

Full Length Article

Towards superhydrophobic coatings via thiol-ene post-modification of polymeric submicron particles

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ABSTRACT

Superhydrophobic coatings find important applications in consumer, commercial and advanced materials industries. Despite the existing approaches, the variety of substrates and different coating compositions necessitates the availability of several simple and versatile strategies for creating these functional coatings. This work demonstrates a facile and versatile strategy for achieving superhydrophobic coatings via deposition of modified polyvinylidene fluoride (m-PVDF) microparticles and subsequent thiol-ene surface functionalization of the microparticles with perfluorodecyl-1-thiol. The “ene” functionalities of the m-PVDF microparticles are achieved via dehydrofluorination of PVDF. The obtained coatings exhibit up to 160° static water contact angle. We show that the hydrophobic properties of the coatings are dependent upon the surface coverage of the substrate with the microparticles and the functionalization with the perfluorodecyl groups. Raman spectroscopy was used to provide insight into the thiol-ene functionalization of the superhydrophobic coatings.

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1. Introduction

Superhydrophobic (SH) coatings provide the benefit of water repellency that are highly desirable for both consumer and advanced industrial applications [1]. These coatings are typically characterized by their ultrahigh water contact angle (WCA) of 150° or higher [1–12]. To accomplish such ultrahigh WCA, sufficient surface roughness and/or texturing in addition to the intrinsic hydrophobicity are required according to the Wenzel and Cassie-Baxter models [13–16]. Moreover, the wide variety of functionalities such as anti-icing, self-cleaning (especially, for solar panels), and anti-corrosion, necessitates the development of several strategies to impart the surface roughness required to accomplish the SH coatings [1,11].

Inspired by unique designs in nature, such as lotus leaves, several strategies have been developed to create SH and other functional coatings. Classical examples of surface texturing strategies include laser microstructuring [17], surface wrinkling [4,10,18], particle fixation [19,20], polymer deposition and mineralization [21], multilayer formation [22,23], fiber modification [5], elastocapillary engineering [24], and templating [25]. Despite several

advances, alternative simpler ways to generate textured surfaces for SH applications are still desirable. Deposition of particles that can be functionalized with hydrophobic groups are attractive as the process is amenable to different substrates, adaptable to large scale, and benefit from several deposition methods including spray, dip, and spin coating. Deposition of microparticles comprising diatomaceous earth of different morphologies has been demonstrated to provide superhydrophobicity when modified with hydrophobic functionalities [26–30]. Blum and coworkers have demonstrated the dependence of the SH properties upon the surface density of diatomaceous earth and the extent of its modification with fluorinated groups [28,30].

Inspired by the excellent results from the deposition of microparticles, we explored a simple and versatile strategy that offers SH coatings by the deposition of polymeric microparticles that are readily functionalized via thiol-ene click chemistry. Thiol-ene and thiol-yne click reactions are well known for facile surface modification and creation of functional surfaces [4,6,31–34]. Essentially, the click reaction entails a photoinitiated radical addition to the unsaturated group by the thiol functionality [33]. Therefore, the deposition of the polymer microparticles provides the textured coating whereas, a fluorinated thiol reacts with the unsaturated groups on the polymer surface to afford the superhydrophobicity. This approach offers the advantages of facile and scalable coating process.

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In this initial report, we demonstrate the formation of a superhydrophobic coating comprising polymer microparticles that are end-functionalized with perfluorinated molecules. The preparation and spectroscopic characterization of alkene-functionalized microparticles is provided. The measure of static WCA was used to characterize the hydrophobicity of the coatings. The effect on the WCA of the surface density of microparticles is evaluated based upon the number of spray coating cycles.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF) was obtained under the trade name Kynar® Powder Grade 301 from PennWalt Corporation, PA. Potassium hydroxide (KOH) and 1H,1H,2H,2H-perfluorodecyl-1-thiol (PFDT) were obtained from Aldrich and used as received. Tetrabutylammonium hydroxide (TBAH) and (3-mercaptopropyl)-trimethoxysilane (MPTMS) were obtained from Aldrich and used as received. Ethanol (200 Proof) was obtained from Pharmco-Aaper. Ultraviolet exposure was carried out using Newport-I series equipment with UVA, UVB, and UVC filter accessories.

2.2. Preparation of modified PVDF microparticles

The dehydrofluorination of PVDF was conducted with modification to reported procedures [35,36]. To a 2-g quantity of the PVDF powder in a falcon tube was added 20-g of aqueous KOH solution (1.8 M) and 5-g ethanol. After ensuring uniform dispersion, 2 mL of TBAH was dispensed dropwise into the PVDF dispersion. After 5 min of gentle shaking by hand, the dispersion was subjected to mechanical shaking (or sonication) for about 10 min to ensure a stable dispersion is obtained. The brown dispersed phase is described as modified PVDF (m-PVDF). The m-PVDF dispersion was centrifuged (6000 rpm, 15 min), decanted, and re-dispersed in ethanol to make a 10 wt% dispersion. The centrifugation, decantation and re-dispersion in ethanol was repeated twice. The final re-dispersion was conducted to obtain a 5 wt% m-PVDF dispersion in ethanol which was preserved for further experiments.

