Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

pH-responsive Superomniphobic Nanoparticles as Versatile Entrant for Encapsulating Adhesive Liquid Marbles

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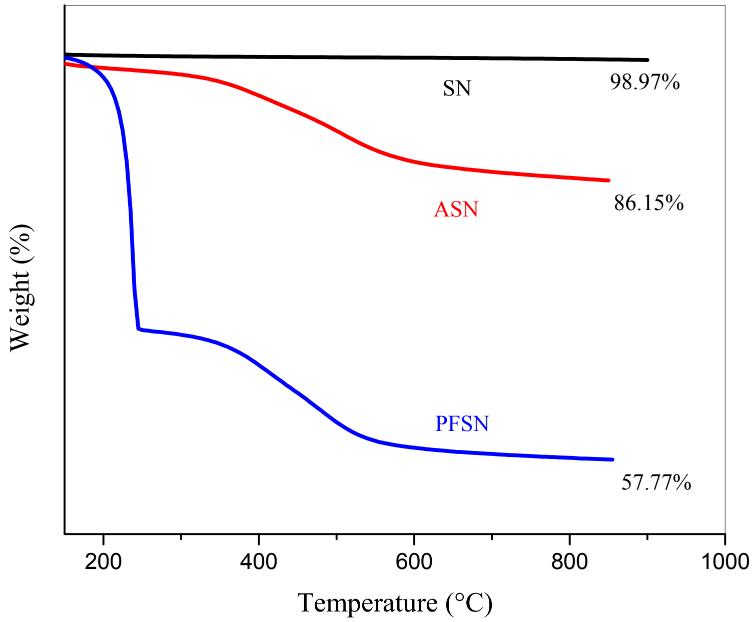
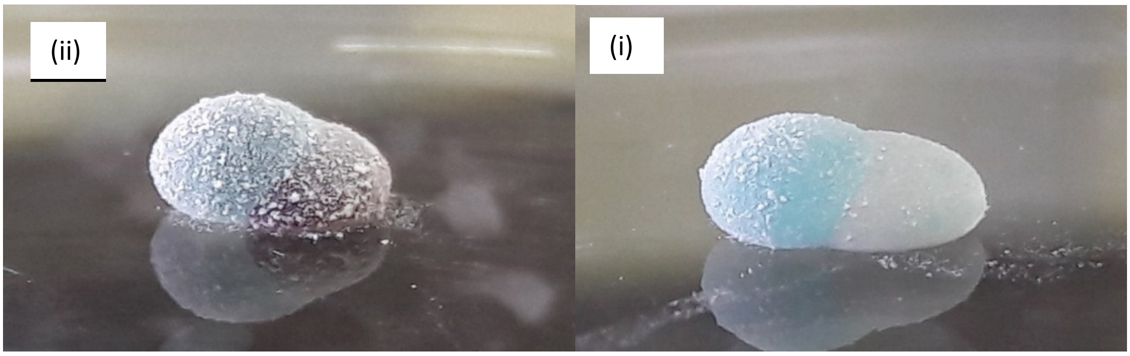


SI1. TGA of pristine silica (SN), APTES silica (ASN) and PFSN

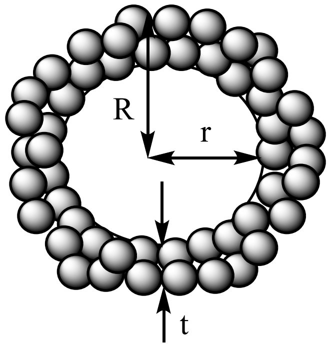


SI2. Hybrid liquid marbles of (i) water/DI and (ii) water/epoxy

SI3. Calculation for the thickness of PFSN powder coating on water, epoxy and PDMS marbles

