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Liquid marble formation using hydrophobic powders

P. McEleney, G.M. Walker*, I.A. Larmour, S.E.J. Bell

School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, BT9 5AG Northern Ireland, UK

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ABSTRACT

This work aims to investigate and quantitatively measure "liquid marble" phenomena using hydrophobic powders (granules). The hydrophobic powders based on a copper substrate were prepared by a silver deposition technique of particle sizes 9 μm, 20 μm and 320 μm and of contact angle with water approaching 160°. The hydrophobic powder poly-methylmethacralate (PMMA) particle size 42 μm and contact angle of 120° was also used to determine the effect of powder density on liquid marble stability. The experimental investigations indicated that for successful formation of liquid marbles a number of variables in addition to hydrophobicity need to be considered, namely: powder density; powder particle size; powder shape; liquid marble formation technique. It was found that liquid marbles were formed using all four powders to varying extents, with a low powder particle size forming more stable liquid marbles. In a series of gravimetric tests, adhered powder mass on liquid marbles was found to be directly proportional to the water droplet surface area. A more complete coverage of the water drops were found with PMMA powder than the hydrophobic granules. Moreover, a further procedure was developed to increase the mechanical strength of the liquid marble, by polymerising methylmethacrylate (MMA) on the surface of a PMMA powder – liquid marble, with the aim of maintaining water within a more robust PMMA – liquid marble shell. This technique may prove to be a novel way of encapsulating drug compounds, such as gentamicin sulphate, for PMMA bone cement.

1. Introduction

1.1. *Liquid marble formation*

In conventional wet granulation theory, it is assumed that only liquids can form a surface film around a solid and that solids do not take part in film formation around a liquid [1]. However, from the pioneering work of Aussillous and Quéré [2,3], it is now known that hydrophobic powder particles can spread over a liquid creating a surface film. The spreading coefficient that was originally defined for solid over liquid spreading, λ_{SL}, gave the tendency of a solid to form bonds at the initial liquid-powder interface. This was subsequently re-defined as the tendency of a solid to spread over or adhere to a liquid binder, called solid spreading nucleation, furthermore the theory indicates that for liquid marble formation it is necessary that the spreading coefficient is positive [4,5].

Limited studies have been carried out to investigate if the driving force behind liquid marble creation is related to solid spreading nucleation, λ_{SL}, but Hapgood and Khanmohammadi [6] have suggested that bulk motion may be required for liquid marble formation and that although the positive solid spreading coefficient may provide a quantitative method to predict whether a liquid marble will be formed or not, it may also be possible that the formation may be driven entirely by a physical flow mechanism. An alternative approach has been taken by Forny et al. [7] who carried out a study on the mixing conditions required to encapsulate water with silica nanoparticles. High shear mixing was shown to be very effective, with liquid marbles forming in approximately 10 s. With the most hydrophobic silica powder, up to 98% (w/w) water was able to be encapsulated with powder.

The presence of the solid particles influences the shape of the drop and it deforms laterally forcing a contact area of radius R_0. A small drop is quasi-spherical apart from the base and therefore the drop radius, R_0, can be taken as approximately half of the overall drop thickness. Fig. 1 illustrates a small non-wetting drop at atmospheric pressure, P_0. The pressure, P, inside the drop is given by the Laplace law [3],

$$P = P_0 + \frac{2\gamma_{LV}}{R_0} \tag{1}$$

where γ_{LV} is the liquid–vapour surface tension. Crossing the interface therefore induces an overpressure, $\Delta P = 2\gamma_{LV}/R_0$, however the weight of the drop applied over a surface area of πR_0^2 induces a pressure,

$$\Delta P \pi \ell_0^2 \approx \frac{4\pi}{3}\rho g R_0^3 \tag{2}$$

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* Corresponding author. Tel.: +44 28 9097 4172; fax: +44 28 9097 4627.
E-mail address: g.walker@qub.ac.uk (G.M. Walker).

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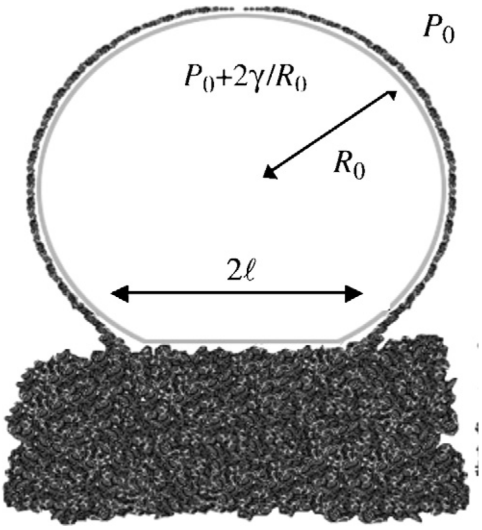

Fig. 1. A small non-wetting drop on a solid surface illustrating liquid marble formation.

where ρ is the fluid density and g is acceleration due to gravity. From this we can define the radius of the contact zone as

$$\ell = \left(\sqrt{\frac{2}{3}}\right) R_0^2 k \tag{3}$$

where k is the inverse of the capillary length,

$$k^{-1} = \sqrt{\frac{\gamma_{\mathrm{LV}}}{\rho g}} \tag{4}$$

Aussillous and Quéré [3] found that experimental data were in good agreement with the model proposed in Eq. (3) and it indicates that the contact radius increases much quicker than for an uncoated droplet of liquid in partial wetting for which the contact is given by

$$\ell = R_0 \sin\theta_{\mathrm{e}} \tag{5}$$

Recent work by Gao and Mc Carthy [8] has reported limitations of the materials used by previous researchers to create liquid marbles, particularly if they are ever to be used as reservoirs for reagents or microreactors, reasons being summarised as follows:

- The liquids have a tendency to evaporate.
- Many organic reagents are not soluble in these solvents.
- Water and glycerol are reactive (nucleophilic and proton donors) and will interfere with many chemical reactions.
- Hydrophobic silica and lycopodium contain Si–O bonds that are reactive under nucleophilic, basic or acidic conditions.

An alternative method has recently been presented where liquid marbles were formed using Ionic liquids on chemically inert fluoropolymer particles, termed ionic liquid marbles [8].

Notwithstanding previous studies in this area, the primary aim of this work is to investigate and quantitatively measure “liquid marble” phenomena using hydrophobic (granules). Specifically, this work intends to investigate how the physical characteristics of the powder, i.e., hydrophobicity, powder density, powder particle size, powder shape, affect liquid marble formation.