2.3. Preparation of glass substrates

Glass substrates were initially pre-cleaned with 1.8 M KOH solution and rinsed with deionized water and/or isopropanol (IPA). After drying under nitrogen gas (N₂), the glass substrates were silanized by spin-coating an ethanol solution of MPTMS. After oven-heating (65 °C) for 15 min, the substrates were rinsed with IPA and dried under N₂.

2.4. Preparation of superhydrophobic coatings

The m-PVDF dispersion (sonicated for 10 min) was spray-coated onto a thiol-functionalized glass slide held vertically and about 15–20 cm from the nozzle of the airbrush (Paasche Model H). Spraying from left to right and back to left makes a complete coating cycle. Except otherwise note, four coating cycles were used. The coated glass was subjected to UV exposure for 3 min (averagely 12 mW/cm² or less). The glass surface was then hand-coated with PFDT (~0.2 mL/cm²) and subjected to UV exposure using similar conditions as noted before. Excess PFDT were removed by rinsing with profuse amounts of acetone. The coating on the glass was dried under N₂.

2.5. Characterization

The hydrodynamic size (R_h) for the m-PVDF dispersed in ethanol was measured using dynamic light scattering on a Malvern Zetasizer Nano-ZS (ZEN). Micro-Raman spectra of the untreated PVDF and m-PVDF, before and after treatment with the thiol (PFDT), were measured using a JY Horiba LabRam spectrometer with 532 nm laser excitation. Water contact angle (WCA) was measured on a goniometer equipped with a high speed digital camera.

2.6. DFT calculation

All calculations used Density Functional Theory (DFT) methodology [37] as implemented in the Gaussian 09 series of computer programs. We employed the M06 functional, and all-electron, valence triple- ζ plus polarization and diffuse function 6-311+G(d, p) basis sets were used [38,39]. Calculations were performed in the gas phase. All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis.

3. Results and discussion

Fig. 1 shows the rapid and facile dehydrofluorination [35] of the PVDF to give unsaturated functional groups on the particle surface. This is accompanied by the change of the PVDF from white to brown particles that are well dispersed in ethanol. It is noted that the dehydrofluorination did not proceed within an hour in the absence of the TBAH, which is a phase transfer catalyst. However, an instantaneous formation of the brown color, consistent with the dehydrofluorination, resulted upon addition of the TBAH [35,40].

Fig. 2 shows Raman spectra for the neat PVDF and the modified PVDF (m-PVDF) which are represented in Fig. 1. The strong CH₂ Raman band around 2985 cm⁻¹ of the PVDF is nearly disappeared to give a weak peak around 3030 cm⁻¹ in the m-PVDF. This is consistent with the loss of alkyl and formation of alkenyl C–H groups. In addition, two new peaks centered around 1133 and 1523 cm⁻¹ are present in the spectra for the m-PVDF (Fig. 2B); these are attributed to conjugated alkenyl functionality on the m-PVDF microparticles [35,41,42]. It is noted that the weak band around

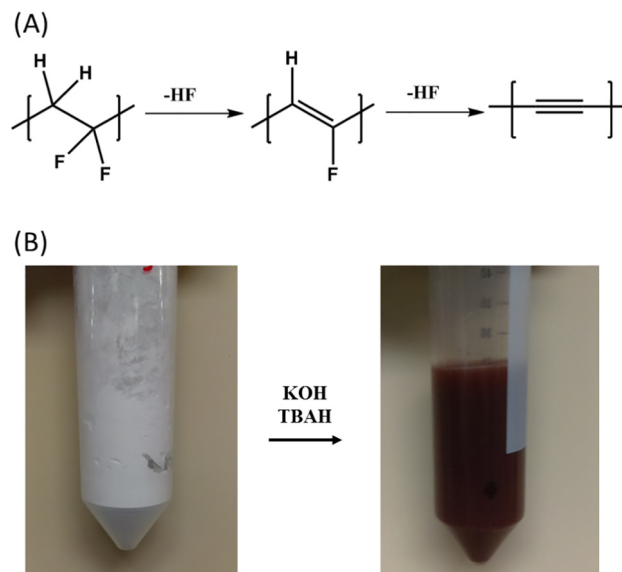


Fig. 1. Dehydrofluorination of PVDF. (A) Chemical equation, and (B) pictures of color changes of PVDF powder from white to brown during reaction with TBAH. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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