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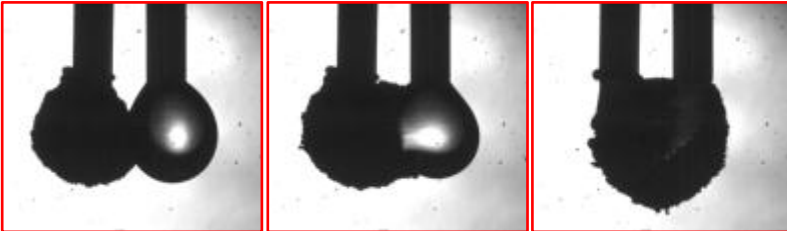
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Observations of liquid marble and water droplet interactions and stability



Coalescence of a liquid marble and a water droplet



Wetting between a capsule and a water droplet

ARTICLE

Liquid Marble and Water Droplet Interactions and Stability

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The interactions between two individual water droplets were investigated in air using a combination of coalescence rig and high speed video camera. This combination allows the visualization of droplet coalescence dynamics with millisecond resolution which provides information on droplet stability. Bare water droplets coalesced rapidly upon contact, while droplet stability was achieved by coating the droplets with polystyrene particles carrying pH-responsive poly[2-(diethylamino)ethyl methacrylate] hairs (PDEA-PS particles) to form liquid marbles. The asymmetric interaction of a water droplet (pH 3 or 10) armoured with the PDEA-PS particles (liquid marble) with a bare droplet at pH 3 exhibited intermediate stability with coalescence observed following an induction time. The induction time was longer for the pH 10 liquid marble, where the PDEA-PS particles have a hydrophobic surface, than in the case of a pH 3 liquid marble, where the PDEA-PS particles have a hydrophilic surface. Furthermore, film formation of PDEA-PS particles on the liquid marble surface with toluene vapour confirmed capsule formation which prevented coalescence with the neighbouring water droplet instead wetting the capsule upon contact within 3 milliseconds. This study illuminates the stability of individual particle-stabilized droplets and has potential impact on processes and formulations which involve their interaction.

Introduction

There is increasing interest in the ability of solid particles to stabilize soft dispersed systems including emulsions, foams and liquid marbles (dry liquid). It has been established that physicochemical properties such as the hydrophilic-hydrophobic balance of the particle surface, interparticle interactions and solution/gas conditions have significant impact on the physical, structural and mechanical properties of these systems. Liquid marbles¹⁻⁵, which are liquid droplets stabilized with solid particles at gas-liquid interfaces, have attracted increasing attention in view of their potential applications in cosmetics^{6,7}, transport & microfluidics^{1,8-11}, miniature reactors^{12,13}, personal & health care products¹⁴, sensors¹⁵⁻¹⁷, accelerometers¹⁸, gas storage^{19,20} and actuators^{21,22}. Relatively hydrophobic particles that can adsorb at the gas-liquid interface are generally used in order to stabilize these liquid-in-gas dispersed systems. Solid particles which can stabilize liquid marbles include surface-modified lycopodium powder^{23,24}, hydrophobic silica particles²⁵⁻²⁸, carbon black^{29,30}, carbon nanotubes³¹ or small organic molecule powders³², and increasingly, organic polymer particles³³⁻⁴⁴. In principle, such synthetic polymer particles should be particularly attractive as liquid marble stabilizers, because their surface chemistries can be readily designed using various functional monomers. Due to this advantage, it is possible to confer stimulus-responsive character to liquid marbles: it has been reported that liquid marbles, which can be disrupted by external stimuli such as pH and temperature, can be fabricated using stimulus-responsive polymer particles^{35,37,39-42}. Another attractive feature of polymer particles is film forming ability, which has been widely deployed in the paint, adhesive and paper industries⁴⁵. Film formation of polymer

particles adsorbed to the water droplet surface leads to rigid capsules with reduced pore size between particles and within flocs and the evaporation speed of the liquid marble internal water can be suppressed^{43,44}.

The instability of liquid marbles is generally attributed to the wetting of the solid particles adsorbed to the air-liquid interface, which results in the disruption of the liquid marbles and coalescence with their neighbours⁴⁶. When the internal liquid penetrates the solid particle layer on the droplet surface and makes contact with the substrates upon which the liquid marbles contact (*e.g.* liquid, solid), liquid marble disruption and disintegration and coalescence occurs. As the liquid penetration rate is a key determining step in liquid marble stability against coalescence, a long wetting time (and therefore long induction time) thereby enhances liquid marble stability. Considering liquid marbles as functional materials with a promising future, it is crucial to establish methods to characterise their stability towards coalescence.

In this study, the interactions between two individual water droplets surrounded by air were investigated, using a coalescence rig equipped with a high speed camera based on the method developed by Ata⁴⁶. This setup has the advantage of allowing the visualization of droplet coalescence and wetting dynamics with high temporal resolution (millisecond order). This approach has been successfully used previously to investigate the stability of either two air bubbles^{47,48}, or oil droplets^{49,50} either bare or armoured with particles (*e.g.* glass and sub-visible polymeric particles) surrounded by aqueous solution. Here, the stability, wetting and coalescence behaviour of individual water droplets armoured with polystyrene particles carrying pH-responsive poly[2-(diethylamino)ethyl

methacrylate] hairs (PDEA-PS particles) brought into contact with water droplets were examined in air as a function of the pH of the inner water phase, and the degree of film formation of the PDEA-PS particles on the droplet surface. This work is the first to investigate the shape and morphological changes of liquid marbles and capsules during wetting and coalescence with millisecond resolution. The investigations of pairwise interactions were conducted in symmetric and asymmetric modes. This study provides information on the stability of individual liquid marbles which is crucial to develop a detailed understanding of liquid-in-gas soft dispersed systems.

Experimental

Materials. The chemicals used for the synthesis of PDEA-PS particles are the same as those used in our previous study⁴⁴. Styrene, α,α' -azobisisobutyronitrile (AIBN), 2-(diethylamino)ethyl methacrylate (DEA, 99%), isopropanol (IPA, 99%), toluene ($\geq 99.0\%$) were purchased from Sigma-Aldrich. 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086) was purchased from Wako Chemicals, Japan. Sodium hydroxide pellets for analysis (EMSURE® ISO) were purchased from Merck KGaA, Germany. Hydrochloric acid (32 %) was purchased from Ajax Finechem Pty Ltd. Millipore Milli-Q water was used in all experiments.