2. Experimental materials and methods

2.1. Experimental materials

Hydrophobic copper powders of three different particle sizes, developed at QUB [9], were used in this work (powder of particle size approximately 9 μm (denoted SH10); 200 mesh powder, approximately 20 μm particle size (denoted SH200); 40 mesh powder of approximately 320 μm particle size (denoted SH40). The three powders are virtually identical in terms of density and chemical composition but provide variation in terms of particle size. The hydrophobic copper particles of all sizes were prepared by the same method. Copper powder (ca. 40 g, 400 mm, 99.5%, Aldrich) was washed with 0.5% HNO3 (70%, J.T. Baker) and deionised water. The particles were shaken in 0.02 M $AgNO_{3(aq)}$ (70 cm^3, AnalaR, BDH Chemicals Ltd.) for several minutes. The powder was filtered, rinsed with deionised water and dried at 70 °C. The powder was immersed in 100 cm^3 of a 0.1 M 1-decanethiol (96%, Alfa Aesar) solution in ethanol (Absolute ACS grade, J.T. Baker). The mixture was shaken intermittently and left overnight. The powder was filtered, rinsed with absolute ethanol and dried at 70 °C [9].

The poly-methylmethacralate (PMMA) bone cement used was the commercially available CMW® 1 (CMW Laboratories Ltd., Blackpool, UK). This material is used extensively in orthopaedic surgery, principally in hip and knee replacement. Bone cement is used as a grout between the prosthetic implants and bone during cemented joint replacement. Its primary function is as a grouting material, to allow load transfer between the prosthetic components and the bone to enable normal joint function, post-operatively. The bone cement also contains antibiotic (typically in the form of gentamicin sulphate) to prevent post-operative bacterial infection. A summary of the physical properties of the SH particles and PMMA powder is given in Table 1. Distilled water was used to form a liquid marble for all experiments.

2.2. Experimental methods

2.2.1. Digital microscopy

Marble specimens were examined under microscope using a Nikon Eclipse series digital microscope (Nikon Co., Japan) and images were analysed using LUCIA G 4.21 (Labtech, Wilmington, MA, USA). Marbles were formed in a small weigh boat and typically viewed vertically at 5× magnification.

2.2.2. Liquid marble formation and gravimetric testing

Multiple setups were trialled to ascertain the best method of carrying out gravimetric tests on liquid marbles. The most successful method involved the formation of liquid marbles on powder placed in a hemi-spherical clock glass, illustrated in Fig. 2(a).

Previous trials with a Petri dish quite often ended in marble collapse during movement as the steep angle created during tilting tends to move a marble quite quickly, increasing the likelihood of impact against the glass sides, which was fairly often destructive. Weigh boats have sides that are at an angle greater than 90° to the base, and typically liquid marbles rolled in a weigh boat were more likely to survive impact on the sides than in a petri

Table 1
Characteristics of SH particle and PMMA systems.

	PMMA	SH10	SH200	SH40
Contact angle[a]	120°	157°	157°	157°
Mean particle size[b] (m)	42×10^{-6}	9×10^{-6}	15×10^{-6}	320×10^{-6}
Particle density ($kg\,m^{-3}$)	1080	8960	8960	8960

[a] Determined using a Camtel Coda 100 surface tension analyser.
[b] Determined using a Helios laser diffractometer.

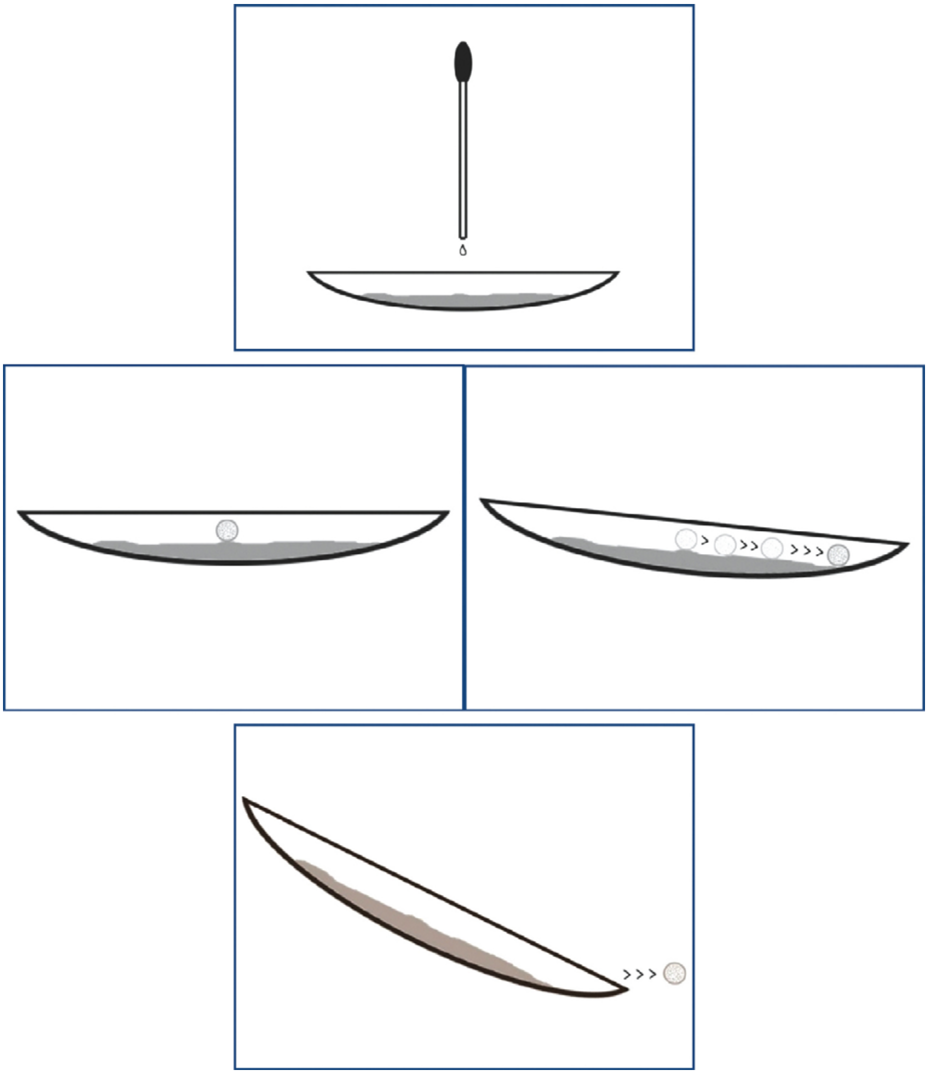

Fig. 2. Clock glass setup; (a) water drop is placed on the powder surface below, (b) clock glass is agitated/tilted to allow powder to fully cover water surface, (c) the liquid marble is then rolled towards the edge and (d) finally exits the setup.

dish. However it was observed that replacing these methods with a clock glass allowed for the greatest control of movement. The hemispherical shape allows for more gentle movement and therefore greater control of both marble motion and marble formation could be achieved. This was particularly important when capturing still images of the objects at different stages of surface coverage. This setup also allowed for much easier removal of the marbles with much less powder loss from the bulk.

