Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Novel Micron-thick Brick Cladding of Polyfluorosilicone Acrylates, A Case Study of Conservation of Historic Brick Wall in Hongcun Village

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Experimental Section

Materials

Trifluoroethyl methacrylate (G03, 96+%), hexafluorobutyl methacrylate (G02, 96+%) and dodecafluoroheptyl methacrylate (G04, 96+%), were supplied by XEOGIA Fluorine-Silicon Chemical Co., Ltd. Isobornyl methacrylate (IBOMA, 85%) was purchased from Sahn Chemical Technology Co., Ltd. Styrene (St, 99.5+%), acrylic acid (AA, 99.5+%) and benzoyl peroxide (BPO, 99.7+%) were from Sinopharm Chemical Reagent Co., Ltd. 3-(trimethoxysilyl)propyl methacrylate (KH-570, 98%) was provided by Jining Huakai Resin Co., Ltd. Dimethyl carbonate (DMC, 99+%) and ethanol (EtOH, 99.5+%) were supplied by Shanghai Gaoyun Chemical Co., Ltd. All reagents and solvent were used as received without further purification. The old bricks with dimensions 22 cm × 10 cm × 4 cm were obtained from Hongcun Village, Yi County, Anhui Province, 300 years ago and cut into 5 cm × 5 cm × 1 cm for water vapor permeability test, 1 cm × 1 cm × 2 cm for the water contact angle measurement, water absorption by total immersion, freeze-thaw cycles test and soluble salts aging test.

Synthesis of polyfluorosilicone acrylates

The polyfluorosilicone acrylates were prepared via a radical initiated solution polymerization. All the polymerizations were carried out in a 250-mL three-neck flask equipped with a reflux condenser, a mechanical stirrer, an inlet for nitrogen gas and a thermometer and heated in the oil bath. Based on different contents of KH-570 (wt%: 5, 10, 15) and IBOMA (wt%: 0, 10), a series of polyfluorosilicone acrylates materials were prepared and designated as FS/S-5, FS/S5, FS/S-10 and FS/S-15, respectively.

Synthesis of FS/S-5

The mixture of 6 g of G04, 11 g of St, 2 g of IBOMA, 1 g of KH-570 and 0.16 g of the initiator (BPO) was added into the flask. Then, the mixture was stirred and slowly heated to 85 °C. After the viscosity of polymer solution was increased to a certain extent, 0.6 g AA and 80 g DMC were added to the system. Then the system was maintained until the viscosity of the polymer solution was no longer increased. Finally, the temperature was cooled to room temperature and the transparent viscous liquid was obtained.

IR (KBr): v [cm^{-1}] =2946, 1455, 1393 (CH_3); 1723 (C=O); 1247, 1171 (C-F); 1110 (Si-O-Si) and 701, 758 (aromatic C-H). ^{19}F NMR (600 MHz, $CDCl_3$) [δ/ppm] =-71.76 – -75.90 (m, 9F, $-CF_3$), -184.66 – -189.52 (m, F, -CHF-), -208.02 – -212.30 (d, F, $-CH_2CF-$).

Synthesis of FS/S5

The mixture of 6 g of G04, 13 g of St, 1 g of KH-570 and 0.16 g of the initiator (BPO) was added into the flask. Then, the mixture was stirred and slowly heated to 85 °C. After the viscosity of polymer solution was increased to a certain extent, 0.6 g AA and 80 g DMC were added to the system. Then the system was maintained until the viscosity of the polymer solution was no longer increased. Finally, the temperature was cooled to room temperature and the transparent viscous liquid was obtained.

IR (KBr): v [cm^{-1}] =2930, 1454, 1390 (CH_3); 1744 (C=O); 1249, 1170 (C-F); 1107 (Si-O-Si) and 700, 758 (aromatic C-H). ^{19}F NMR (600 MHz, $CDCl_3$) [δ/ppm] =-71.74 – -76.17 (m, 9F, $-CF_3$), -184.63 – -189.49 (m, F, -CHF-), -207.98 – -212.14 (d, F, $-CH_2CF-$).

