Journal of Colloid and Interface Science 470 (2016) 31–38

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Polymer grafted hard carbon microspheres at an oil/water interface

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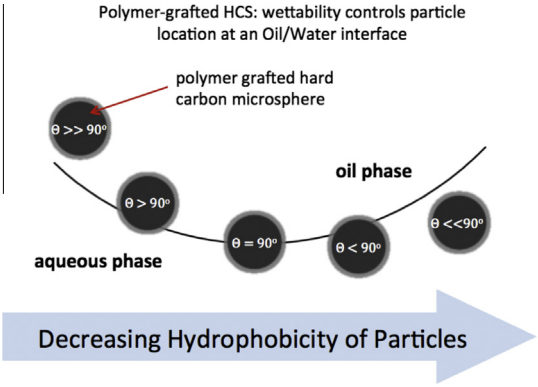
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 November 2015
Revised 12 February 2016
Accepted 16 February 2016
Available online 17 February 2016

Keywords:
Pickering emulsion
Wettability
Carbon microspheres
Polymer ATRP
Steric repulsion

ABSTRACT

Pickering emulsions offer an established method of stabilizing oil-in-water emulsions as either an alternative to surfactants or as an additive together with surfactants, providing greater colloidal stability even at low particle concentrations. This work presents a novel experimental approach to study the influence of several system parameters on the effectiveness of Pickering emulsion systems. Specifically, a dodecane oil drop stabilized by hard carbon microspheres in an aqueous saline solution is used as a model system to obtain both quantitative and qualitative information on the effectiveness of the microspheres as a function of their surface wetting properties. The test setup, in which a macroscopic oil drop is brought into contact with a test surface in a controlled motion and environment, allows for several aspects of the test (for e.g., oil drop size, approach velocity, normal force, solution ionic strength, temperature, pH, and presence of surfactants) to be potentially controlled and studied precisely. To demonstrate the capabilities of the experimental set-up, hard carbon microspheres are modified with a poly(styrenesulfonate) shell through ATRP in order to tune the wettability of the particles through choice of polymer, which are then used to stabilize a dodecane oil drop in an aqueous saline solution. The particles effectively form a steric barrier preventing the spreading of an oil drop on hydrophobic surfaces and also preventing the coalescence of stabilized oil drops.

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http://dx.doi.org/10.1016/j.jcis.2016.02.038
0021-9797/

1. Introduction and background

During an oil spill, dispersed oil droplets have the potential to spread on a variety of marine surfaces including deep-water coral communities [1,2], sea dwelling mammals [3,4], fish [5,6], birds [7–9], and coastal plant life in wetlands and marshes [10–12] through exposure or ingestion. The most basic damage-mitigating response to an oil spill is to prevent the adhesion of these oil droplets to surfaces altogether. In previous work [13], we demonstrated that highly hydrophilic surfaces submerged in an aqueous phase were resistant to oil spreading. As marine surfaces range in surface energies (i.e., wetting properties) and topography (i.e., roughness), a practical approach is to sufficiently stabilize dispersed oil drops such that they do not spread on surfaces. Pickering emulsions [14] offer a potential solution [15–19]. In terms of the total interfacial energy for a given droplet, a product of the interfacial energy (γ_{OW}) and the interfacial area (a_{ij}), surfactants lower the interfacial energy between the two phases and particles at the interface reduce the area over which the oil and aqueous phases interact. Previous research has shown the effectiveness of surfactants [20,21], but also demonstrated the advantages that Pickering Emulsions may offer comparatively [22,23], including greater emulsion stability at low particle concentrations [24], steric interference to agglomeration [25–27], and/or ease of oil recovery [28]. It has been suggested that even with low particle interfacial coverage, particles aggregate toward each other (on neighboring drops) and provide steric hindrance to coalescence [29].

Neither surfactants nor particles alone provide the optimal solution, and a combination of both will likely provide the best combination for desired small drop formation and long lasting stability [30]. Research has shown that a synergistic effect can be found when the right conditions (i.e., surface charge, solution pH and ionic strength, concentrations of particles, mixing energy, etc.) are met [31,32].

Pickering emulsions as a treatment for oil spills would ideally be comprised of abundant and non-toxic materials such as carbon, clay, and silica particles. Binks and Whitby looked into the environmental conditions and particle size effects on silica nanoparticle stabilized oil-in-water emulsions [33], while others expanded on this idea by controlling particle wettability using surfactants (hexamethyldisilazane) [29] and acid treatments (oleic acid) [34]. Silica particles approximately 200 nm in diameter were treated using oleic acid to go from a hydrophilic state to being hydrophobic by the self-assembly of an oleic acid monolayer around the particles. Katepelli et al. have researched the possibility of modified carbon black, negatively charged through carboxyl terminated functionalization, as a possible source for particle stabilized emulsions [30]. Monodispersed hard carbon spheres (HCS) were used to stabilize water-in-trichloroethylene emulsions by forming an ordered monolayer coating at the interface [35]. Additionally, hydrophobically modified biopolymers (i.e., chitosan) have been shown to be effective at oil spill remediation [36]. The use of asymmetric (Laponite clay discs) [37] and non-rigid particles has also been investigated [38].