For the majority of gravimetric tests either a weigh boat or a clock glass was used to form a liquid marble. Marbles were formed by placing a single drop of water on each powder with a dropper. Note that the size of liquid marbles could be altered by adding more liquid to a drop on the surface. However, the liquid marbles used for the gravimetric analysis were single drops which did not have excess liquid inserted. The marbles were observed to keep an approximately spherical shape until a certain volume was reached, where the liquid tended to spread outward producing a puddle-like shape. Note that although drop sizes were altered for experimental purposes, liquid mass was typically only varied within a range between 5 mg and 100 mg (between 2 mm and 5 mm diameter approx.), with no single drop exceeding 230 mg (7.5 mm diameter approx.) throughout the experiments.

A simple more repeatable method was adopted where marbles were rolled out of the bed destructively, illustrated in Fig. 2(b)–(d).

It must be noted that there is a tendency for a liquid marble to deposit a trail of particles along the glass exit route if the marble is removed very quickly. Moving a marble quickly across a powder gives it a tendency to pick up more powder particles during motion, which may be the reason why more of a significant trail appears to be formed at higher exit velocities. It is observed that marbles exiting the setup in this fashion are fully covered. An alternative mechanism may be that the higher exit velocity means that the liquid marble surface experiences more attrition, especially of any relatively loose aggregates on the liquid marble surface. It is possible however that the extent of surface coverage may be less in this setup than what would be observed through heavy marble agitation and lift removal. It could also be possible that lifting liquid marbles off a surface provides a mechanism for loss of powder coverage, particularly at small particle diameters, although this was not observed.

The mass of each liquid droplet placed on the surface was recorded and upon liquid marble formation and subsequent removal, the mass of adhered powder could be recorded. The mass of water was used to calculate drop surface area, and hence, powder mass versus water surface area for the different powders was plotted. Liquid marble formation was investigated for three different hydrophobic copper powders and also PMMA.

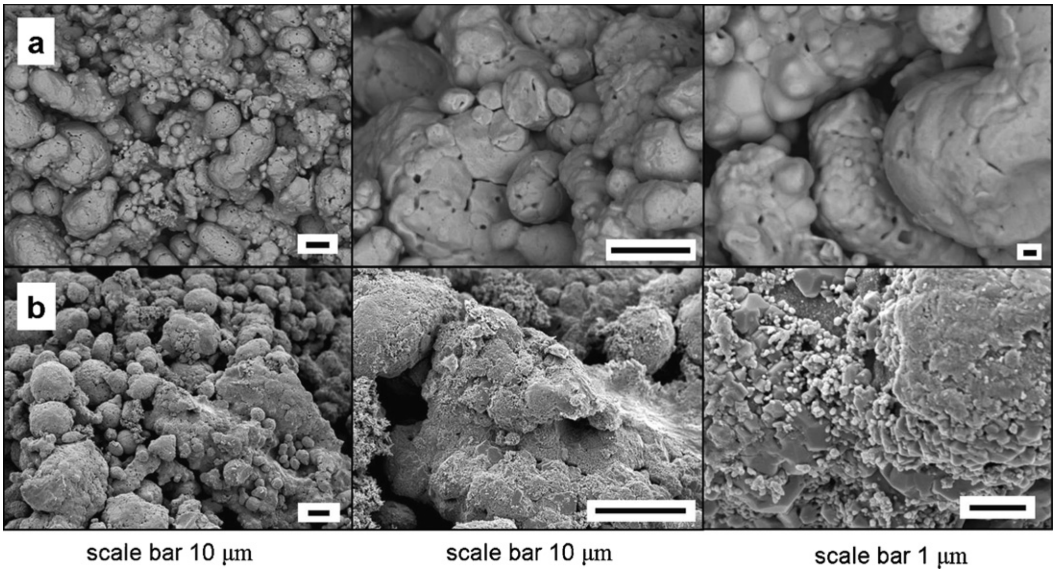

Fig. 3. SEM images at different magnifications of (a) an uncoated ≤400 µm copper particle and (b) a similar particle following electroless deposition of Ag not its surface. The macroscopic granular structure is not changed by the coating process and does not contribute to the hydrophobicity, which arises only as a consequence of the nanotextured Ag deposit.

3. Results and discussion

3.1. SH powder characteristics

Fig. 3 illustrates SEM images at different magnifications of (a) an uncoated ≤400 µm copper particle and (b) a similar particle following electroless deposition of Ag onto its surface. The macroscopic granular structure is not changed by the coating process and does not contribute to the hydrophobicity, which arises only as a consequence of the nanotextured Ag deposit. The apparent contact angle of a water droplet placed on a bed of dry particles is approximately 157° [9].

3.2. SH marble characteristics

Liquid marbles formed by each material were found to have their own distinct characteristics. Varying degrees of rolling or agitation were required for each material, yielding marbles of different surface coverage. Of the hydrophobic granules studied, SH 10 was observed to form the most complete marbles and allowed for the greatest ease of marble formation. Very little rolling or agitation is required to form a liquid marble on SH 10 powder. Fig. 4(a)–(c) illustrate different stages in the SH 10 marble forming process with (d) image of a partially formed SH 10 marble.

Note in Fig. 4(b) that the powder does not distribute evenly over the water surface but instead accumulates in a sheet like manner. This phenomena has been described in previous work of Forny et al. [7], who suggest that this results from attractive lateral capillary immersion forces, where particles move across the drop surface until they aggregate into a film.

In terms of formation, SH 200 powder exhibits similar behaviour to SH 10 although requiring slightly more agitation to form. SH 200 marbles are observed to form completely during motion, however particles at the top of SH 200 marbles have a tendency to recede back once the marble is at rest. Fig. 5(a)–(c) shows different stages of formation for a SH 200 marble. Fig. 5(d) indicates how particles typically recede back.

SH 40 liquid marbles were not observed to fully form utilising any technique. A significant amount of agitation was necessary even for the adherence of powder to a small fraction of a water droplet surface. SH 40 marbles were also the most difficult to handle once formed as they could be quite difficult to move without causing collapse. At most, between 60 and 70% powder–water surface coverage was attainable when rolling or agitating a water droplet on SH 40 powder. Fig. 6 illustrates the different stages of surface coverage for a SH 40 marble. Fig. 7 illustrates the typical fraction of surface coverage observed for SH marbles. As fairly similar particle shape is exhibited by marbles on all three types of SH powder, it would seem most probable that there is a particle size effect (i.e., particle mass effect) where the attainable surface coverage decreases with increasing particle mass.

