

## Supporting Information

### **Non-elastic Glassy Coating with Fouling Release and Resistance Abilities**

Runze Chen, Qingyi Xie, Haohang Zeng, Chunfeng Ma\*, Guangzhao Zhang\*

*Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China*

\* Corresponding Author

Chunfeng Ma, E-mail: [msmcf@scut.edu.cn](mailto:msmcf@scut.edu.cn)

Guangzhao Zhang, E-mail: [msgzzhang@scut.edu.cn](mailto:msgzzhang@scut.edu.cn)

## **Experimental Section**

### **Materials**

Dodecafluoroheptyl methacrylate (DFMA) from Dayang Chemical was used as received. Poly(ethylene glycol) methyl ether methacrylate (PEGMA,  $M_n = 475$  g/mol), triethoxyoctylsilane (KH832), 3-mercaptopropyl triethoxysilane (KH580), and tetraethyl orthosilicate (TEOS) from Aladdin were used as received. Azobisisobutyronitrile (AIBN) from Aladdin was purified by recrystallizing in methanol. Tetrahydrofuran (THF), hydrogen chloride (HCl) and isopropanol (IPA) were from Sinopharm and THF was distilled by  $\text{CaH}_2$ . Artificial seawater (ASW) was prepared following ASTM D1141-98 (2003). Sylgard 184 silicone elastomer base and curing agent from Dow Corning were used to prepare PDMS with the 10:1 base/agent weight ratio.

### **Synthesis of Silane-terminated Telomer**

DFMA (4.00 g, 10.0 mmol), PEGMA (4.75 g, 10.0 mmol), KH580 (1.19 g, 5 mmol) and AIBN (0.02 g, 0.2 wt%) were mixed with 15.0 mL THF. The solution was added to a 100 mL Schlenk tube stirring for 12 h under nitrogen at 70 °C. Afterwards, the solution was precipitated in hexane and dried under vacuum at 25 °C overnight. The product is defined as telomer according to the IUPAC recommendations.<sup>1</sup> The telomer is designated as FP. To extract the roles of PEG and DFMA another two telomers were prepared. Following the same protocol, one without DFMA was synthesized at a molar ratio of 4:1 (PEGMA : KH580) and designated as P. Another without PEGMA was at a molar ratio of 4:1 (DFMA : KH580) and designated as F. The <sup>1</sup>H NMR

spectra of FP, P and F with assigned protons are shown in Figure S1-S3. The characterization data are showed in Table S1-S2.

### **Preparation of Telomer-tethered Organic-inorganic Hybrid Coating**

The hybrid coatings were prepared by facile sol-gel process from TEOS, KH832 and FP. For convenience, the FP-tethered hybrid coatings are designated as HC-FP-x. Typically, HC-FP-15 hybrid coating was prepared by mixing TEOS (2.09 g, 10 mmol), KH832 (2.73 g, 10 mmol), FP (0.73 g) and isopropanol (5 mL) in a round bottom flask stirring for 1 h. To promote the hydrolysis of silane, 0.1 M HCl (1.2 mL) was added dropwise to the flask gently. After stirring for 12 h at room temperature, the transparent solution was dropped on glass slide (for transmittance test and adhesion test), PET (for flexibility test), steel (for adhesion test), epoxy resin fiberglass panel (for adhesion test, nanoindentation, fouling release test, atomic force microscopy, surface wettability and mass loss test), silicon slide (for antibacterial assay and anti-diatom assay) and non-treated polystyrene 24-well tissue culture plate (for bacterial biofilm assay). The thickness was controlled by a tetrahedral wet film fabricator and determined by a coating thickness gauge (Phynix, Model Surfifix). Then, all coatings dried at 60 °C for 24 h and stored at room temperature for at least 7 days to ensure cure completely. Following the same protocol, HC-FP-0, HC-FP-5, HC-FP-10, HC-P-15 and HC-F-15 were prepared.

### **Characterization**

*Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR).* All samples using CDCl<sub>3</sub> as solvent were determined by an NMR spectrometer (Bruker, Model AV600).

