

Supplementary Information

One step fabrication of superhydrophobic polymeric surface from an acrylic copolymer containing POSS by spraying

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Experimental section

Materials

Methacryloisobutyl polyhedral oligomeric silsesquioxane (MA-POSS, C₃₅H₇₄O₁₄Si₈, formula weight 943.64) was supplied by Hybrid Plastics Inc (USA). Bovine serum albumin (BSA) and bovine fibrinogen (BFG) were obtained from Sigma Chemical Company. Butyl acrylate (BA), methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Kemiou Chemical Co., Tianjin, China. All the monomers were purified by washing with 5 wt% NaOH aqueous solution and water, respectively, and dried with CaCl₂ and distilled under vacuum. Methyl isobutyl ketone (MIBK) and Benzoyl peroxide (BPO) were also purchased from Kemiou Chemical Co., Tianjin, China. Other chemicals were used as received without further purification.

Synthesis of the POSS-acrylic copolymer (PAC)

The POSS-acrylic copolymer was prepared by radical solution polymerization. In short, MIBK (6g) and BPO (0.15g) were placed in flask and heated to 80°C for 30 min. A solution of MMA (6g), BA (4.5g), HEMA (1g), MA-POSS (1.2g) and MIBK (5g) was dropwise added into the flask within 2 h. After about 3h, the amount of BPO (0.07g) and MIBK (3g) solution was added into the flask. The reactants were stirred for another 6 h at 80°C. The entire operation was conducted under a constant stream of nitrogen. At the end of the reaction, the resulting production was precipitated in hexane, and dried under vacuum at 60°C for 24 h.

Preparation of the superhydrophobic POSS-acrylic copolymer (SPAC) coating

A certain amount of the prepared POSS-acrylic copolymer was dissolved in ethyl acetate to form 10 wt% solutions. The superhydrophobic POSS-acrylic copolymer (SPAC) surface was obtained by spraying the copolymer solution over substrate under appropriate air pressure (0.6MPa) and then dried at room temperature. During the spraying process, the nozzle of spray gun with diameter of approximately 0.2~1 mm is kept at a certain distance from the substrate. The room temperature and relative humidity are $\sim 25 \pm 5^\circ\text{C}$ and $40 \pm 5\%$, respectively. The thickness of the sample coatings are $25 \pm 2.1\mu\text{m}$, which is measured by Coating Thickness Gauge (PTG-3550).

Preparation of hydrophobic POSS-acrylic copolymer (HPAC) coating

The HPAC films were prepared by spin-coating of the copolymer/MIBK solution on the substrate at room temperature. The spinning speed was set at 200 rpm (5 s) and 2000 rpm (10 s) for the first and second steps, respectively. The room temperature and relative humidity were $\sim 25 \pm 5^\circ\text{C}$ and $40 \pm 5\%$, respectively.

Characterizations

FT-IR spectra of samples were recorded between 4000 cm^{-1} and 500 cm^{-1} in a Bio-Rad FTS-135 spectrophotometer using KBr pellet technique. The molar mass distribution was determined in a Waters 1515 gel permeation chromatography (GPC) with THF as the eluent flowing at 1 mL/min. Polystyrene standards were used to generate a calibration curve. The diluted copolymer solution was deposited onto a copper net and stained with phosphotungstic acid solution. TEM micrographs were taken with JEOL JEM100CXII transmission electron microscope. The surface morphology of the SFAC coatings was observed with a scanning electron microscope (SEM, FEL Nova Nano 430). The surface composition of coating was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using at a 90° take-off angle. Water contact angles and sliding angles on the surfaces at 25°C were measured with a modified optical contact angle meter system with cold plate (Dataphysics OCA40). The cumulation particle size distribution curve of liquid droplets formed in spraying process was tested with a spray laser particle size analyzer (JL-3000, Chengdu Jingxin Powder Analyse Instrument CO., LTD) and the room temperature and relative humidity were $\sim 25 \pm 5^\circ\text{C}$ and $40 \pm 5\%$, respectively.

Protein adsorption experiments¹ were carried out with BSA and BFG solutions. First, the samples with an area of $10 \times 10\text{ mm}^2$ were immersed in phosphatic buffer solution (PBS, pH 7.4), and equilibrated with PBS for 12 h. Then the samples were dunked in PBS containing BSA or BFG with a concentration of 1 mg/ml, and incubated at 37°C for 2 h. After rinsed slightly with PBS solution and double distilled water, the membrane was placed in a washing solution (2% sodium dodecyl sulfate at 37°C) and shaken for 2 h to remove the adsorbed protein. The protein concentration in the washing solution was determined by using the MICROBCA Protein Assay Reagent Kit, and then the adsorbed protein amount was calculated. The experiments were repeated three times.