3.3. PMMA marble characteristics

PMMA powder behaves quite differently from the SH materials in terms of liquid marble formation. When a droplet of water is placed on a PMMA surface, marble formation can quite often be instantaneous, particularly for larger drops. It would appear that even the slightest of impact forces can cause immediate PMMA spreading over the water surface. This type of behaviour has been reported in previous literature [4,5], where a bulk flow mechanism was proposed. This mechanism suggests that the initial solid spreading is caused by surface motion due to internal flow, which in turn entrains the solid particles dragging them up over the surface. PMMA particles are of a much lower density (typically 1080 kg m^{-3}) than the copper powder based SH materials (8960 kg m^{-3} approx.). This means that less force would be required to move these particles along the surface of the droplet, which could suggest agreement with the bulk flow mechanism proposed by Hapgood and Khanmohammadi [6].

Marbles formed on SH materials typically appeared to have one monolayer (or less) of solid particles across the water surface. Similar behaviour was noted by Aussillous and Quéré during their experiments with lycopodium liquid marbles [3]. Upon extensive agitation however, it would appear that more particle layering can result. PMMA liquid marbles when extensively agitated can be observed to collect clumps of material, i.e. much more variation in particle layering.

The radius of the contact zone, l, was observed to vary during liquid marble formation using PMMA, therefore the observed data were correlated with the theoretical values calculated from Eq. (3).

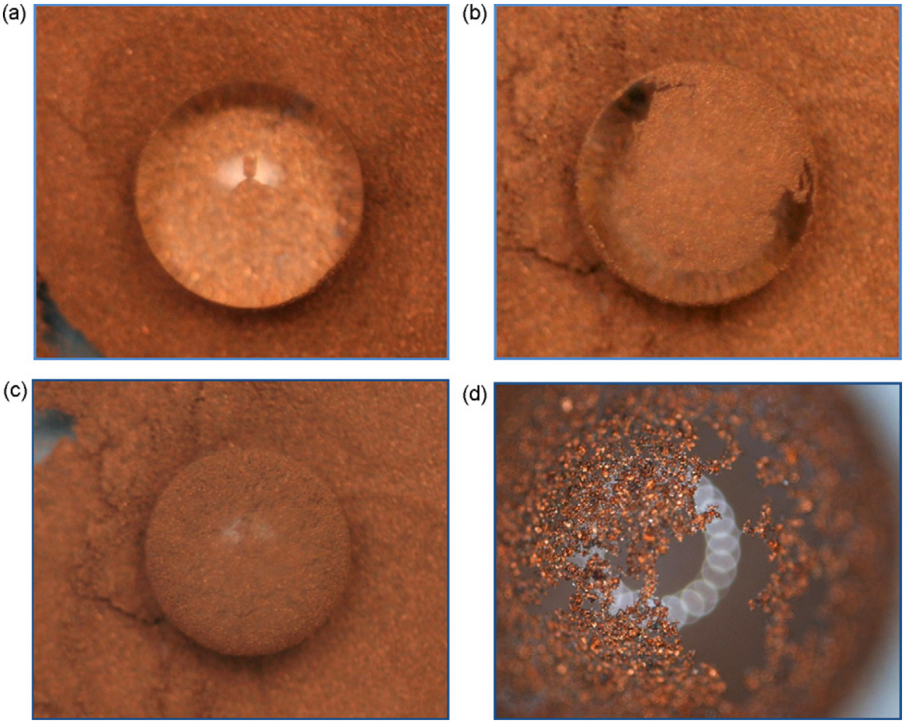

Fig. 4. (a) Water drop at rest on SH 10 surface, (b) partially formed liquid marble, (c) SH 10 liquid marble, and (d) close up of partially formed SH 10 marble (liquid marble approximately 2 mm in diameter).

Fig. 8 shows various images of PMMA liquid marbles. The low density of PMMA powder coupled with its regular spherical shape and small particle size would appear to allow more powder adhesion to the water surface than the SH materials. The radius of the contact zone during initial contact of PMMA and water is illustrated in Fig. 8a and indicates quite a broad contact zone. Fig. 8b shows a PMMA-water liquid marble with approximately 50% surface coverage, showing more sphericity and a lower contact zone than the initial contact. Fig. 8c shows a fully formed PMMA-water liquid marble, showing good sphericity and a low contact zone. The radii of

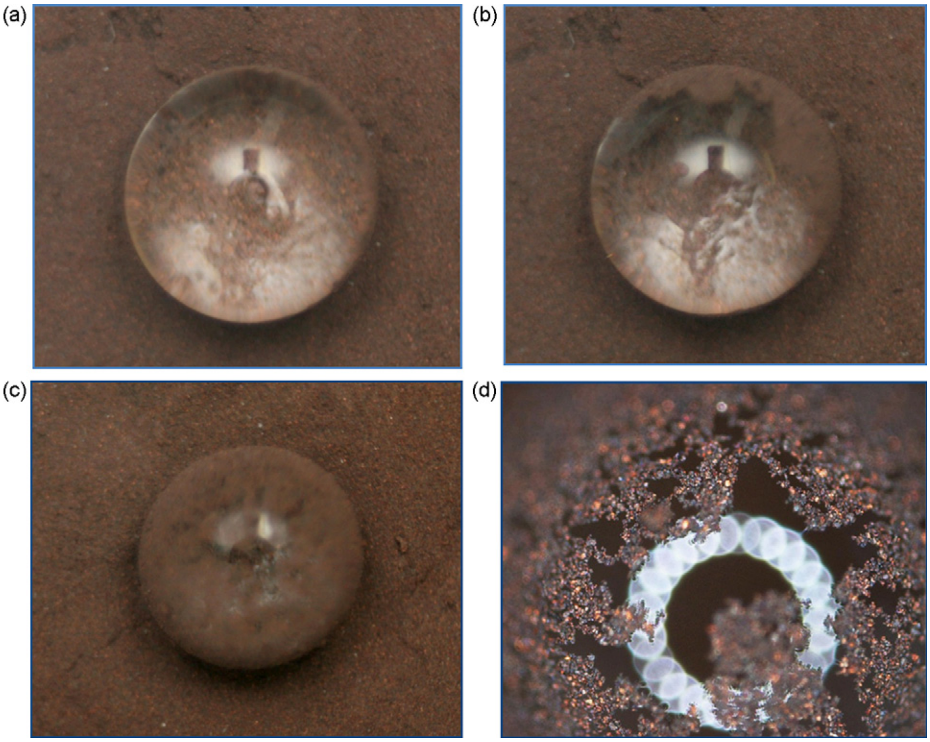

Fig. 5. (a) Water drop at rest on SH 200 surface, (b) water droplet with partial coverage, (c) SH 200 liquid marble, and (d) noting that top particles are observed to recede back (liquid marble approximately 2 mm in diameter).

