Highly Liquid-Repellent, Large-Area, Nanostructured Poly(vinylidene fluoride)/ Poly(ethyl 2-cyanoacrylate) Composite Coatings: Particle Filler Effects

Manish K. Tiwari,[†,‡] Ilker S. Bayer,[§] Gregory M. Jursich,[†] Thomas M. Schutzius,[†] and Constantine M. Megaridis*[,†]

Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, and Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

ABSTRACT Super-repellent nanostructured composite coatings applied over large areas by spray and subsequent thermal treatment are reported. Solution blending of poly(vinylidene fluoride) and poly(ethyl 2-cyanoacrylate) is implemented to formulate filler particle dispersions used to apply these coatings. The wettability of these coatings is manipulated using hydrophobic poly(tetrafluoroethylene) and hydrophilic zinc oxide particle fillers or their combination. The resulting coatings feature contact angles up to 164° for water and 154° for a water and isopropyl alcohol mixture (9:1 weight ratio; surface tension ~40 mN/m). A self-cleaning ability is revealed by droplet roll-off angles below 10°. The results show that the fillers affect the coating surface energy and surface roughness, in turn influencing the wettability of the coatings.

KEYWORDS: superhydrophobicity • liquid repellency • hierarchical surface structure • nanostructured composite • polymer blend • filler particles • surface energy

I. INTRODUCTION

Lightweight and flexible, polymer-based nanocomposite coatings are useful in a broad range of applications (1). The incorporation of functional particle fillers in such coatings naturally influences the material properties of the coated surface. More specifically, the addition of fine particles influences the coating surface morphology, ultimately affecting wettability. Many naturally occurring surfaces, such as plant leaves (e.g., lotus, *Nelumbo nucifera*; rice, *Oryza sativa*) (2), wings of insects (e.g., blue butterflies, *Morpho aega*), etc., possess a sophisticated hierarchical microscale-to-nanoscale surface texture, which results in their high water repellency. In fact, the hierarchical texture of these natural surfaces is responsible for their superhydrophobicity (sessile droplet contact angles above 150°) and "self-cleaning" ability demonstrated by low roll-off (sliding) angles of water droplets (2). No natural material shows such high liquid repellency in the absence of surface texture roughness. Inspired by this realization, many groups have demonstrated synthetic superhydrophobic surfaces using one of three different approaches in nanotechnology (top-down, bottom-up, or mixed), as described in recent reviews (3). By manipulating the morphology of materials with low-energy functional groups (e.g., $-CF_3$ and $-CF_2$), some researchers have designed surfaces with high repellency to low surface tension liquids, such as oil (4) or alcohol (5). The low surface energy of these materials, however, poses a formidable challenge in obtaining coatings with high adhesion. Both high adhesion and scalability of superhydrophobic coatings to large areas are needed for practical applications.

In this paper, we demonstrate wet-processed composite coatings that rely on good particle dispersion of nanosized hydrophilic and submicrometer-sized hydrophobic particles to control the liquid repellency of the coatings. Although a number of previous works have shown the feasibility of obtaining superhydrophobic surfaces from nanocomposites [see reviews 3b and 6, for example] with fabrication techniques that are potentially scalable to large areas, the problem of low adhesion has not been addressed. In this work, a polymer blend of poly(vinylidene fluoride) (PVDF) and poly(ethyl 2-cyanoacrylate) (PECA) is used to facilitate good particle dispersion and high coating adhesion. The solution blending of PVDF with PECA was achieved by controlled polymerization of the ECA monomer in a cosolvent medium as described in 7. Submicrometer-sized hydrophobic poly(tetrafluoroethylene) (PTFE) particles and nanosized hydrophilic zinc oxide (ZnO) particles are combined in different proportions to control the coating surface energy and morphology. These controlled factors allow tunable wettability of the composite coatings prepared by spraying dispersions of filler particles in PVDF/PECA polymer blend solutions. The influence of the filler particle content

---

* Corresponding author. Phone: +1 312 996-3436. Fax: +1 312 413 0447. E-mail: cmm@uic.edu.