Particle synthesis

Submicrometre-sized PDEA-PS latex particles were synthesized by the dispersion polymerization of styrene using a PDEA macro-initiator (mean degree of polymerization = 60) and VA-086 azo initiator in IPA at 80 °C, as described previously^{39,40}. The PDEA macro-initiator was synthesized by atom transfer radical polymerization of DEA using 2,2'-azobis[2-methyl-N-(2-(2-bromoisobutyryloxy)ethyl) propionamide] as an initiator in IPA at 25 °C and was purified by passing through a silica column. The PDEA macro-initiator (6.55 g), VA-086 (0.59 g) and styrene monomer (30.0 g) were added to IPA (300 mL) in a round-bottomed 500 mL flask containing a magnetic stirrer bar. The number of moles of azo groups used in this polymerization formulation was 1.0 mol% based on styrene monomer. The reaction mixture was vigorously stirred at room temperature until the macro-initiator, VA-086 initiator and monomer had dissolved completely. The reaction mixture was purged with nitrogen gas for 30 min in order to remove dissolved oxygen. The styrene polymerization commenced after placing the reaction vessel in an oil bath set at 80 °C. The reaction was allowed to proceed for 168 h with continuous stirring at 500 rpm under a nitrogen atmosphere. These PDEA-PS latexes were purified via ten centrifugation-redispersion cycles (typically 6,000 rpm for 30 min) using a centrifuge (Hitachi CF16RXII centrifuge). Each supernatant was replaced with fresh IPA and then water, and the final purified latex was freeze-dried for 48 h. The dried PDEA-PS powder was ground using a pestle and mortar before use. An SEM image of the particles is shown in Fig. S1.

Stability of water droplets

The experimental setup used in this work is based on the method of Ata⁴⁶ (Fig. 1). Briefly, two water droplets (bare droplet or liquid marble) were located at the end of stainless steel capillaries (0.69×1.07 mm I.D×O.D). The right droplet was then moved towards the left one using a linear actuator, until they were just touching (no visible gap between the droplets). In the case of the bare water droplet-bare water droplet interaction experiments, hanging droplets with a diameter of 2.9 mm ($\pm 5\%$) at the major horizontal length were produced in air at adjacent capillaries with the aid of independent microsyringe pumps (Sarasota, FL), which is equivalent to a volume of 15 μL . In the case of particle-armoured water droplets, the liquid marbles were attached to the end of the

capillary as follows. Water droplets (15 μL) were deposited onto the dried PDEA-PS particle powder bed using a micropipette (Nichipet EX, Nichiryo, Transferpette®, BRAND GMBH+CO KG). By gently rolling the water droplet on the powder bed for 30 s-2 min, the droplet was entirely encapsulated by the PDEA-PS powder. The liquid marble was then attached to the end of the capillary filled with aqueous solution of identical pH as that of the inner aqueous solution of the liquid marble (within 30 s after preparation of liquid marble). The liquid marble was contacted with the other liquid marble/bare water droplet within 5 min after being attached to the capillary. In order to prepare the polymer capsule samples, liquid marbles stabilized with the PDEA-PS particles suspended from the capillary were film formed by exposure to toluene vapour as follows. The liquid marble was brought into a glass vessel ($5.70 \times 10^{-5} \text{ m}^3$ volume and $9.57 \times 10^{-4} \text{ m}^2$ base area) containing 3 mL toluene and covered with an Al foil lid with *ca.* 2-cm diameter hole for a period of 1, 2 or 4 min. The interaction experiments were conducted approximately 5 min after this toluene vapour treatment. When the asymmetric bare water droplet-liquid marble/capsule interaction experiments were conducted, the volume of bare water droplet was controlled for the droplet to have the same height as the liquid marble.

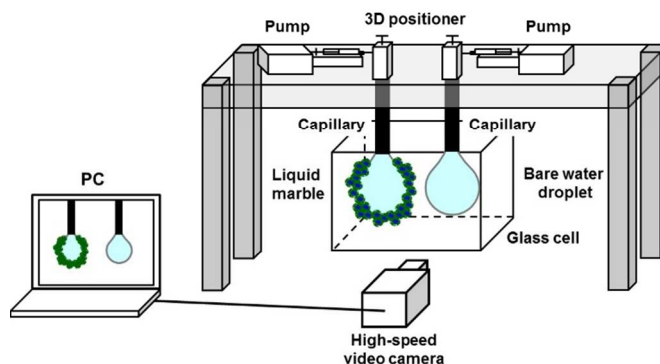


Figure 1. Experimental configuration for investigation of water droplet interaction in air based on the method of Ata [46]. The setup was placed on a vibration isolation table.

The entire process (from before the droplets were in contact until after coalescence) was recorded using a high speed video camera (Phantom 5, Vision Research). Videos were recorded at a resolution of 512×256 and 1024×512 with a frame rate of 10-300 frames per second for induction time calculations and 2100 or 2127 frames per second for post coalescence analysis using the Phantom 6.30 (Nikon) software. The induction time for bare water droplet-bare water droplet interactions was calculated by subtracting the time associated with the frame before coalescence started minus that of the frame where the droplets initially touched. The induction time for the liquid marble-bare water droplet systems was determined using a stop watch. Here, the induction time is the time taken for liquid to penetrate the particle layers at the surface of the liquid marble and subsequently displace the intervening air gap and rupture to form a single large droplet. In some cases, especially with the capsule, no coalescence was observed. However, the droplet was seen to wet the capsule. In such cases two characteristic times were determined to quantify the interfacial stability. The adhesion time is the time required to initiate wetting of the liquid marble capsule surface. The second characteristic time is the wetting time, which corresponds to the complete spreading (or wetting) of the PDEA-PS coating by the droplet. Both times were determined using the same method as that used for calculation of induction time between two bare water droplets. The videos taken for post coalescence analysis of the

droplets (or liquid marbles/capsules) were analysed using ImageJ **Symmetric interactions**

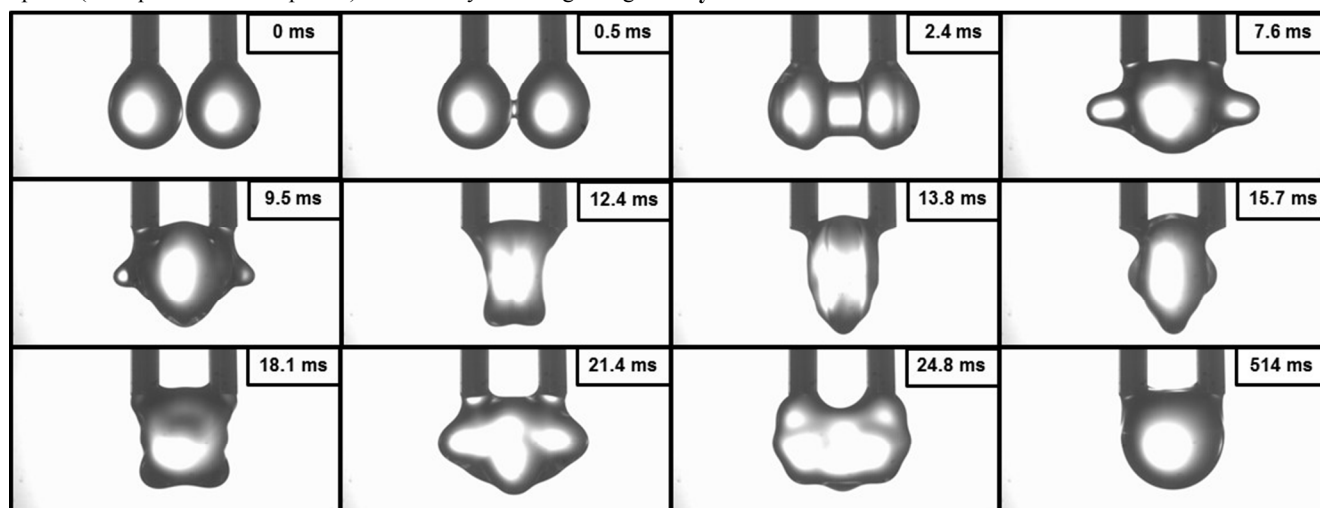


Figure 2. Selected images taken from video footage of the coalescence between bare water droplets with pH 3. The coalescence between bare water droplets with pH 10 was similar to that with pH 3. The time shown for each image is the time since coalescence relative to the frame before coalescence occurs. The outer diameter of the capillaries is 1.07 mm which acts as an appropriate scale bar.