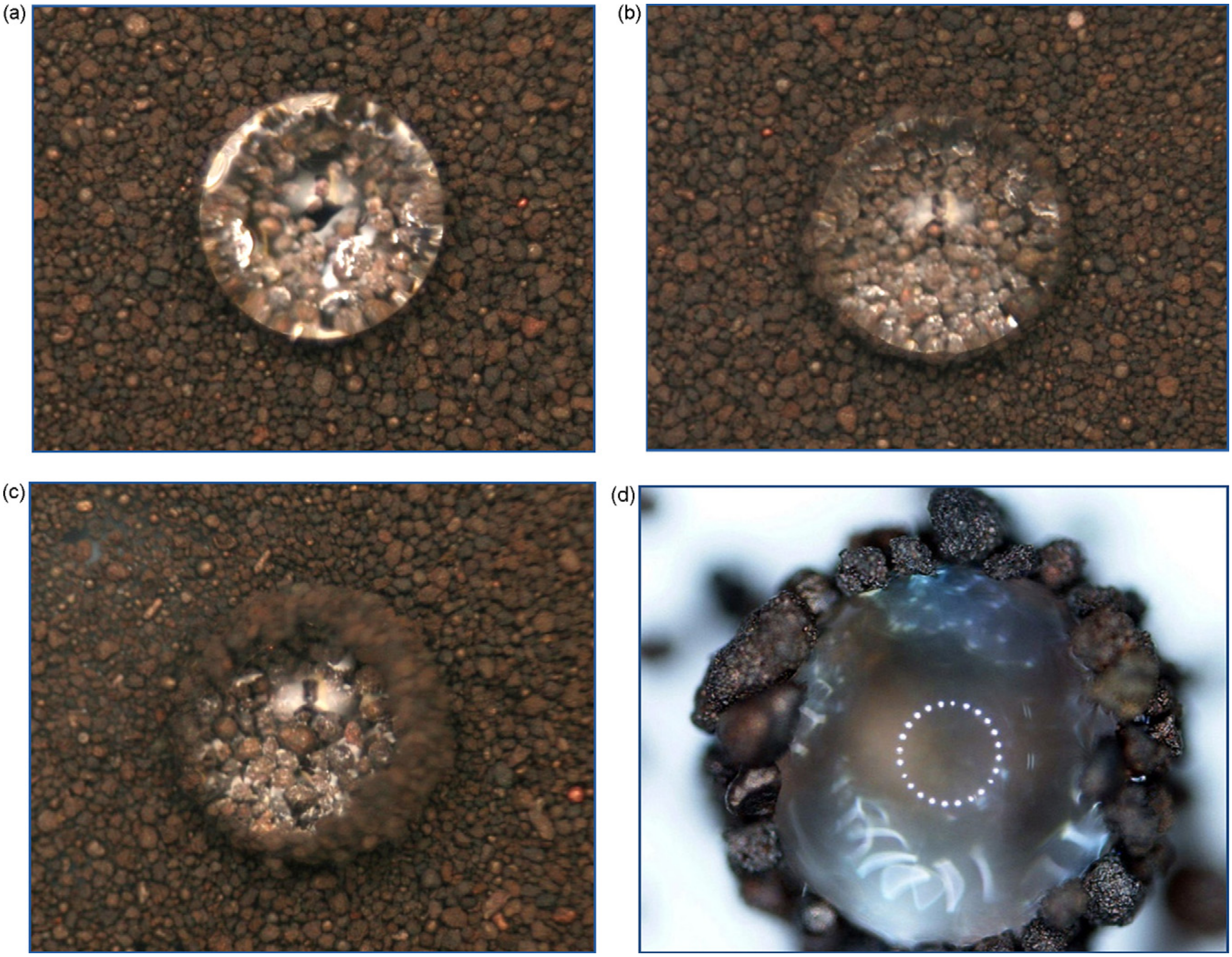

Fig. 6. (a) Water drop at rest on SH 40 surface (base particles can be seen through the drop), (b) partial formation, (c) close to maximum attainable surface coverage and (d) closer image of image SH40 marble formation (liquid marble approximately 2 mm in diameter).

the initial ($l_{\text{partial wetting}}$) and final ($l_{\text{liquid marble}}$) liquid marble contact zones were observed and correlated to the theoretical radius of the contact zone (l, as defined in Eq. (3)), with the data presented in Table 2.

A summary is given in Table 3 comparing some observations of the marbles formed from each powder type. In terms of mechanical properties, it appeared that SH 10 and SH 200 were the easiest to manipulate, i.e. marbles were easily divided. PMMA could be manipulated also, however the high fraction of open water surface area on SH 40 marbles made it almost impossible to separate them. SH 10, SH 200 and PMMA all formed liquid marbles quite readily. It was noted on occasion however that SH 200 particles could fall back into the powder bulk from the liquid surface if a drop was only partially covered, suggesting that the larger particle size

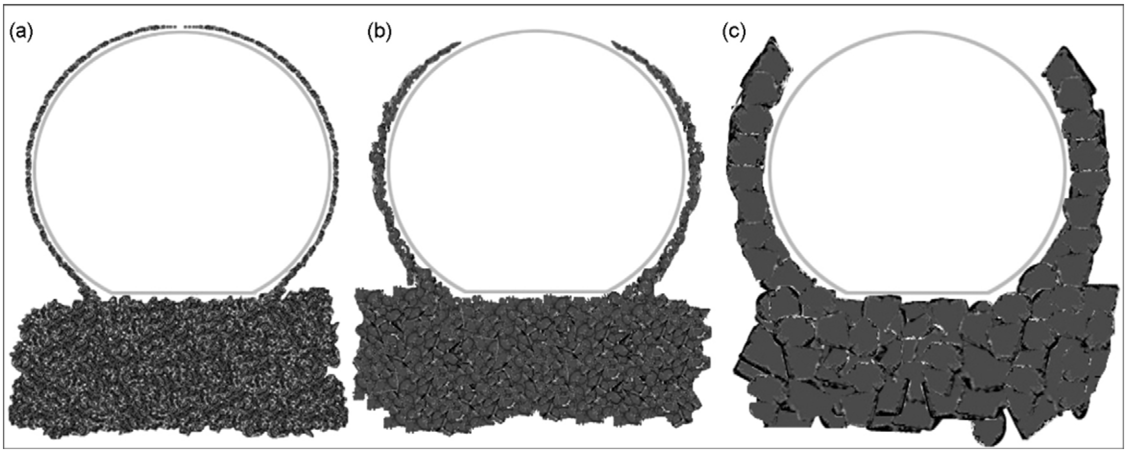

Fig. 7. Schematic diagram of typical attainable powder–water surface coverage (side view) for (a) SH 10 (lowest particle size), (b) SH 200 and (c) SH 40 (largest particle size).