Received for review December 15, 2009 and accepted February 24, 2010

[†] University of Illinois at Chicago.

[‡] Current address: Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology, Zurich 8092, Switzerland.

[§] University of Illinois at Urbana-Champaign.

DOI: 10.1021/am900894n

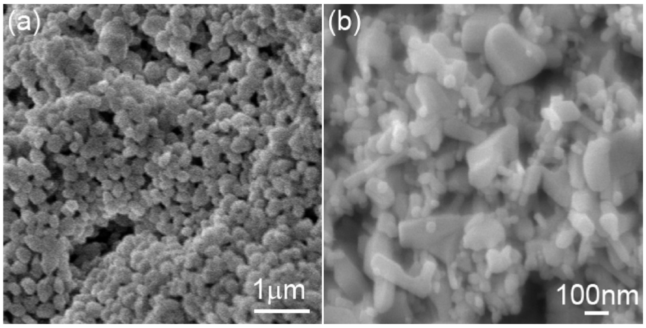

FIGURE 1. SEM images showing the morphology of the filler particles used in this work. Image analysis of the PTFE particles (left) designated a mean diameter of 260 nm (standard deviation 54.2 nm). The ZnO particles (right) have a bimodal size distribution. The smaller particles are primarily spherical, with an average diameter of 74.6 nm (standard deviation 23.4 nm). For the larger particles, which are irregular in shape, the mean value of the maximum dimension is 236 nm (standard deviation 60 nm). The corresponding mean for the minimum dimension is 109 nm (standard deviation 36 nm).

on the wettability of the coatings is quantified in terms of the sessile droplet contact angle and droplet roll-off angle measurements performed with two different liquids, namely, water and a 90/10 wt % water/isopropyl alcohol mixture. It was observed that at sufficiently high content of each type of filler particle, the water contact angle for the coatings approached or exceeded 150°, which is considered a threshold value for superhydrophobicity. The self-cleaning (8) property of these coatings was evaluated in terms of roll-off angle measurements of droplets placed on a tilting stage.

II. EXPERIMENTAL SECTION

A. Materials. Poly(vinylidene fluoride) (PVDF) pellets (M_w $\sim$530 000 Da), ethyl 2-cyanoacrylate (ECA) monomer, reagent-grade acetone, *N*,*N*-dimethylformamide (DMF), and isopropyl alcohol (IPA) were all obtained from Sigma-Aldrich, USA. The fillers used include submicrometer particles of poly(tetrafluoroethylene) (PTFE; Sigma-Aldrich, USA) and nanoparticles of zinc oxide (ZnO; Alfa-Aesar, USA). Figure 1 displays scanning electron microscopy (SEM) images of PTFE particles (a) and ZnO particles (b), as purchased. Particles of each type were dispersed in acetone and sonicated for 10 min before being left to dry on a clean stainless steel surface and subsequent SEM observations. SEM images were obtained using a Philips XL30 environmental scanning electron microscope after all samples were sputter-coated with a 5-nm-thick layer of platinum. Figure 1a displays fairly monodisperse PTFE particles, which are predominantly spherical in shape. Image analysis of about 100 particles defined the average diameter as 260 nm, with a standard deviation of 54.2 nm. Figure 1b displays ZnO particles with a bimodal size distribution. The smaller ZnO particles are primarily spherical, with an average diameter of 74.6 nm and a standard deviation of 23.4 nm. The larger ZnO particles are irregular in shape, displaying maximum and minimum dimensions. Image analysis designated the mean value of the maximum dimension as 236 nm with standard deviation 60 nm. The corresponding values for the minimum dimension were 109 and 36 nm, respectively. Thus, because of their larger size, the PTFE particles are expected to contribute only to the microscale texture of the coatings, while the ZnO particles would contribute to both micro- and nanoscale texture.