Thickness of particles coating on water droplet

Method 1: Composite Method



Parameters for thickness estimation

Volume of liquid (water) droplet =5 µL

Mass of liquid (water) droplet =0.005 g

Density of liquid (water) droplet (ρ_w) =1 g/mL

Volume of liquid droplet (V_w) =4/3 π r^3

Radius of water droplet (r) =1.06096 mm

Mass of 5µL water marbles = 0.0054 g

Mass of coated PFSN = mass of marbles – mass of water droplet = 0.0004g

Density of PFSN (ρ_{PFSN}) = 2.4 g/mL

Volume of PFSN required to form 5µL water marbles (V_{PFSN}) = mass of PFSN/ density of PFSN =0.166667 µL

Volume fraction of PFSN to form marbles = 0.032258

Volume fraction of water to form marbles= 0.967741

Equivalent density of marbles = $\rho_w \times V_w + \rho_{PFSN} \times V_{PFSN}$

= 1×0.967741+2.4×0.032258

= 1.04516 g/mL

Volume of marbles = mass of marbles / equivalent density of marbles= 5.16667µL

Volume of marbles = 4/3 π R^3

Radius of marbles (R) = 1.072624 mm

Thickness of PFSN particle coating (t) = R – r =11.664µm

Method 2: Gravimetric Method

Total Volume of water marble = volume of water droplet + volume of particles

= 5 +0.166667 = 5.166667µL

Volume of marbles = 4/3 π R^3

Radius of marbles (R') =1.07262 mm

Thickness of PFSN particle coating (t) =Radius of Marble (R') – Radius of droplet (r) = (1.07262-1.06096) mm= 11.6638 μm

Thickness of Particles Coating on Epoxy Droplet

Method 1: Composite Method

Volume of liquid (epoxy) droplet = 5 μL

Mass of liquid (epoxy) droplet =0.006 g

Density of liquid droplet (epoxy) =1.2 g/mL

Volume of liquid droplet = 4/3 π r^3

Radius of epoxy droplet (r) =1.06096 mm

Mass of 5μL epoxy marbles = 0.0067 g

Mass of coated PFSN = mass of marbles – mass of epoxy droplet= 0.0007g

Density of PFSN = 2.4 g/mL

Volume of PFSN required to form 5μL epoxy marbles = mass of PFSN/ density of PFSN

=0.29166667μL

Volume fraction of PFSN to form marbles = 0.055118

Volume fraction of epoxy to form marbles =0.944881

Equivalent density of marbles =$\rho_e \times V_e + \rho_{PFSN} \times V_{PFSN}$

= 1.2×0.944881+2.4×0.055118

=1.26614 g/mL

Volume of marbles = mass of marbles / equivalent density of marbles = 5.29167μL

Volume of marbles = 4/3 π R^3

Radius of marbles = 1.081205 mm

Thickness of coated particles (t) = R – r =20.2453 μm

Method 2: Gravimetric Method

Total Volume of epoxy marble = volume of epoxy droplet + volume of particles

= 5 + 0.29166667 = 5.29166667 μL

Volume of marbles = 4/3×π R^3

Radius of marbles = 1.081204 mm

Thickness = Radius of Marble – Radius of droplet

Thickness = 20.2449μm

Thickness of Coating Particles on PDMS Droplet

Method 1: Composite Method

Volume of liquid (PDMS) droplet = 5 μL

Mass of liquid (PDMS) droplet =0.004825 g

Density of liquid droplet (PDMS) =0.965 g/mL

Volume of liquid droplet = 4/3 π r^3

Radius of PDMS droplet r =1.06096 mm

Mass of 5μL PDMS marbles = 0.0057 g

Mass of coated PFSN = mass of marbles – mass of PDMS droplet =0.000875g

Density of PFSN = 2.4 g/mL

Volume of PFSN required to form 5μl PDMS marbles = mass of PFSN/ density of PFSN

=0.3645833μL

Volume fraction of PFSN to form marbles =0.0679611

Volume fraction of PDMS to form marbles =0.932038

Equivalent density of marbles = $\rho_{PDMS} \times V_{PDMS} + \rho_{PFSN} \times V_{PFSN}$

= 0.965×0.9320238+2.4×0.0679611= 1.062509 g/mL

Volume of marbles = mass of marbles / equivalent density of marbles = 5.364657 μL

