be tested when the overlayer is subjected to external forces, objects, or interfaces that strip away the liquid. To better understand the ability of our system to withstand these types of forces, we tested two distinct situations designed to cause system failure defined by the loss of slippery function. The first was intended to test the ability of the samples to withstand the repeated removal of the liquid overlayer without allowing the system to self-replenish (on a timescale of minutes), while the second examined the self-replenishment abilities of the system, which occurred on a timescale of hours.

Experiments to examine the ability of the infused polymer system to retain its slippery properties involved examining the contact angle hysteresis (CAH) of infused and control samples
during repeated exposure to air-water interfaces (Fig. 3A). Previous reports have indicated this to be a rigorous testing method, as the introduction of such an interface causes a wrapping layer of lubricant to form around water droplets that ultimately sheds with the droplet and over time results in the stripping of the overlayer.\textsuperscript{56,57} Glass slides were dip-coated with PDMS of 5:1, 10:1, and 20:1 mixing ratios, cured, and infused with 10 cSt silicone oil. Tensiometry, or the Wilhelmy Plate method, was used to periodically measure each sample’s contact angle hysteresis with water, an established measure of slipperiness.\textsuperscript{37,58}

Figure 3B shows the CAH of both control (solid bars) and infused (points) samples as a function of number of dipping cycles. The CAH for the non-infused 10:1 control sample is between 46° and 90°, in agreement with previous results for the same type of PDMS samples cured between 60° and 100°C.\textsuperscript{37} When infused, all samples retain a lower CAH when faced with repeated lubricant stripping compared to their non-infused controls. The values for all infused samples are lower than that of their respective controls in the timeframe tested. The 20:1 control samples show a CAH of ~95°, compared to samples infused with 10 cSt oil that appear to reach an equilibrium value of 40° after 60 dipping cycles; the 10:1 controls displayed CAH values of ~65° compared to 45° when infused. The 5:1 samples showed the lowest CAH for both, with controls averaging approximately 35° and infused controls 10° after 60 dips.

In all cases, there is variation in the CAH values, with 20:1 samples in particular showing large error bars at 20 dips. These variations, as well as the overall increasing trend in CAH with decreasing curing agent concentration in this system may be explained by the fact that the Young equation describing contact angle and surface tensions in a three-phase system assumes that the substrate is perfectly flat.\textsuperscript{59} This is not necessarily the case in our system, as the PDMS surfaces,
particularly the 20:1 samples, are soft and potentially deformable at very small length scales. In this case, decreased PDMS stiffness could be playing an increasing role in the greater contact angle hysteresis observed for 20:1 samples than for 5:1 samples as the lubricant is stripped away, since the 20:1 samples have a lower E (Fig. 2) and are more deformable. Such observations have been confirmed as “contact line deformation” by others.58

