Supporting Information

Design of 'Tolerant and Hard' Superhydrophobicity to Freeze Physical Deformation

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Experimental Section:

Materials: [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS), Octadecyl acrylate (ODAc), pentaerythritol triacrylate (3-Acl; molecular weight: 298.29 g/mol), dipentaerythritol penta-acrylate (5-Acl; molecular weight: 524.51 g/mol), sodium dodecyl sulphate (SDS), hexadecyltrimethylammonium bromide (CTAB), triton x-114, methylene blue were obtained from Sigma Aldrich (Bangalore, India). Ethanol was procured from Changshu Hongsheng Fine Chemical. Sodium chloride, magnesium chloride, calcium chloride, magnesium sulphate, sodium hydroxide was purchased from Emparta (Merck Specialties Private Limited). HCl was purchased from Fischer Scientific (Mumbai India). Polyurethane fabric was procured from Amazon India. Melamine sponge was purchased from AR Acoustics LLP Maharashtra. Adhesive tape, sand paper, knife was procured from a local shop in Guwahati city (Assam, India). Milli-Q grade water was used for all experiments.

General Considerations: KRUSS Drop Shape Analyser-DSA25 instrument with an automatic liquid dispenser was used for the measurement of contact angle under ambient condition. Field emission scanning electron microscope (FESEM) images were taken using Sigma Carl Zeiss scanning electron microscope (a thin layer of gold was done on the sample before imaging). FTIR-ATR spectra were recorded using PerkinElmer instrument. Mechanical properties were measured using 5kN Electromechanical Universal Testing Machine. Digital pictures were captured using a canon power shot SX420 IS digital camera.

Fabrication of RMT1, RMT2A and RMT2B Coated Superhydrophobic Material: Both melamine foam and polyurethane fabric was washed with acetone prior to apply dip coating. Reaction mixture RMT1 was prepared by mixing 6 ml of 3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS) and 9 g of Octadecyl acrylate (ODAc) in 24 ml of ethanol. Next polyurethane fabric and melamine foam was dipped in the reaction solution and kept for 10 min under agitation followed by drying in oven at 70 ^{0}C to obtain the superhydrophobicity. RMT2A reaction mixture was prepared by mixing 6 ml of [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS), 3.12 g Octadecyl acrylate (ODAc) and 1.78 g pentaerythritol triacrylate (3-Acl) in 24 ml of ethanol. RMT2B reaction mixture was prepared by mixing 6 ml of [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS), 3.12 g of Octadecyl acrylate (ODAc) and 1.88 g of Dipentaerythritol penta-acrylate (5-Acl) in 24 ml of ethanol. Same fabrication procedure mentioned for RMT1 coated materials was followed to prepare the RMT2A and RMT2B coated substrates.

Tailoring Mechanical Property of Superhydrophobic Material: Reaction mixture of RMT2B comprises of three reactants [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTMS), octadecyl acrylate (ODAc) and dipentaerythritol penta-acrylate (5-Acl). To demonstrate tailored mechanical property, a series of reaction mixtures has been prepared where the 5-Acl concentration has been varied from 0 mM to 140 mM—keeping the ratio of acrylate group to primary amine group identical (1:1). In these series of reaction mixtures, the amount of AEAPTMS remained unaltered—but the concentrations of 5-Acl and ODAc changed. Hence, the increase in the concentration of 5-Acl in the reaction mixture of RMT2B, reduced the concentration of ODAc in order to maintain the acrylate to amine functional groups as 1:1. The superhydrophobic coating with tailored mechanical property was achieved by dipping the selected soft substrate in the respective reaction mixture for 10 minutes. On increasing the concentration of 5-Acl in RMT2B, the mechanical property has been gradually improved. Details of reactants amount in different reaction solution is given in the table below.

Concentration of 5-Acl (mM)	Amount of 5-Acl (g)	Amount of ODAc (g)	Amount of Aminosilane (ml)
0	-	9	6
20	0.31	7.98	6
40	0.62	7.01	6
60	0.94	6.03	6
80	1.25	5.06	6
100	1.57	4.09	6
120	1.88	3.11	6
140	2.21	2.14	6

Table S1: Accounting the detailed formulation of reaction mixture that provided superhydrophobic coating with tailored mechanical property.

Mechanical Performance of the Prepared Coatings: Mechanical properties of the synthesized superhydrophobic materials were determined using 5kN Electromechanical Universal Testing Machine. For measuring the compressive strength, both bare and coated (RMT1, RMT2A and RMT2B) melamine foams were cut with the dimension of 4 cm × 2.5 cm × 2.5 cm. For tensile strength measurement, bare and coated (RMT1, RMT2A and RMT2B) polyurethane fabric of dimension 5 cm × 2 cm was used. All the experiments were performed under ambient conditions.

Physical and chemical durability: Different physical and chemical durability tests were performed on both superhydrophobic melamine foam and polyurethane fabric. Detailed procedure for all the durability tests were explained in the section given below.

Sand Paper Abrasion Test: 400 grit abrasive sand paper (2 cm radius) was rubbed manually in back-and-forth direction across the superhydrophobic melamine foam of area 2 cm x 1 cm with an applied pressure of 25 kPa for about a distance of 250 cm. The same sand paper abrasion test was carried out for superhydrophobic polyurethane fabric. The fabric (7 cm x 2 cm) was rubbed with sand paper of size 3 cm x 1 cm in backward and forward direction for 3000 cm distance with an applied pressure of 25 kPa. Afterwards, the antiwetting property for both melamine foam and polyurethane fabric was measured through contact angle experiment. Coloured water droplet was placed on abraded area of both substrates for visual inspection of water wettability.