(National Institutes of Health).

In this study, interaction experiments were conducted in two modes: symmetric (both droplets were bare or coated) and asymmetric (a coated and a bare droplet). All the experiments were conducted in air (relative humidity, 29-57 %; temperature, 19-22 °C). The whole setup was placed on a vibration isolation table. Before each experiment, the cleanliness of the setup was tested by bringing two bare water droplets together approximately 30 s after they were formed. If the droplets coalesced within a single video frame interval (< 0.003 s), the setup was considered to be clean. The experiments were repeated at least 5 times. The mean induction or adhesion (wetting) time was determined together with the standard deviation (shown as error bars in figures).

Wetting behaviour

To test the wetting of the particles, a floc of particles was placed on a glass slide under a single water droplet (pH 3 or 10). The floc was moved up to the droplet. The process was recorded to determine if the aggregate adhered to the surface of the water droplet or was partially immersed in the water droplet depending on the pH of the droplet. Conversely, contact angles for water droplets (15 μ L) placed on the dried PDEA-PS particle powder bed were measured using an Excimer SImage02V apparatus at 25°C. The adhesion and immersion wetting behaviour of the particles was also characterised using the experimental setup used to investigate the interaction of water droplets with videos recorded at 40 fps. The immersion wetting of the PDEA-PS particles was assessed by recording the count rate within a cuvette in a Malvern Zetasizer Nano ZS containing different pH aqueous solutions. The mean count rate was measured to determine the background. A known mass of particles was placed on the surface of the solution and the mean count rate was measured for 25 s every 30 s over a period of 60 min.

Results and discussion

Observations of symmetric droplets interactions will be discussed first, followed by asymmetric interactions. Regarding the induction and wettings times characterising the stability of the droplets, see Table 1.

The stability of an interacting droplet pair is defined by the time taken for coalescence to occur. An increase of induction time indicates higher stability of the droplet pair. The initial approach in this study was to investigate the interaction between two individual water droplets (in the presence and absence of particles adsorbed to the air-water interface) as a function of pH. Bare water droplets coalesced rapidly (within one video frame interval or 0.003 s) for pH 3.0, 6.5, and 10.1 droplets (Table 1). The coalescence of bare droplets (15 μ L) starts with the formation of a bridge (neck), see Fig. 2. While the neck expands, surface waves, or ripples, are observed on the surface of the droplet. Bulges are formed at the extremities of the droplet, which then retract as the droplet is compressed. Multiple expansion and compression cycles followed with the surface of the droplet appearing highly deformable. At all pH values investigated, similar coalescence behaviour was observed.

The air-water surface is known to be negatively charged above an $i_{ep} \sim 4$ and slightly positively charged below the i_{ep} ⁵⁷⁻⁵⁵ and there should be a weak short-ranged electrostatic repulsion between the pair of interacting water droplets at both pH 3 and 10. However, any repulsive force operating in air will be dominated by the longer ranged van der Waals attractive force and rapid coalescence occurred. The induction times observed for water droplets in air in this study (see Table 1) agree with previous studies⁵⁶ and were similar to those observed for air bubbles in aqueous media in no added electrolyte (< 0.003 s)⁵⁷. It should be noted that the solutes used to adjust the pH here are known to have little effect on the stability of air bubbles in water at the concentrations used^{58,59} and are assumed to act similarly on water droplets in air.

Previous studies of emulsion and bubble systems have shown that the stability of oil-water or air-water interfaces is enhanced in the presence of solid particles, because the presence of particles at the interface creates a steric barrier against coalescence⁴⁷⁻⁵⁰. First, we fabricated liquid marble samples by contacting the water droplet hanging on the capillary end to the dried PDEA-PS particle powder bed until complete coating of the air-water interface by the powder was attained. The surfaces of the resultant liquid marbles were very rough due to coating with an excess quantity of large PDEA-PS flocs, the presence of which was difficult to minimise using this method. Subsequently we fabricated the liquid marble samples by picking pre-prepared liquid marbles up on the capillary tip (see

Experimental). This method reduced the quantity of excess PDEA-PS particle flocs on the marble surface. All of the results shown used the latter method. Scanning electron microscopy studies confirmed the PDEA-PS particle coating layer thickness of $151 \pm 24 \mu\text{m}^{44}$.

Table 1. Summary of water droplet interaction investigated using coalescence apparatus^d. Upper row shows coalescence, no wetting/coalescence or wetting. Middle and lower rows show induction or adhesion (wetting) time and number of flocs detached from the liquid marble into air phase, respectively.

		Left side droplet ^{b)}									
		pH 3 bare droplet	pH 10 bare droplet	pH 3 LM	pH 10 LM	pH 3 LM (1 min ^{c)})	pH 3 LM (2 min ^{e)})	pH 3 LM (4 min ^{c)})	pH 10 LM (1 min ^{c)})	pH 10 LM (2 min ^{c)})	pH 10 LM (4 min ^{c)})
Right side droplet ^{b)}	pH 3 bare droplet	coalescence < 0.003 s	-	coalescence 86 ± 24 s	coalescence 230 ± 117 s	coalescence 2 ± 1 s	wetting 0.008 ± 0.003 s ^{d)} (0.019 ± 0.004 s) ^{e)}	wetting 0.008 ± 0.003 s ^{d)} (0.019 ± 0.003 s) ^{e)}	coalescence 5 ± 4 s	wetting 0.005 ± 0.002 s ^{d)} (0.017 ± 0.003 s) ^{e)}	wetting 0.004 ± 0.001 s ^{d)} (0.028 ± 0.017 s) ^{e)}
	pH 10 bare droplet	-	coalescence < 0.003 s	no wetting nor coalescence -	no wetting nor coalescence -	wetting < 0.003 s ^{d)} (0.019 ± 0.003 s) ^{e)}	wetting < 0.003 s ^{d)} (0.026 ± 0.004 s) ^{e)}	wetting < 0.003 s ^{d)} (0.018 ± 0.004 s) ^{e)}	wetting < 0.003 s ^{d)} (0.018 ± 0.002 s) ^{e)}	wetting < 0.003 s ^{d)} (0.018 ± 0.001 s) ^{e)}	wetting < 0.003 s ^{d)} (0.024 ± 0.0003 s) ^{e)}
		-	-	0-1 flocs	1-11 flocs	0-6 flocs	0 floc	0 floc	0-4 flocs	0 floc	0 floc
		-	-	0 floc	0 floc	0 floc	0 floc	0 floc	0 floc	0 floc	0 floc

No coalescence occurred between liquid marbles (pH 3 and 10) with or without toluene vapour treatment within 30 min.