**Figure 3.** (A) Schematic of longevity testing setup. Glass slides supporting infused PDMS layers are repeatedly dipped into water, stripping the liquid overlayer. (B) Change in contact angle hysteresis of 5:1, 10:1, and 20:1 infused PDMS upon repeated dipping into water. The solid bars represent the range of control values measured for each mixing ratio. The infused 5:1 PDMS retains the lowest contact angle hysteresis, indicating a more slippery surface. Error bars represent standard deviation for n = 3 independent experiments.
The second major contributor to functional longevity – replenishment – is difficult to measure directly under dynamic conditions. Therefore, we used optical microscopy under ambient in-air static conditions to visualize surfaces of infused PDMS. Previous work has shown that changes in surface microtexture morphology can be used to observe the accumulation of a liquid overlayer.\textsuperscript{60} In the study presented here, samples were prepared by first removing all excess surface oil via absorption with a lint-free cloth to simulate complete overlayer stripping. This wiping created surface scratches, which were used as visual markings. The disappearance of these markings was taken to be indicative of overlayer replenishment. Figure 4A qualitatively demonstrates these observations via time-lapse optical microscopy, with 20:1 showing noticeable replenishment at 30 min. Figure 4B shows quantitatively that 20:1 PDMS replenishes significantly faster than 10:1 and 5:1, which have similar replenishment profiles. The time to 95% replenishment is 2.5 h for 20:1, 5.75 h for 10:1, and 5.25 h for 5:1 samples, with the latter two showing no significant difference (P > 0.05). This is expected, as the lower crosslinking density of 20:1 better facilitates the movement of oil molecules out of the matrix,\textsuperscript{26} and as 10:1 and 5:1 have similar infusion characteristics (Fig. 1A). Another contributing factor may be a lower compatibility of the oil for the matrix with increasing base to crosslinker ratio, which may promote separation of the liquid from the solid substrate.\textsuperscript{61,62}
Figure 4. (A) Visualization of differences in initial overlayer replenishment. Scale bars, 100 μm. (B) Replenishment rates of 5:1, 10:1, and 20:1 PDMS infused in 10cSt silicone oil, showing 20:1 is significantly different from 5:1 and 10:1. Error bars represent standard deviation for n = 3 independent experiments. Inset: Zoom of the data from time = 0 to time = 1.2 h.

D. Resistance to bacterial adhesion

Given the differences in ability to sustain low CAH under interfacial disturbances and the replenishment among infused samples made with different curing agent ratios, we determined which behavior was dominant in practical applications by measuring bacterial adhesion to 10 cSt silicone oil-infused 5:1, 10:1, and 20:1 PDMS samples under continuous, orbital-shaking growth conditions. Minimal to no background protein adhesion was observed on infused samples incubated in culture medium alone after removal, washing, and staining (Supplementary Fig. 3), in agreement with previous results on similarly-handled surfaces after contact with blood and cell
Surface topography of the samples was controlled by molding all samples on flat polystyrene and the same *E. coli* culture was used to ensure no differences in the mechanosensing systems among the bacteria in the tests. Furthermore, X-ray photoelectron spectroscopy results on this PDMS material at different crosslinker mixing ratios have shown no trend in changes in surfaces elements as a function of cross-linker concentration.\(^{39}\)

Samples exposed to bacteria were subjected to multiple sonication and vortexing cycles to ensure that all bacteria were removed from the surface.\(^{17}\) An in-depth analysis of *E. coli* associating with liquid layers over infused PDMS can be found elsewhere;\(^ {17}\) however, for this work we hypothesized that if stability of a low CAH is more important for resisting bacterial adhesion, then, based on our other data, 5:1 should show fewer adherent bacteria than other mixing ratios compared to its non-infused control; conversely, if replenishment is more important, then 5:1 should perform similarly to 10:1 PDMS, with 20:1 demonstrating the lowest number of adherent cells.

Figure 5 shows the number of colony forming units (CFUs) adherent on the infused samples, normalized to non-infused controls. The CFU counts were normalized to their own controls to account for difference in bacterial adherence caused by stiffness, as previous work by Song et al.\(^ {7}\) exploring the relationship between PDMS stiffness and bacterial adhesion in static culture has shown that significantly fewer cells attached to PDMS mixed at a 5:1 ratio than a 20:1 ratio when inoculated at densities of between 10⁵ and 10⁷ cell/mL (an inoculation density of 10⁶ cell/mL was used in the experiments reported here). A somewhat similar trend was observed in our results, with absolute CFU values of 2.6x10⁵ (+/- 7.1x10⁴), 4.3x10⁵ (+/- 1.2x10⁵), and 10x10⁵ (+/- 5.2x10⁵) cells/mL recorded for the 5:1, 10:1, and 20:1 infused samples, respectively, and
values of $7.3 \times 10^5 (+/- 4.7 \times 10^5)$, $2.6 \times 10^5 (+/- 2.2 \times 10^5)$, and $8.5 \times 10^5 (+/- 7.1 \times 10^5)$ cells/mL recorded for non-infused samples. The differences in the trend for the control values and larger standard deviations compared to previous published work may be due to the use of a shaking culture and more aggressive surface removal methods. However, when normalized, the data presented in Figure 5 shows corrected CFU counts of 0.35 (+/- 0.1) for the 5:1 samples compared to 1.65 (+/- 0.46) and 1.23 (+/- 0.62) for the 10:1 and 20:1 samples, respectively. These data suggest that the 5:1 samples are resisting bacterial adhesion better than the 10:1 or 20:1 samples, and that stability of CAH, as opposed to replenishment, is the dominant factor in bacterial resistance. This echoes our results on apparently improved longevity of 5:1 over 10:1 and 20:1 PDMS when faced with repeated overlayer stripping, as shown in Figure 3.