The molecule weight of telomer ( $M_n$ ) was calculated by the equation:

$$M_n = M_{KH580} + M_{PEGMA} \frac{H_{KH580} A_{PEGMA}}{H_{PEGMA} A_{KH580}} + M_{DFMA} \frac{H_{KH580} A_{DFMA}}{H_{DFMA} A_{KH580}}$$

where  $A$  is the integration of resonances.  $A_{PEGMA}$  is for the methyl in PEGMA (3.4 ppm),  $A_{KH580}$  is for the methylene in KH580 (2.5 ppm),  $A_{DFMA}$  is for the methyne in DFMA (5.5 ppm).  $M_{KH580}$ ,  $M_{PEGMA}$  and  $M_{DFMA}$  are 238, 475 and 400 g/mol respectively.  $H_{KH580}$ ,  $H_{PEGMA}$  and  $H_{DFMA}$  are the number of protons per proton-bearing group assessed (2 methylene protons per KH580, 3 methyl protons per PEGMA and 1 methyne proton per DFMA).

*Differential scanning calorimetry (DSC).* A differential scanning calorimeter (Netzsch, Model 204 F1) was used to measure the glass transition of the telomers. The samples were heated to 90 °C for annealing and then cooled down to -60 °C at the maximum cooling rate of the instrument. Then it was scanned from -60 to 90 °C at a heating rate of 10 °C·min<sup>-1</sup>. The  $T_g$  values were determined as the midpoint between the onset and the end of a step transition by TA Instruments Universal Analysis 2000 software.

*Thickness measurements.* A coating thickness gauge (Phynix, Model Surfex) with a FN 1.5 Sonde probe was used to measure the thickness of coatings. The coating coated on the substrate was placed on a steel. The thickness was measured by the probe and recorded as  $T_1$ . The corresponding substrate was placed on the steel and the thickness was measured as  $T_0$ . The thickness of coating was calculated by  $T_1 - T_0$ .

*Transmittance Spectra Measurements.* All samples were coated on cleaned glass. The visible spectra of coatings were recorded by a UV-vis spectrophotometer (Agilent, Model Cary 3500).

*Flexibility Tests.* HC-FP-0 and HC-FP-15 were coated on a PET film (thickness: 0.2 mm). The coated film was bent into a U cross section with a side-to-side distance of 0.5-cm diameter. Then, the force was released to return the film to its original shape, completing a bending circle. Each coating was bent and released 100 times. The thickness of each coating is  $\sim 50 \mu\text{m}$ .

*Adhesion Tests.* An automatic tester (PosiTest, Model AT-A) was used to measure the adhesion of coatings to the epoxy resin panel according to ASTM D4541-09.<sup>2</sup> The average adhesion strength was obtained by detaching six cylindrical aluminum studs glued on different regions of each coating. Before test, the coating surface is lightly abraded by a knife to ensure good adhesion to substrate. The diameter of studs was 20 mm and the pull rate was set at 0.2 MPa/s.

*Nanoindentation Tests.* Nanoindentation was performed by a nanoindenter (Anton Paar, Model TTX-NHT<sup>3</sup>) equipped with Berkovich diamond tip at room temperature. Eight different regions of each sample were tested using Oliver-Pharr method to quantify the hardness ( $H_{IT}$ ) and elastic modulus ( $E_{IT}$ ). The approach speed was set at 2000 nm/min and the stiffness threshold was  $500 \mu\text{N}/\mu\text{m}$ . Considering that PDMS and HC-P-15 are soft materials, we increased the approach speed to 4000 nm/min and decreased the stiffness threshold to  $100 \mu\text{N}/\mu\text{m}$  following the application reports provided by Anton Paar. The hardness ( $H_{IT}$ ) was calculated from load-displacement curve by the equation:<sup>3,4</sup>

$$H_{IT} = \frac{F_{max}}{A_p}$$

where  $F_{max}$  is the maximum load, and  $A_p$  is the contact projected area under the

corresponding load. For quasi-static nanoindentation test, the reduced modulus is calculated by the equation:

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}}$$

where S is the slope of the upper portion of the unloading curve and A is the tip contact area.  $E_{IT}$  can be obtained by equation:

$$E_{IT} = E_r \cdot (1 - \nu^2)$$

where  $\nu$  is the Poisson ratio of samples. In this study, the Poisson ratio of PDMS was determined as 0.5, and others were determined as 0.3. The higher the  $H_{IT}$  value, the more difficult the surface is to be damaged. The higher the  $E_{IT}$  value, the more rigid the coating is.