^{a)} 19.4-22.3 °C, 29-57 RH%

^{b)} Right-side droplet approached to left-side droplet.

^{c)} Toluene vapour treatment time.

^{d)} Adhesion time: Time required to initiate wetting of the liquid marble capsule surface.

^{e)} Wetting time: Time for the bare water droplet to fully wet the film-formed liquid marble (to spread on the film-formed liquid marble surface).

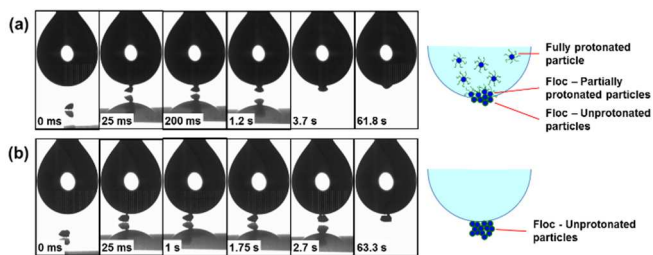


Figure 3. Selected images taken from videos showing the contact of a floc of PDEA-PS particles with a 15 μL droplet at (a) pH 3 and (b) pH 10.

Liquid marble pairs were stable against coalescence independent of the pH value of the inner aqueous phase (pH 3.0, 6.5 and 10.1). These liquid marbles were able to be moved apart without coalescence, after initial contact for a period of time (up to 30 min); this emphasizes the excellent stability of these liquid marbles. Note that the liquid marbles became separated from each other after initial contact during the 30 min stability assessment period, because of volume shrinkage of the liquid marbles due to evaporation of some internal water⁴⁴. Particles in the contact region formed a thick bridge of particle layers which inhibited coalescence.

It is of interest to report that stable liquid marbles can in fact be prepared using an acidic inner aqueous droplet. The PDEA-PS particles can be wetted by acidic aqueous solution because of their high hydrophilicity due to protonation of PDEA hairs, which led to difficulty in stable liquid marble formation. Fig. 3 shows the interaction of a particle floc with a droplet at pH 10 and at pH 3. The floc appears to weakly adhere to the pH 10 droplet, and hangs loosely at the base of the water droplet. When the droplet has a pH of 3, the floc is partly immersed and it appears that the wetted

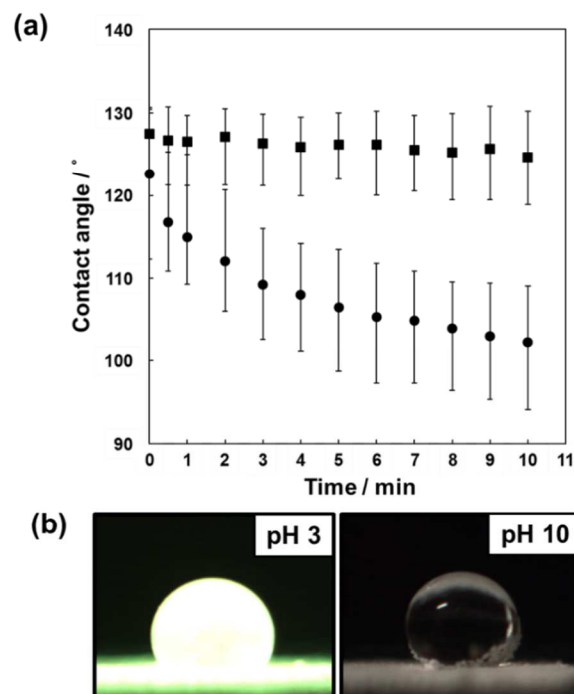


Figure 4. (a) Contact angles of water droplet (15 μL) at (●) pH 3 and (■) pH 10 on a dried PDEA-PS particle powder bed. (b) Digital photographs of water droplets at pH 3 and pH 10 taken after placing on the PDEA-PS particle powder for 2 min (pH 3) and 10 min (pH 10), respectively.