![Figure 5](image)

**Figure 5.** *E. coli* colony-forming units removed from the surface of 5:1, 10:1, and 20:1 PDMS infused with 10 cSt oil after 48 h of growth. All samples are normalized to their own non-infused controls (horizontal dotted line) to account for changes in stiffness: a value below the line indicates fewer bacteria were present on the infused samples than the control, while a value above the line
indicates more bacteria were present on the infused samples. Error bars represent standard deviation for n=5 independent experiments.

E. Surface patterning

To explore how the properties we have defined could be used to enable the rational design of slippery infused polymer surfaces to achieve particular functionalities, such as patterned wettability and adhesion, we used the existing knowledge of PDMS modification by plasma treatment. It is known that treatment with oxygen plasma produces a silica layer on the PDMS surface via oxidation, causing it to become hydrophilic, and that this property may be exploited to promote patterned adhesion of proteins and cells\textsuperscript{22,63} and to provide heightened control in surface-directed microfluidics.\textsuperscript{23,24} To enable the application of our infused PDMS in these fields, we first aimed to determine the effect of oxygen plasma treatment on the slipperiness of our infused polymers by measuring the contact angle hysteresis of 5:1, 10:1, and 20:1 infused PDMS that had been exposed to oxygen plasma before infusion by 10 cSt oil. Figure 6A shows the results, with CAH values of the infused samples at 0 ± 0.1°, 3.5 ± 1.1°, and 31.7 ± 0.3° for the 5:1, 10:1, and 20:1, respectively. For samples that were subjected to plasma treatment before infusion, those values change to 23.4 ± 0.5°, 26.1 ± 1.5°, and 30.7 ± 2.7°. This is presumably due to the fact that the increased hydrophilicity of the surface caused by the plasma treatment makes it less suitable to supporting a hydrophobic oil overlayer, as it has been established that a chemical match between the solid substrate and the liquid overlayer is crucial to maintaining a functioning slippery surface.\textsuperscript{64} A practical application of these results is given in Figure 6B, where the difference in biofilm adhesion between unaltered infused and plasma-treated infused samples is most
pronounced in the 5:1 samples (2.7% biofilm coverage without plasma treatment, 79.1% with), followed by the 10:1 (9.4% coverage without plasma, 33.3% with) and finally 20:1 (49.7% coverage without plasma, 75.0% with). The greatest difference in biofilm coverage on 5:1 samples may correspond to their greater difference in CAH between plasma-treated and untreated, as shown in Figure 6A.

