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ORIGINAL PAPER

Liquid marbles containing petroleum and their properties

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Abstract Liquid marbles (non-stick droplets) containing crude petroleum are reported. Liquid marbles were obtained by use of fluorinated decyl polyhedral oligomeric silsequioxane (FD-POSS) powder. Marbles containing crude petroleum remained stable on a broad diversity of solid and liquid supports. The effective surface tension of marbles filled with petroleum was established. The mechanism of friction of the marbles is discussed. Actuation of liquid marbles containing crude petroleum with an electric field is presented.

Keywords Liquid marbles · Crude petroleum · Friction · Low energy oil transportation, effective surface tension · Electrical actuation

1 Introduction

Liquid marbles are non-stick droplets encapsulated with micro- or nano-scaled solid particles (Mahadevan 2001; Aussillous and Quéré 2001, 2004, 2006) Since liquid marbles were introduced in the pioneering works of Aussillous and Quèrè (2001), they have been exposed to intensive theoretical and experimental research (McHale et al. 2009; Arbatan and Shen 2011; Bormashenko et al. 2009a, 2011, 2013a; Planchette et al. 2012, 2013; Laborie et al. 2013). An interest in liquid marbles arises from both their very unusual physical properties and their promising applications. Liquid marbles present an alternate approach to superhydrophobicity, i.e., creating a non-stick situation for a liquid/solid pair. Usually, superhydrophobicity is achieved by a surface modification of a solid substrate. In the case of liquid marbles, the approach is opposite: the surface of a liquid is coated by particles which may be more or less hydrophobic (Zang et al. 2013). Marbles coated by graphite and carbon black, which are not strongly hydrophobic, were also reported (Dandan and Erbil 2009; Bormashenko et al. 2010a).

A variety of media, including ionic liquids and liquid metals, could be converted into liquid marbles (Gao and McCarthy 2007; Sivan et al. 2013). Liquid marbles were successfully exploited for microfluidics (Venkateswara Rao et al. 2005; Xue et al. 2010; Bormashenko et al. 2008, 2011, 2012), water pollution detection (Bormashenko and Musin 2009), gas sensing (Tian et al. 2010), electrowetting (Newton et al. 2007), blood typing (Arbatan et al. 2012), and optical probing (Zhao et al. 2012). Respirable liquid marbles for the cultivation of microorganisms and Daniel cells based on liquid marbles were reported recently by the group led by Shen (Tian et al. 2013; Li et al. 2013). Stimulus (pH, UV, and IR)-responsive liquid marbles were reported by several groups (Dupin et al. 2009; Nakai et al. 2013a, b). The stability of marbles is crucial for their microfluidics and sensing applications. Marbles possessing increased mechanical and time stability were prepared by Matsukuma et al. (2013). It is noteworthy that liquid marbles retain non-stick properties on a broad diversity of

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solid and liquid supports (Bormashenko et al. 2009b, c). Actually, liquid marbles are separated from the support by air cushions in a way similar to Leidenfrost droplets (Biance et al. 2003). The state-of-the-art in the study of properties and applications of liquid marbles is covered in recent reviews (McHale and Newton 2011; Bormashenko 2011, 2012). The majority of groups concentrated their efforts on the study of properties of marbles containing liquids possessing a high surface tension such as water, liquid metals, and ionic liquids, whereas reports devoted to marbles containing organic liquids are still scarce (Xue et al. 2010). Our study is devoted to manufacturing marbles containing crude petroleum, characterized by relatively low surface tension (γ) is in the range of 28–33 mJ/m^2 (Francis and Bennett 1922; Harvey 1925). We also demonstrate new possibilities in micro-manipulation of crude petroleum with the use of liquid marbles.

2 Experimental

Petroleum was supplied by Givot Olam Oil Ltd. Liquid marbles were manufactured with the use of fluorinated decyl polyhedral oligomeric silsequioxane (FD-POSS) powder. FD-POSS was synthesized according to the protocol described in detail by Mabry et al. (2008). FD-POSS powder is strongly hydrophobic and was successfully used by Xue et al. for manufacturing marbles of both aqueous solutions and organic liquids (Xue et al. 2010). FD-POSS powder particles were imaged with SEM (JEOL JSM 6510 LV, Japan). Highly developed topography of FD-POSS particles, displayed in Fig. 1, strengthening their pronounced inherent hydrophobicity is noteworthy.

