Mechanically robust nanoparticle stabilized transparent liquid marbles

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Optically transparent liquid marbles were made from water and glycerol drops embedded in surface-treated fumed silica nanoparticles. The mechanical robustness of such liquid marbles is shown to be greater than similar marbles made from microparticulate poly(tetrafluoroethylene), both under compressive and tensile loading conditions. Using liquid evaporation data and environmental scanning electron microscope images, we demonstrate that their robustness may be attributed to a nanoparticulate elastic thin film that self-assembles on the liquid-vapor interface. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2959853]

Since Aussillous and Quere[1] proposed their use, liquid marbles have held the potential to effortlessly move liquids in microfluidic devices. Liquid marbles are formed when hydrophobic particles self-organize on the liquid-vapor (LV) interface[2] thereby encapsulating a small volume of liquid. The presence of the particles on the free surface causes the effective liquid-solid interfacial tension to decrease substantially resulting in nonwetting conditions even with a liquid that would inherently wet the surface in the absence of the particles. These marbles consequently exhibit a remarkably high contact angle ($>150°$) and low hysteresis.[3]

Most previous studies on liquid marbles have used microparticulate materials for their formation.[2,4,5] While these particles help create liquid marbles, the particulate layer that is protecting the marble from rupturing is not sufficiently robust. A robust liquid marble would remain intact while bouncing against other marbles or with the wall during the process of its transport. Nanoparticle stabilized interfaces have been reported for the case of air bubbles.[6] However, colliding bubbles do not tend to be as destructive toward each other as colliding liquid marbles owing to much lower inertia. It is known that the ability to employ liquid marbles as carriers in microfluidic devices is currently limited by their mechanical robustness.[4]

In this letter, we report on remarkably robust, transparent, and extremely mobile (low hysteresis) liquid marbles of glycerol and water formed using hydrophobized nanoparticulate fumed silica. The fumed silica powder is obtained as aggregates of $200-500$ nm long chains of 3.27 nm beads [see atomic force microscope (AFM) image in Fig. 1(a)] with a very high ($100-200$ m^2/g) BET surface area. We demonstrate that the liquid marbles created with these particles will withstand higher compressive and tensile load prior to rupture in comparison with marbles made from microparticulate materials. This is attributable to uniform coverage of the LV interface by the nanoparticles [compare environmental scanning electron microscope (ESEM) images in Figs. 1(b) and 1(c) with 1(d)].

Marbles made from microparticulate material are opaque [see inset in Fig. 1(d)]; hence it is not possible to optically interrogate the material contained in the liquid marble. We, herein, report on liquid marbles made from nanoparticulate material that are almost entirely transparent. The contents of these liquid marbles can therefore be probed optically during their transport, a property that may be useful in biofluidic devices. For example, biological fluids can be "marbled up" and transported[5] or stored[7] while being able to optically monitor the cell health, concentration or other characteristics.

Liquid marbles were made with fumed silica nanoparticles donated by Cab-O-Sil[8] as well as microsized poly(tetrafluoroethylene) powder (referred to as μPTFE) with particles of size $7-12$ μm (effective surface area of $1.5-3$ m^2/g). The fumed silica nanoparticles were surface-