Knife Scratch Test: Both superhydrophobic foam and fabric was scratched manually with a sharp knife for multiple times in different directions randomly. Then wettability of both substrates was checked by placing coloured water droplet on scratched area of substrates and also through measuring contact angle.

Adhesive tape peeling test: An adhesive tape was attached on the surface of superhydrophobic melamine foam and polyurethane fabric with an applied load of 500 g for having a proper contact between the surface and adhesive tape. Then the adhesive tape was removed manually from the surface of the material. This procedure was repeated for 250 times. Thereafter, the water wettability was inspected through digital images and contact angle measurement.

Chemical Durability Test: To test the chemical durability, superhydrophobic melamine foam and polyurethane fabric was exposed separately to diverse chemically harsh aqueous media such as extremes of pH (pH 1 and pH 12), artificial sea water (solution of 0.226 g $MgCl_2$, 0.325 g $MgSO_4$, 2.673 g NaCl, and 0.112 g $CaCl_2$ in 100 mL of deionized water), river water (Brahmaputra, Assam, India) surfactants contaminated water (1 mM sodium dodecyl sulphate and 1 mM dodecyltrimethylammonium bromide, Triton-X) for 30 days. Impact of these harsh chemicals on the antiwetting property of the substrates was measured through contact angle and also checked visually through digital images.

Laundering Test: The washing durability was done following a standard procedure (AATCC Test Method 61-2006 Test No 2A) where the superhydrophobic fabric was washed at 40 ^{o}C for 45 min in presence of 0.37 wt% SDS surfactant. This procedure was repeated for 250 times.

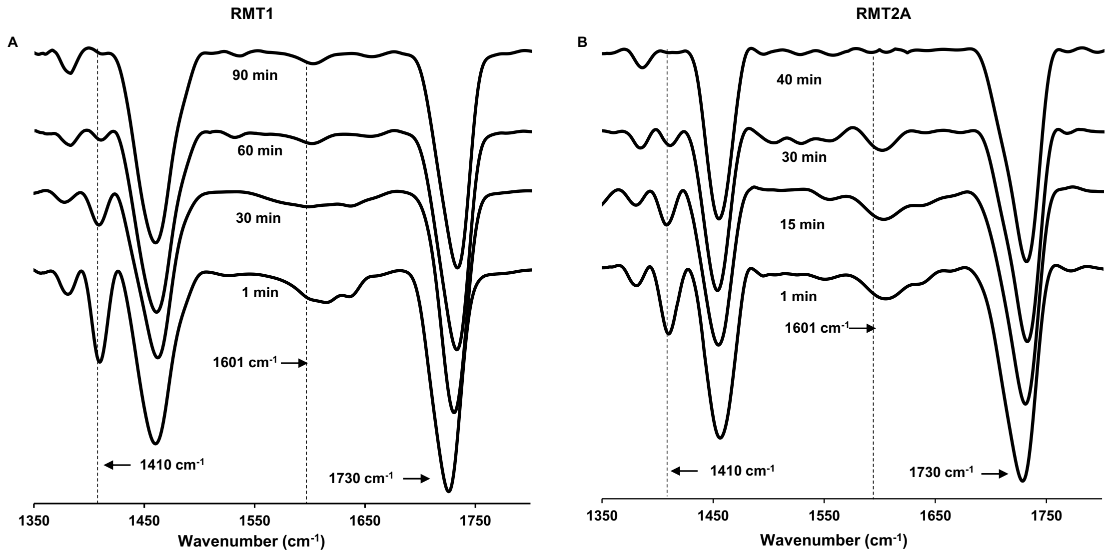

Figure S1. A) FTIR-ATR spectra for the reaction mixture RMT1 at regular time interval with the progression of the reaction- 1 min, 30 min, 60 min and 90 min. B) FTIR-ATR spectra at different time interval for the reaction mixture RMT2A depicting the progression of reaction – 1 min, 15 min, 30 min and 40 min.