The creation of oil-in-water Pickering emulsions or water-in-oil Pickering emulsions is based on many factors, two of which are the volume ratio of oil to water and the wettability of the particles. While surfactants have Janus-like properties, particles sit at an interface based on the wettability [39] and their wetting properties can dictate the type of emulsion formed (i.e., oil-in-water or water-in-oil). Hydrophobic particles typically generate water-in-oil emulsions, and hydrophilic particles usually generate oil-in-water emulsions. These properties have been thoroughly characterized by Binks in the literature [40,18], with other experiments advancing the theories through controllable wettability [41] and use of both hydrophobic and hydrophilic particles that assemble simultaneously at an interface to create stable emulsions [42].

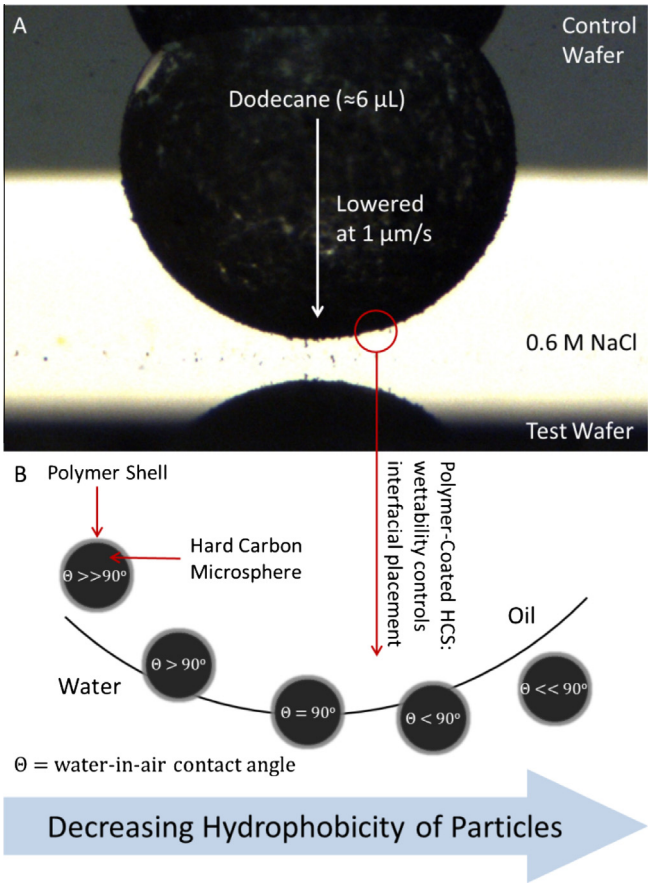

Fig. 1. (A) Optical image of an oil droplet (volume ≈ 6 µl, diameter ≈ 2.5 mm) attached to a control flat silicon wafer prior to contact with a test surface immersed in a saline aqueous solution. The control wafer is attached to a force sensor, which provides quantitative data on the normal forces exerted between the control and test wafer surfaces. Polymer grafted carbon microparticles reside at the oil/water interface. (B) Schematic illustration showing the location at which a polymer modified carbon microparticle resides at an oil/water interface based on its wetting properties.

Uniform hard carbon spheres (HCS) are attractive due to their biocompatibility [43], the reason for their high interest in foods, cosmetics, and drug delivery [44,45]. On their own the hydrophobic HCS can stabilize small droplets (1–10 µl) that represent a similar range of droplet sizes one would find for dispersed oil drops resulting from an oil spill [46]. With an appropriate polymer coating, the wettability and depth location at which particles sit at the oil–water interface can be controlled (Fig. 1). Recently a single step method for covalent immobilization of benzyl bromide atom transfer radical polymerization (ATRP) initiators onto fully pyrolyzed HCS [47] and boron nitride nanotubes [48] was developed by Ejaz et al. through a radical fixation method. This method provides a high density of surface immobilized initiators resulting from the well-known fact that graphitic materials like carbon black are strong radical scavengers. Once functionalized, high density polymer brushes can be grafted from these sites.

In this work, we present a novel experimental approach allowing for greater control over several experimental conditions and in situ and real-time observation of the steric repulsion on a macroscopic scale; the test setup in which an oil drop is brought into contact with a test surface in a very controlled motion and