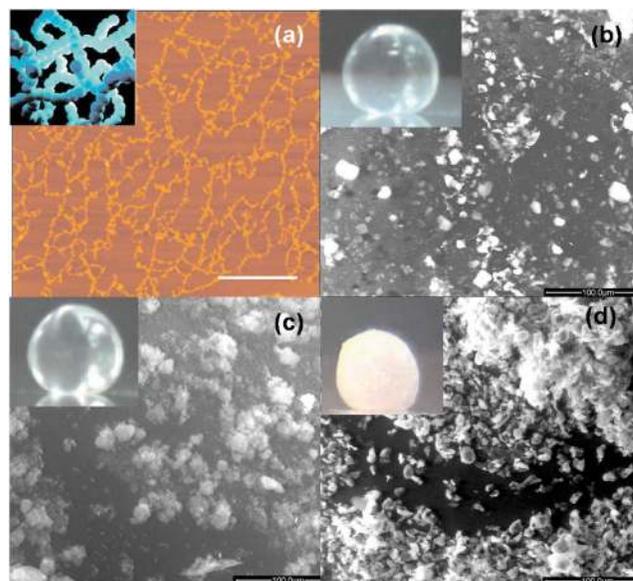FIG. 1. (Color online) (a) AFM micrograph of nHMDS fumed silica particles deposited on a silica wafer showing the entangled particle network (Scale: 2 μm). (Inset) a cartoon representing silica nanoparticles. Glycerol liquid marbles (inset) and corresponding ESEM micrographs of LV interface with (b) nHMDS, (c) nDMDCS treated fumed silica particles and (d) μPTFE LV interface.
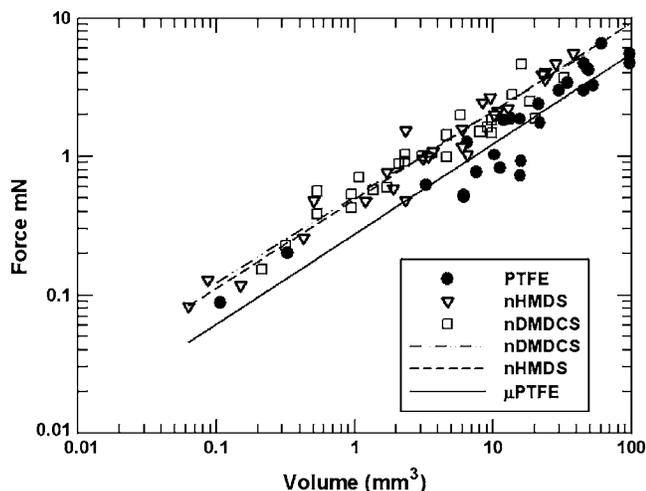
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FIG. 2. Force at rupture vs volume for μPTFE, nHMDS, and nDMDCS marbles.

treated with two distinct hydrophobic chemicals, hexamethyldisilazane (referred to as nHMDS) and dimethyldichlorosilane (referred to as nDMDCS), which exhibit BET surface areas of 225 and 105–145 m^2/g respectively. Distilled water was used to make water marbles for the evaporation experiment and glycerol was used for ESEM imaging owing to its low volatility.

The process of preparing the liquid marbles is initiated by embedding glycerol or water drops of desired size on the hydrophobic particulate material placed in a glass dish. The particles spontaneously self-organize[1] on the LV interface causing the drop to become nonwetting. The excess particles are then shed by rolling the drop in a new glass dish resulting in a liquid marble.

We present evidence of mechanical robustness of the nHMDS and nDMDCS liquid marbles in comparison with μPTFE using two sets of experimental measurements— tensile load test data and liquid evaporation data. Firstly, direct measurements of tensile robustness of the marbles are presented through measurements of the force that a marble can withstand while being compressed between a pair of parallel smooth silicon wafers. As the marble is compressed, the LV interfacial area and Laplace pressure in the marble increase, finally causing it to rupture. Lafuma and Quere[9] note that the Laplace pressure Δp in a marble compressed between two parallel plates is given by $\Delta p = 2\gamma|\cos \theta^*|/h$, where γ is the surface tension, θ^* is the contact angle made by the marble with the solid surface in the compressed state, and h is the spacing between the parallel plates. The force experienced by the marble just prior to rupture is given by $F = \Delta p A_c$, where $A_c \approx V/h$ is the plate/marble contact area and V is the marble volume. Figure 2 is a plot of F versus V. The curves in this figure are a power-law fit to the experimental data of the form $F = C_0 V^\alpha$ ($R^2 \geqslant 0.9$ in all cases). It can be observed from this plot that nHMDS ($C_0 = 0.51$, $\alpha = 0.62$) and nDMDCS ($C_0 = 0.49$, $\alpha = 0.64$) marbles can withstand a higher load prior to rupture in comparison with μPTFE ($C_0 = 0.27$, $\alpha = 0.65$) marbles of similar volume. From comparing the values of C_0, it can be concluded that the nHMDS and nDMDCS marbles can withstand 81% higher force than μPTFE. This is direct evidence of the mechanical robustness of nDMDCS and nHMDS marbles. This increased robustness could be due to increased particle-particle

interaction in marbles from nanoparticulate materials.[7] Forny *et al.* hypothesized that this interaction is due to mechanical entanglement of the fumed silica particles, which forms a particulate network on the LV interface.[7] The particulate network, as on the silica wafer in Fig. 1(a), acts like an elastic membrane protecting the liquid marble. Similar behavior was also recently reported with intact gold nanoparticulate membranes stretched over microcavities.[10]