*Pseudobarnacle Removal Tests.* The tests were conducted following the standard ASTM D5618 (2011).<sup>5</sup> Five cylindrical aluminum studs with the diameter of 10 mm were glued on different regions of each coating using two-component epoxy adhesive (Araldite® Rapid Epoxy Adhesive, Huntsman), where the adhesive has been widely used to simulate barnacle adhesive.<sup>6-8</sup> A shear force was applied with a force gauge (SUNDOO, Model SH-500) to the aluminum studs, parallel to the surface, at a constant speed (~4.5N/s).

*Surface Wettability Measurements.* A contact angle goniometer (Biolin, Model KSV NIMA) was used to measure static water contact angles by placing drops of liquid (3  $\mu$ L) on the surface of coatings at room temperature using sessile method. An average contact angle value was measured from five different regions of each sample. The surface energy of each sample was calculated from water and diiodomethane contact

angles using Owens-Wendt-Rabel-Kaeble method.<sup>9</sup>

*Atomic Force Microscopy (AFM).* All samples were coated on epoxy panels and measured by an atomic force microscope (Park Systems, Model XE-100) using a non-contact mode. Area-scan measurements ( $5 \times 5 \mu\text{m}^2$ ) were conducted on six different regions of each sample to determine the topography and phase image. The value of  $R_q$  (the root mean square of the surface roughness height) was used to quantify the surface roughness of coatings. The light and dark region on AFM phase image reflects the phase separation of telomer and hybrid matrix.

*Mass Loss Measurements.* Before immersing in ASW, the weight of each uncoated panel ( $20 \times 20 \text{ mm}^2$ ) was measured and recorded as  $W_p$ . Then, the panels were coated with samples and the weight ( $W_0$ ) was recorded. The coatings were soaked in ASW at 25 °C. After 14 days, the coatings were taken and rinsed with Millipore-Q water to clean the surface carefully. After drying at 110 °C for 2 h, the weight of each coating was measured and recorded as  $W_t$ . The mass loss ratio was obtained by  $(W_0 - W_t) / (W_0 - W_p) \times 100\%$ . The average mass loss was calculated by triplicate samples.

*Antibacterial Assays.* A marine bacteria *Pseudomonas* sp. isolated from marine subtidal biofilms was selected as model,<sup>10</sup> which was cultured following our previous procedure.<sup>11</sup> Silicon slides coated with samples were placed in non-treated polystyrene 24-well tissue culture plate. Each coating was immersed in 1 mL of bacterial suspension (10<sup>8</sup> cell/mL) at 30 °C and cultured for 4 h before the assay. Then, the bacteria were stained with LIVE/DEAD BacLight Bacterial Viability Kit for 30 min and rinsed with ASW twice to wash out the weakly attached bacteria and

extra dye. Finally, the adhered bacteria on coatings were observed by fluorescent microscope (Zeiss, Model Scope A1).

*Anti-biofilm Assays.* The anti-biofilm property of coatings was evaluated using bacteria *Pseudomonas* sp. The samples were casted in 24-well plates and placed in oven at 60 °C for 3 days to remove the residual solvent. Then, each coating was soaked in 1 mL of bacteria suspension ( $10^8$  cell/mL) and the plates were sealed by sealing films. The bacteria were incubated in an incubator at 30 °C. After two days, the suspension was removed by pipette and the plates were gently rinsed with ASW to take weakly attached or planktonic biofilm away. The biofilm was fixed by methanol and dried at room temperature. Afterwards, the fixed biofilm was stained with crystal violet (0.3 wt% aqueous solution) and rinsed with ASW to remove the extra dye. Finally, the dye was extracted with acetic acid (33 wt% aqueous solution) and measured by a photometer at 589 nm to obtain the OD value (optical density) as biomass.