FD-POSS powder was spread uniformly on a superoleophobic surface, manufactured according to the procedure described by Bormashenko et al. (2013b). Petroleum droplets with

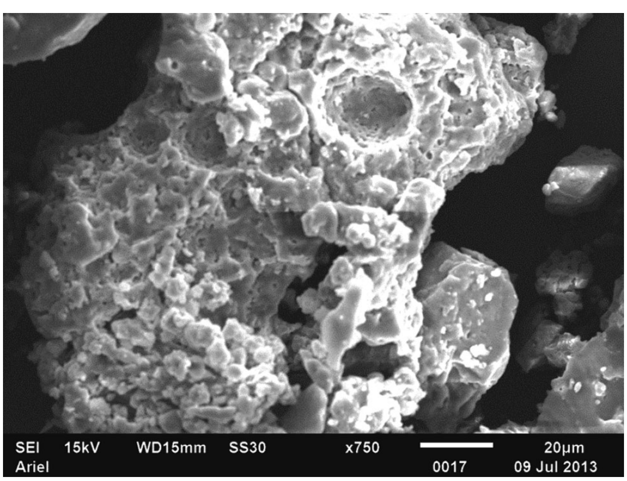

Fig. 1 SEM image of FD-POSS particle. The scale bar is 20 µm

a volume of 5–400 µL were deposited using a precise micro-syringe on the layer of FD-POSS powder. Rolling of petroleum droplets resulted in the formation of petroleum marbles enwrapped with the FD-POSS powder, as depicted in Fig. 2.

The kinematic viscosity of petroleum was established with a conventional Ostwald viscometer. The kinematic viscosity ν at ambient conditions was established as 1.48×10^{-6} m^2/s. The relative density of the crude petroleum oil measured with a pycnometer at ambient conditions was 0.79 g/cm^3.

3 Results and discussion

3.1 Effective surface tension of marbles containing crude petroleum

Liquid marbles prepared according to the procedure described in the experimental section remained stable for a long

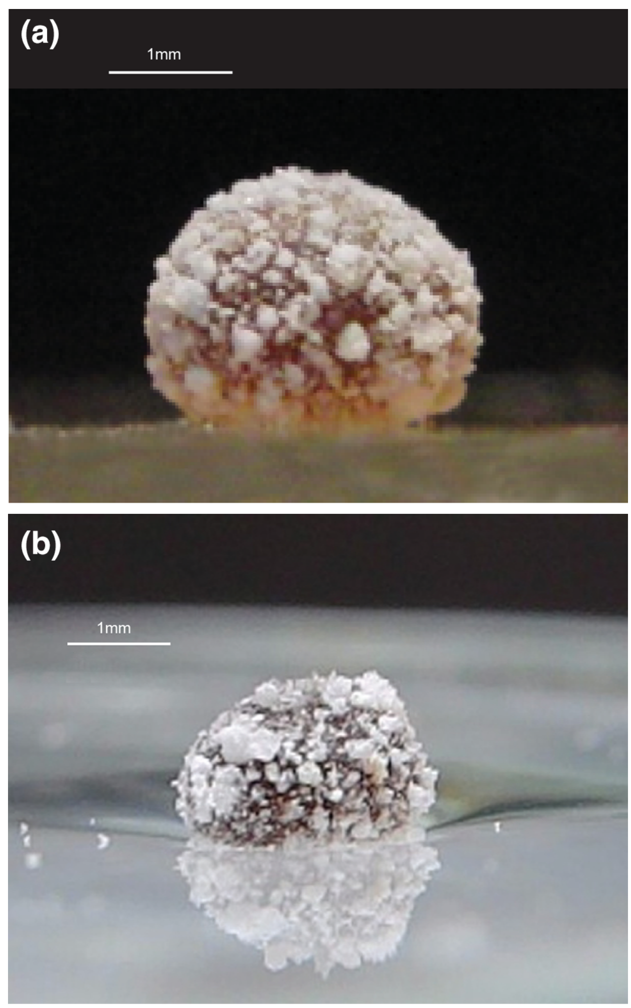

Fig. 2 **a** 10 µL liquid marble of crude petroleum coated with FD-POSS powder. **b** 20 µL liquid marble of crude petroleum coated by FD-POSS supported by 26 wt% NaCl water solution