We next present data pertaining to the rate of evaporation of the liquid contained in the marble, obtained using a thermogravimetric analyzer (TGA). The objective of this experiment is to demonstrate the mechanism for the robustness presented in Fig. 2. In this TGA experiment, the liquid marbles were placed on a foil-wrapped alumina pan and allowed to evaporate in a controlled environment. The initial mass difference between all the samples was maintained to be less than 1.5 mg (6–7.5 mg). Air with 20% relative humidity at 25 °C was used as the drying medium. Four data sets were obtained from liquid marbles of each hydrophobic material. For baseline comparison, we present evaporation data from a plain sessile water drop evaporating under similar concentration gradient conditions, temperature, and initial contact angle.

It is well known[11] that a sessile drop evaporates following the "D^2 law" that states

$$D(t)^2 = D(0)^2 - Kt. \tag{1}$$

Here $D(t)^2$ is a measure of the LV interfacial area at an instant of time, t, and K is the diffusion rate constant that is a function of the ambient vapor concentration gradient as well as the initial contact angle for a sessile drop. However, in the case of liquid marbles, the diffusion process is impeded by the presence of the hydrophobic particles on the LV interface.[12] For this case, Eq. (1) is modified to read

$$D(t)^2 = D(0)^2 - \eta Kt. \tag{2}$$

Here η is a factor that takes the resistance to diffusion through the particle layer into account. This resistance to diffusion is dependent on the nature of the particle-particle interaction on the LV interface. By taking the ratio of the measured average rate of evaporation of the μPTFE, nHMDS, and nDMDCS liquid marbles to that of the plain drop ($\eta = 1$) under the same temperature and vapor concentration gradient conditions, we calculate a value for η.

Figure 3(a) is a plot of the normalized surface area of the liquid, $A = D(t)^2/D(0)^2$ (calculated as $[m(t)/m(0)]^{2/3}$ from the TGA data) versus nondimensional time, $\tau = v(\rho_v/m(0))^{2/3}t$, where v is the diffusivity of water vapor in air, $m(0)$ is the initial mass of the marble, ρ_v is the saturated air density, and t is time in seconds. Three distinct regimes can be observed in each curve in Fig. 3(a). An initial heat up regime is observed for very short values of τ during which time the marbles are observed to show little reduction in A. The second regime (referred to herein as the "linear regime") is marked by a region where A is observed to decrease linearly with τ following Eq. (2). The last regime (referred to herein as the "nonlinear regime") is characterized by a nonlinear relationship between A and τ. The dimensionless rate of evaporation, ηK, in the linear regime ($50 < \tau < 70$) for the plain drop, μPTFE, nDMDCS, and nHMDS liquid marbles are, respectively, measured to be 0.00434 ± 0.000014, 0.0044 ± 0.000189, 0.00421 ± 0.000131, and
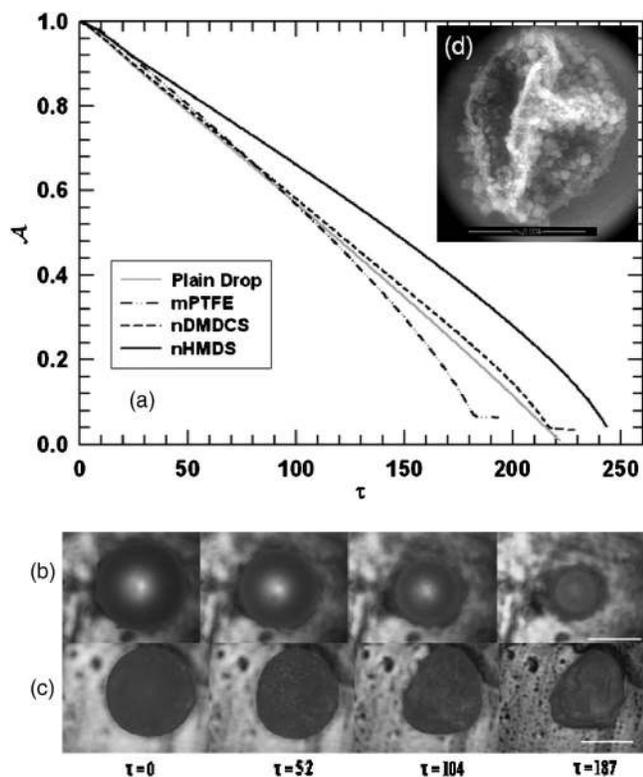
FIG. 3. (a) Nondimensional surface area, A vs τ. Optical micrographs of an evaporating marble formed from (b) nHMDS fumed silica and (c) μPTFE. (d) ESEM image of a buckled evaporating nHMDS marble. [Scale bar represents 1 mm for (b) and (c) series of images and 400 μm for image (d)].

