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Polymeric Gels

Fluorogel Elastomers with Tunable Transparency, Elasticity, Shape-Memory, and Antifouling Properties**

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Abstract: *Omniphobic fluorogel elastomers were prepared by photocuring perfluorinated acrylates and a perfluoropolyether crosslinker. By tuning either the chemical composition or the temperature that control the crystallinity of the resulting polymer chains, a broad range of optical and mechanical properties of the fluorogel can be achieved. After infusing with fluorinated lubricants, the fluorogels showed excellent resistance to wetting by various liquids and anti-biofouling behavior, while maintaining cytocompatiblity.*

Developing materials and devices with tolerance to diverse operating conditions is fueled by technological needs. Optical lenses, flexible electronics, and soft robotics require multifunctional materials with tunable optics, mechanics or actuation coupled with resistance to surface contamination.[1–4] Furthermore, biological implants, such as catheters and artificial blood vessels, need materials with controllable mechanics while exhibiting sustained biocompatibility and anti-biofouling properties to prevent infection. Exemplary technologies harness multicomponent systems with specific chemical moieties to tune the surface chemistry.[5–10] However, such multicomponent systems create excessive complexity that often sacrifices certain useful properties, while not fully avoiding the loss in function resulting from surface contamination. Moreover, the molecular mechanisms that prevent liquid contamination are generally different from those involved in the prevention of biofouling, which makes integration of both functions in one material fundamentally difficult.[11–14] For example, hydrophilic coatings such as poly(ethylene glycol) (PEG) are often used for the prevention of nonspecific bioadhesion, while hydrophobic surfaces are usually required for liquid repellency. Here we develop a family of multifunctional, omniphobic perfluorinated elastomers that combine exceptional liquid repellency with tunable optics, mechanics, and shape memory. By controlling the crystalline state of the polymer chains, a broad range of optical and mechanical properties can be achieved. Fluorinated lubricants were further infused into the perfluorinated elastomers to yield a new type of organogels, namely “fluorogels”, which demonstrated broad antifouling against water, hydrocarbon oils, proteins, cells, and blood while maintaining excellent cytocompatibility.

The fluorogels were designed from selected perfluorinated alkyl acrylate monomers and a fluorinated macromolecular crosslinker. Specifically, 2-perfluorooctylethyl acrylate (PFOEA) or 2-perfluorohexylethyl acrylate (PFHEA) were mixed with perfluoropolyether dimethacrylate (PFPE-DMA) in different ratios to yield fluorogels (naming convention: monomer-volume %). It was envisioned that the morphology of the fluorogel polymer network could be precisely tuned from semi-crystalline to amorphous by specifying the identity and/or amount of monomer in the matrix.[15–17] As evidenced by differential scanning calorimetry (DSC; Figure 1 a), melting and crystallization phase transitions were noted only for PFOEA-based gels with a monomer content greater than 50 %, as enthalpy changes were not observed for PFHEA-based gels between −70 and 150 °C. The length of the fluorinated side chain of PFOEA is sufficient for crystallization while that of PFHEA does not provide crystallization.[15,16] The magnitude of the change in

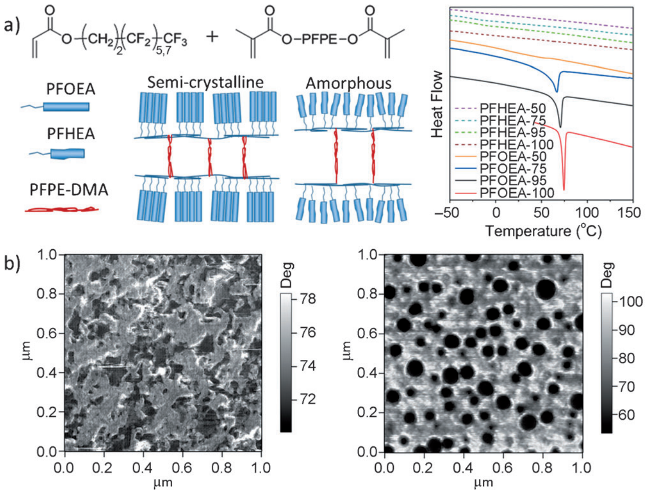

Figure 1. a) Chemical design of the fluorogels, molecular configuration of the side chains, and DSC analysis of the fluorogels. b) Tapping-mode-phase AFM images of PFOEA-100 (left) and PFOEA-50 (right) fluorogel film prepared on glass slides, indicating that the surface of PFOEA-100 films is notably more homogeneous than that of PFOEA-50. Domains of different softness were observed in PFOEA-50, which may be ascribed to semi-crystalline and amorphous regions from the PFOEA side chain and PFPE crosslinker, respectively.