Table 1. Composition of Particle Dispersions in PVDF + PECA Blend Solutions Used To Make Composite Coatings

ingredient	concentration (wt %)
20 wt % PVDF dissolved in DMF	8.3
8 wt % PECA dissolved in a DMF/ acetone mixture	13.9
filler particles	2−20
acetone	75.8−57.8q(balance)

B. Controlled Polymerization of ECA and Blending with PVDF. A cosolvent-based technique was used to control ECA polymerization and facilitate blending with PVDF in solution, as reported elsewhere (7) and described briefly below. In a glass flask equipped with a water-cooling jacket, the ECA monomer was dissolved in acetone to obtain a 33 wt % ECA monomer solution. Using a syringe pump, equal weights of DMF and acetone were slowly introduced into the ECA solution, with continuous stirring until the final concentration of ECA in the solution reached 8 wt %. During this process, a thickening of the mixture was observed. The final mixture was stored overnight at room temperature. DMF is known to act as a catalyst in rapid anionic polymerization of ECA. However, in a cosolvent system, in which the relative amount of DMF in solution is adjusted, the anionic polymerization reaction of ECA progresses more slowly. Through such a slow polymerization, a poly(ethyl 2-cyanoacrylate) (PECA) polymer formed, which was used as an adhesion-enhancing and filler-dispersing component in polymer particle dispersions described below.

PVDF pellets were dissolved in DMF at 70 °C to obtain a separate 20 wt % solution. The PVDF and PECA solutions so prepared were miscible in any proportion and were diluted with acetone, as required for subsequent spraying. The blending of the two polymer solutions was performed at room temperature to obtain a PVDF/PECA weight ratio of 3:2.

C. Dispersion Preparation and Wettability Tests. To prepare the dispersion of filler particles in the PVDF/PECA blend solution, the fillers were added directly and shaken mechanically without the addition of dispersants or surfactants. The PVDF/PECA weight blend ratio was kept constant at 3:2, to provide an optimum level of filler dispersibility and adhesion of the nanocomposite coatings. PVDF in the polymer blend helps keep the surface energy of the dispersant low, which facilitates the formation of low-surface-energy composites. The dispersions were sprayed on aluminum foils using a Paasche VL siphon feed airbrush with a 0.73-mm spray nozzle. The dispersions remained stable during the entire spraying process. Table 1 shows the composition details of the dispersions used to make the present coatings. The fillers included submicrometer-sized PTFE particles, ZnO nanoparticles, or their combinations. The choice of these two fillers was made in order to determine the effect of the filler surface energy on the designed nanocomposite coatings. PTFE particles are typical hydrophobic (low-surface-energy) fillers, while ZnO particles are typical hydrophilic (high-surface-energy) fillers. The coated foils were heated at 125 °C for 45 min to cure the coatings and remove any solvent residuals. Aluminum foil was chosen as the substrate to demonstrate the mechanical flexibility of the resulting coatings. It is important to point out that the present coatings are not substrate-limited; we have also tested them on glass slides, steel plates, and printable fabrics with good results.

Sessile droplet contact angles were measured by an optical image acquisition system described elsewhere (9). The liquids were water and a 9:1 weight ratio water + IPA mixture. Droplet roll-off angles were measured by gently placing each droplet on coated aluminum foil mounted on a tilt stage (with an angle graduation accuracy of 1°) and gradually inclining the stage until the droplet rolled down the plate. The droplet roll-off angle was the minimum inclination angle at which a sessile droplet started rolling. This technique offers a more severe test of the self-