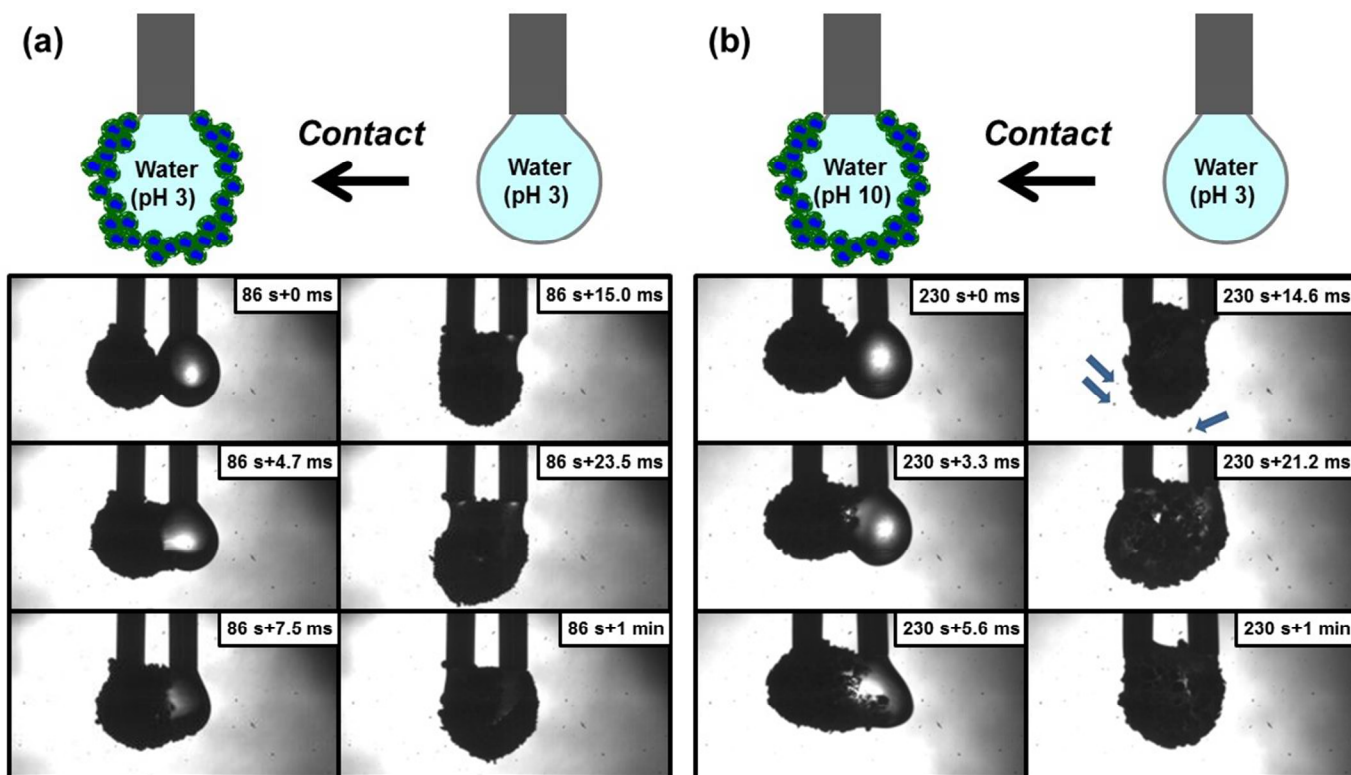


Figure 5. Selected images taken from video footage of the coalescence between a PDEA-PS particle-stabilized liquid marble with (a) pH 3 or (b) pH 10 and a bare water droplet (pH 3). The time shown in each image indicates the coalescence time + time elapsed since coalescence. Arrows in (b) show flocs detached from the liquid marble. The outer diameter of the capillaries is 1.07 mm which acts as an appropriate scale bar.

perimeter slightly increases with time (which is approximately 60 s after the contact of the floc with the droplet). In order to characterise pH-dependent wetting behaviour, contact angle measurement of water droplets on a PDEA-PS particle powder bed were conducted (Fig. 4). At pH 10, the powder bed was not wetted by water and the contact angles were almost constant at approximately 126° , which was attributed to pinning of the water droplet at the rough surface of the dried PDEA-PS powder. On the other hand, a water droplet at pH 3 started to wet the powder bed and the contact angle gradually decreased from 122° to 102° over a ten min period. (Note that the contact angle is still above 90° , which is sufficient to form a liquid marble.) In addition, the droplet became white and turbid within two min after placement of the water droplet on the powder, which confirms dispersion of the protonated hydrophilic PDEA-PS particles into the aqueous phase. It is noteworthy that the pH of the water droplet on the PDEA-PS powder increased from pH 3 to 5-6, which was confirmed using pH indicator paper. This is explained by the consumption of protons in the protonation of the PDEA hairs on the PDEA-PS particles (Note that pH of the inner water of the analogous liquid marble also increased from 3 to 6-7, 5 min after preparation). Possible reasons for the observed stability of the liquid marble with an acidic inner aqueous droplet are therefore that (i) insufficient protons were supplied to the PDEA-PS particles to protonate many of the PDEA-PS particles, and/or that (ii) pinning effects due to the rough surface of the PDEA-PS particle flocs were in operation^{60,61}.

Pairs of liquid marbles after toluene vapour treatment (1 min, 2 min and 4 min) also showed high stability against coalescence independent of the internal aqueous phase pH. These capsules did not coalesce when in contact for up to 30 min, which demonstrates the excellent stability of the PDEA-PS films formed on the droplet surfaces.

Asymmetric interactions

Liquid marbles

Interestingly, the observed stability is very different for the asymmetric interaction between a liquid marble and a bare water droplet. Fig. 5 shows high-speed camera images illustrating coalescence of a liquid marble with pH 3 or 10 and bare water droplet at pH 3. Before coalescence, it is clear that the bare water droplets have smooth surfaces and the liquid marbles have rough surfaces (roughness, $64 \pm 36 \mu\text{m}$) due to the presence of the PDEA-PS powder. During the dynamic coalescence process, both the droplet and marble surfaces exhibit less deformation than was evident in the coalescence of bare droplets in Fig. 2. No bulging was observed even on the extremity of the droplet side. The liquid marble appears to engulf the droplet, which is possible since the particles are loose on the particle-free air-water interface and can redistribute themselves. The result of the coalescence of a liquid marble with a bare droplet is a larger liquid marble with some packing defects (see Fig. 5). It is noted that doubling the volume of the $15 \mu\text{L}$ liquid marble increased the relative surface area by approximately 59 % (assuming spherical droplets). The practical implications are that liquid marbles may sustain small changes in volume (i.e. surface area) for example due to a change in density of the liquid (e.g. change in temperature) while retaining their overall integrity.

The induction time for the coalescence of a liquid marble (pH 10) and a bare water droplet (pH 3) system was determined to be 230 ± 117 s, which was longer than that determined for a liquid marble (at pH 3) and bare water droplet (at pH 3) at 86 ± 24 s. This difference is attributed to the difference in wetting/penetration behaviour of water from within the liquid marble into the particle powder coating (see Figs. 3 and S2). It is worth noting that the period observed for the wetting/penetration was longer than that

needed for protonation of the diethylamino groups (expected in /less than 1 millisecond⁶²). One possible explanation for the slow wetting observed here could be orientation of the polar surface diethylamino groups towards the inside of the particles during drying, with a subsequent finite reorientation time for these groups to make contact with the aqueous phase⁶³. Another possible reason would be a pinning effect^{60,61}: it should take time for the acidic water to wet the rough PDEA-PS powder surface. On the other hand, when the bare water droplet at pH 10 contacted a liquid marble at pH 3 or 10, no wetting nor coalescence occurred for at least 30 min and they could be readily separated (Fig. 6). Sometimes PDEA-PS flocs were transferred to the bare water droplet surface from the liquid marble while in contact as shown.

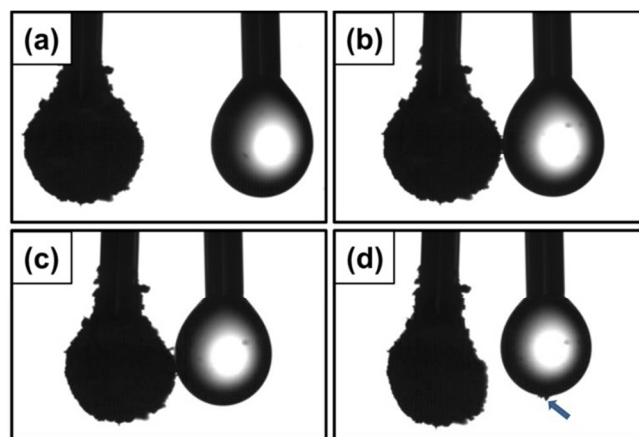


Figure 6. Selected images taken from video footage of the contact between a PDEA-PS particle-stabilized liquid marble at pH 10 and a bare water droplet at pH 10: (a) prior to contact, (b) initial contact, and after contact for (c) 3 min and (d) 60 min. An arrow in (d) shows a floc transferred from the liquid marble to the bare water droplet. The outer diameter of the capillaries is 1.07 mm which acts as an appropriate scale bar.