To further demonstrate how this finding could be applied, 5:1 PDMS samples were placed underneath a shadow mask, plasma treated, then infused to create discrete adhesive and slippery regions before incubation with *E. coli*. Figure 6C shows the mask and the resulting patterned biofilm formation. The results show that the differences in slipperiness with plasma treatment can be leveraged to create patterned biofilms. However, such patterning will require further optimization. Under certain conditions, biofilm growth can stretch across and over slippery liquid-infused regions. This biofilm bridging is thought to be due to proteins and smaller biofilm clusters settling between the patterned areas. Insufficient shadow mask-surface contact may also be playing a role. Future experiments that will be important in exploring the limits of this system’s tunability involve determining how intricately the wettability may be patterned with plasma treatment and better understanding the longevity of plasma-treated samples. Nevertheless, with further research this approach may offer a patterning method which is both low-cost and simple.
**Figure 6.** (A) Contact angle hysteresis of infused PDMS either exposed to O₂ plasma or left untreated before infusion. Error bars represent standard deviation for n = 3 independent experiments. (B) Crystal violet staining of *E. coli* biofilms grown on plain and plasma-treated 10 cSt oil-infused PDMS of varying mixing ratio. Scale bars, 5 mm. (C) *E. coli* biofilm patterning on 5:1 PDMS after exposure to O₂ plasma (right) through a mask (left). Scale bars, 150µm.

**IV. CONCLUSIONS**

In this work, we characterize the tunability of systems of silicone oil-infused PDMS with varying curing agent concentration and oil viscosity. We develop a model to correlate equilibrium swelling with PDMS mechanical properties and oil viscosity. The resulting good fit to experimental data enables us to predict equilibrium mechanical properties of infused PDMS systems with any combination of curing agent concentration and oil viscosity. In exploring the effect of curing agent concentration and oil viscosity on both the rate of infusion and total oil uptake, we find that while there are differences in both the swelling rate and total oil uptake
between oil viscosities, systems of 20:1 PDMS swell significantly more than those of 10:1 or 5:1 mixing ratio, which swell similarly. Building from the infusion data, we develop an additional model to extract diffusivity values for different combinations of curing agent concentration and oil viscosity. We find that infusion lowers the Young’s modulus of the system to a greater extent in 20:1 and a lesser effect in 5:1 samples. Nevertheless, a wide range of resulting stiffnesses is achievable, dependent primarily on crosslinking density rather than the oil viscosity.

Investigation into the longevity of the immobilized liquid overlayer showed that after stripping via repeated exposure to an air-water interface, there is a large difference in CAH among 10 cSt oil-infused PDMS mixtures, with the 5:1 base to curing agent ratio showing less change. Observations of surface replenishment of the stripped overlayer indicate that 20:1 PDMS replenishes roughly twice as fast as 10:1 and 5:1, which have similar replenishment profiles, mimicking their infusion characteristics. Tests of 10 cSt systems against biofilm adhesion showed superior adhesion resistance of 5:1 infused PDMS samples. Leveraging existing knowledge of how plasma treatment affects CAH of PDMS, we synergistically combined the superior performance of 10 cSt oil-infused 5:1 PDMS in CAH suppression and anti-fouling tests to spatially control bacterial growth via patterned plasma exposure.

These promising initial results indicate that the infused PDMS system may be rationally designed and tuned to create substrates with patterned wettability, a feature useful in tissue engineering,\textsuperscript{6,16,20,21} cell mechanobiology,\textsuperscript{2,22} microfluidics,\textsuperscript{23,24} diagnostics,\textsuperscript{25–27} the development of microbial fuel cells,\textsuperscript{67} and the development of arrayed assay platforms for accelerated multiplexing evaluation,\textsuperscript{68} which might be used for the determination of antibiotic resistance and study of bacterial interactions with other species. Moreover, patterned wettability can be combined
with the topographical\textsuperscript{69–71} and mechanical tunability\textsuperscript{6,7,20,21} of PDMS to provide further degrees of control for a desired application. Given this wide range of potential applications, future in-depth chemical and mechanistic studies will be useful to further understand the system. However, the work presented here is a crucial step towards enabling the rational design of infused PDMS, and elucidate the degree of tunability of this class of immobilized liquid layers.