Synthesis of FS/S-10

The mixture of 6 g of G04, 10 g of St, 2 g of IBOMA, 2 g of KH-570 and 0.16 g of the initiator (BPO) was added into the flask. Then, the mixture was stirred and slowly heated to 85 °C. After the viscosity of polymer solution was increased to a certain extent, 0.6 g AA and 80 g DMC were added to the system. Then the system was maintained until the viscosity of the polymer solution was no longer increased. Finally, the temperature was cooled to room temperature and the transparent viscous liquid was obtained.

IR (KBr): v [cm^{-1}] =2941, 1455, 1382 (CH_3); 1724 (C=O); 1246, 1172 (C-F); 1106 (Si-O-Si) and 700, 759 (aromatic C-H). ^{19}F NMR (600 MHz, $CDCl_3$) [δ/ppm] =-71.73 – -76.16 (t, 9F, $-CF_3$), -184.67 – -186.66 (m, F, -CHF-), -207.88 – -211.99 (d, F, $-CH_2CF-$).

Synthesis of FS/S-15

The mixture of 6 g of G04, 9 g of St, 2 g of IBOMA, 3 g of KH-570 and 0.16 g of the initiator (BPO) was added into the flask. Then, the mixture was stirred and slowly heated to 85 °C. After the viscosity of polymer solution was increased to a certain extent, 0.6 g AA and 80 g DMC were added to the system. Then the system was maintained until the viscosity of the polymer solution was no longer increased. Finally, the temperature was cooled to room temperature and the transparent viscous liquid was obtained.

IR (KBr): v [cm^{-1}] =2947, 1455, 1380 (CH_3); 1726 (C=O); 1246, 1173 (C-F); 1103 (Si-O-Si) and 701, 759 (aromatic C-H). ^{19}F NMR (600 MHz, $CDCl_3$) [δ/ppm] =-71.76 – -75.84 (m, 9F, $-CF_3$).

Characterization

FTIR. The FTIR spectra of the polymers were obtained with an AVATAR 370 FTIR spectrometer (Nicolet, USA), at a resolution of 4.000 cm^{-1} and an accumulation of 16 scans.

NMR analysis. The ^{19}F NMR spectra of the polymers were obtained by a Bruker AVANCE III HD 600 MHz NMR Spectrometer (Bruker, Switzerland) using $CDCl_3$ as the solvent.

Gel permeation chromatography (GPC). The molecular weight and polydispersity were determined by Waters 1515 gel permeation chromatography (Waters, USA). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min. The samples were prepared dissolving 2 mg polymer in 1.2 mL THF.

The glass transition temperature. The glass transition temperature of the polymers was obtained using a TA Q500 HiRes (TA Instruments, USA) differential scanning calorimeter. The scanning rate was 10°C/min from −50 °C to 250 °C under nitrogen atmosphere.

The properties of the polyfluorosilicone acrylates. The viscosity of the four polymer solutions (3 wt%) was determined with an NDJ-8S numerical viscometer (Shanghai Lichen Instrument Technology Co., Ltd., China) according to ISO 2884-1974. The pencil hardness of the polymer films was measured with a QHQ-A pencil sclerometer (Zhenwei Testing Machinery Co Ltd, China) according to ISO 15184:1998. The adhesion was measured with a QFH paint film adhesion tester according to ISO 2409:2013 by cross cut test. Impact resistance was measured with a QCJ-120 impact tester according to the standard ISO 6272-2:2011. The surface water contact angle of the polymer films was measured according to GB/T 30693−2014 on an OCA 15EC video-based measuring system (EASTERN-DATAPHY (HK), China). Water absorption of polymer films was measured by gravimetric variation before and after immerging the polymer films into deionized water for 24 h. The corrosion resistance to acid and alkali was carried out with water solution of 5.0 wt% sulfuric acid and 5.0 wt% sodium hydroxide respectively at room temperature for 30 d.

