



Robust amphiphobic coatings from bi-functional silica particles on flat substrates

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ABSTRACT

Robust oil- and water-repellent or amphiphobic particulate coatings were prepared from epoxy glue and bi-functional silica particles bearing poly(2-perfluorooctylethyl methacrylate) (PFOEMA) and poly(acrylic acid) (PAA) coronal chains. To prepare the particles, silica was first co-grafted in a one-pot process by poly[3-(triisopropoxy)silyl]propyl methacrylate]-*block*-poly(2-perfluorooctylethyl methacrylate) (PIPSMA-*b*-PFOEMA or P1) and poly[3-(triisopropoxy)silyl]propyl methacrylate]-*block*-poly(*tert*-butyl acrylate) (PIPSMA-*b*-PtBA or P2). P1 and P2 grafted onto silica because of the sol–gel reactions between the surface silanol groups of silica and the PIPSMA blocks of the two polymers. The sol–gel reactions also occurred between the different PIPSMA blocks of P1 and P2, resulting in a crosslinked anchoring PIPSMA layer. This layer was topped by the PFOEMA and PtBA chains. Cleavage of the *tert*-butyl groups of the PtBA chains yielded PAA corona chains. The particles bearing both PAA and PFOEMA could be dispersed in trifluorotoluene and sprayed onto an epoxy film that was partially cured on a glass plate to yield a rough particulate coating. The curing of the particles with the glue at 120 °C for 30 min bonded the AA units and the glycidyl groups of the epoxy glue and exposed the low-surface-tension PFOEMA chains. At P1 mass fraction of $f_1 \geq 80\%$ relative to P1 and P2, the coatings were superhydrophobic and repelled diiodomethane strongly. Furthermore, the coatings resisted trifluorotoluene extraction and abrasion tests if the PAA chains existed in sufficient amounts with P2 weight fraction (f_2) $\geq 5\%$.

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1. Introduction

Coatings that repel both water and oil are omniphobic or amphiphobic. Amphiphobic coatings that possess water and oil contact angles larger than 150° are superamphiphobic [1–5]. Superamphiphobic coatings are useful. For example, they may be applied onto the inner wall of oil-transporting pipelines to reduce drag and sludge deposition [6,7]. A reduced drag helps save energy and transportation cost. Cost saving also results from the lowered pipeline down time due to sludge removal. Deposition of marine organisms such as barnacles, diatoms and algae on ships is also a serious issue, resulting in increased fuel consumption [8–10]. This problem may similarly be alleviated by a superamphiphobic coating. Amphiphobic coatings can also be applied on the screen of an iPad or other handheld electronic devices to minimize buildup of smudges or fingerprints [11,12].

While advantageous, superamphiphobic coatings are difficult to prepare on flat substrates such as glass windows or metal sheets.

Organic liquids such as cooking oils have surface tensions ~ 30 mN/m [13]. For such an oil to achieve a contact angle of $>90^\circ$ on a flat coating, the coating should have a surface tension $\leq \sim 7.5$ mN/m [4,14,15]. This value is achievable only by CF₃ surface groups [16] and thus limits the usable coating materials to fluorine-containing compounds or polymers, which are expensive. Even on fluorinated polymers, the maximal achievable contact angles on flat films for water, diiodomethane, and hexadecane with the surface tensions of 72.1, 50.8, and 27.5 mN/m are only $\sim 120^\circ$, $\sim 100^\circ$, and $\sim 80^\circ$, respectively [17]. To increase the contact angles of the former two liquids to $>150^\circ$, surface roughness on the nanometer and micrometer scales is needed via the creation of textures or bumps [18–24]. To help push up the apparent contact angles of hexadecane and other liquids that have contact angles $<90^\circ$ on a flat substrate of the same chemical composition, these features need to be fabricated to contain re-entrant surfaces [1,2,25]. Re-entrant surfaces are those hidden under overhangs and can be, for example, the surfaces of the gills of a standing mushroom or the bottom half of a sphere [1,2]. While overhangs can be readily prepared from lithography, they are difficult to prepare from the bottom-up approaches [4]. Therefore, there have been only ~ 100 publications by 2011 on superoleophobic coatings [4]. Reports on superamphiphobic coatings on flat substrates were

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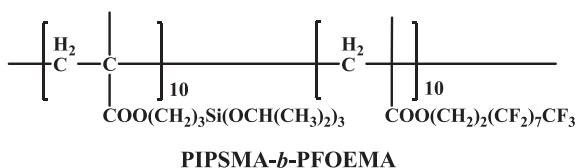
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even fewer because some of these reported superoleophobic coatings did not repel water [26] or were created on intrinsically rough substrates such as textiles [27–29].

Superamphiphobic coatings have been prepared from two approaches: the top-down and bottom-up approaches. In the top-down approach, nano- or/and micro-features are first created on a flat surface and their surfaces are then fluorinated to render superamphiphobicity. Methods used to fabricate these surface features have included lithography [30], anisotropic plasma etching [31], templating [32], electrospinning [1,2,5], and mechanical shaping [33]. While the key to the bottom-up approach is the assembly of the particles into an architectural film, three scenarios can be differentiated depending on the sequence of particle assembly and fluorination. In the first scenario, the particles are first assembled and the surfaces of the resultant coating are then fluorinated [34]. In the second scenario, coating formation and fluorination are accomplished simultaneously [11,35]. In the third scenario, pre-fluorinated particles are deposited to roughen a surface [36–38]. While the top-down approach can produce elegant and sophisticated surface features, the bottom-up approach is more practical.