time and demonstrated low rolling friction. Marbles remained stable on a diversity of solid and liquid substrates including water and aqueous NaCl solutions, as shown in Fig. 2a, b.

The effective surface tension of the marbles was measured according to the maximal puddle height method. We increased the volume of crude petroleum oil in a marble from 10 to 400 μL and measured its maximal height, H (see Fig. 3). The effective surface tension was calculated as described in detail by Aussillous and Newton (Aussillous and Quéré 2006; Newton et al. 2007):

$$r_{\mathrm{eff}} = \frac{\rho g H^2}{4} \tag{1}$$

The effective surface tension of crude petroleum marbles coated with the FD-POSS powder was established as 30.2 ± 0.2 mJ/m^2. The obtained value is close to the surface tension of the crude petroleum aforementioned in the Introduction Section (Francis and Bennett 1922; Harvey 1925). The reported value should be taken with a certain care due to the pronounced hysteretic nature of the effective surface tension of liquid marbles, which was demonstrated recently (Bormashenko et al. 2013a). Regrettably, we did not manage to establish the hysteresis of the surface tension of marbles containing petroleum, because the method of pumping of a “pendant marble” turned out to be unfeasible for the marbles containing low surface tension liquids.

3.2 Mechanisms of friction of crude petroleum liquid marbles

The mechanism of friction of rolling liquid marbles is rather complicated. The energy dissipation rate $\frac{\mathrm{d}E}{\mathrm{d}t}$ under liquid marbles rolling is given by

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}E_{visc}}{\mathrm{d}t} + \frac{\mathrm{d}E_{CL}}{\mathrm{d}t}, \tag{2}$$

where $\frac{\mathrm{d}E_{\mathrm{visc}}}{\mathrm{d}t}$ describes the viscous dissipation under rolling, and $\frac{\mathrm{d}E_{CL}}{\mathrm{d}t}$ is the energy dissipation rate due to the disconnection (de-pinning) of the contact line, at which a marble contacts the solid support. The viscous dissipation may be calculated as follows (Landau and Lifschitz 1987):

$$\frac{\mathrm{d}E_{visc}}{\mathrm{d}t} = \eta \int_{V_d} (\nabla \vec{u})^2 \mathrm{d}V. \tag{3}$$

Here V_d is the volume over which viscous dissipation occurs, η is the viscosity of the liquid, and $\vec{u}$ is the velocity field in the droplet. When a liquid marble contains a sufficiently viscous liquid (such as glycerol) it will stop rolling mainly by the viscous dissipation (Bormashenko et al. 2010b). Thus, the stopping distance of the marble S possessing an initial velocity of the center of mass U may be estimated as follows:

$$S \cong 1.5 \frac{\rho U R^5}{\eta a^3} \cong 1.5 \frac{U R^5}{\nu a^3}, \tag{4}$$

where $R = \sqrt[3]{\frac{3V}{4\pi}}$ is the radius of the marble (V is its volume), a is the radius of the contact area (shown in Fig. 3), ρ is the density, and υ is kinematic viscosity (Bormashenko et al. 2010b). We measured the stopping distance of marbles with a simple device depicted in Fig. 4: 12 μL crude petroleum marbles rolled downhill, and the velocity U was measured with a rapid camera at the origin of the horizontal portion of its pathway (see Fig. 4). Marbles rolled on the horizontal glass slides across the distance S necessary for their eventual deceleration, and the stopping distance of marbles S was measured. A series of 10 experiments were performed to establish the averaged value of the stopping distance.