Volume of marbles = 4/3 π R^3

Radius of marbles = 1.0861534 mm

Thickness of coated particles (t) = R – r =25.1934μm

Method 2: Gravimetric Method

Total Volume of PDMS marble = volume of PDMS droplet + volume of particles

= 5 + 0.3645833μL

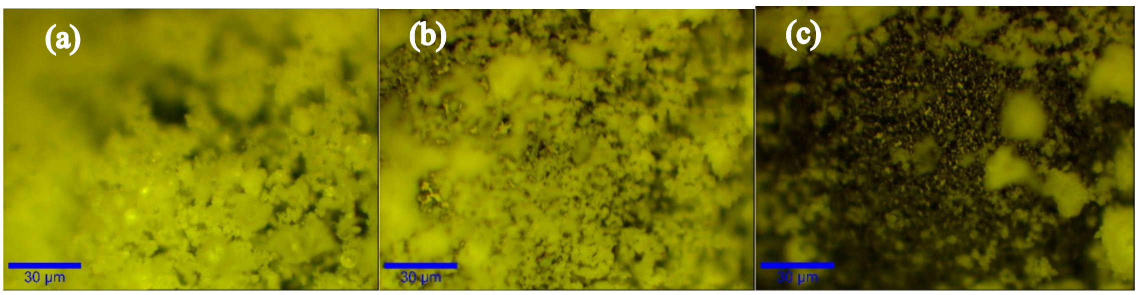
= 5.3645833μL

Volume of marbles = 4/3 π R^3

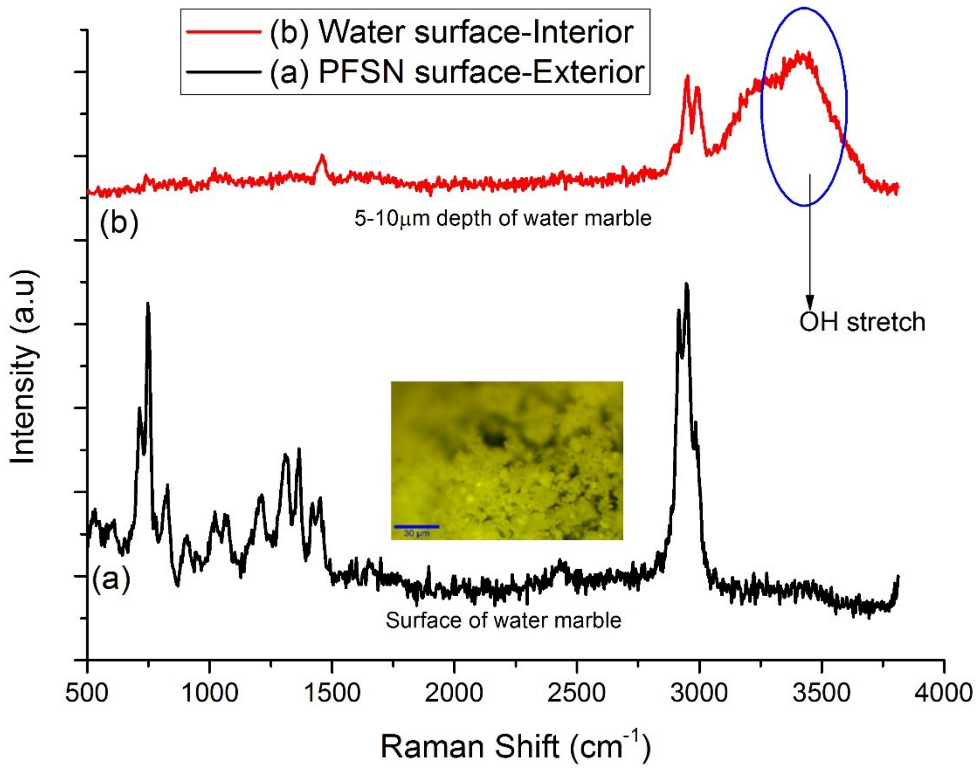
Radius of marbles =1.086148 mm

Thickness = Radius of Marble – Radius of droplet =25.18849μm

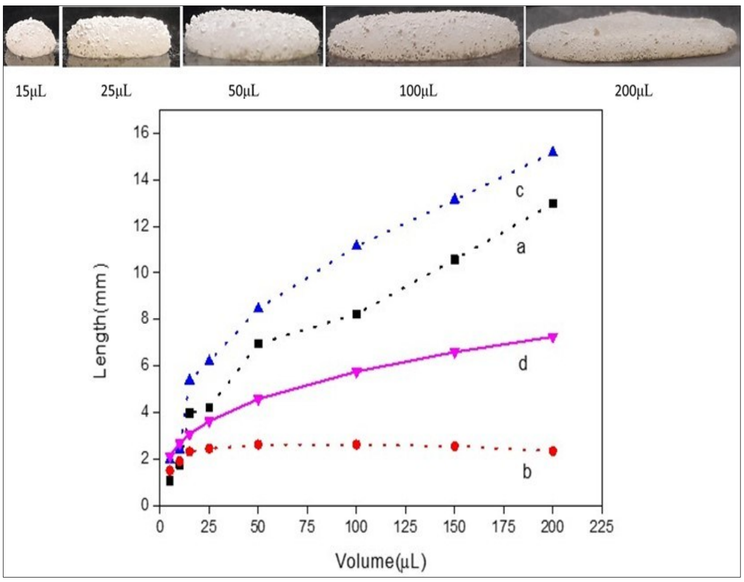
The depth of the coated particle layer of the liquid marble was determined using Raman Spectroscopy. An agglomerated distribution of PFSN particles were observed by confocal microscope (see Figure SI4 (i)) in each case (water, epoxy and PDMS marbles). Attempts were made to estimate the depth of the coated layer of PFSN through the corresponding Raman shift at the surface of the marble (exterior, predominantly of PFSN) and then through the thickness of the coated layer (interior, predominantly of the confined liquid). We were able to get a secondary Raman Shift of the corresponding inner liquids (thanks to the non-uniform coating of PFSN) which gave an approximate estimate of the thickness of each marbles (Typical Raman Shift of water marbles is shown in SI4(ii)). As evident from SI4(ii), Raman spectrum corresponding to top surface of liquid marble indicate no peaks corresponding to OH groups (a) whereas (b) (secondary Raman shift interior of the liquid marble) exhibited presence of OH group at a certain depth from the PFSN coated exterior surface. From this, we estimated the depth of the coated layer for water and epoxy marbles which are approximately 5-10 μm and 15-20 μm respectively. It was interesting to note that the obtained values are in good agreement with the thickness estimation by gravimetric method. As mentioned in the manuscript, the formation energy of epoxy and PDMS marbles are very low compared to water and they both interact rapidly with the particles. Therefore, it was observed that their shell thickness drops down at a faster rate with time due to the increased rate of particle-liquid interaction. This led to the presence of trace amounts of PDMS over the silica particle within a short span of time making the depth determination of the coated particle impossible especially in the case of PDMS marbles. Since water and epoxy marbles showed almost similar values for the coating depth/ thickness by both methods, we hypothesize that the thickness estimation by gravimetric method for PDMS marbles should also hold good. However, we would like to emphasize that, though slight variations are observed with mathematical calculations and Raman method estimation (mainly the depth of the coated layer), both methods are just approximations and the obtained values also are approximate.



