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Nonsolvent-induced phase separation synthesis of superhydrophobic coatings composed of polyvinylidene difluoride microspheres with tunable size and roughness

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ABSTRACT

Polyvinylidene difluoride (PVDF) microspheres are synthesized using the non-solvent induced phase separation (NIPS) method. The diameters of the microspheres are varied from 0.3 μm to 2.8 μm by controlling the amount of water added to a solution of PVDF in dimethylformamide. Sphere aggregates are created from spun-on films whose thickness is tuned in the range 6.5–16.5 μm by varying the spin-casting rotational velocity. Spin-casting with optimized parameters results in high-surface-area films that are among the most superhydrophobic non-templated polymer coatings to date, with water contact angles up to 171°, hysteresis less than 12°, and slide angle as low as 3°. We model the dependence of sessile water contact angle on the morphological properties of the films, including not only the sphere diameter, but also nanoscale roughness of the microsphere surfaces and the geometries of macroscopic fingers formed by the aggregated spheres.

1. Introduction

Within the last decade, research into microsphere technologies has progressed to enable a range of applications in fields such as pharmaceuticals [1,2], biological sensors [3,4], photonics [5], and, recently, superhydrophobic materials [6]. Further, microspheres with central voids have desirable compressive, acoustic, and tensile properties when organized into syntactic foams [7–9]. Research has now begun to focus on enhanced control of these microspheres with the goal of efficient, reliable fabrication of micro-objects possessing desirable bulk or unit performance [10]. Microspheres of several polymers have been realized: Zhang et al. recently prepared fluorinated polystyrene (PS) microspheres through distillation precipitation polymerization [11], while poly-epsilon-caprolactone (PCL) microspheres have been thoroughly studied as a degradative delivery vehicle with production methods including emulsion solvent extraction, hot melt, solution-enhanced dispersion, and spray drying [12].

One particularly intriguing methodology for microsphere growth is non-solvent-induced phase separation (NIPS). NIPS describes the process in which a ternary solution of solvent, non-solvent, and polymer components separate into a bi-phase system of polymer-rich and polymer-poor regions [13]. The introduced non-solvent—which is

nevertheless miscible with the existing solvent—is the driving force behind the separation, creating a solvent/non-solvent phase which is generally allowed to evaporate from the system [14]. By controlling external parameters, percolation activity of this polymer-poor phase can be altered to introduce unique surface morphologies [15]. Recently, NIPS has been used as a growth procedure for polymer microspheres. Piacentini et al. combined membrane emulsification with NIPS to produce polyethersulfone (PES) microspheres [16], while Gao et al. leveraged a coupled method of NIPS and electrospray technology to fabricate hierarchically porous polymethyl methacrylate (PMMA) microspheres capable of superhydrophobic performance [17].

Synthetic superhydrophobic surfaces are desirable due to their droplet shedding [18–20], anti-sticking [21,22], and self-cleaning [23–25] tendencies, as well as other valuable characteristics [26]. As shown by widespread studies of the lotus leaf [27], [28], a hierarchical, multi-scale surface structure incorporating both micro- and nano-scale features can yield exceptionally desirable hydro-static and –dynamic properties, including water contact angle (θ^*), hysteresis, and slide angle (SA) [29]. One feasible material for mimicking such structures is polyvinylidene difluoride (PVDF), an abundant, inexpensive, and easily malleable thermoplastic fluoropolymer [30]. A flat PVDF surface has been variously reported [31,32] as having an inherent water contact

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angle of between 82° and 95° , and this contact angle can be considerably raised by surface roughening and the induction of a composite (*i.e.* Cassie–Baxter [33]) interface in which a small fraction of the solid surface's projected area is in contact with the liquid.

The motivation to produce extremely rough surfaces from PVDF has spurred multiple efforts within the last several years: Zheng et al. [34] showed that alkali conditions during chemical bath deposition of PVDF improve θ^* to 155° and SA to 4° , while Wang et al. [35] proposed a PTFE/PVDF composite fabricated through mechanical hot press and abrasion with a θ^* greater than 160° and SA less than 5° . Many other methods have returned similar θ^* and SA characteristics [35–38]. In addition, there have been several attempts to achieve superhydrophobicity with PVDF–carbon nanotube/graphene composites [39–41]. Finally, one of the more promising cost-effective production procedures has been put forth by Peng et al., who showed θ^* of 150° through simple immersion baths [42].

Previous work using the NIPS technique in conjunction with PVDF, however, has focused primarily on porous membrane formation, as opposed to the creation of aggregates of microspheres. Sphere aggregates are expected to be preferable to porous membranes for water repellence, because to achieve low contact-angle hysteresis and slide angle one actually desires a composite (liquid–solid and liquid–air), Cassie–Baxter-like interface with as small a liquid–solid fraction as possible, and spheres that have aggregated to form a surface with many asperities are more likely to offer a low solid-area fraction than an essentially flat membrane perforated by pores. An intermediate morphology composed of spherule-reminiscent PVDF structures has been observed [43,44], although no optimization was performed on the material's properties and the highest resultant contact angle was 110° , little different from that of a flat surface [45]. There thus remains a need for a comprehensive investigation of the parameters governing the formation of PVDF microspheres. We provide here the first detailed study of the formation of PVDF microsphere aggregates *via* NIPS. We demonstrate the ability to control the sphere size and surface roughness to determine overall wettability by modulating the diffusion rate of the solvent. These structures are shown to possess superhydrophobic performance that is superior to any previously reported polymeric material, and have the potential to be cast or sprayed on to any surface.