For marbles possessing an initial velocity of the center of mass $U = 0.028$ m/s, the stopping distance S was established as $S = 7.7 \pm 0.2$ mm. Substituting $R = 1.42$ mm, $a = 1.16$ mm established for 12 μL crude petroleum marbles and $\nu = 1.48 \times 10^{-6}$ m^2/s (see the Sect. 2) into Exp. 4 yields the estimation $S \cong 100$ mm, which is an order of magnitude larger than the experimentally established $S = 7.7$ mm. This means that the condition:

$$\frac{dE_{visc}}{dt} << \frac{dE_{CL}}{dt} \tag{5}$$

takes place for marbles filled by the crude petroleum. Thus, the energy dissipation under rolling is mainly due to the

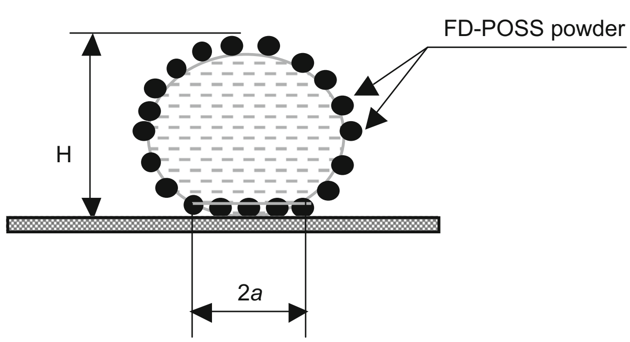

Fig. 3 Scheme illustrating the maximal high height method of the measurement of the effective surface tension of liquid marbles

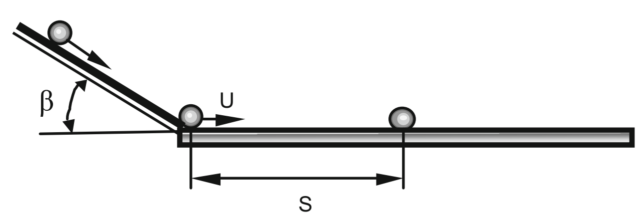

Fig. 4 Sketch of the experimental device used for the study of friction of liquid marbles. Marbles rolled from a height of 2 cm, $\beta = 15^0$.

disconnection (de-pinning) of the triple contact line, consuming the energy. This situation is typical for marbles containing low viscosity liquids (Bormashenko et al. 2010b). Low-energy transport of crude oil, exploiting non-stick lotus effect-inspired surfaces, was discussed recently (Wang et al. 2013). Non-stick liquid marbles filled with crude oil present a distinct alternative to lotus effect-based solutions.

3.3 Actuation of liquid marbles containing crude petroleum with an electric field

The effect of an electric field on crude petroleum oil marbles was studied. Crude petroleum oil marbles (20 μL) were placed on a glass slide located between two plain electrodes (as shown in Fig. 5); the electric field was increased from 0 to 10^6 V/m by a power supply Pasco (model SF-9586), as shown in Figs. 5, 6.

When the electric field reached $E \cong 1.2 \times 10^6$ V/m, the marble started to stretch until it touched the upper electrode, as depicted in Fig. 6. The value of the electric field necessary for electrical actuation of marbles filled with crude petroleum may be estimated as follows: The dimensionless constants ξ_1, ζ_2 describing the sensitivity of the marble to the electric field could be introduced (Bormashenko et al. 2012). The constant ξ_1 describes interrelation of electrically induced effects and gravity:

$$\xi_1 = \frac{\varepsilon_0 \varepsilon}{\rho g R} E^2, \tag{6}$$

where ε and ρ are the dielectric constant and density of the marble, respectively. The constant ξ_2 describes the interrelation of electrically induced and surface phenomena:

$$\xi_2 = \frac{\varepsilon_0 \varepsilon R}{\gamma_{\text{eff}}} E^2. \tag{7}$$

When $\xi_1 \cong \xi_2 \cong 1$ takes place, the marble becomes sensitive to the electric field. Substituting $\varepsilon = 2.1$, $\rho \cong 800\ \text{kg/m}^3$, and $\gamma_{eff} \cong 30\ \text{mJ/m}^2$ yields the electric field E^* necessary for electrical actuation of petroleum-based marbles the estimation $E^* \cong 10^6$ V/m, which is in an excellent agreement with the experimental findings.