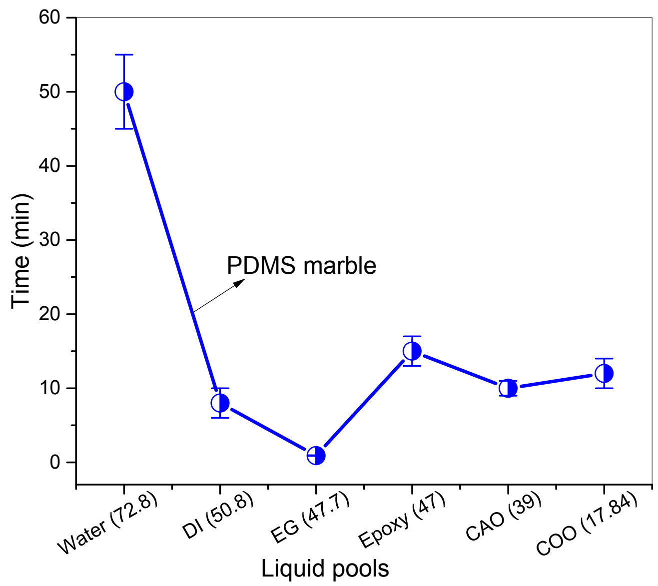
SI4 (i). Distribution of particles on the marbles of (a) water, (b) epoxy and (c) PDMS obtained from Confocal Raman spectrometer



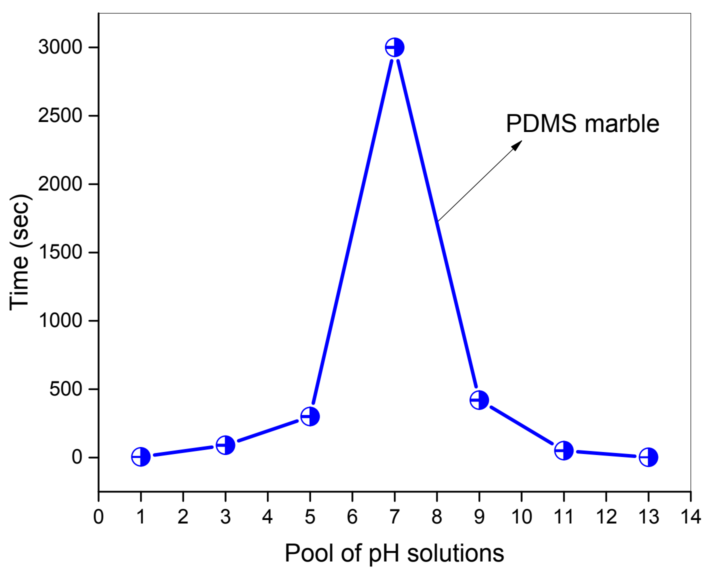
SI4 (ii). Typical Raman shift for water marbles



SI5. Relationship between *a,b,c* of PDMS marbles with varying volume. The solid curve *d* is the theoretical diameter of a quasi-spherical droplet with various volumes.



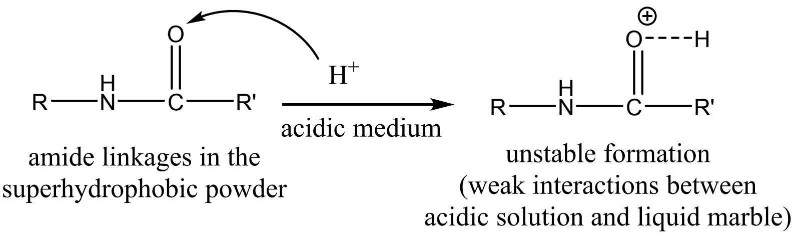
SI6. Stability of PDMS marbles in different liquid pools



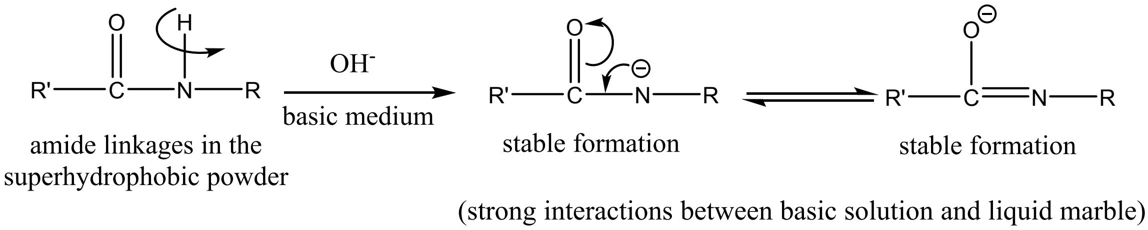
SI7. Stability time of PDMS marbles in various pH pools