Platelet adhesion tests¹ were conducted on HPAC, SPAC and PVC (for comparison) surface ($10\text{ mm} \times 10\text{ cm}$). Then platelet-rich plasma (PRP) was obtained by centrifuging citrate anticoagulated rabbit whole blood at 1200 rpm for 10 min at room temperature. All the samples were equilibrated with phosphate buffered saline (PBS, pH 7.4) for 24h, and then immersed in PRP for 1 h at 37°C . After gently rinsing with PBS for three times to remove non-adherent platelets, the platelets on the samples were fixed using 2.5% glutaraldehyde solution for 10 h. The films were gently rinsed with PBS then dehydrated sequentially with 30%, 50%, 70%, 90%, and 100% gradient solution of ethanol/ water (v/v) for 30 min each, and subsequently allowed to dry at room temperature and finally sputter-coated with gold. Platelet adhesion and deformation on surfaces were observed by scanning electron microscopy (SEM, FEL Nova Nano 430), and the number of platelet adhesion on different surfaces were also calculated from the SEM pictures.

Results

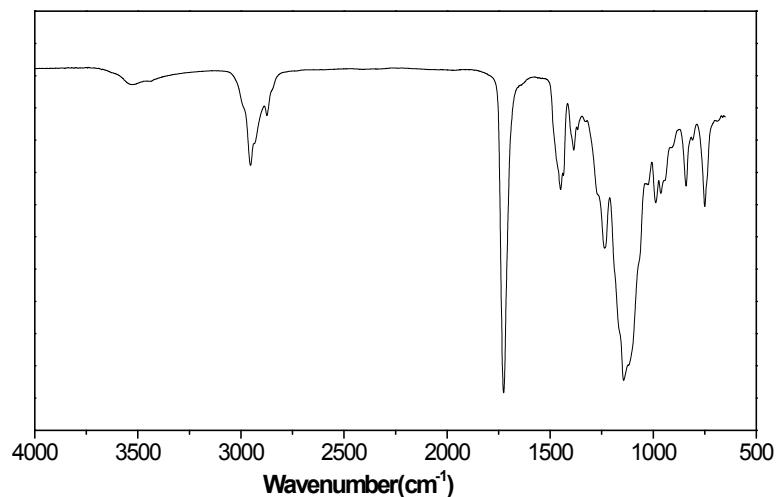


Fig. S1 FT-IR spectrum of the POSS-acrylic copolymer

Fourier transform infrared spectroscopy (FT-IR) was performed on Perkin-Elmer Spectrum One (USA) using KBr pellets. FT-IR spectrum of the POSS-acrylic copolymer was shown in Fig. S1. The characteristic stretching peaks of C-OH, C-H, and C=O group were shown at 3550 cm^{-1} , 2850~3000 cm^{-1} , and 1740 cm^{-1} , respectively. The peak at 1250 cm^{-1} was the characteristic bonds of C-O in ester group of the copolymer, and the peak at 1000~1100 cm^{-1} was attributed to the characteristic bonds of Si-O-Si. Meanwhile, peak at 1640 cm^{-1} , which was attributed to the stretching vibration of C=C group, disappeared, indicating the almost all monomers have been polymerized.

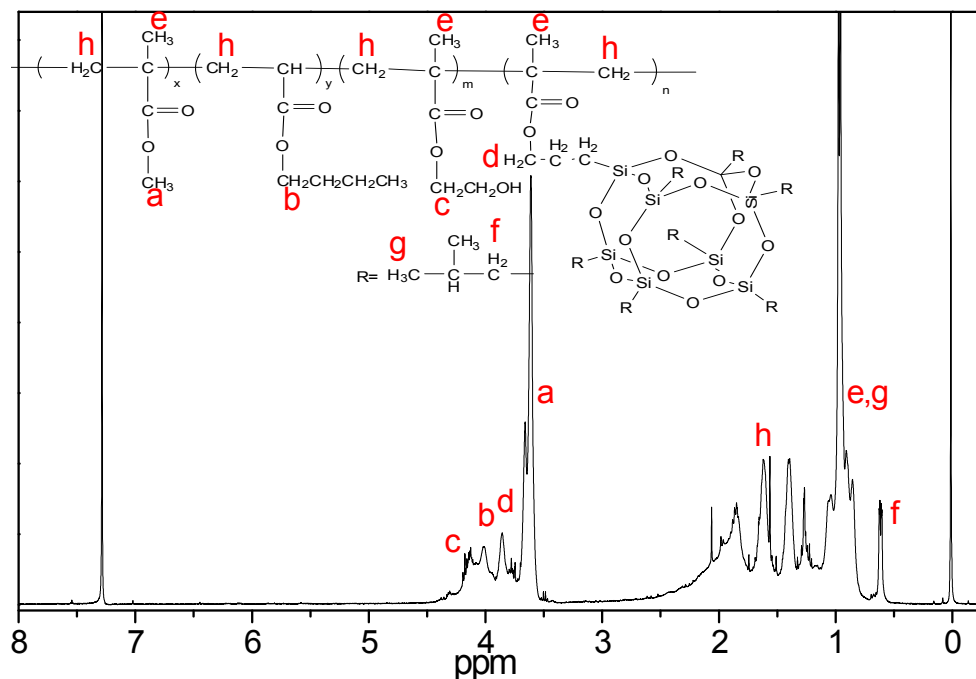


Fig. S2 $^1\text{H-NMR}$ spectrum of the POSS-acrylic copolymer.