The established value of E^* supplies to both of the dimensionless constants ξ_1, ζ_2 the value close to unity, this is not surprising, because the radius of 20 μL marbles is close to the capillary length $l_{ca} = \sqrt{\frac{\gamma_{\text{eff}}}{\rho g}} \cong 2$ mm, thus the capillary and gravitational energies of marbles are comparable.

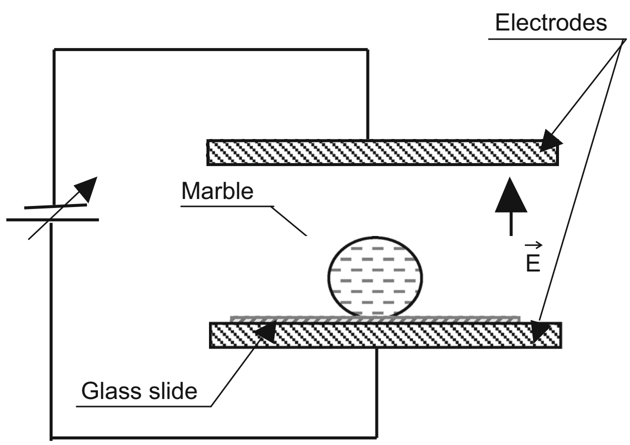

Fig. 5 Experimental setup used for investigation of marbles shape exposed to an electric field

4 Conclusions

We conclude that the use of decyl polyhedral oligomeric silsequioxane powder allows manufacturing of liquid marbles containing crude petroleum. The effective surface tension of the marbles was established as 30.2 ± 0.2 mJ/m^2. The mechanisms of friction of the liquid marbles filled with crude petroleum were examined. The viscous dissipation is negligible for rolling marbles containing crude petroleum. The energy dissipation under rolling of marbles is mainly due to the disconnection of the triple contact line. Liquid marbles containing crude petroleum can be actuated by electric fields of 10^6 V/m. The mechanism of the electrical actuation of liquid marbles containing crude oil is

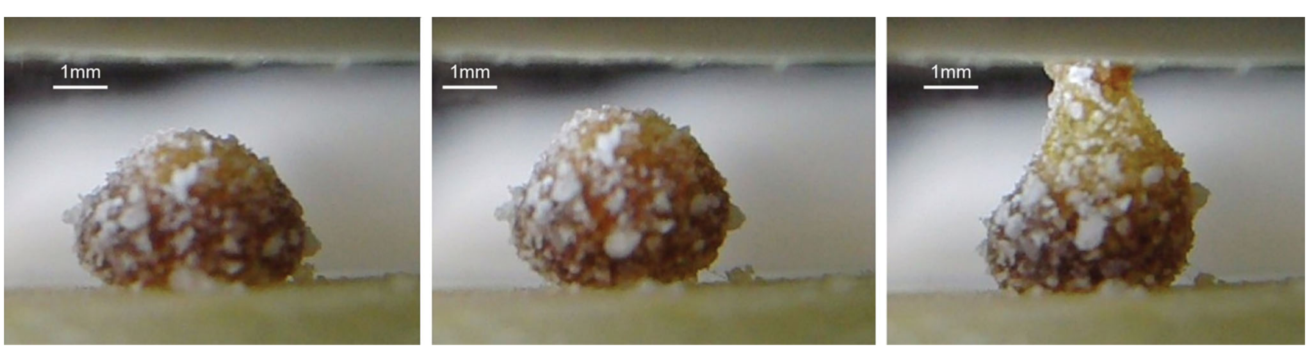

Fig. 6 The sequence of images illustrating the behavior of a 20 μL crude petroleum oil marble exposed to an electric field; the left image depicts the initial state of the marble and the right shows the marble exposed to the electric field of $E \cong 10^6 \frac{V}{m}$

discussed. Liquid marbles allow effective manipulation of micro-volumes of crude oil.

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