*Anti-diatom Assays.* The marine diatom *N. incerta* (*Navicula incerta*) was incubated following our previous procedure.<sup>11</sup> Silicon slides coated with samples were placed in 24-well plates. 1 mL of *N. incerta* suspension (chlorophyll content is 0.50 µg/mL) was added to each plate well and cultured at 25 °C for 24 h. Then, the silicon slides were rinsed with ASW to wash out the weakly attached and planktonic diatom. Afterwards, ten random regions of triplicate slides were observed by a microscope (Zeiss, Model Scope A1) to quantify the average diatom density of each sample.

**Table S1.** Characterization data of the telomers.



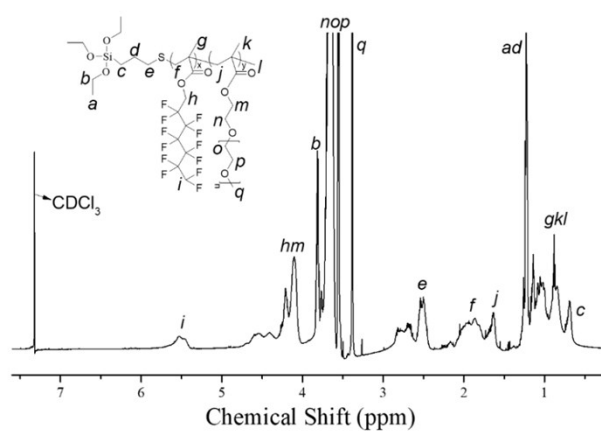
Sample	DFMA/PEGMA/KH590 <sup>a</sup>	DFMA/PEGMA/KH590 <sup>b</sup>	$M_n^c$ (g/mol)	$T_g^d$ (°C)
FP	2/2/1	1.9/1.7/1	1800	7.8
P	0/4/1	0/4.1/1	2200	/
F	4/0/1	3.5/0/1	1650	34.6

<sup>a</sup> Feed molar ratio. <sup>b</sup> Molar ratio in telomers determined by <sup>1</sup>H NMR. <sup>c</sup> Molecule weight was determined by <sup>1</sup>H NMR. <sup>d</sup> Glass transition temperature was determined by DSC.

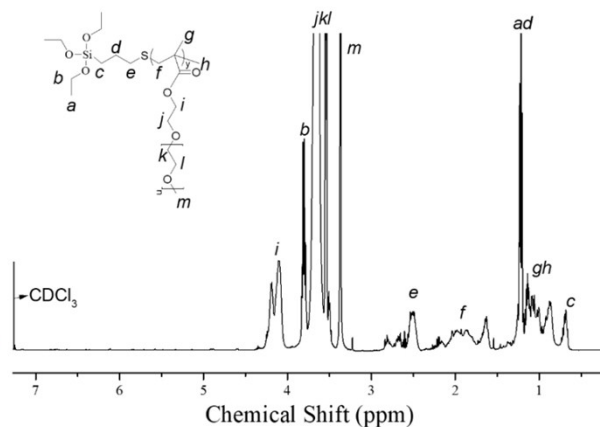
**Table S2.** Composition of raw hard coatings (units: g).

Sample	TEOS/KH832	FP/P/F	Modulus <sup>a</sup> (GPa)	Adhesion <sup>b</sup> (MPa)
HC-FP-0	2.08/2.77	0/0/0	0.29	0.86
HC-FP-5	2.08/2.77	0.24/0/0	0.34	1.36
HC-FP-10	2.08/2.77	0.48/0/0	0.38	1.36
HC-FP-15	2.08/2.77	0.73/0/0	0.42	1.36
HC-P-15	2.08/2.77	0/0.73/0	0.11	1.20
HC-F-15	2.08/2.77	0/0/0.73	1.00	0.70