Thermogravimetric analysis (TGA). Thermogravimetric analysis was investigated at a heating rate 10 °C/min under nitrogen atmosphere in the temperature range 25-600 °C by TA Q500 HiRes (TA Instruments, USA).

UV-Vis transmittance. Optical transmittance spectra of polymer films from 280-800 nm were recorded on a UV-2501PC UV-vis spectrometer (Shimadzu, Japan).

Water contact angle. Water contact angle of the treated ancient bricks surface was measured using an OCA 15EC video-based measuring system (EASTERN-DATAPHY (HK), China) at room temperature (RT, 25 °C). The droplet of distilled water (5 μL) was placed on the surface of the treated brick sample, and the water contact angle test was completed within 10 seconds. Water contact angle of the sample was the average value of five measurements on different positions at the sample surface.

Water absorption by total immersion. The water absorption of the treated and untreated brick samples was calculated by determination of the weight for dry sample (M_1) and the weight of totally water-saturated sample for 24 h (M_2):

$$\text{Water absorption (wt\%)} = (M_2-M_1)/M_1\times100 \quad (1)$$

Freeze-thaw cycles test. The treated and untreated brick samples were soaked in water for 12 h, followed by freezing at -20°C for 12 h after absorbing excess surface water with a filter paper. This process was repeated 50 times in this experiment.

Soluble salts aging test. The treated and untreated brick samples were immersed in a 10 wt% sodium sulfate (Na_2SO_4) solution for 4 h, then all the samples were taken out and allowed to stand at ambient temperature for making the salt precipitates few hours. Then all were washed with deionized water and moved to the oven under 60 °C for 4 h. This process was repeated for 30 times in this experiment.

Penetration depth. The penetration depth of each solution was measured by cutting the specimens vertically and moistening the cross section. The hydrophobic zone then showed up much lighter than the wet material.

Water vapor permeability. For the water vapor permeability, the treated and untreated brick samples were fixed on the top of containers that were partially (1/2) filled with water. Then, the containers fixed and sealed with brick were placed in a climatic chamber, kept at R.H. 40%±1 and at constant temperature of 25±1 °C. The containers were weighted every 24 h to determine the mass of water vapor passing though the surface unit under controlled conditions. Then water vapor transmission rate (WVTR) expressed in g/(m^2·d) was defined as:

$$WVTR=\Delta m/(A\cdot t) \quad (2)$$

Where: Δm is the weight change (g), A is the area exposed to water vapor (m^2), t is the time when Δm occurred (24 h). In our case, Δm was calculated as the average of five consequent values of the daily difference in weight.

Colorimetric measurements. The total color difference between the treated and untreated brick samples (ΔE*) was evaluated by the use of L*a*b* coordinates of CIE 1976 scale [1] and is defined as:

$$\Delta E=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad (3)$$

Where ΔL* is the lightness difference; Δa* is the red/green difference; and Δb* is the yellow/blue difference.

SEM analysis. Morphology of the treated and untreated brick samples was observed using an Apollo 300 scanning electron microscope (Shanghai China Science Xinxin International Trade Corp. Ltd., England) at an accelerating voltage of 15 KV. All specimens were sputter-coated with gold prior to examination.