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the heat flow decreased with decreasing monomer content in PFOEA-based gels, suggesting that the amount of PFOEA side chains available for packing into semi-crystalline domains decreases with increasing crosslinker content, which was also further evidenced by atomic force microscopy (Figure 1 b, Figure S1). Additionally, robust thermal stability was observed for these fluorogels, as determined by thermal gravimetric analysis; 0.5 % total mass loss for PFOEA-50 at 134 °C, 2 % total mass loss at 265 °C, and 50 % total mass loss occurred around 375 °C, respectively (Figure S2).

Defining the morphology of the fluoropolymer network allows for control over the physical properties and corresponding behavior of the material. The transparency ranged from opaque to transparent, and the mechanical properties extended from a stiff, rigid plastic to a soft elastomer with the modulus spanning three orders of magnitude (Table S1). The PFOEA-100 samples were rigid (elastic modulus, *E*, of ca. 200 MPa) and opaque (transmission of ca. 0 %) where the large crystalline domains contributed to light scattering and high modulus. PFOEA-based networks became increasingly flexible, soft, and transparent with increasing content of crosslinker, which breaks up the semi-crystalline domains. PFHEA-based samples were all clear and soft because of the amorphous nature of the network and the short-chain perfluoroalkyl monomer, with the modulus depending inversely on the monomer content and reaching ca. 0.1 MPa for PFHEA-95 (Figure 2 a–b).

A thermally induced crystalline–amorphous transition enabled tunable optical and mechanical properties for the fluorogels with notable semi-crystallinity. For example, a film of PFOEA-95 turned transparent when it was heated above 70 °C, and reverted back to opaque after cooling down to 25 °C (Figure 2 c,(1) and (2) and Figure S3). Crosslinked polymers with high degrees of crystallinity have been shown to exhibit thermally responsive shape-memory behavior.[18,19] Heating a semi-crystalline fluorogel, such as PFOEA-95, above its transition temperature resulted in a soft and processable material that retained any acquired shape after cooling (Figure 2 c,(3) and (4)). After re-heating above the transition temperature, the fluorogel recovered its initial shape because of the covalent crosslinks (Figure 2 c,(5) and (6)).

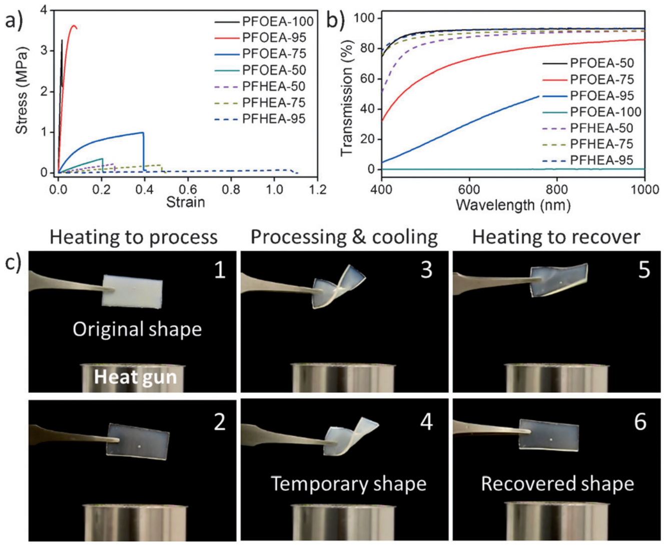

Figure 2. Tunable mechanical and optical properties of the fluorogels. a) Tensile and b) optical tests for the fluorogels of different compositions. Samples of 1 mm thickness were prepared for all the optical measurements. c) Demonstration of the shape-memory behavior of PFOEA-95: 1 and 2) converting a rigid film (white) to a soft and flexible (transparent) film upon heating with a heat gun; 3 and 4) twisting a soft film and keeping the shape when cooling down; 5 and 6) recovering the original shape upon heating.