The deposition of pre-fluorinated particles is an effective way to amphiphobic coatings. For example, we have recently coated silica particles [39] using a diblock copolymer poly[3-(triisopropoxy-silyl)propyl methacrylate]-*block*-poly(perfluorooctylethyl methacrylate) or PIPSMA-*b*-PFOEMA or P1 (Scheme 1). Catalyzed by HCl, the PIPSMA block hydrolyzed to yield silanol groups that readily coupled with the surface silanol groups of silica via siloxane bonds, Si–O–Si [40]. Also, the silanol groups condensed with each other, yielding a crosslinked PIPSMA layer that was covalently attached to the silica [39]. Evidently, the surface of the particles was enriched with the PFOEMA block. Also, the chain density in this grafted P1 unimolecular diblock copolymer layer could be increased somewhat by increasing the P1 to silica mass ratio used in the grafting experiment. Casting these particles bearing a saturated P1 layer onto glass produced coatings that had static contact angles of 154 ± 2 and $149 \pm 2^\circ$, respectively, for diiodomethane and hexadecane.

A fundamental problem with this method is that the fluorinated particles do not bind with any substrate or adhere to each other. Campos et al. [17] recently reported on the spraying of a dispersion containing fluorinated silica particles and a curable fluorinated rubber resin to get stable superamphiphobic coatings. While effective, these coatings might be costly because of the use of fluorinated resin as the binder. We recently proposed to prepare robust amphiphobic coatings by using fluorinated bi-functional particles that bear mostly fluorinated surface units and some reactive functional groups [37]. These particles would be cast with an epoxy or polyurethane glue on a substrate and then cured. Since these glues are known to bind with many substrates, our hypothesis was that bond formation between the functional groups of the bi-functional particles and glue would ensure the durability of the particulate coating. The coating would still be amphiphobic if the particle surfaces bear mostly fluorinated units that can top the unreacted functional groups.



Scheme 1. Chemical structure of PIPSMA-*b*-PFOEMA.

We have previously demonstrated that this approach was viable for improving durability of amphiphobic coatings by using polymer particles that bore a random copolymer on their surfaces [37]. The copolymer consisted of 20 mol% hydroxyethyl methacrylate (HEMA) units and 80 mol% HEMA that was fluorinated by perfluorononanoyl chloride (FEMA). Since the fluorinated nonanoyl group was much longer than hydroxyl groups, it was thus not surprising that the resultant particulate films were superhydrophobic and highly oil repellent, exhibiting diiodomethane contact angles upto $141 \pm 2^\circ$.

Silica particles are probably easier to prepare than polymer particles and have properties and applications different from those of bi-functional polymer particles. Also, bi-functionality can be rendered differently. Instead of using a random copolymer, bi-functionality can, for example, be achieved via two types of polymer chains such as PFOEMA and poly(acrylic acid) (PAA). This research was initiated mainly to examine the suitability of this new type of bi-functional particles for robust amphiphobic coatings.

To address this issue, we prepared the needed bi-functional silica particles in two steps. First, the particles were co-grafted with two types of polymer chains, which were P1 and PIPSMA-*b*-PtBA (P2), where PtBA denotes poly(*tert*-butyl acrylate). Then, PtBA was hydrolyzed to poly(acrylic acid) (PAA) so that it could react with the glycidyl components of an epoxy glue. The particles were then cast on a pre-cast and partially cured epoxy film and were further cured with the epoxy glue. The resultant composite coatings were subsequently evaluated for their amphiphobicity and stability against solvent extraction and abrasion.

2. Experimental section

Materials and reagents. Tetrahydrofuran (THF, Caledon, >99%) was distilled after it had been refluxed with sodium and a small amount of benzophenone and had developed a deep purple color. The solvent α,α,α -trifluorotoluene (TFT, 99%) was purchased from Aldrich. HCl (4.0 M in dioxane) was purchased from Aldrich and was diluted with THF to 1.0 M before use. The epoxy glue mixture, designed for transmission electron microscopy specimen embedment, was purchased from Cedarlane Laboratories Limited. The kit consisted of four components, which were Araldite 502 (bisphenol A diglycidyl ether + dibutyl phthalate), Embed-812 (1,2,3-propanetriol + a polymer bearing pendent chloromethyl oxirane groups), DDSA (dodecynyl succinic anhydride), and DMP-30 (epoxy tertiary amine accelerator or 2,4,6-tris(dimethylaminoethyl)phenol), and these components were suggested to be used at the weight ratios of 17.0/27.5/55.0/1.45–1.80 for a curing mixture.

Silica particles were synthesized following the Stöber method [36,41] and the detailed procedures for their synthesis and purification are described in recent reports [39,42]. P1 and P2 were prepared via anionic polymerization using 1,1-diphenyl-3-methylpentyl lithium as the initiator. This initiator was generated *in-situ* from the reaction between *sec*-butyl lithium with 1,1-diphenyl ethylene [43]. The repeat unit numbers were determined by comparing the ^1H NMR peak integrals corresponding to protons in a given block with the peak integrations representing the phenyl protons of the initiator.

Silica coating. Silica was coated with P1 and/or P2 in TFT/THF using HCl as the catalyst. While THF was a selective solvent for PtBA, TFT solubilized both PtBA and PFOEMA. TFT was used to ensure the dispersion of the final particles. Unless otherwise mentioned, silica particles were always coated using the standard conditions, which involved performing the grafting reaction at 21°C for 10 h in a TFT/THF solvent mixture at a THF volume fraction (f_{THF}) of 9.1%. The molar ratio between PIPSMA, HCl, and water was 1/1/2 ($n_{\text{Si}}/n_{\text{HCl}}/n_{\text{H}_2\text{O}}$). The weight ratio used between polymers consisting of P1 and/or P2 and SiO_2 ($m_{\text{P}}/m_{\text{S}}$) was 0.08/1.00.

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