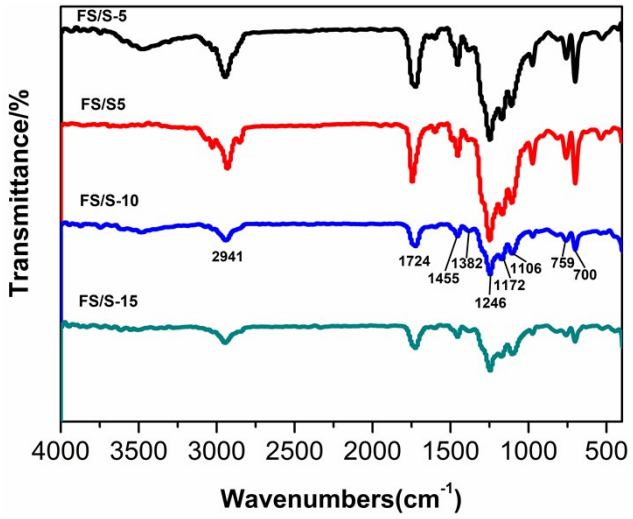

Fig. S1. FTIR spectra of FS/S-5, FS/S5, FS/S-10 and FS/S-15.

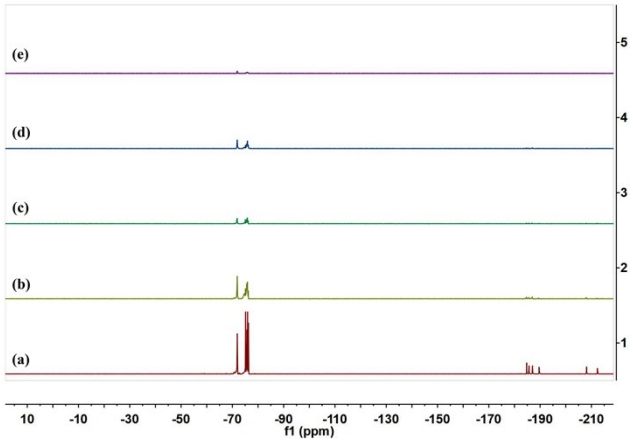

Fig. S2. ^{19}F NMR spectra of (a) G04, (b) FS/S-5, (c) FS/S5, (d) FS/S-10, and (e) FS/S-15.

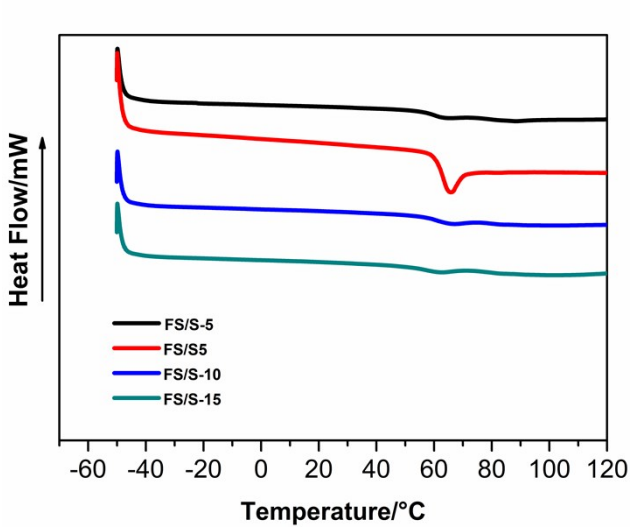

Fig. S3. DSC curves of different polyfluorosilicone acrylates.

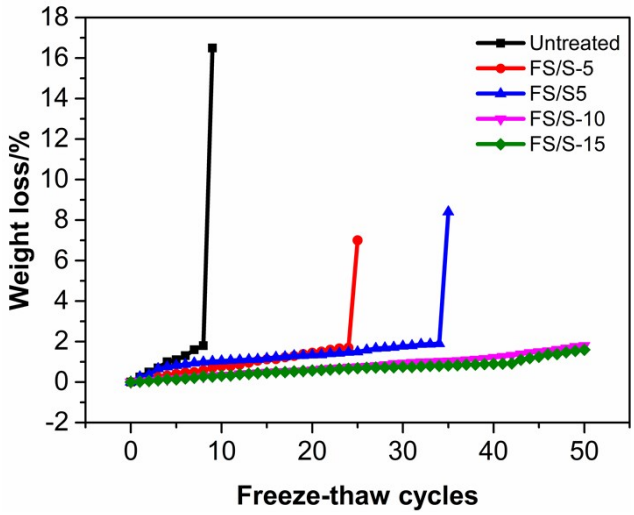

Fig. S4 Weight loss of samples during the freeze-thaw cycles.