The nonwetting properties of the fluorogels were exemplified by superior chemical resistance to most organic solvents such as pentane, hexane, toluene, and ethanol (Table S2). As a class of fluorinated elastomers, the fluorogels were subsequently investigated for their swelling properties. The fluorogels were slightly swollen by some halogenated solvents such as chloroform or trifluoroethanol, and showed great affinity for fluorinated solvents such as 3MFC-70 and DuPont Krytox oils (Figure S4), which are commonly used as lubricants in liquid-infused materials to achieve interfacial slipperiness and universal repellency because of their immiscibility with most other liquids.[20,21] Several days were required for the fluorogels to reach equilibrium swelling, and larger extents of swelling were noted with FC-70, a small molecule, compared to Krytox 100, a macromolecule (Figure 3 a–b). Furthermore, the magnitude of swelling increased

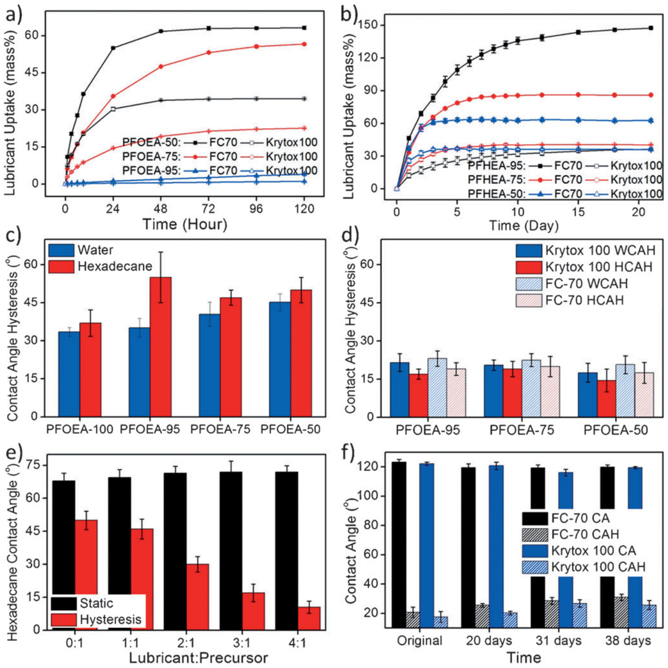

Figure 3. a and b) Mass uptake of different lubricants and time-dependent swelling dynamics for a) PFOEA-50 and b) PFHEA-95 fluorogels. c–f) Wetting properties of PFOEA-based fluorogels: c) contact angle hysteresis of water (WCAH) and hexadecane (HCAH) on a bare fluorogel; d) WCAH and HCAH on lubricant-swollen fluorogels; e) contact angle and hysteresis of hexadecane on fluorogels prepared by the one-pot method, specifically, PFOEA-50 mixed with FC-70 in different volume ratios; f) contact angle (CA) and contact angle hysteresis (CAH) of water on lubricant-swollen PFOEA-50 fluorogels incubated under ambient conditions at different time points.

with decreasing modulus for the fluorogels swollen by FC-70 as swelling is promoted by mixing the polymer with solvent and is discouraged by stretching the network strands.[22]

These unique swelling and chemical resistance abilities make the fluorogels suitable as matrices for liquid-infused materials. The bare fluorogels were found to be omniphobic; droplets of water or hexadecane, with contact angles of about 120 and 70° (Figure S5), respectively, did not spread or pin on the substrates but slid away upon tilting. The contact angle hysteresis values were relatively high, that is, 40–55° for hexadecane and 33–48° for water on bare PFOEA-based gels. Although several days may be required to completely swell the fluorogels, the material properties were evaluated after 24 h of lubricant infusion to minimize the time and amount of lubricant required for applications. With an overcoated lubricant layer, swollen fluorogels exhibited slippery properties with water or hexadecane sliding angles less than 10°. To decouple the effect of the thick lubricant layer from the swollen gel, the surface was wiped dry to remove the excess lubricant layer after swelling. As shown in Figure 3 c–d, the contact angle hysteresis of water or hexadecane decreased down to around 15–20° for PFOEA-based fluorogels after swelling in FC-70 for 24 h. Similar results were observed when the swelling liquid was changed to Krytox 100, and for PFHEA-based fluorogels.