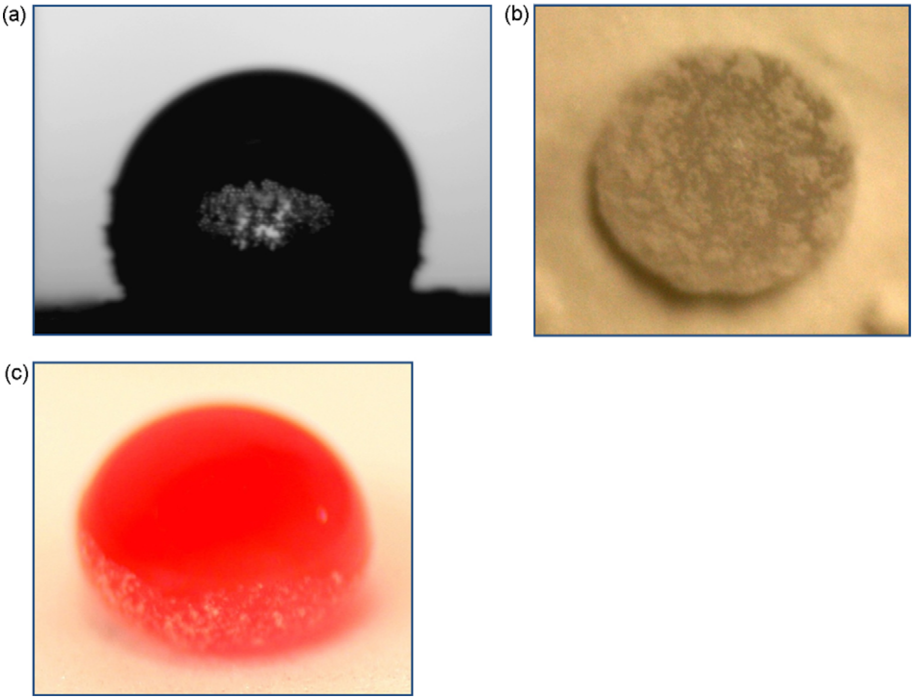

Fig. 8. PMMA marble (a) initial viewed from side), (b) dyed water drop for enhanced visibility (note particles adhered to drop base), (c) fully coated PMMA marble.

Table 2
The theoretical and observed radii of the initial ($l_{\text{partial wetting}}$) and final ($l_{\text{liquid marble}}$), droplet contact zones.

	Theoretical[a]	Observed
R_0 (mm)	0.750	0.750
$l_{\text{liquid marble}}$ (mm)	0.170	0.220
l_{lm}/R_0	0.226	0.293
$l_{\text{partial wetting}}$ (mm)	0.650	0.690
l_{pw}/R_0	0.866	0.892

[a] l, as defined in Eq. (3).

(and therefore larger particle weight) tends to gives an unstable marble powder structure this could also be attributed to weak particle–particle attachment. SH 40 marbles were however known to resist impact even with such low percentage powder coverage. This impact was induced by moving the "marbles" from the powder bed onto a solid surface. The large particle size of SH 40 most likely acts as a protective barrier, stopping an impact medium (such as glass) from coming in contact with the fluid interior.

Table 3
Comparison of liquid marble formation characteristics.

	SH 10	SH 200	SH 40	PMMA
Forms stable liquid marble (full coverage)	Yes	Yes[a]	No	Yes
Forms liquid marble in motion (full coverage)	Yes	Yes	No	Yes
Observed to form more than one monolayer	Yes[b]	Yes[b]	No	Yes
Difficulty of forming, ranked 1–4 (with 1 being the most difficult to form)	3	2	1	4
Difficulty of movement, ranked 1–4 (with 1 being the most difficult to move)	4	3	1	2

[a] Only for small diameter droplets.
[b] Not significantly more than one layer.

3.4. Liquid marble gravimetric analysis

Fig. 9 shows a plot of SH 10 powder mass against drop surface area. A fairly linear trend is observed suggesting that adhered powder mass is directly proportional to drop surface area ($R^2 = 0.923$). Experimental error associated with recording liquid marble mass is one potential reason for the deviation from linearity. Another possibility could be that weight contamination occurred (to a small degree), i.e. extra powder could have been entrained. Gravimetric data were plotted for SH 200 in Fig. 10, again illustrating a linear relationship of powder mass against water surface area ($R^2 = 0.913$).

SH 40 proved extremely difficult to handle during gravimetric testing. A SH 40 bed of particles tends to get disturbed very easily and even the slightest movement can result in the loss of particles from the bulk powder, therefore a wide object such as a clock glass was required to ensure maximum retention of the SH 40 powder in the bulk. When attempting to roll SH 40 marbles off a clock glass

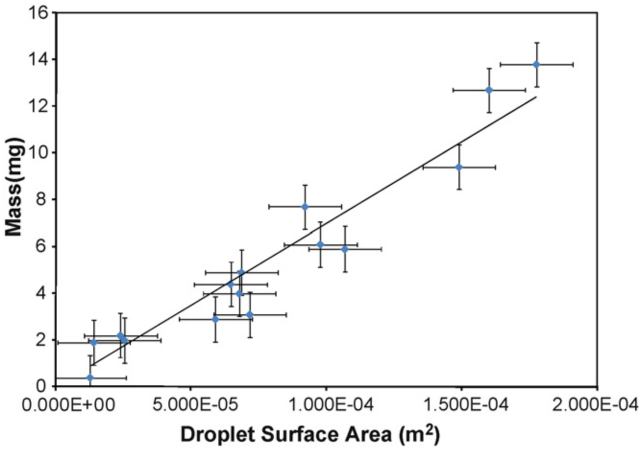

Fig. 9. SH 10 powder mass versus droplet surface area.