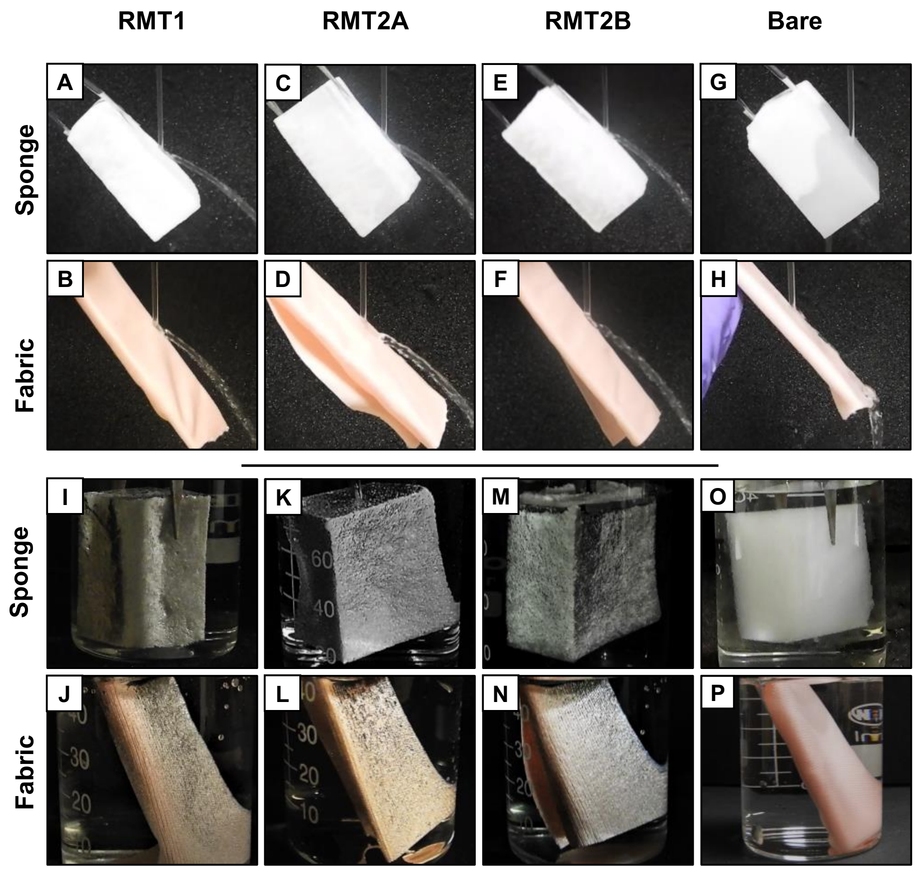

Figure S2. A-H) Digital images showing the impact of stream of water after hitting the substrates (melamine formaldehyde sponge and polyurethane fabric) coated with reaction mixtures- RMT1 (A-B), RMT2A (C-D), RMT2B (E-F) and bare substrates (G-H). Water jet readily bounced away upon hitting the coated (RMT1, RMT2A and RMT2B) substrates whereas the bare substrates are completely wetted. I-P) Digital images of substrates (melamine formaldehyde sponge and polyurethane fabric) coated with three different reaction mixtures- RMT1 (I-J), RMT2A (K-L), RMT2B (M-N) and bare substrates (O-P) on submerging under water. Appearance of shinny interface under water for all the substrates coated with these three different reaction mixtures revealed the presence of metastable trapped air whereas the bare substrates become completely wetted upon submerging under water.

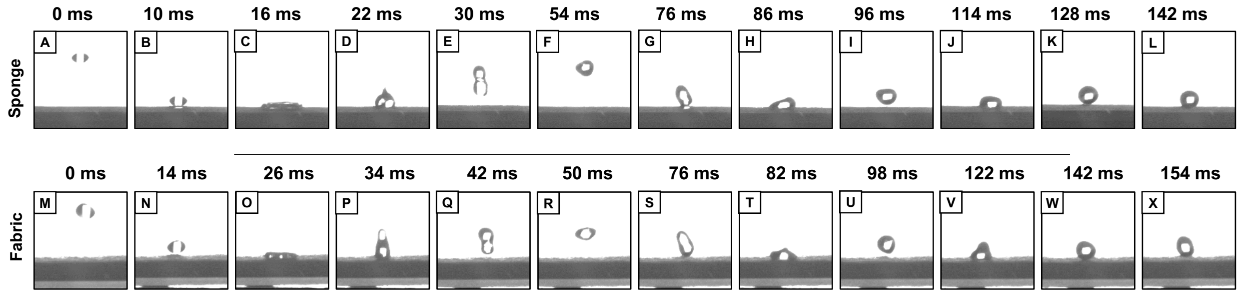

Figure S3. A-X) Images captured with high speed camera to demonstrate the impact and bouncing behaviour of water droplet (20 µL, dropped from 25 cm distance) on RMT2B coated superhydrophobic sponge (A-L) and fabric (M-X). See Movie 1.

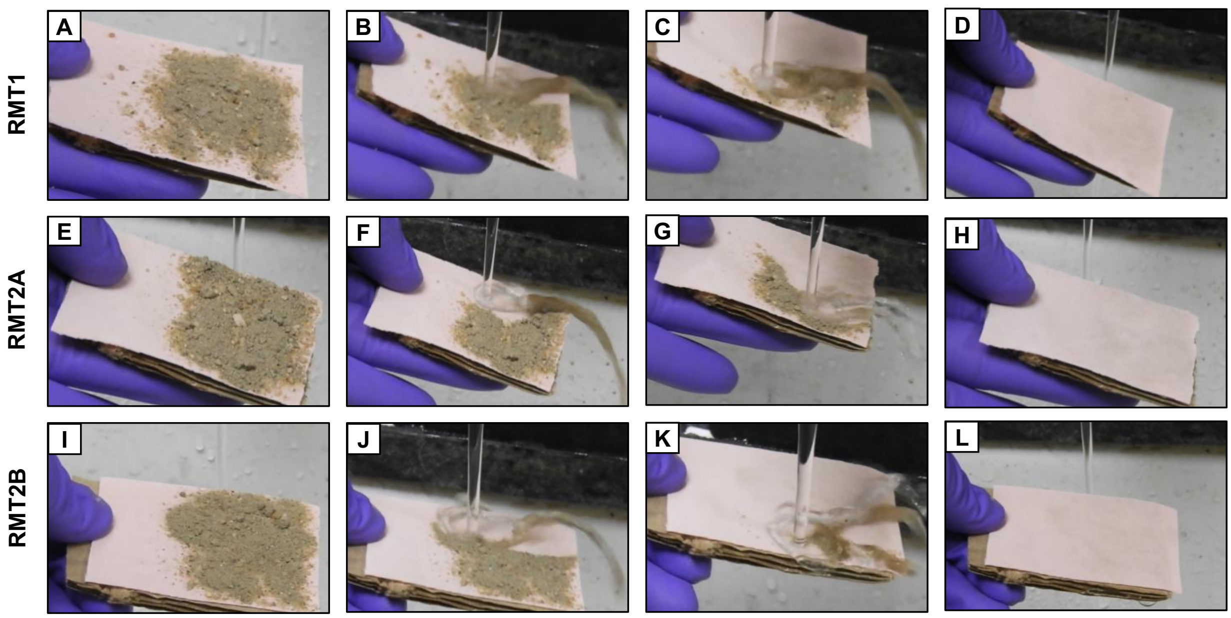

Figure S4. A-L) Digital images depicting the self-cleaning performance of deposited dust and dirt particles on RMT1 (A-D), RMT2A (E-H) and RMT2B (I-L) coated superhydrophobic fabrics.