0.0034 $\pm$ 0.000116. From these measured rates of evaporation, we can calculate η for μPTFE, nDMDCS, and nHMDS to be 101%, 97%, and 78%, respectively. This indicates that the evaporation process in nHMDS liquid marbles encounters a higher resistance than from μPTFE or nDMDCS.

The data in Fig. 2 show insignificant statistical variation in the robustness of nDMDCS and nHMDS marbles. However, their respective resistances to diffusion (η) are markedly different. This is explained by the fact that the BET surface area of nHMDS is higher than nDMDCS, which indicates increased aggregation on the LV interface in the case of nDMDCS [see Fig. 1(c)] in comparison with nHMDS [see Fig. 1(b)]. Therefore while the fumed silica particulate network exists in the case of nDMDCS liquid marbles, it offers significantly lower resistance to diffusion owing to increased particle aggregate sizes on the LV interface.

We next present evidence of buckling to demonstrate the robustness of the nanoparticulate liquid marbles under compressive loads. As the volume of the liquid marble decreases due to evaporation, the particulate film on the marble surface becomes thicker and is subject to compressive stresses, eventually causing it to buckle. Similar buckling of the liquid free surface during evaporation was also observed recently in the context of Leidenfrost drops.[13] Figures 3(b) and 3(c) are time sequenced images of evaporating liquid marbles for nHMDS and μPTFE, respectively. As can be observed from these images, the μPTFE liquid marbles take on an increasingly wrinkled shape in comparison with nHMDS. The wrinkled shape causes the surface area per unit volume to increase. As a result, the evaporation rate in the nonlinear regime for a μPTFE marble increases with τ. In comparison, it can be observed from Fig. 3(b) that the shape of the nHMDS marble remains spherical for a larger values of τ. The nonlinear regime observed in Fig. 3(a) is a result of this buckled free surface that causes the average surface area per unit volume to increase [see ESEM image of a wrinkled marble in the inset of Fig. 3(d)]. The transition to nonlinear regime and wrinkling occurs at an earlier τ for μPTFE than nHMDS, demonstrating robustness under compressive load conditions.

The results observed in Fig. 3(a) in the linear regime are explained with the aid of Fig. 1. Figures 1(b) and 1(d) show ESEM micrographs of the surface distribution of the nHMDS nanoparticulate material and μPTFE powder on a glycerol marble, respectively. It has to be noted that the LV free energy of glycerol and water as well as the solid-liquid surface free energies of glycerol or water on μPTFE as well as nHMDS are similar, indicating that the effective distribution of the particles on the surface would be the same for the two fluids if they were of the same morphology. The black region observed in Fig. 1(d) indicates where liquid glycerol is exposed. In addition, it can be observed that μPTFE forms clusters on the liquid surface. In comparison, Fig. 1(b) shows that the liquid surface is more uniformly covered with nanoparticles, as is evidenced by the gray region.

In conclusion, nHMDS and nDMDCS particles form stable, robust, and transparent liquid marbles in comparison with μPTFE. This is attributable to increased particle-particle interaction, owing to the significantly higher BET surface area of the nanoparticulate material. In the present context, the fumed silica particulate network on the liquid free surface acts like an "elastic" membrane that makes these liquid marbles extremely robust mechanically in comparison with conventional liquid marbles made from microparticulate hydrophobic powders such as μPTFE.

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