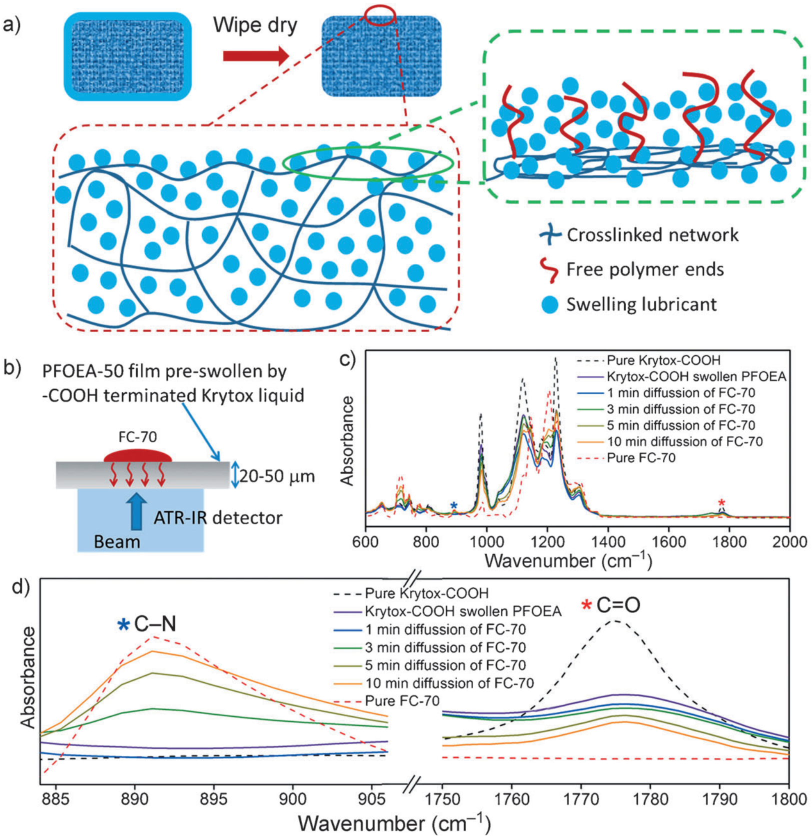

Figure 4. a) Schematic depicting the presence of the lubricant dispersed throughout the polymer network and diffusing to the polymer surface, with the free polymer chains at the swollen gel surface that reduce friction and provide slipperiness. b–d) Analysis of lubricant diffusion in fluorogels by ATR-IR spectroscopy: b) schematic of the experimental setup, c) full spectrum, d) C–N (blue star; left) and C=O (red star; right) stretch peaks from ATR-IR analysis of pure FC-70, pure Krytox-COOH, Krytox-COOH-swollen PFOEA-50, and Krytox-COOH-swollen PFOEA-50 with FC-70 diffusion at 1, 3, 5, and 10 minutes. The increase of the C–N signal and the decrease of the C=O signal with increasing diffusion time imply that the Krytox-COOH was diluted or even replaced by the diffusion of FC-70.

As an alternative to swelling fluorogels post-fabrication, the lubricant may be incorporated into the fluorogel through a one-pot method by adding the lubricant to the precursor solution. Water and hexadecane contact angle hysteresis values decreased with increasing Krytox lubricant concentration, reaching less than 10° at a lubricant:precursor volume ratio of 4:1 (Figure 3 e and Figure S6). Fluorogels prepared by either post-fabrication swelling or the one-pot method exhibited viscoelastic rheological properties, and the modulus decreased with increasing concentration of the lubricant (Figures S7, S8).