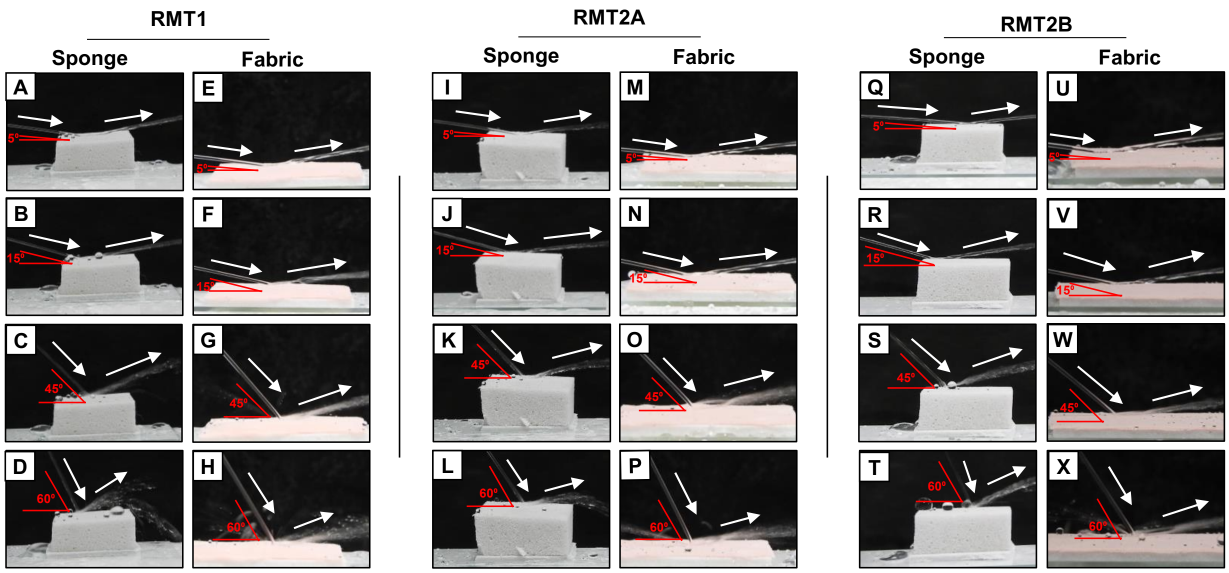

Figure S5. A-X) Digital images of water jet that bounced off on RMT1 coated sponge (A-D) and fabric (E-H), RMT2A coated sponge (I-L) and fabric (M-P), RMT2B coated sponge (Q-T) and fabric (U-X) over a wide range of incident angles (5^0, 15^0, 45^0, 60^0). See Movie 2 and Movie 3.

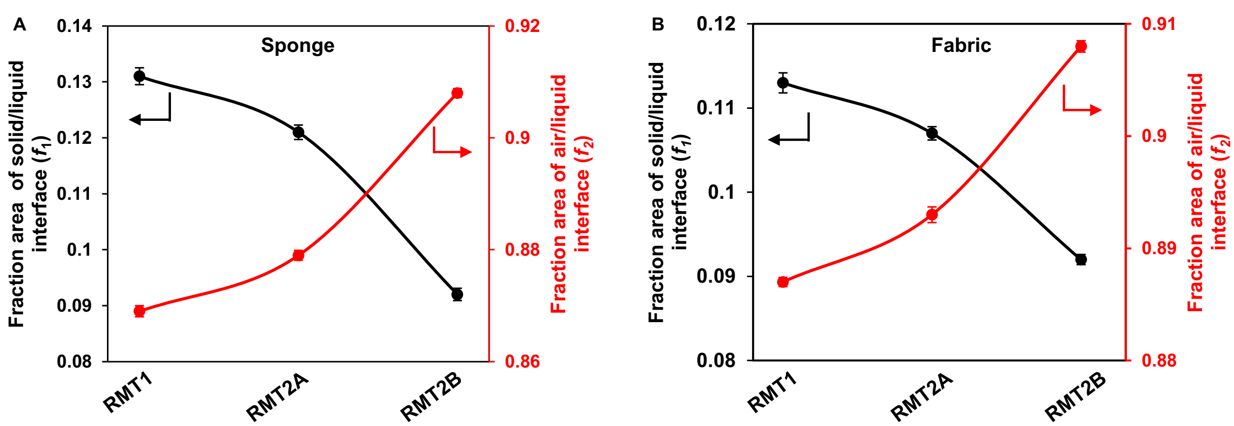

Figure S6. A) Graph showing the fraction of contact area of solid/ water interface (*f1*) and air/ water interface (*f2*) for melamine formaldehyde sponge coated with three different reaction mixtures- RMT1, RMT2A and RMT2B. B) Graph showing the fraction of contact area of solid/

water interface (*f1*) and air/ water interface (*f2*) for polyurethane fabric coated with three different reaction mixtures- RMT1, RMT2A and RMT2B.