The $^1\text{H NMR}$ result of POSS-acrylic copolymer in Fig. S2 could confirm its structure by the typical δH (ppm) at about 3.65(a), 3.8~4.1 (b, d), 4.2 (c), 0.8~1.0(e, g), 0.6(f), and 1.65 (h).^{2,3}

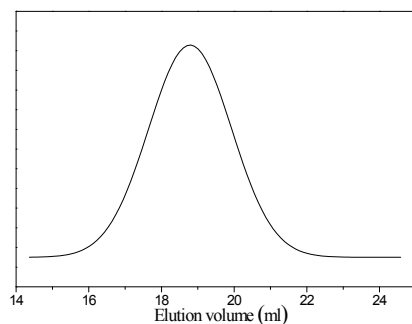


Fig. S3 GPC curve of the POSS-acrylic copolymer. The number-average molecular weight is 35,000 and the polydispersity index is 1.91.

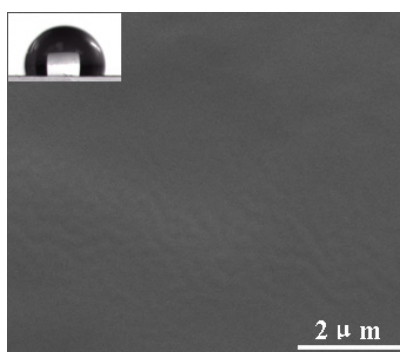


Fig. S4 SEM image of the surface of hydrophobic POSS-acrylic copolymer (HPAC), and the inset shows the water contact angle. The contact angle value of HPAC coating is $106 \pm 2.3^\circ$

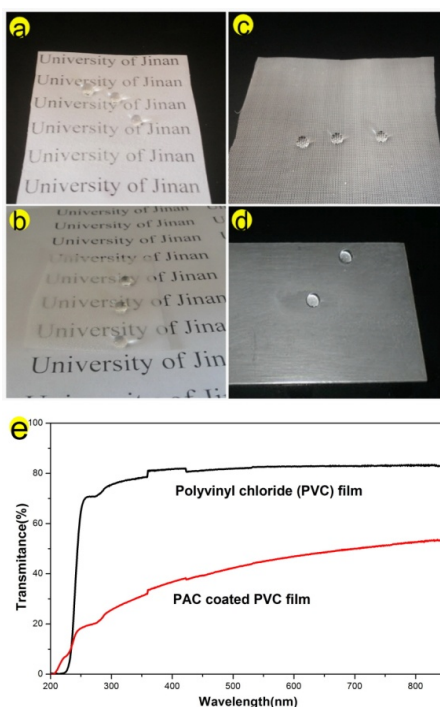


Fig. S5 Photographs of water droplets on the spray-coated (a)paper, (b)PVC film, (c) steel mesh and (d)aluminum plate. (e) Ultraviolet visible transmittance spectra of the PVC film and PAC-coated PVC film.

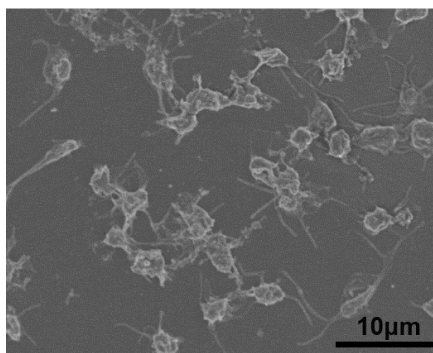


Fig. S6 SEM image of the platelets adhesion on PVC surface

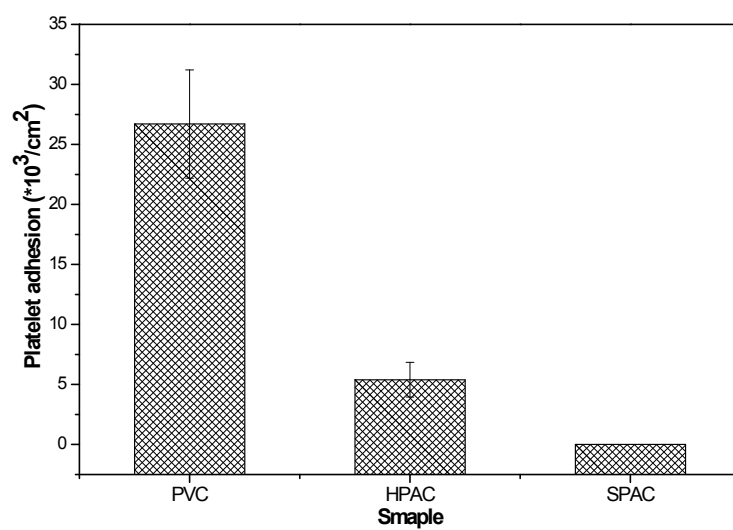


Fig. S7 Number of the platelets adhesion on the surfaces of PVC, HPAC and SPAC from the SEM pictures.

References

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