During the coalescence of two droplets, a rapid oscillation of the projected area of the resulting droplet was observed. Fig. 7(a) shows the normalised relative projected area of a coalescing droplet (heretofore shortened to as the ‘projected area’), that is the difference between the projected area and the average projected area divided by the average projected area, as a function of time. Using the coalescence of water droplets (pH 3) as an example, the oscillation in its entirety appears damped (Fig. 7(a)) although the values of the individual peaks are not monotonically decreasing when considering small time frames (Fig. 7(b)). As such, the dampening cannot be quantified with an equation as in the case of coalescing pairs of air bubbles^{57,64-66}. Nevertheless, the oscillatory motion of the projected area merits comparison. Fig. 7(b) shows that the presence of particles on one of the droplets caused a slight decrease in the period of the oscillation of the projected area. In addition, the amplitude of the oscillation at similar times is lower when one droplet is covered with particles. Fig. 7(c) shows the relative amplitude of the frequency of the oscillation of the projected area determined by Fast Fourier Transform (FFT) analysis. This confirms that the movement of the interface during the coalescence-induced oscillation is slightly faster for the asymmetric coalescence of a liquid marble with a bare droplet than for the coalescence of two bare droplets. It is believed that the frequency of the oscillation of the liquid marble/water droplet couplet is faster due to the reduction in the amplitude of the oscillation. In other words, the larger amplitude of the oscillation of the projected area in the case of bare

water droplets means that a longer time is required to complete a cycle, which decreases the oscillation frequency. It is also interesting to note that the frequency peaks for the liquid marble/droplet couplets (Fig. 7(c)) are wider than for the coalescence of two water

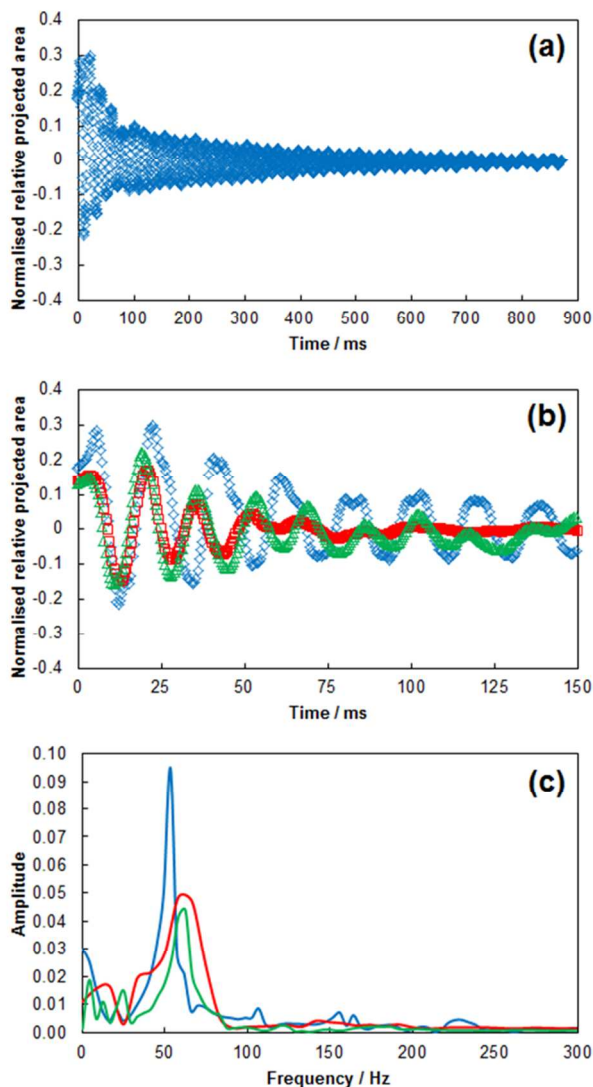


Figure 7. (a) Normalised relative projected area of coalescing droplets as a function of time. Coalescence of two bare droplets at pH 3. (b) Normalised relative projected area in the early stages of coalescence for two bare droplets at pH 3 (\diamond); one liquid marble and a bare droplet both at pH 3 (\square); and one liquid marble at pH 10 and a bare droplet at pH 3 (\triangle). (c) Fast Fourier Transform frequency analysis for the coalescence of two bare droplets at pH 3 (blue); one liquid marble and a bare droplet both at pH 3 (red); and one liquid marble (pH 10) coalescing with 1 bare droplet (pH 3) (green).

droplets. It is hypothesised that the asymmetric interaction of the rigid liquid marble surface with the mobile droplet surface promotes (upon the creation and expansion of the neck as clearly seen in Fig. 2 for bare droplets) the formation of waves of different frequencies in the water and liquid marble halves which exhibit destructive interference.

The properties of the interface are critical for some applications. This is controlled by the type of particles (and the formation of an

intervening film, if any). In the case of a bubble-rich solution (i.e. foam), the coalescence of a few bubbles may trigger several coalescence events, which results in a partial collapse of the foam^{67,68}. The presence of particles may produce lamellae which are more resistant to vibrations caused by the coalescence of surrounding bubbles⁶⁹. As a consequence, the structural integrity of the foam (i.e. bubbles) is enhanced. Although foam systems are known to be more sensitive than emulsions⁷⁰ and probably liquid marbles, it is theorised that a system in which the liquid marbles are more rigid may prevent the catastrophic collapse of bulk liquid marble formulations thus extending their shelf-life. It was also noted that PDEA-PS particles were detached from the droplet surface during the post-coalescence dynamic motion (see Table 1). Considering that the total air-water interfacial area available to be coated with the PDEA-PS particles becomes larger after the asymmetric coalescence of a liquid marble with a bare water droplet, detachment of excess PDEA-PS flocs weakly adhered to the liquid marble surface should occur, rather than rejection of particles adsorbed directly to the air-water interface. Interestingly, the single large water droplet obtained after coalescence was almost completely covered with PDEA-PS particles, which indicates significant rearrangement of the PDEA-PS particles to the air-water interface: excess PDEA-PS flocs adhering to the liquid marble surface attach to bare air-water interface after coalescence with the aid of the energy released through coalescence.

Further understanding of the impact of droplet pH on the asymmetric interactions above was obtained through investigation of the wetting behaviour of water droplets on a PDEA-PS particle powder bed (Fig. 4). These contact angle studies indicate an increase in the water penetration rate as the particle hydrophilicity increases at pH 3. It can therefore be expected that the PDEA-PS particles adsorbed at the liquid marble surface can disperse into the aqueous phase, if the particles come into contact with an acidic solution as shown in Fig. S2. In the interaction of the bare droplet (pH 3) and liquid marble (pH 3), the particles can be dispersed into both the inner water of the liquid marble and the contacting bare water droplet. Thus the wetting interfaces will meet and coalescence will occur in a shorter time, when compared with the interaction of a bare droplet (pH 3) and liquid marble (pH 10) system. In this case the particles can only be dispersed into the contacting bare water droplet, but air pockets will be present for longer on the inside of the powder coating. These concepts are summarised in Fig. 8.