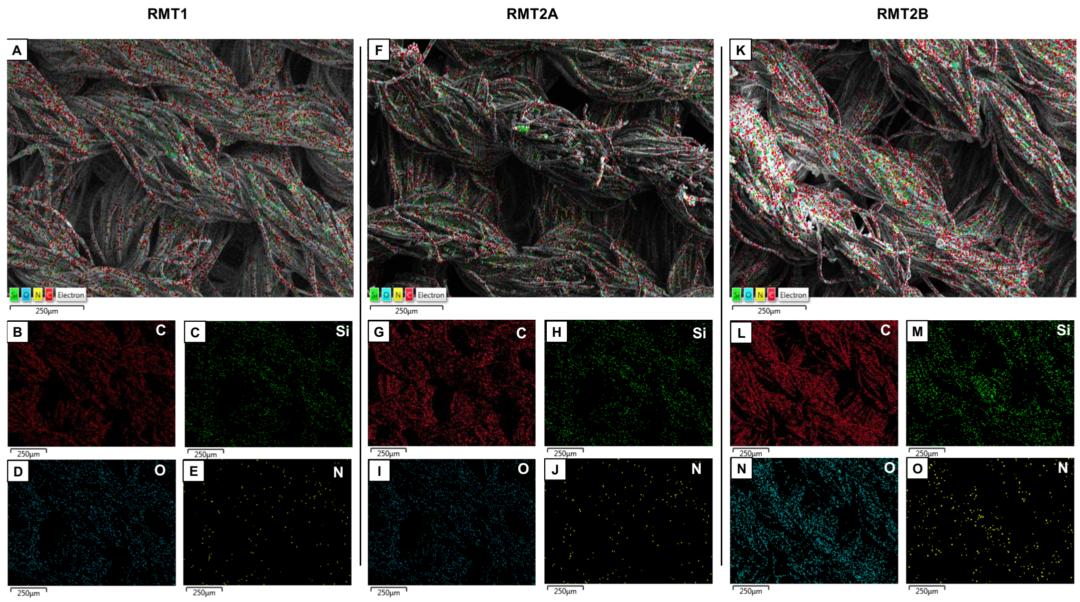

Figure S7. A-O) Energy-dispersive X-ray spectroscopy (EDX) images for polyurethane fabric coated with three reaction mixtures – RMT1 (A-E), RMT2A (F-J) and RMT2B (K-O).

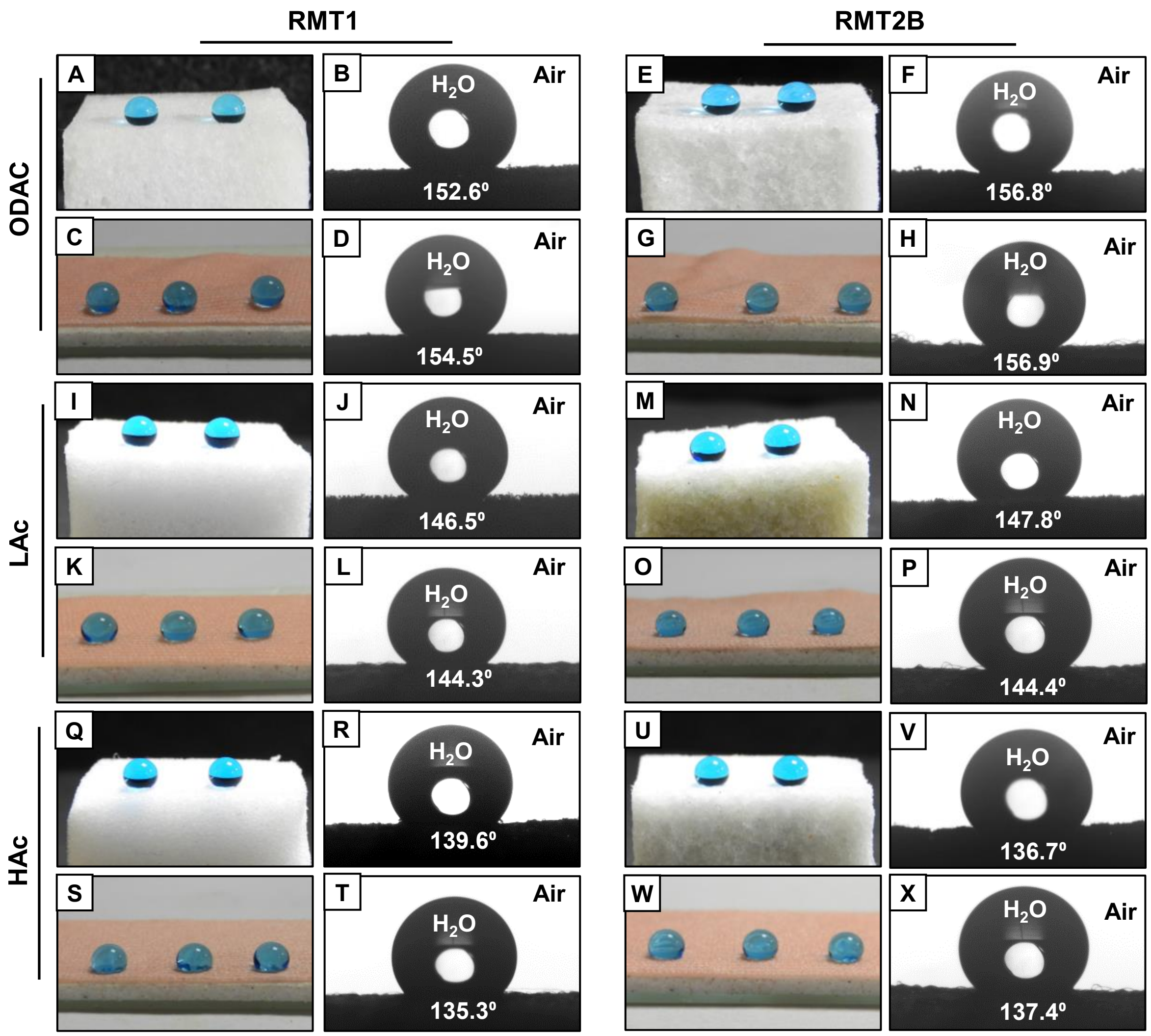

Figure S8. A-X) Digital images (A, C, E, G, I, K, M, O, Q, S, U and W) and contact angle images (B, D, F, H, J, L, N, P, R, T, V and X) for the substrates (melamine formaldehyde sponge and polyurethane fabric) coated with two different reaction mixtures RMT1 and RMT2B where hydrophobic acrylate moiety in the reaction mixtures has been varied from ODAc (A-H) to its two lower analogues acrylates i.e., LAc (I-P) and HAc (Q-X).