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Caitlin Howell (Fig. 7) is an Assistant Professor of Biomedical Engineering at the University of Maine. She began her career at the University of Maine, studying biology with a minor in mathematics and working in any research lab that would take her. After a brief experience as an ornithology field hand in the Maine woods—where the birds and ecology PhD students were amazing but the bugs were most decidedly not—she landed in the lab of Professor Jody Jellison, a leader in the field of fungal wood decay. While proving herself through the enthusiastic washing of dirty glassware, she learned how to do real science from Dr. Jellison and her PhD student at the time, Jonathan Schilling. But above all, she learned how something that may not be very glamorous on the surface (like wood decay) can be fascinating when you look closer and start wondering why and how. In her senior year, she received the Ron Cockcroft award from the International Research Group on Wood Protection to travel to Tromso, Norway to share the results of her research with the international community, as well as an NSF Teaching Fellowship to share her newly-discovered passion for science with over 80 local middle school students each week.

After completing a Master’s degree using ever larger machines to look at ever smaller bits of decaying wood, Caitlin was very lucky to be introduced to Professor Michael Grunze of the University of Heidelberg in Germany. In his Applied Physical Chemistry group there he created specifically defined surfaces using tricks of physics and chemistry, then studied how those surfaces interacted with the world. She was thrilled when he invited her to come to Germany to earn her PhD, which was supported by an NSF Graduate Research Fellowship. Over the next three years, she worked with Dr. Patrick Koelsch as well as Professor Michael Zharnikov, Dr. Dmitri Petrovykh, and many other talented chemists, physicists, and engineers to understand how biological molecules such as DNA organized themselves at interfaces. Although it was initially challenging both to live in a different country and learn to communicate with researchers in very different disciplines, it soon became clear that her colleagues were equally excited about uncovering the mysteries of Nature and how they could be used to accomplish specific goals. Through their kindness and willingness to take the time to break down the barriers between the fields, Caitlin’s colleagues worked with her to answer critical questions at the intersection of biology, chemistry, and physics that none of them could have answered alone. She finished her PhD with 11 publications, 7 of which as first author, all contributing to the greater understanding of the organization and orientation biological molecules on abiotic surfaces.

Near the end of her PhD, Caitlin began to think about how amazing it was that people could take an understanding of Nature and using it to build new materials that could act in
defined ways—otherwise known as engineering. This line of reasoning led her to Professor Joanna Aizenberg at Harvard University, who was working as part of the Wyss Institute for Biologically Inspired Engineering where they looked to nature for breakthrough solutions to a wide variety of challenges. Joining as a postdoctoral researcher, Caitlin worked with Professor Aizenberg, senior Wyss scientist Michael Aizenberg, and a series of phenomenal collaborators, research assistants, and students to develop pitcher plant-inspired slippery surfaces for controlling the adhesion of biological materials to surfaces. After a year, she received a Wyss Technology Development Fellowship, which allowed her to not only continue to develop these specialized surfaces, but also to begin to work with companies on translating the technology to the market where it could begin to make a difference in people’s lives. Caitlin’s work with Professor Aizenberg and her team and collaborators at the Wyss Institute saw the development of self-replenishing vascularized polymers, slippery surfaces for releasing sheets of cells, as well as the first uses of liquid-infused materials in vivo to reduce blood clot formation, infection, and instrument fouling.

In 2016, Caitlin joined the Faculty back at the University of Maine. She founded her lab to combine the knowledge gained during her undergraduate, graduate, and postdoctoral work: building specialized surfaces and interfaces to control biological interactions. Together with her amazing students and academic as well as industrial partners, she continues to work toward understanding Nature, then using that knowledge to create the next generation of materials that will save the world. Although she continues to be regularly amazed at all the things she doesn’t know, she has learned a few useful things in her relatively short career that help when things get tough:

1. Although it may not always feel it, it helps to remember that we are incredibly lucky: the beauty and complexity of Nature is breathtaking, and we are the people who get to work toward understanding it every day! While getting paid! What better job could there possibly be?

2. Nothing is better than equally enthusiastic, competent, and hardworking colleagues and collaborators. They are worth their weight in gold, so once you find them, do everything you can to keep them. Science is best as a team sport, and a good team makes all the difference.