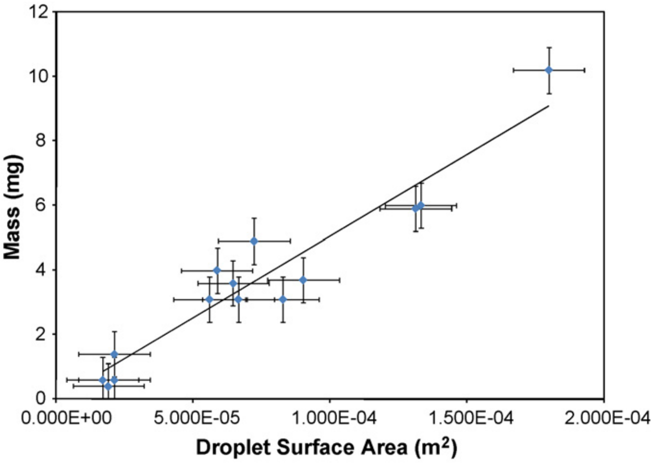

Fig. 10. SH 200 powder mass versus droplet surface area.

destructively, the marbles had a tendency to stick to the glass at the edge regardless of exit velocity. Trials of other methods of SH 40 marble removal from a particle bed were conducted but were also met with a significant tendency to cause marble collapse. As a result, very limited data could be gathered for SH 40 marbles. Fig. 11 is a plot of the limited data that were available, however these liquid marbles were inherently unstable, as illustrated in the relatively low R^2 value.

The gravimetric experimental data for PMMA powder liquid marbles is shown in Fig. 12. Again the data the show a linear trend with an R^2 value of 0.906. Table 4 is a summary comparing gravimetric results for each of the 4 materials used. It can be seen that SH 40 marbles (despite the low surface coverage) have the highest powder mass per unit water surface area, owing to large particle size.

The PMMA mass per unit droplet surface area is much higher than the SH copper based powders which can be attributed to the low density and mass of individual PMMA particles and possibly particle sphericity, whereby more spherical particles would have a lower particle–liquid contact and thus less resistance to flow over the liquid surface. The quantitative gravimetric data in Table 4, suggest that multiple layers of PMMA particles tend to occupy the droplet surface compared with the SH materials. Moreover, the quantitative gravimetric data for the SH copper powders indicates that only the SH10 produces liquid marbles with complete monolayer coverage. This is in agreement with visual observations, illustrated in Figs. 4–6, where SH200 and particularly SH40 particles were seen to slide off the surface of the liquid marbles.

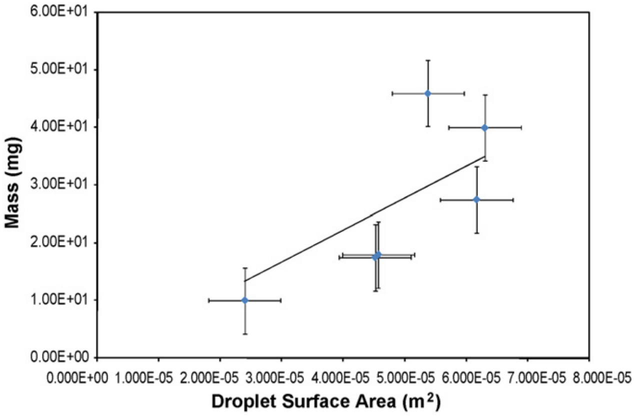

Fig. 11. SH 40 powder mass versus droplet surface area.

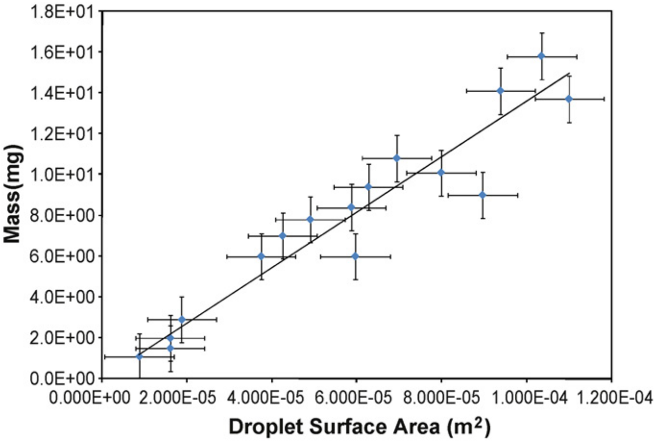

Fig. 12. PMMA powder mass versus droplet surface area.

3.5. Solid spreading phenomena

During microscopic investigation of the liquid marble phenomena, PMMA particles were observed to spontaneously “climb” up the surface of a liquid water drop when the drop was completely at rest, eventually covering the entire surface of the sphere. No agitation or marble rolling was performed during this period. These phenomena were subsequently filmed and images at four different time intervals can be viewed in Fig. 13.

It was noted that a temperature gradient between the top of the water droplet and the droplet base may have existed as a result of exposure to the microscope light, causing convection driven flow inside the drop. Considering the three possible mechanisms of convection driven flow; Rayleigh–Bénard (buoyancy-driven) convection typically results a downward flow at the liquid surface which was assumed as not applicable in this instance as the solid particles are observed to flow upwards along the drop sides. Spatially non-uniform evaporation, or the “coffee stain” phenomena, could be a possibility in this system as there is a fixed contact line. However, the characteristic upward flow of the Marangoni effect

Table 4
Quantitative gravimetric data comparison of liquid marbles.

	SH 10	SH 200	SH 40	PMMA
Average powder mass per droplet surface area (kg m^{-2})	0.0698	0.0505	0.556	0.1361
R^2 from linearization	0.923	0.914	0.541	0.907
Particle size (m)	9.000E−06	1.500E−05	3.200E−04	4.300E−05
Particle vol. (m^3)	3.815E−16	1.766E−15	1.715E−11	4.161E−14
Particle density (kg m^{-3})	8.960E+03	8.960E+03	8.960E+03	1.080E+03
Particle mass (kg)	3.418E−12	1.583E−11	1.537E−07	4.494E−11
Particle projected surface area (m^{-2})	6.359E−11	1.766E−10	8.038E−08	1.451E−09
No. of particles per m^2	2.042E+10	3.191E+09	3.619E+06	3.029E+09
For a 1 mm drop (diameter, m)	1.000E−03	1.000E−03	1.000E−03	1.000E−03
Drop volume (m^3)	5.233E−10	5.233E−10	5.233E−10	5.233E−10
Drop surface area (m^2)	3.140E−06	3.140E−06	3.140E−06	3.140E−06
No. of particles per droplet	6.412E+04	1.002E+04	1.136E+01	9.510E+03
No. of particles in monolayer	4.938E+04	1.778E+04	3.906E+01	2.163E+03
No. of particle layers on droplet	1.30	0.56	0.29	4.40

Note: The mass of the particles enclosing the water droplet was measured, knowing the particle size and density the number of particles can be estimated. The number of particles in a monolayer is based on the surface area of water droplet and the projected area of individual particles.