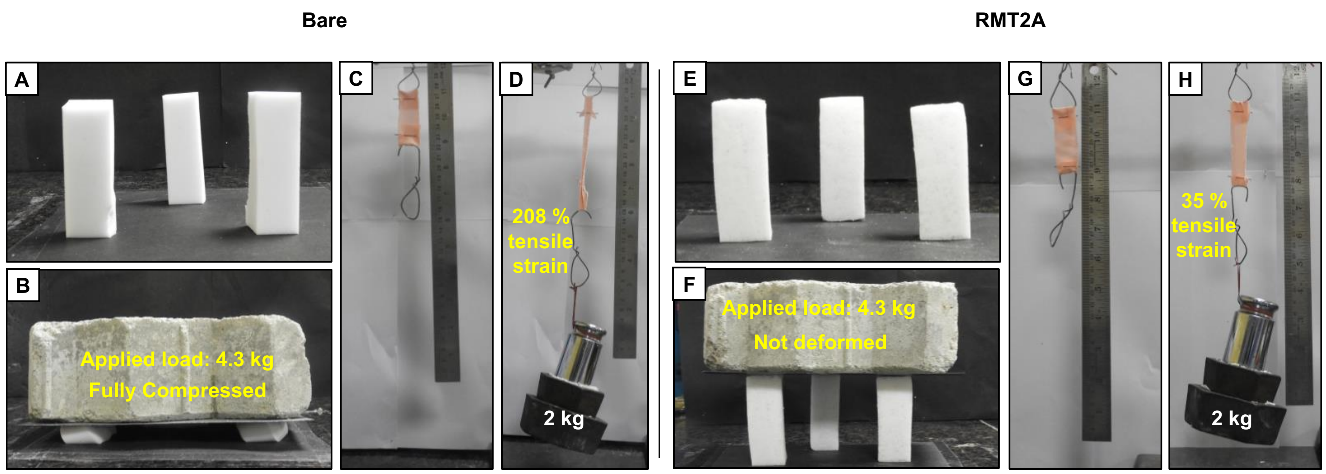

Figure S9. A-H) Digital images illustrating the extent of deformation of the bare and RMT2A coated substrates (melamine formaldehyde sponge and polyurethane fabric) on applying load. Bare melamine foam (A-B) and polyurethane fabric (C-D) experienced large amount of deformation on applying load of 4.3 kg and 2 kg respectively, however melamine sponge coated with RMT2A (E-F) can withstand 4.3 kg without any deformation whereas RMT2A coated polyurethane fabric (G-H) shows 35 % tensile strain upon applying 2 kg external load.

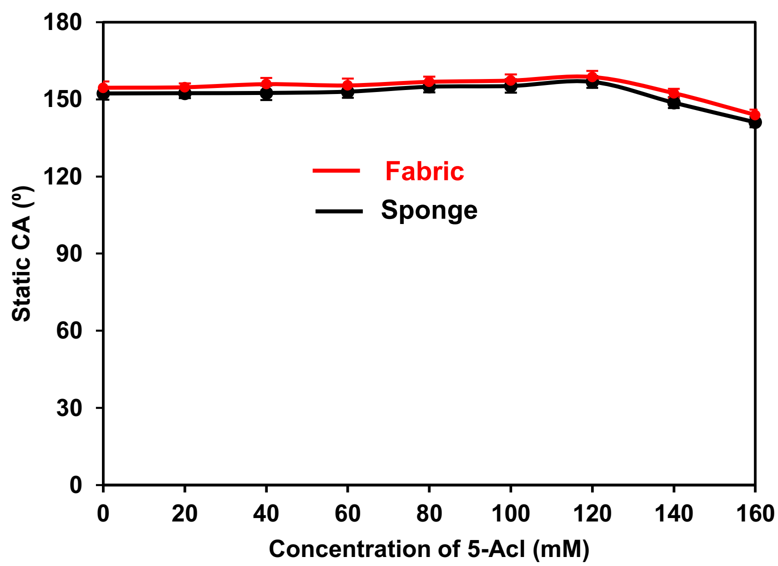

Figure S10: Plot showing the change in static contact angle value of beaded water droplet on both sponge and fabric on increasing the concentration of 5-Acl in RMT2B reaction mixture.