2. Methods³

2.1. Microsphere synthesis

Aluminum scanning electron microscopy (SEM) sample-mounting pegs were cleaned by sonication in acetone for 15 min. A 20 wt% polymer solution was created by dissolving PVDF pellets into dimethylformamide (DMF) in an $80 \pm 2^\circ\text{C}$ water bath for three hours. Quantities of water ranging from 0.06 to 5.51% of total mass were loaded into the solution. The solution was then vortex-mixed for five minutes. An aluminum SEM peg with diameter 12.7 mm was drop-cast with 50.0 μL of the polymer solution and then spun at between 1100 rpm and 2600 rpm for 30 s. Immediately after spinning, the pegs were submerged in deionized water for 30 min at $90 \pm 2^\circ\text{C}$. After removing the samples from the water, they were air-dried and then pumped under dynamic vacuum at room temperature overnight to ensure that the pores of the resulting polymeric film were free of solvent and water. Aluminum SEM pegs were used purely for convenience and the substrate material is not expected to limit applicability of the coating. Provided that a substrate is flat enough to facilitate spinning and capable of being wetted by the PVDF/DMF solution, the coating is expected to be applicable to the substrate.

2.2. Scanning electron microscopy

After formation and drying, PVDF films were imaged by scanning electron microscopy (FEI Quanta 3D FEG) at 10 kV with a secondary electron detector.

2.3. Sessile drop contact angle, slide angle, and hysteresis measurements

Sessile drop contact angle measurements were performed using 5 μL droplets dispensed from a Hamilton Model 1710 LT syringe with threaded plunger. Droplets were imaged from the side with a 4X objective (Olympus Plan Achromat), a 30 mm focal-length achromatic doublet (Thorlabs, Newton, NJ), and a CMOS image sensor (Thorlabs DCC1645C) [46]. Contact angle hysteresis was obtained by mounting each sample in turn on to a tilt stage and moving it at a rate of 0.25°s^{-1} while imaging a static droplet at ≥ 15 frames per second. The advancing and receding contact angles were determined from the last video frame captured before droplet motion began. Hysteresis is the difference between advancing and receding angles. Slide angle was determined to be the inclination of the tilt stage at which droplet motion began. Sessile contact angle measurements were extracted from images using the Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA) analysis package [47], while hysteresis values were obtained using the Dropsnake package [48], both in ImageJ [49]. Values reported for contact angle, slide angle, and hysteresis are the average of five measurements taken at separate locations on a sample. The test liquids used were, in descending order of surface tension, γ , water ($\gamma = 72.8 \text{ mN/m}$ [50]), glycerol ($\gamma = 64 \text{ mN/m}$ [50]), thiodiglycol (TDG, $\gamma = 54 \text{ mN/m}$ [50]), polyethylene glycol diacrylate 700 Da (PEGDA, $\gamma = 42.3 \text{ mN/m}$ [51]), dipropylene glycol (DPG, $\gamma = 33.9 \text{ mN/m}$ [50]), and methanol ($\gamma = 22.7 \text{ mN/m}$ [50]).

2.4. Film thickness measurement

The PVDF films were gently scratched with a razor blade, taking care not to cut into the aluminum substrate, and film thicknesses were then measured using a Dektak 3030 stylus profilometer.

3. Results and discussion

3.1. Dependence of sphere size/roughness and θ^* on water loading

Fig. 1 shows scanning electron micrographs of PVDF microsphere clusters that were produced on aluminum substrates. As the water content of the spun-on PVDF solution increases, the sphere size after decomposition decreases. Microspheres with diameters ranging from 3 μm down to 250 nm were fabricated using the NIPS technique and a 20 wt% PVDF solution. This dependence of sphere size on the amount of water added is consistent with previous reports by Matsuyama [52,53]. By adding more water, the polymer degree of saturation increases and a larger number of smaller particles precipitate upon submersion in the water bath.

Fig. 2 shows the relationship between the loaded water fraction and $\cos \theta^*$. Meanwhile, Fig. 3 shows how the average sphere size depends on water loading fraction. Sphere sizes were extracted from SEM images of the specimens. Taking Figs. 2 and 3 together (see also Table 1), we note that for sphere diameters above about 500 nm (occurring for water loadings $< 2 \text{ wt}\%$), θ^* increases (*i.e.* $\cos \theta^*$ decreases) as the average sphere size reduces. At a water loading of 1.72 wt%, θ^* reaches a peak value of $170.5 \pm 1.0^\circ$, which is far superior to that of a flat PVDF surface. For the higher water loadings, however, which give rise to sphere sizes below 500 nm, the trend in θ^* reverses, and θ^* begins to decrease with decreasing sphere size. This effect implies that the water mass loading fraction influences properties other than sphere diameter, such as individual spheres' surface roughness or their geometrical arrangements, affecting the wetting properties of the surface in different ways.

³ Materials were obtained from Sigma-Aldrich unless otherwise stated.

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