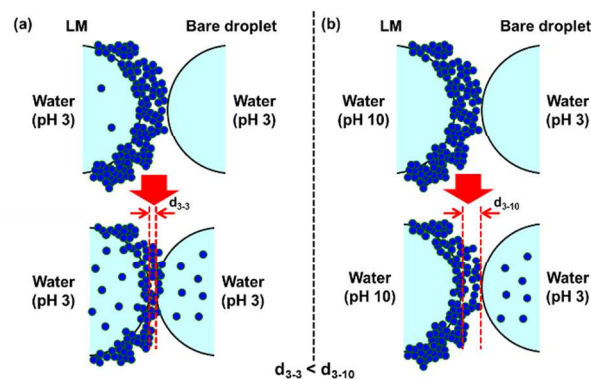
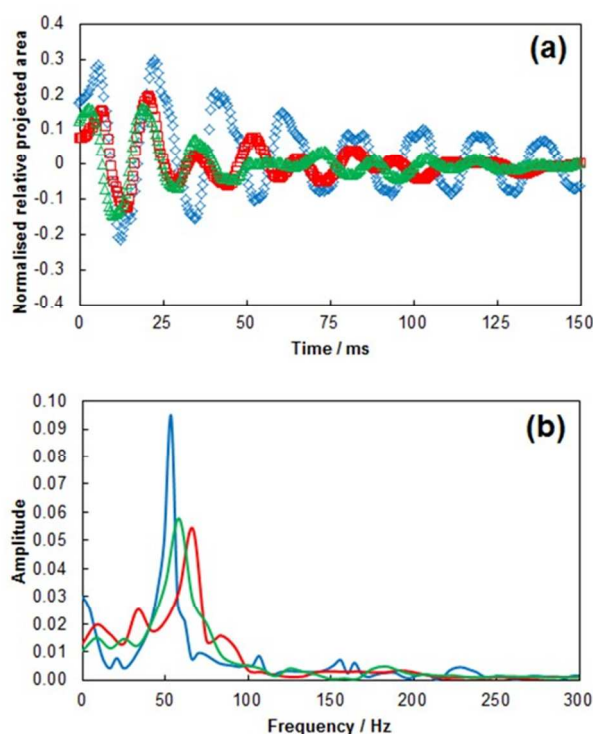


Figure 8. Scheme illustrating interaction between liquid marble at (a) pH 3 or (b) pH 10 and bare water droplet (pH 3). The PDEA-PS particles/flocs can disperse into any acidic aqueous phase, which leads to a decrease in the distance between water interfaces followed by more rapid coalescence.

The contact angle formed by a particle at the interface (air-water) is related to the adhesion of the particles. The difference in



hydrophobicity of the particles in relation to the pH of the water phase may influence the removal of particles from the surface due to vibration (e.g. coalescence, handling). It is worth noting that the

Figure 9. (a) Normalised relative projected area of coalescing droplets as a function of time. Coalescence of two bare droplets at pH 3 (\diamond); one liquid marble toluene treated for 1 minute and a bare droplet both at pH 3 (\square); and one liquid marble at pH 10 toluene treated for 1 minute and a bare droplet both at pH 3 (\triangle). (b) Fast Fourier Transform frequency analysis for the coalescence of two bare droplets at pH 3 (blue); one liquid marble toluene treated for 1 minute and a bare droplet both at pH 3 (red); and one liquid marble at pH 10 toluene treated for 1 minute and a bare droplet at pH 3 (green).

number of detached PDEA-PS flocs appears to be larger in the case of the pH 10 system compared to the pH 3 system as reported in Table 1. This is attributed to the greater wettability of the PDEA-PS flocs by pH 3 water than pH 10 water as shown in Fig. 3. The protonation of the PDEA-PS particles causes a local increase in pH. It is speculated that the PDEA-PS particles, which remain on the flocs at the air-water interface, may be partly protonated (i.e. hydrophilic) and thus provide a greater adherence of the floc to the droplet (see schematic in Fig. 3). Such particulates will be less likely to detach from the surface of the droplet.

Capsules

Liquid marbles at pH 3 or 10 after 1 min toluene vapour-treatment also coalesced with a contacting bare water droplet (pH 3) as shown in Fig. S3. The induction time was found to have decreased significantly compared to the untreated marbles discussed above, with coalescence occurring within 2 ± 1 s, and 5 ± 4 s, for 1 min toluene vapour-treated liquid marbles with inner water at pH of 3 and 10, respectively. These shorter induction times are attributed to the thinner PDEA-PS particle layer between water droplets and

incomplete film formation after this brief toluene treatment⁴⁴. Scanning electron microscopy studies indicated that the PDEA-PS particle layer thickness on the liquid marble surface decreases from 151 μm to 112 μm , which indicates the distance between water fronts decreased by approximately 40 μm as shown schematically in Fig. S4. There is another possible reason that water penetrates further into the particle layer due to the lower interfacial tension between the particles and water during toluene vapour treatment and thus the distance between water droplets decreased. The surface tension of water under toluene vapour for 1 min was determined to be 67.1 mN/m at 25°C (Note that the air-pure water surface tension was measured to be 72.1 mN/m), and the interfacial energy between the water exposed to toluene vapour and PDEA-PS particles swollen with toluene should be low enough for the water to wet the PDEA-PS powder. On the other hand, liquid marbles with pH 3 or 10 after 1 min vapour treatment were wetted by bare water droplets with pH 10, rather than coalescing (see Table 1). Note that the adhesion times were found to be less than 10^{-3} s, which indicates wetting rather than coalescence (cf. induction times of liquid marbles coalescing with water droplets in Table 1).

Again, the coalescence dynamics of the droplets was studied by comparing the projected area. In Fig. 9(a), the data for the coalescence of two pH 3 water droplets (Fig. 6(a)) is included for comparison. The coalescence of a droplet (pH 3) with a 1 min-toluene treated capsule (pH 3 and 10) caused a somewhat irregular oscillation (in amplitude of the projected area). Again, this is believed to be the result of the asymmetric interaction of a rigid-shell droplet with a compliant surface droplet yielding greater irregularities in the oscillation periodicity (i.e. broader frequency distribution). Fig. 9(b) shows the FFT frequency analysis performed on the curves shown in Fig. 9(a). As observed for the rupture of liquid marbles against bare droplets in Fig. 6, a breaking capsule increased the oscillation frequency by reducing the amplitude of the oscillation.

Once again the fact that capsules, like liquid marbles, provide a rigid envelope appears to result in destructive interference of the different wave frequencies when coalescing with a mobile fluid. Since the integrity of the capsules is sensitive to impacts⁴⁴, a reduction in the perturbation caused by surrounding failing capsules may improve bulk handling following the same argument stated above. Furthermore, when capsule breakage occurred, the number of detached flocs seemed to decrease with an increase of toluene vapour treatment time (see Table 1).