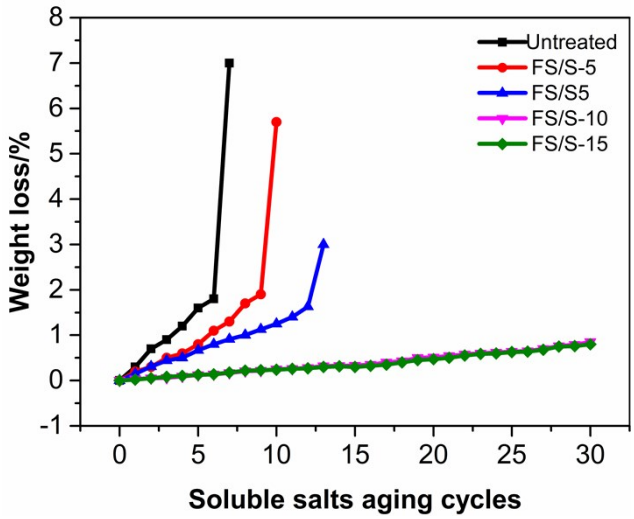

Fig. S5 Weight loss of samples during the soluble salts aging cycles.

Table S1. Effect of fluorinated monomer on properties of the polyfluorosilicone acrylates polymers[a]

Properties	Fluorinated monomer		
	G03	G02	G04
Pencil hardness[b]	5H	5H	6H
Adhesion[b]	Gt 0	Gt 0	Gt 0
Contact angle (°)[c]	88	93	95
Water absorption (wt%)[c]	6.99	4.20	1.17
5 wt% NaOH (30d)[c]	shedding	Unchanged	Unchanged
5 wt% H_2SO_4 (30d)[c]	Unchanged	Unchanged	Unchanged

[a] KH-570 content is 10 wt%. [b] Polymer films were cast on the tinplate substrates. [c] Polymer films were cast on a glass substrate.

Table S2. Effect of G04 content on properties of the polyfluorosilicone acrylates polymers[a]

Properties	G04 content (wt%)			
	10	20	30	40
Pencil hardness[b]	6H	6H	6H	6H
Adhesion[b]	Gt 0	Gt 0	Gt 0	Gt 0
Contact angle (°)[c]	87	95	99	98
Water absorption (wt%)[c]	5.06	3.36	1.12	1.17
5 wt% NaOH (30d)[c]	Unchanged	Unchanged	Unchanged	Unchanged
5 wt% H_2SO_4 (30d)[c]	Bubble	Unchanged	Unchanged	Unchanged

[a] KH-570 content is 10 wt%. [b] Polymer films were cast on the tinplate substrates. [c] Polymer films were cast on a glass substrate.

Table S3. The molecular weight of the polyfluorosilicone acrylates polymers

Sample	$M_n/10^4$	PDI
FS/S-5	5.8	2.0
FS/S5	6.1	1.7
FS/S-10	6.6	1,6
FS/S-15	6.8	1.8

Table S4. Total colour difference ΔE* of untreated brick samples and brick samples treated with different polyfluorosilicone acrylates cladding agents

Sample	ΔL*	Δa*	Δb*
Pure brick	-	-	-
FS/S-5	-0.23	0.017	-0.9113
FS/S5	-0.1678	0.1143	0.8064
FS/S-10	-0.1143	0.2389	0.9747
FS/S-15	-0.64	0.35	0.9779

Reference

[1] G. Cappelletti, P. Fermo, F. Pino, E. Pargoletti, E. Pecchioni, F. Fratini, S. A. Ruffolo and M. F. La Russa, *Environ. Sci. Pollut. Res*., 2015, **22**, 17733-17743.