The crosslinked network of the fluorogels may retard the loss of lubricant encapsulated in the matrix and maintain function for a long time even if the lubricant is relatively volatile, as in the case of FC-70. Contact angle hysteresis of water remained approximately 25–30° and 20–25° for FC-70- and Krytox 100-swollen samples, respectively, after more than a month (Figure 3 f). As there is no apparent change in the topography of the fluorogels during the swelling process nor excess lubricating layer present after wiping samples dry, the slippery properties and the extended longevity may be attributed to the swollen gel interface coated with a lubricant layer that is constantly replenished at the gel surface because of directional diffusion (Figure 4 a).

We anticipate that the swelling mechanism involves a homogeneous, molecular-level infusion of the lubricant, resulting in a wet, lubricated environment at the gel surface.[23] Free, dangling polymer chain ends, together with the wet environment, can help reduce interfacial friction and thus promote slipperiness of the surface.[24–26] The presence of this lubricating layer on the surface was confirmed by attenuated total reflectance infrared spectroscopy (ATR-IR). As shown in Figure 4 b–d, a thin film (20–50 μm) of PFOEA-50 was swollen with COOH-terminated Krytox oligomer (DuPont, molecular weight, M.W., about 2500 g mol^{-1}), wiped dry and placed onto the detector of the ATR-IR spectrometer. In situ ATR-IR measurements were carried out when a droplet (10 μL) of FC-70 was deposited onto the upper surface of the swollen fluorogel sample. The increasing signal of the C–N bond stretch was observed with increasing diffusion time, showing that FC-70 indeed diffused into the network and reached the other side of the pre-swollen sample. The maintenance of FC-70 at the swollen gel surface (top few microns) was noted up to five days even when the gel was placed in vacuum (Figure S9).

The surface of the fluorogels can also be patterned at the nano- and microscale into any desired topography using soft lithography to generate superhydrophobicity in the absence of lubrication, or omniphobicity with lubrication (Figure S10).