SI8. Interaction of different marbles with acid/basic medium

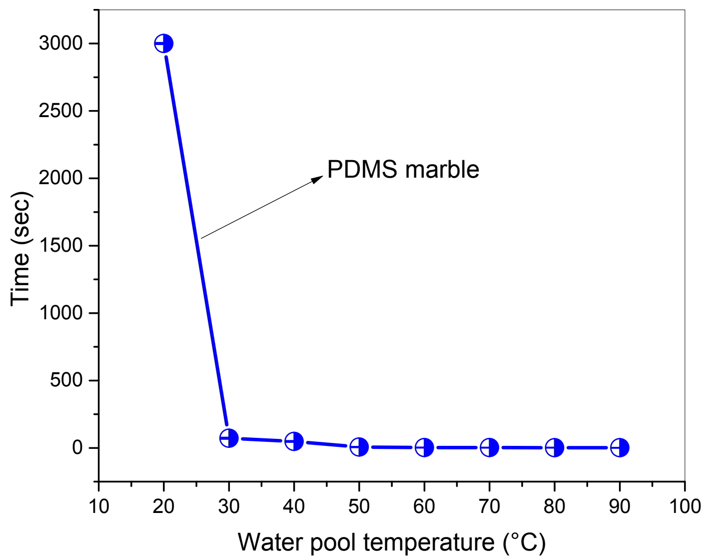
Interactions of liquid marble with acidic solution:



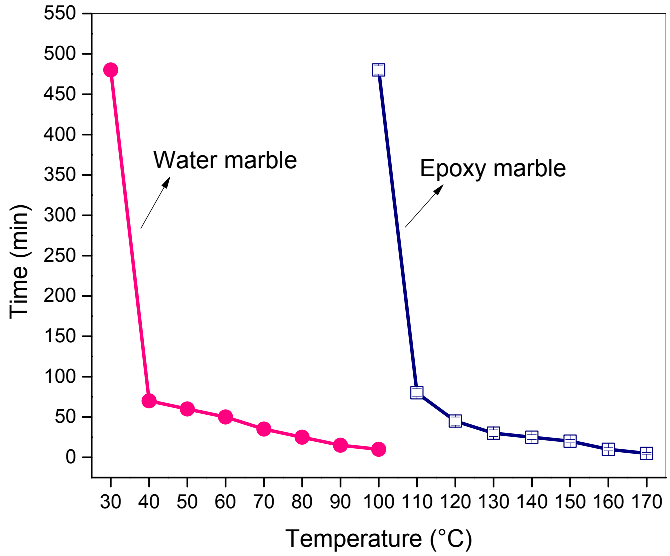
Interactions of liquid marble with basic solution:



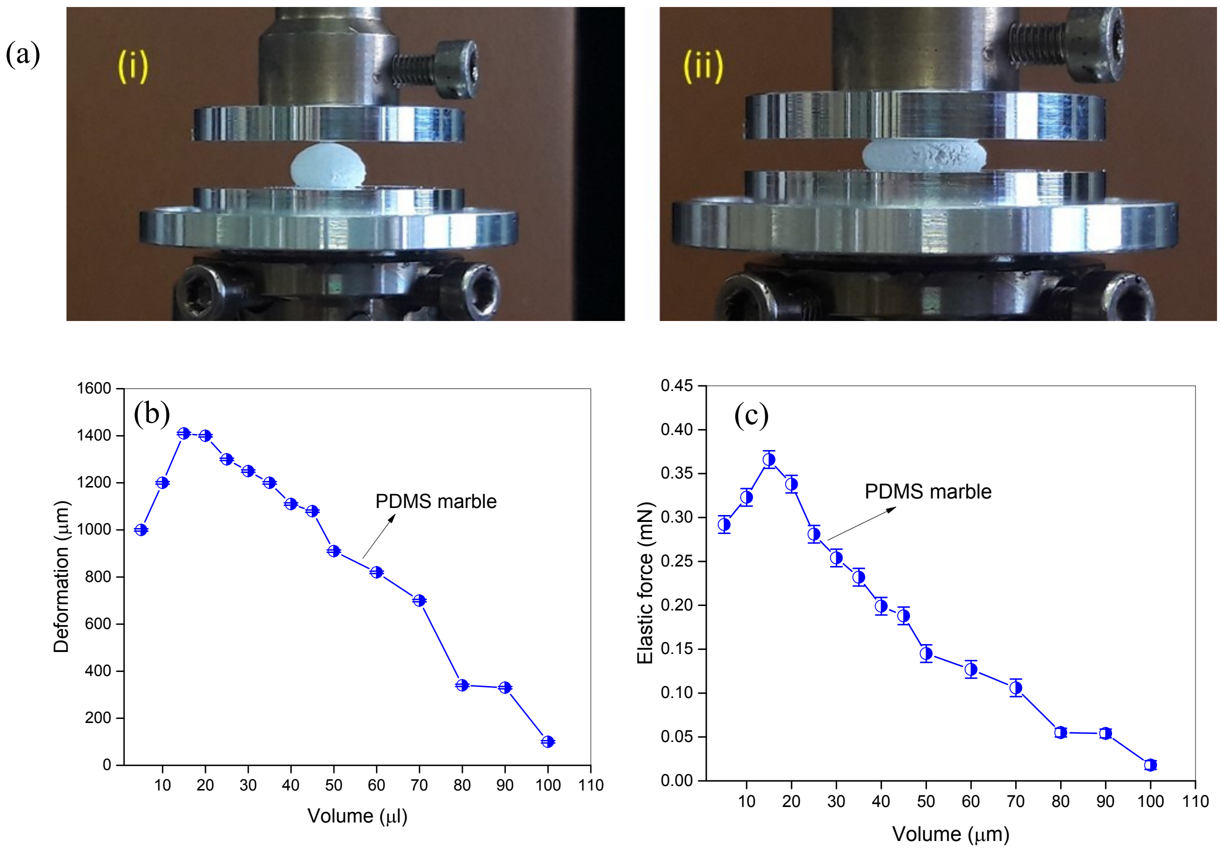
R= silica counter part
R'= perfluoro chain



SI9. Stability time of PDMS marbles in different water pool temperatures

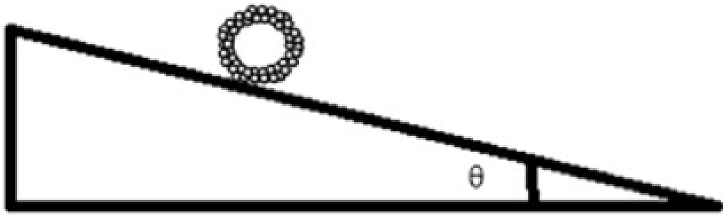


SI10. Stability of liquid marbles at varying temperatures (Since temperature of destabilization for epoxy marbles are above 100 °C, those data is not presented in the graph)

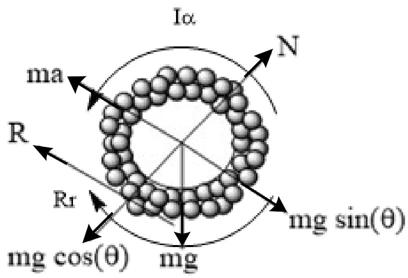


SI11. (a) Marbles (i) before deformation and (ii) after deformation on a highly sensitive parallel pate assembly of HR-3 Hybrid viscometer (TA Instruments) (b) extent of deformation vs varying volume and (c) Elastic force vs varying volume of PDMS marble.