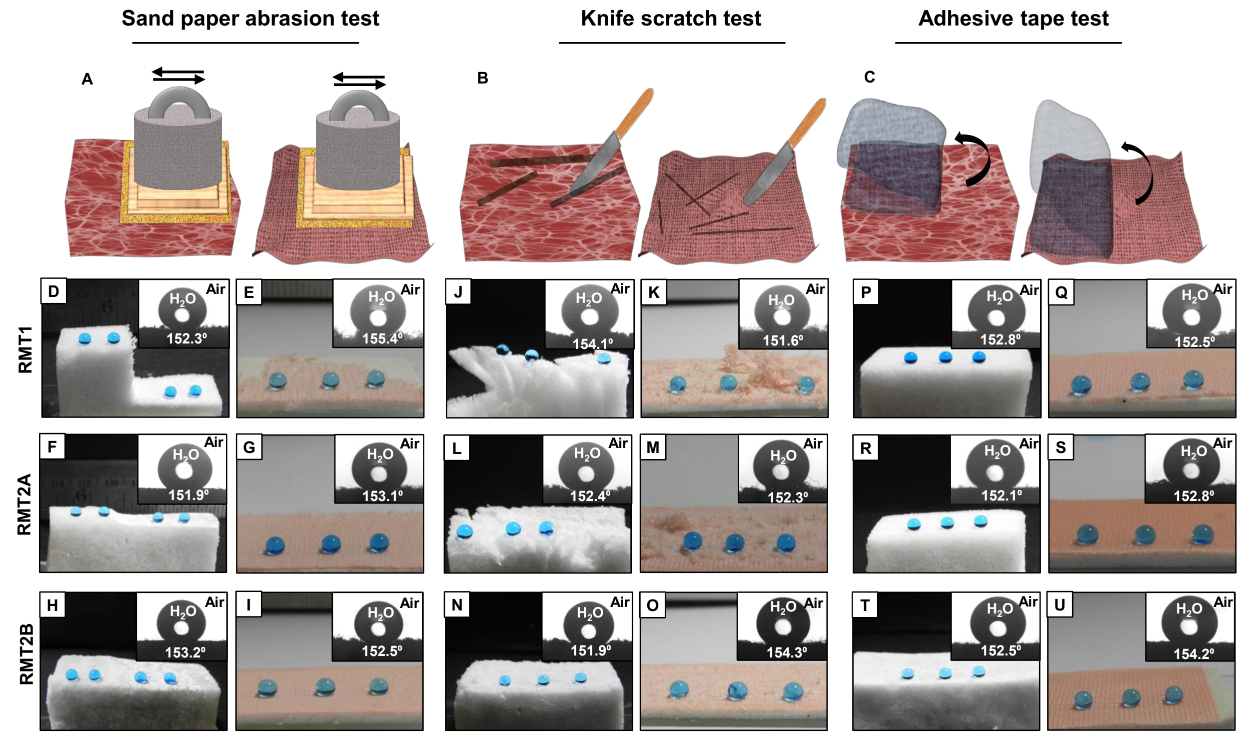

Figure S11. Comparing the durability of superhydrophobic materials that were derived from RMT1, RMT2A and RMT2B. A-C) Schematic representation of different physical abrasive exposures- Sand paper abrasion (A), Knife scratch test (B) and adhesive tape test (C) performed on the coated substrates. D-I) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (D-E), RMT2A (F-G) and RMT2B (H-I) after sand paper abrasion. J-O) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (J-K), RMT2A (L-M) and RMT2B (N-O) after knife scratch test for multiple times. P-U) Digital images and contact angle images (inset) of substrates (melamine sponge and polyurethane fabric) coated with three different reaction mixtures RMT1 (P-Q), RMT2A (R-S) and RMT2B (T-U) after adhesive tape test for 250 times.

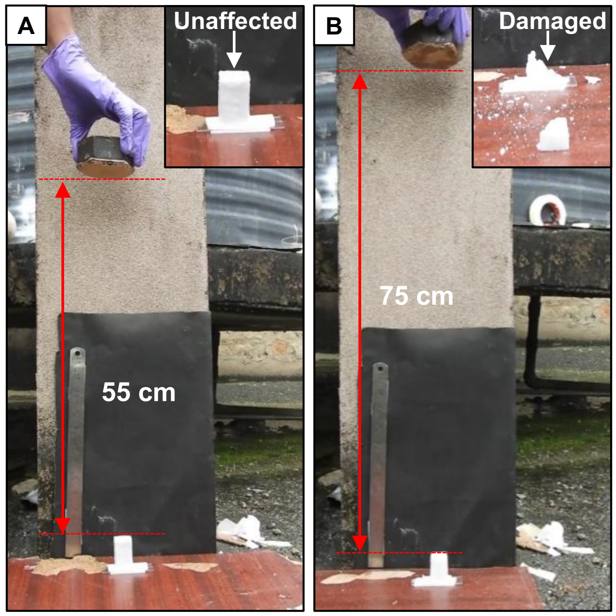

Figure S12: A-B) Digital images depicting the impact of 1 kg external weight from two different heights 55 cm (A) and 75 cm (B) on RMT2A coated sponge. The material failed to sustain the impact of 1 Kg weight from a 75 cm distance.

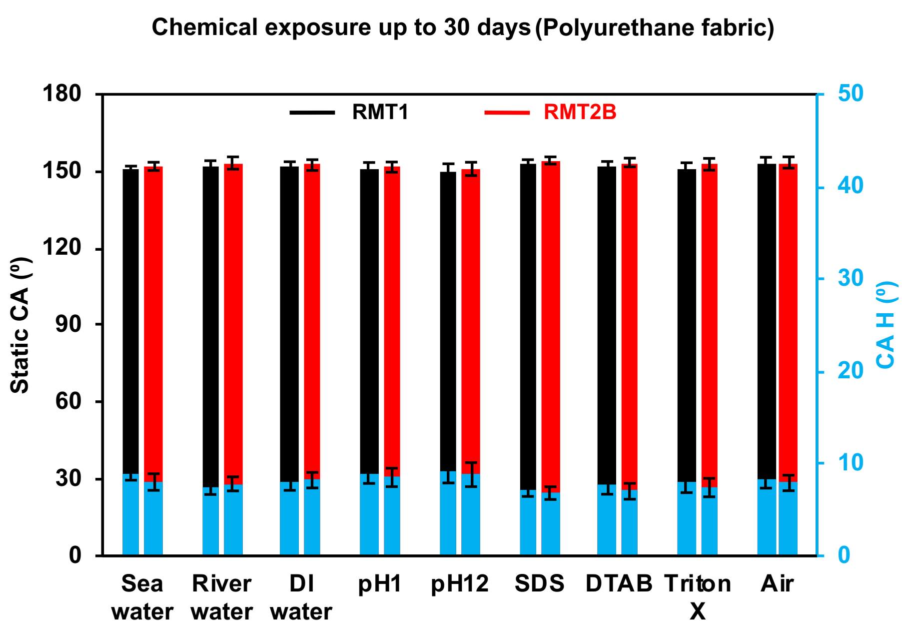

Figure S13. Bar plot of showing the effect of different chemical exposures on polyurethane fabric coated with RMT1 (black) and RMT2B (red) reaction mixtures after 30 days.