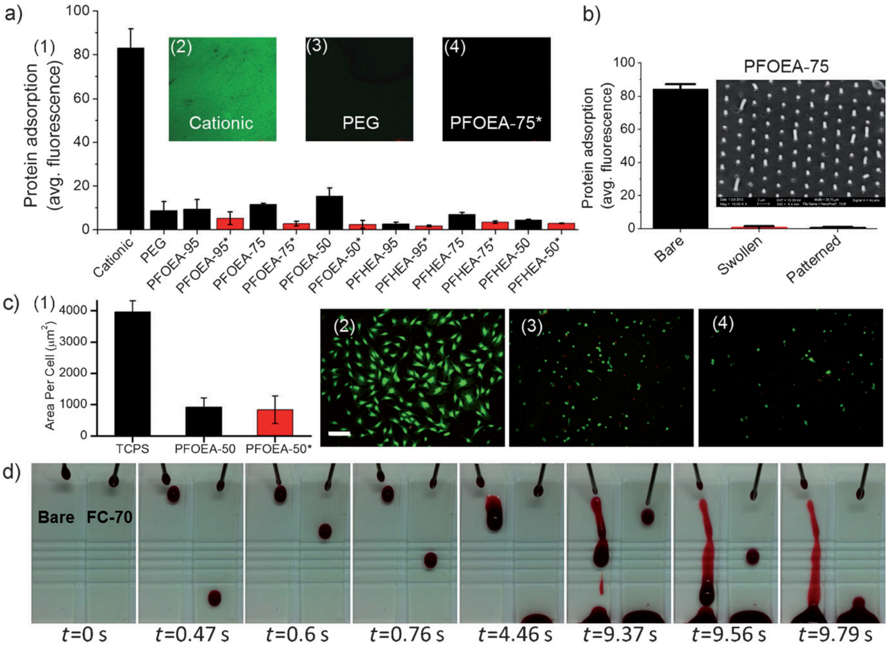

Figure 5. Anti-biofouling behavior of the fluorogels (swollen gels are indicated by an asterisk and marked as red columns). a) Protein adhesion to different fluorogels: 1) average fluorescence intensity of samples exposed to fluorescently tagged BSA protein; 2 to 4) confocal micrographs of 2) cationic hydrogels, 3) PEG hydrogels, and 4) swollen PFHEA-75 samples after incubation with protein; b) spectrophotometric analysis of fluorogels (bare, FC-70-swollen, and post nanopatterning, FC-70-swollen PFOEA-75) exposed to protein. The inset shows an SEM image of the patterned fluorogel. c) Assessing adhesion of mouse embryonic fibroblasts to different substrates: 1) Quantification of cell spreading on substrates; 2 to 4) fluorescent images of samples after incubation with cells for 24 h on 2) tissue culture polystyrene (scale bar = 200 µm), 3) bare PFOEA-50 fluorogel, and 4) FC-70-swollen fluorogel. d) Application of blood to bare and FC-70-swollen PFOEA-50 fluorogels: time lapse images show blood sliding on swollen fluorogels and pinning and streaking on bare fluorogels.

Since the swollen fluorogels showed excellent liquid-repellent characteristics, their anti-biofouling properties were subsequently studied. Biofouling of surfaces can negatively affect the performance of medical devices and sensitivity of diagnostics.[27] To evaluate the biological and anti-biofouling activity of the fluorogels, their interaction with proteins, cells, and blood was assessed. Reduced protein adsorption was noted on both bare and swollen fluorogels relative to a positive control (cationic hydrogels), and the fluorogels performed similarly to an anti-biofouling surface benchmark (PEG hydrogels), as indicated by confocal fluorescence microscopy (Figure 5 a). A closer examination of the protein adsorption onto various fluorogel samples through spectrophotometric analysis showed that both the FC-70-swollen bulk and patterned fluorogels did not display any detectable presence of protein while bare fluorogels showed notable protein adsorption. The interaction of biological cells with the fluorogels was studied for cytocompatibility (Figure S11) and adhesion/spreading behavior (Figure 5 c). The control (tissue culture polystyrene, TCPS) enabled good adhesion and spreading of cells while an about four-fold smaller area per cell was noted after incubation with the fluorogels, indicating that they were mostly unattached, with complete viability. Next, blood bank blood was dispensed on bulk material of FC-70-swollen or bare PFOEA-50 fluorogels. The ability of materials to minimize adhesion of blood to their surface and prevent coagulation finds importance in several medical applications such as dialysis, transfusion, analyte detection, and pathogen removal. Only swollen fluorogels repelled blood, while pinning and streaking of blood on bare fluorogels was observed, which can cause undesired coagulation (Figure 5 d).

In conclusion, lubricant-infused fluorogels are a unique, modular, and customizable polymeric gel system possessing omniphobicity, slipperiness, broad anti-biofouling, tunable mechanical and optical properties, and a shape-memory behavior. Our study provides a general framework for the design of lubricant-infused polymeric gels with controlled properties and functions that should be amenable to a variety of applications. We anticipate that these multifunctional fluorogels can offer unforeseen combinations of tunable properties and antifouling performance, which will enable new technologies and improve performance/efficiency in a range of energy, environmental, and biomedical applications that require long-term operations and/or encounter harsh environmental conditions. Because of its modularity, the family of fluorogels may be expanded by selecting monomers and crosslinkers with different structures, or implementing additives such as fillers or functional monomers. The flexibility and chemical simplicity of the fluorogels may enable integration with a wide range of materials, response to different stimuli, and design of unique behaviors. Both the lubricant and polymer network can be rationally chosen for specific crystalline, optical, swelling, and slippery properties to meet the requirements for a particular application and/or environment.

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Communications

Polymeric Gels

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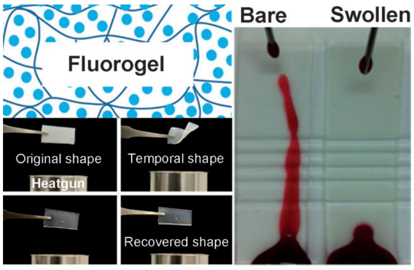
Fluorogel Elastomers with Tunable Transparency, Elasticity, Shape-Memory, and Antifouling Properties



Slippery surfaces: Multifunctional fluorogel elastomers with tunable transparency, mechanics, and shape memory properties are reported. After infusing with fluorinated lubricants, the fluorogels demonstrated broad omniphobicity and antifouling against water, hydrocarbon oils, proteins, biological cells, and blood (see picture) while maintaining excellent cytocompatibility.