Interestingly, the liquid marbles with pH 3 or 10 after 2 or 4 min toluene vapour treatment did not coalesce with the bare water droplets with pH 3 or 10, but instead the bare water droplets wetted the capsule surface (Fig. 10). Even after 1 h liquid marbles containing alizarin dyed-water (at pH 3 or 10) with 2 or 4 min of toluene vapour treatment in contact with a transparent and colourless bare water droplet, the colour of the bare water droplet remained unchanged (see Fig. S5). These results confirmed that the PDEA-PS particles formed a complete film with these longer vapour treatments, and the water inside the capsule did not come into contact with the bare water droplet, and thus no coalescence but simply wetting occurred. It is worth noting that the bare water droplet (pH 10) adhered to the capsule, after increasing the distance between the capillaries (Fig. 11).

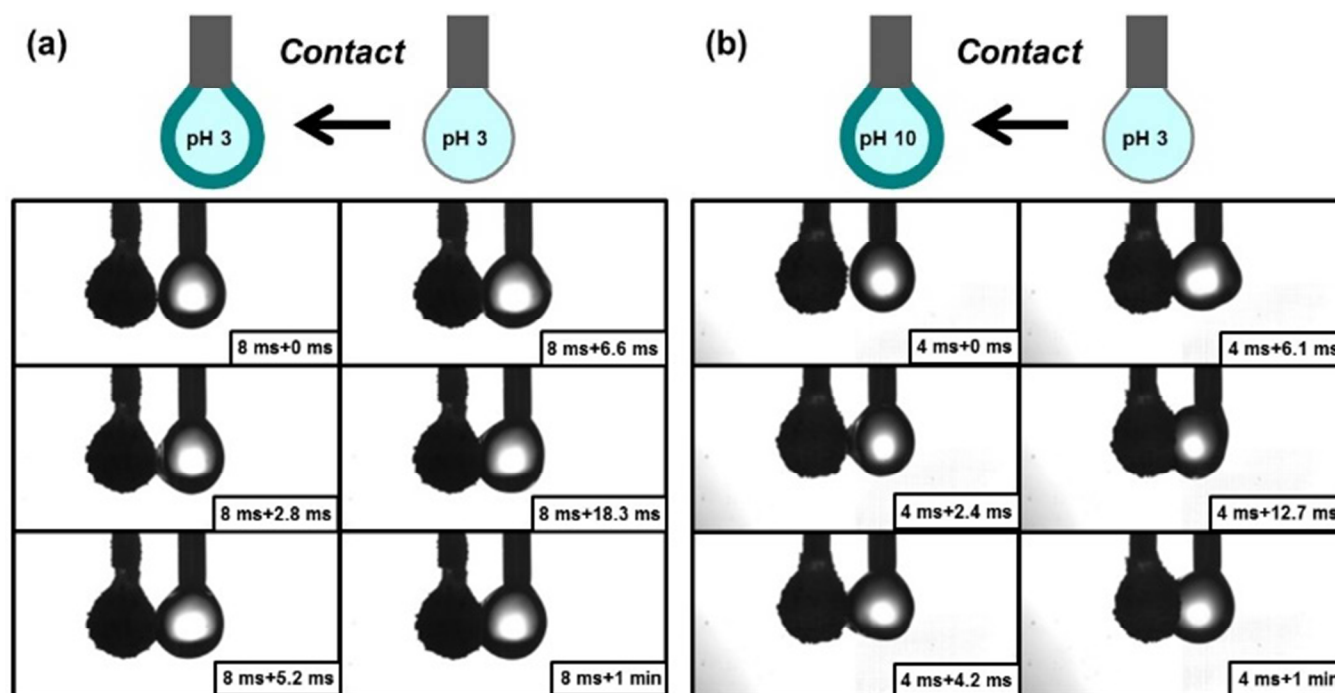


Figure 10. Selected images taken from video footage of the wetting between a capsule at (a) pH 3 and (b) 10 prepared after 4 min toluene vapour treatment of PDEA-PS particle-stabilized liquid marble and a bare water droplet (at pH 10). The time shown in each image indicates the wetting time + time after wetting occurred. The outer diameter of the capillaries is 1.07 mm which acts as an appropriate scale bar.

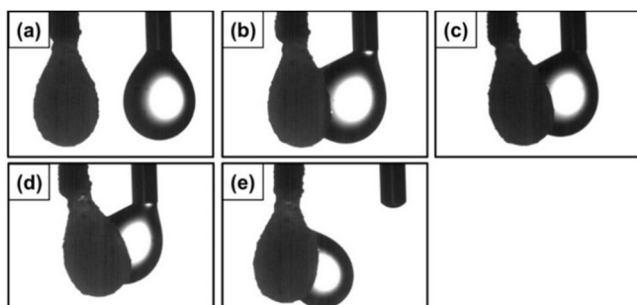


Figure 11. Selected images taken from video footage of the contact between a capsule prepared after 4 min toluene vapour treatment of PDEA-PS particle-stabilized liquid marble at pH 10 and a bare water droplet at pH 10: (a) prior to contact, (b) initial contact, after contact for (c) 30 min and (d) 60 min, and (e) after increasing the distance between the capillaries. The outer diameter of the capillaries is 1.07 mm which acts as an appropriate scale bar.

Conclusions

The stability of individual water droplets armoured with pH-responsive PDEA-PS particles was investigated, in both symmetric and asymmetric modes, using a combination of coalescence rig and high speed video camera which allows the visualization of the droplet coalescence dynamics. The time taken for the PDEA-PS particle powder layers formed after contact of droplets to rupture, known as the induction time, is taken as an indication of droplet stability. Following layer rupture, the oscillatory data extracted from the video footage revealed that the systems exhibited a highly damped motion.

The general observations from this study are: water droplets can be stabilized through the adsorption of PDEA-PS particles at the air-water interface and destabilized by increasing the surface hydrophilicity of the particles by exposure to acidic aqueous solution. The increase in induction time, and therefore droplet stability, in the presence of particles is due to the existence of a steric barrier, and an increase in droplet surface rigidity. Liquid marbles never coalesced with other liquid marbles independent of the internal pH. Liquid marbles can be coalesced by contact with an acidic water droplet, which is due to detachment and dispersal of PDEA-PS particles from the liquid marble surface into the aqueous phase. Moreover, the detachment of particles from the liquid marble surface into the air phase was observed after coalescence: it is the kinetic energy provided by the surface wave during the post-coalescence motion that results in the ejection of excess particles attached to the liquid marble surface as a floc.

Film formation of the PDEA-PS particles on the liquid marble surface upon toluene vapour treatment for at least 2 min prevented contact between the inner water droplet and outer bare water droplet, and therefore no coalescence occurred but wetting was observed instead. After film formation of the PDEA-PS particles on the liquid marble surface, no detachment of particles was observed.

Due to the widespread applications of liquid marbles (and dry liquids) in various industries, it is hoped that these results will provide a deeper insights into their stabilization mechanisms and thus improve multiphase processes which involve these combinations.

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Notes and references

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Electronic Supplementary Information (ESI) available: Details on PDEA-PS particles, dispersability of the PDEA-PS particles into water phase, coalescence between liquid marble after 1 min toluene vapour treatment and bare water droplet, and contact between capsule and bare water droplet. See DOI: 10.1039/b000000x/

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