3. Science is hard—because if it were easy, someone else would have already done it. We are here because we have the capacity to create change, to discover and understand the world around us, and to use that knowledge to improve the lives of our community members as well as our environment. Given the magnitude of what we’re trying to do, it’s natural that turning that capacity into results is challenging. But saving the world is well worth the effort.
The Team. This work is the result of a collaborative effort of a dedicated group of professors, research scientists, postdocs, graduate students, and undergraduate students working on the design and characterization of an innovative materials system so that it can serve a purpose and make an impact outside the laboratory. It is their belief that fundamental research on materials and interfaces will be crucial to addressing several of the issues facing contemporary society, including reducing environmental impact, improving energy efficiency, and fostering sustainability.

Irini Sotiri (Fig. 8) is a graduate research assistant in the Department of Bioengineering at the University of Washington with Professor Buddy Ratner. She received a BS in Materials Science & Engineering with an additional major in Biomedical Engineering from Carnegie Mellon University, then worked as a research fellow at the Wyss Institute for Biologically Inspired Engineering at Harvard University.

Fig. 8. Irina Sotiri.

Amanda Tajik (Fig. 9) recently received her Bachelor of Science (Honours Biochemistry) at the University of Waterloo in Canada. She is starting her master's degree in the Stem Cell and Cancer Research Institute at McMaster University, Canada.

Fig. 9. Amanda Tajik.

Yang Lai (Fig. 10) is a graduate student in the Department of Mechanical Science and Engineering at University of Illinois at Urbana Champaign. Her PhD study focuses on the mechanical characterization of soft and bio materials.

Fig. 10. Yang Lai.
Cathy T. Zhang (Fig. 11) is a Ph.D. student in the Aizenberg group studying the behavior of colloidal assemblies on soft, dynamic interfaces.

Fig. 11. Cathy T. Zhang.

Yevgen Kovalenko (Fig. 12) received his BSc in Biochemistry with Honours from the University of Waterloo in Canada, and is currently a Master’s candidate at the Wine Research Centre, University of British Columbia, Vancouver.

Fig. 12. Yevgen Kovalenko.

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Fig. 13. Carine R. Nemr.

Haylea Ledoux (Fig. 14) received her B.S. in Biological Engineering from the University of Maine in 2014, and currently works as an Associate Scientist at IDEXX Laboratories in Westbrook, ME.

Fig. 14. Haylea Ledoux.

Jack Alvarenga (Fig. 15) is a Research Scientist at the Wyss Institute, where his focus is on the development of novel adaptive materials. He received his B.S. in Physics and M.S. in Materials Science and Engineering from the Rochester Institute of Technology.

Fig. 15. Jack Alvarenga.
**Edythe Johnson** (Fig. 16) received her B.S. in Engineering Sciences from Harvard College in 2016 and is currently working at a startup in Newton, MA.

**Fig. 16.** Edythe Johnson.

**Huseini S. Patanwala** (Fig. 17) received his PhD in Polymer Science from the University of Connecticut in 2017 and is currently a PTD Module and Integration Device Yield Engineer at the Intel Corporation.

**Fig. 17.** Huseini S. Patanwala.

**Jaakko V. I. Timonen** (Fig. 18) is an Assistant Professor of experimental condensed matter physics and leader of the Active Matter Research Group at Aalto University in Finland.

**Fig. 18.** Jaakko V.I. Timonen.

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**Fig. 19.** Yuhang Hu.

**Joanna Aizenberg** (Fig. 20) is Professor of Materials Science and Chemistry, Director of the Kavli Institute for Bionano Science and Technology, and Platform Leader of the Wyss Institute at Harvard University. She is a member of the American Academy of Arts and Sciences, American Philosophical Society, American Association for Advancement of Science and an External Member of the Max Planck Society.

**Fig. 20.** Joanna Aizenberg.


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