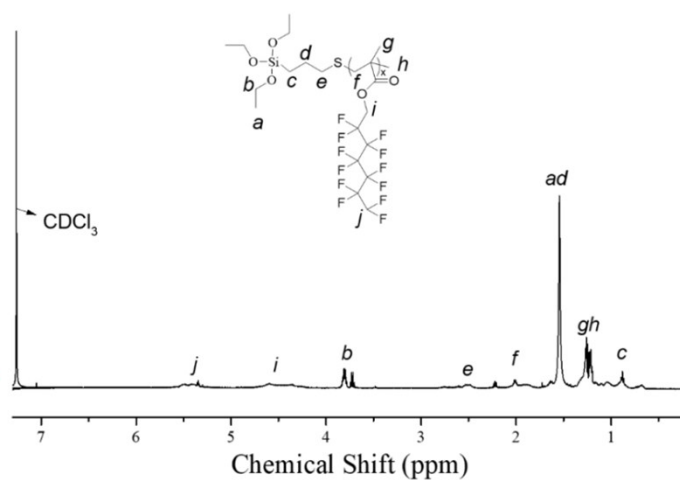
<sup>a</sup> Modulus was determined by nanoindentation. <sup>b</sup> Adhesion was determined on epoxy resin fiberglass panel.



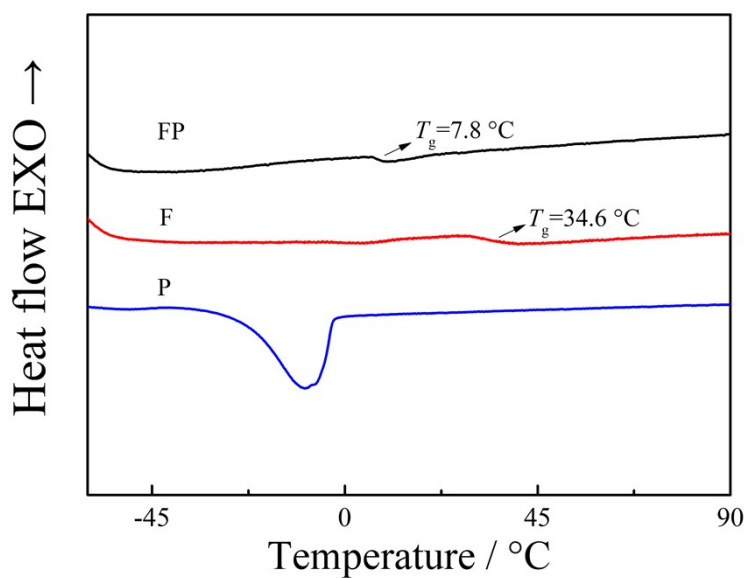
**Figure S1.** <sup>1</sup>H NMR spectrum of telomer FP.



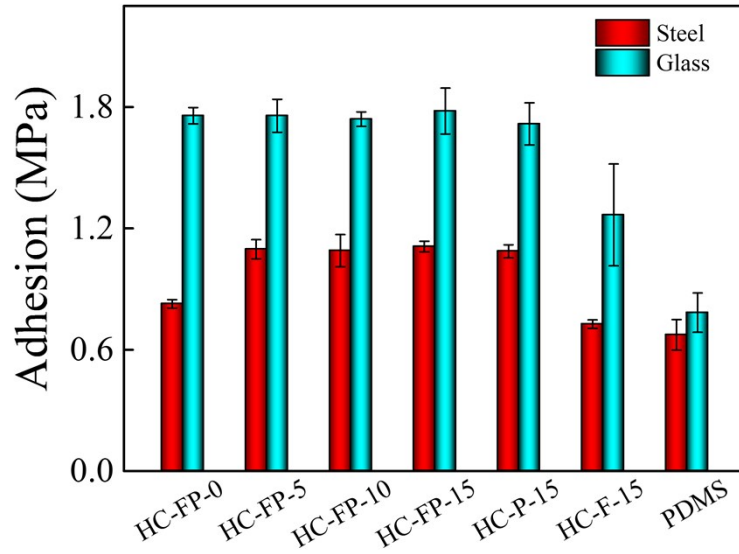
**Figure S2.**  $^1\text{H}$  NMR spectrum of telomer P.