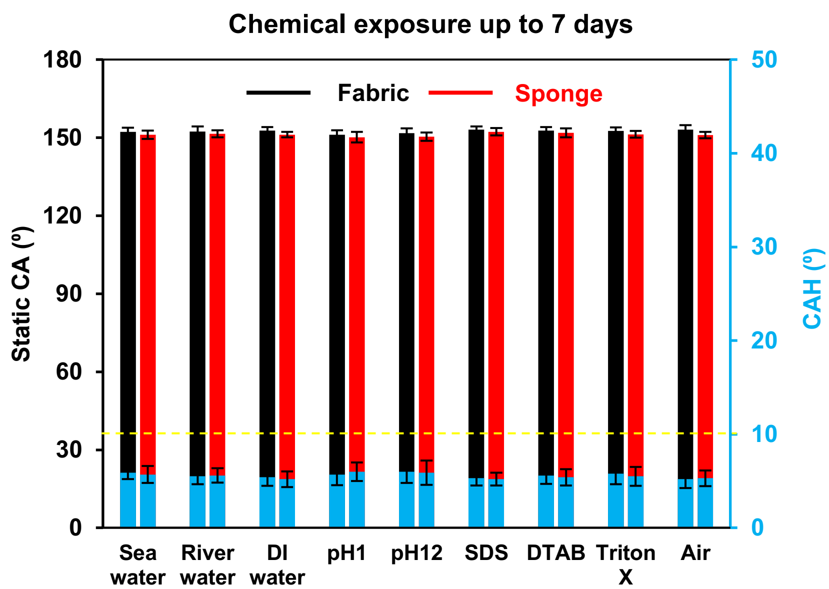

Figure: S14: Bar plot showing the effect of different chemical exposures on RMT2A coated sponge (red) and fabric (black) after 7 days.

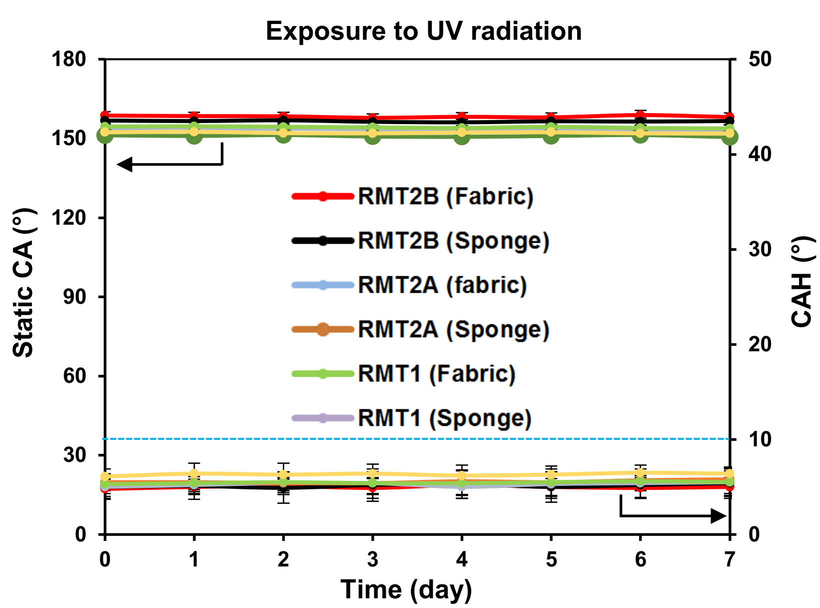

Figure S15: Plot showing the change in static contact angles (CA) and contact angle hysteresises (CAH) of beaded water droplets on RMT2B coated fabric (red) and sponge (black), RMT2A coated fabric (blue) and sponge (brown), RMT1 coated fabric (green) and sponge (purple) after exposure to UV radiation (λmax- 254 nm and 365 nm) for continuous 7 days.

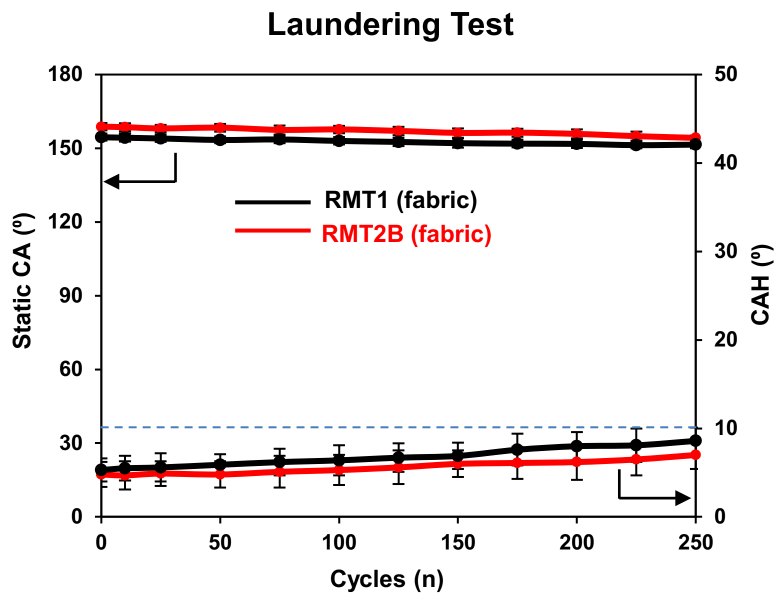

Figure S16. Plot accounting the change in static contact angles (CA) and contact angle hysteresises (CAH) of beaded water droplets on RMT1 (black) and RMT2B (red) coated fabric during repetitive washing test (250 cycles).