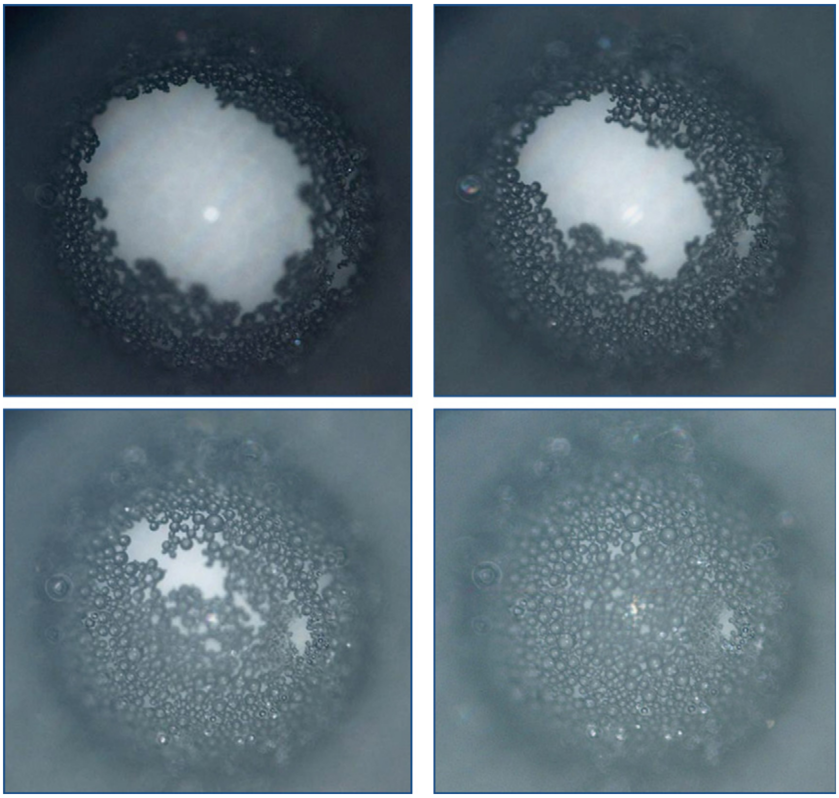

Fig. 13. Images taken under microscope of PMMA spreading over a sessile water drop. Top left image after 300 s; top right image after 400 s; bottom left image after 460 s; bottom right image after 520 s.

seems to fit the observed phenomena best of the three possible mechanisms and maybe induced by evaporation from the top of the droplet which was caused by the over-droplet light source from the microscope.

3.6. Polymerisation of MMA–PMMA liquid marbles

In order to improve the mechanical strength of the PMMA liquid marbles, an experiment was undertaken to coalesce the individual powder particles on the surface of the liquid marble. This was facilitated by dropping some methylmethacrylate (MMA) monomer on a PMMA marble. The MMA liquid was found to spread over the PMMA surface without penetrating into the fluid interior. MMA liquid is totally immiscible with water, therefore if the liquid MMA penetrated the powder coating it would have created a layer adjacent to the surface of water droplet. The MMA/PMMA marble was then exposed to UV-light to polymerise the MMA to produce a shell of PMMA in the shape of the liquid marble. This shell could subsequently be lifted off revealing an empty interior (it is assumed that water exits through the PMMA bed or is evaporated due to the heat released from the bone cement formation reaction. Fig. 14 illustrates some remaining shells from this process. The schematic given in Fig. 15 below outlines the process used to create the bone cement shell.

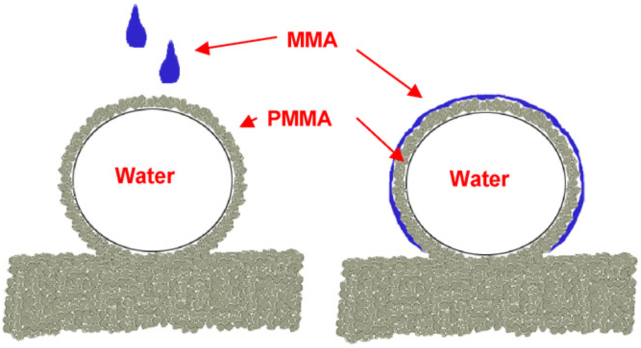

Fig. 15. (a) MMA dropped onto a PMMA liquid marble, (b) MMA is observed to spread over the surface. The MMA and PMMA react forming a shell of bone cement which can be removed intact.

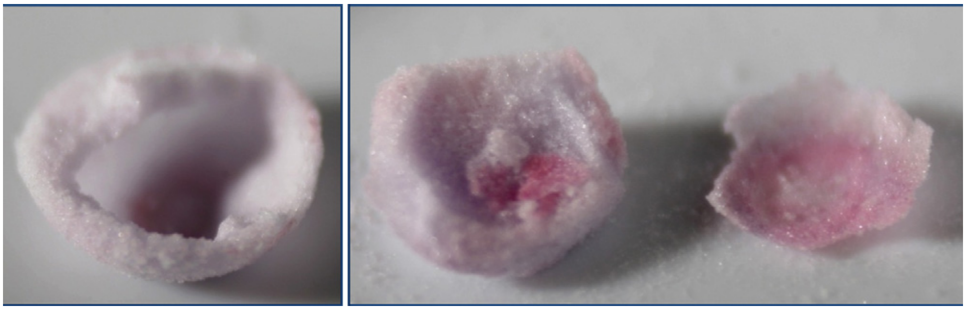

Fig. 14. Shells remaining after the formation of PMMA on a liquid water marble.

4. Conclusions

A summary of liquid marble observations is given in Table 3. The experimental data indicate for the successful formation of liquid marbles, that in addition to the hydrophobicity of the system, powder density and particle size (i.e., particle mass) are important parameters. Adhered powder mass was found to be directly proportional to water surface area for all materials. It was noted that large particle size (SH 40) results in a high powder mass to surface area ratio. It was also observed that PMMA had a relatively high mass to surface area ratio for a material of such density, once again suggesting a difference in surface coverage characteristics. Moreover, a further procedure was developed to increase the mechanical strength of the liquid marble with the aim of maintaining water within a more robust PMMA liquid marble shell. This technique may prove to be a novel way of encapsulating drug compounds, such as gentamicin sulphate, for PMMA bone cement.

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