SI12. Derivation of rolling resistance calculation



(a) Rolling of marble at angle θ



(b) Freebody diagram of marble

Newton second law

$\sum F = ma$

$mg \sin(\theta) - R = ma$ ………… (1)

$\sum M_c = 0$

$I\alpha - Rr = 0$

$I\alpha = Rr$

$\alpha = Rr/I$

$a/r = Rr/I$

$a = Rr^2/I$ ………………… (2)

$I = 2/5\ mr^2$

From equation 1 and 2

$a = 5/7\ g \sin(\theta)$

$R = \mu N$

$N = mg \cos(\theta)$

$R = 2/7 mg \sin(\theta)$

$\mu = 2/7 \tan(\theta)$

where

m = mass of adhesive marble

r = radius of marble

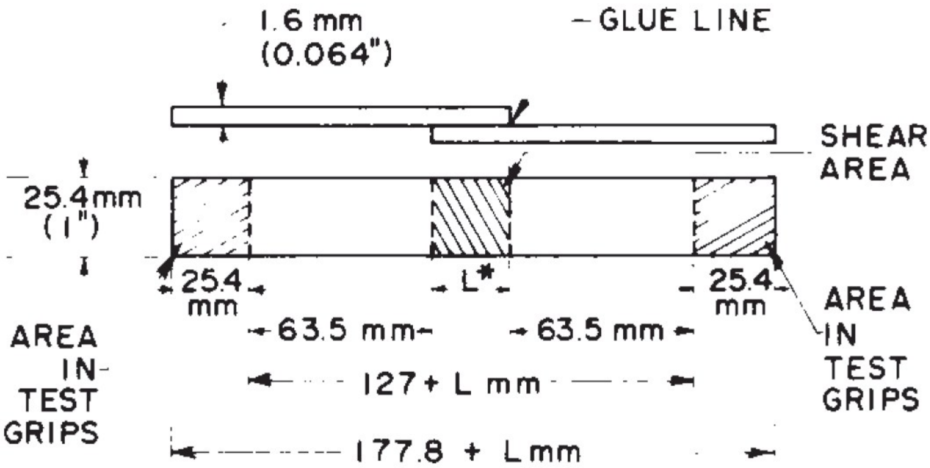
a = acceleration of marble

R = rolling resistance of marble

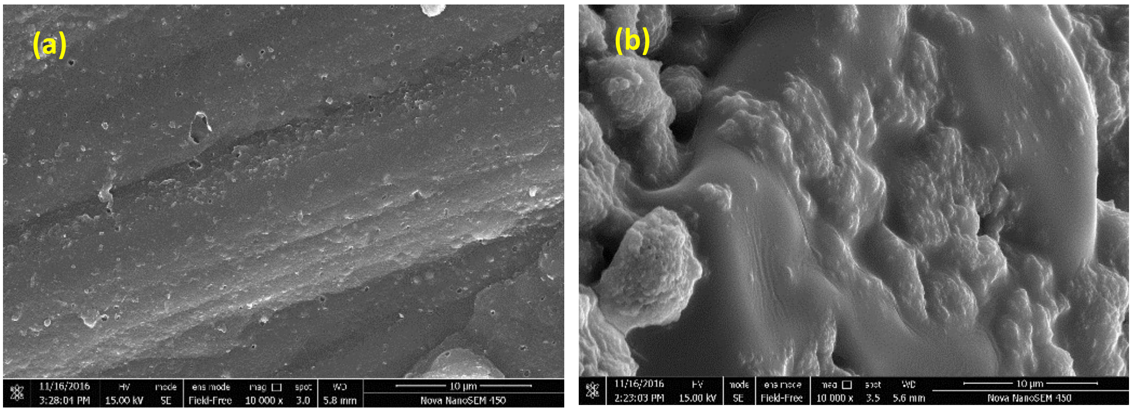
N = normal force of contact

μ = friction coefficient

θ = minimum angle of rolling



SI13. Diagram showing the specimen preparation for Lap Shear strength as per ASTM D1002 standard



SI14. SEM images of the fractured surface of (a) pristine epoxy (b) epoxy with PFSN marble