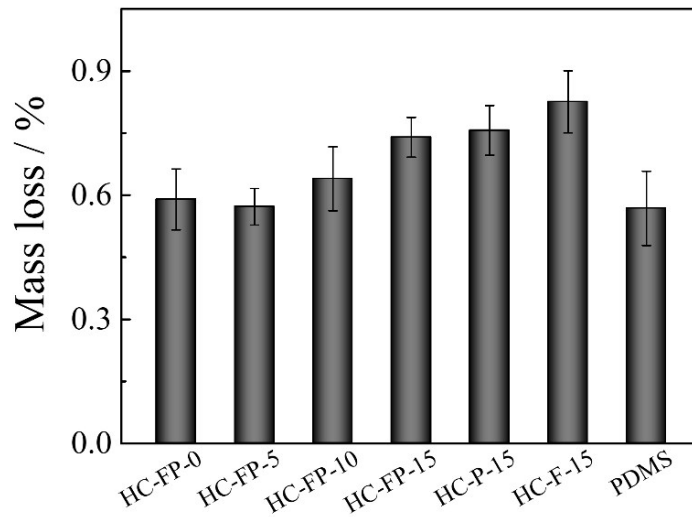
**Figure S3.**  $^1\text{H}$  NMR spectrum of telomer F.



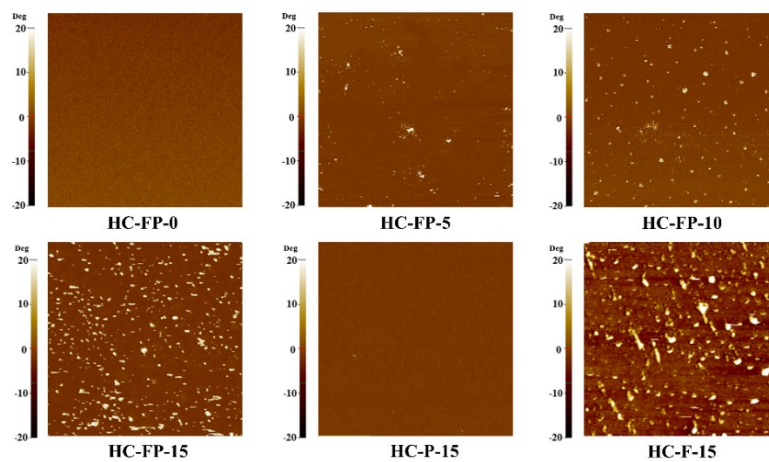
**Figure S4.** DSC heating curve of telomers.



**Figure S5.** Adhesion of the FP contained coatings on steel and glass.



**Figure S6.** Mass loss of hybrid coatings after immersing in ASW for 14 d.



**Figure S7.** The phase images ( $5 \times 5 \mu\text{m}^2$ ) of hybrid coatings by AFM.

## References

- 1 P. Muller, *Pure & Appl. Chem.* 1994, **66**, 1077-1184.
- 2 ASTM D4541-09. Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers; ASTM International: West Conshohocken, PA, 2009.
- 3 Z. Wang, A. A. Volinsky, N. D. Gallant, *J. Appl. Polym. Sci.* 2015, **132**.
- 4 C. Jin, Z. Wang, A. A. Volinsky, A. Sharfeddin, N. D. Gallant, *Polym. Test.* 2016, **56**, 329.
- 5 ASTM D5618-94. Test Method for Measurement of Barnacle Adhesion Strength in Shear; ASTM International: West Conshohocken, PA, 2011.
- 6 M. Berglin, P. Gatenholm, *J. Adhesion Sci. Technol.* 1999, **13**, 713-727.
- 7 J. C. Thomason, M. D. Letissier, P. O. Thomason, S. N. Field, *Biofouling*, 2002, **18**, 293-304.
- 8 A. S. Sebastin, S. Mohanty, S. K. Nayak, *Appl. Polim. Sci.* 2019, **136**, 47720.
- 9 D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* 1969, **13**, 1741.
- 10 Q. M. Peng, Z. Xin, Q. Y. Xie, C. F. Ma, G. Z. Zhang, *Langmuir* 2019, **35**, 12257-12263.
- 11 Q. Y. Xie, Q. N. Xie, J. S. Pan, C. F. Ma, G. Z. Zhang, *ACS Appl. Mater. Interfaces* 2018, **10**, 11213.