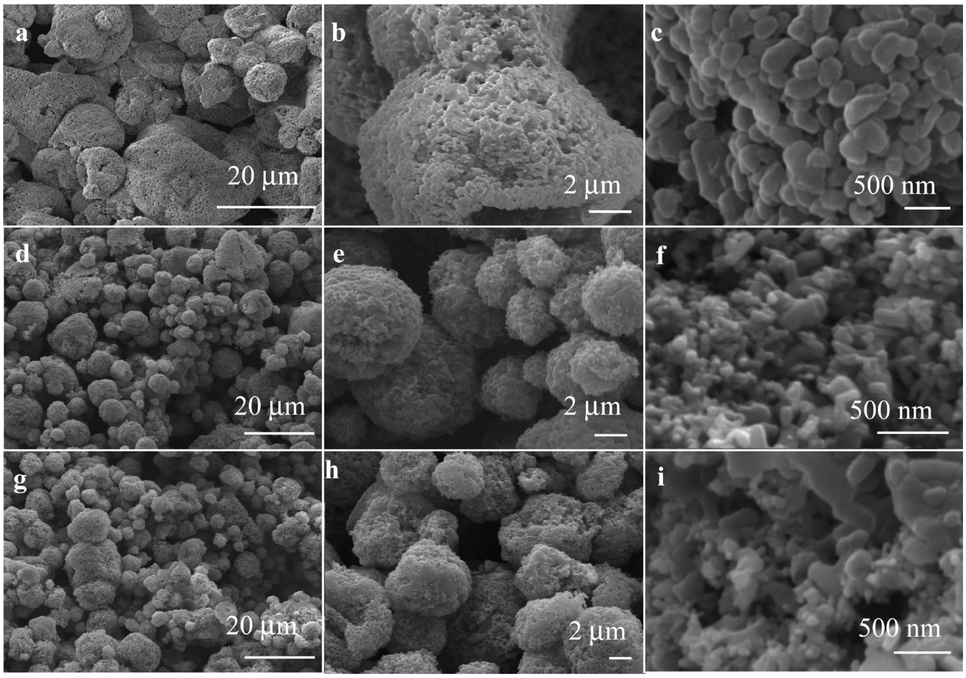

FIGURE 2. Morphology of nanostructured composites with 12 wt % concentration of three types of fillers: (a−c) submicrometer-sized PTFE particles; (d−f) ZnO nanoparticles; (g−i) PTFE + ZnO particles (50/50 wt %). The microscale roughness results from particle clusters that are bound together by the polymer blend (binder) in all three cases.

cleaning ability as compared to placing the liquid droplet on a preinclined surface (10).

III. RESULTS AND DISCUSSION

The addition of submicrometer-sized or nanosized particle fillers is intended to influence the surface texture of the resulting composite coatings. Because of the high particle content used, the particles should form microscale clusters with a PVDF + PECA blend filling the interspaces, thus holding them together. These clusters provide the micrometer-scale roughness, while the inclusion of nanoparticles provides the nanoscale roughness on top of the micrometer-sized clusters. Such particle organization results in a hierarchical microscale-to-nanoscale roughness, which is known to produce superhydrophobicity on natural and artificial surfaces. In this work, the influence of micro/nanoscale surface morphology on hydrophobicity was tested by adding different combinations of submicrometer-sized PTFE particles and ZnO nanoparticles separately and jointly (50/50 wt %). Figure 2 demonstrates the hierarchical morphology in composite coatings resulting from such micro/nanoparticle−polymer systems. In the figure, for each filler case, three images with progressively increasing magnifications (from left to right) are shown, in order to clarify the hierarchical morphology. Parts a−c in Figure 2 are images of coatings containing only PTFE particles, parts d−f are of coatings with only ZnO particles, and parts g−i are of coatings with a PTFE + ZnO particle mixture. The low-magnification images of Figure 2 (left column) clearly show the clustering of the primary units to form porous polydisperse microstructures. For example, Figure 2a depicts clusters of PTFE particles with sizes in the range 5−20 μm. The smaller ZnO particles form clusters in the range 2−10 μm, as seen in Figure 2d. The coating structures seen in Figure 2a,d,g result from the earlier dynamic interactions between the PVDF + PECA matrix and the filler particles not only through the spray impact stage but also during the heat treatment. When the PTFE and ZnO fillers were combined, the resulting surface morphology (Figure 2g) resembled that of the ZnO-only case (compare with Figure 2d) but also included the nanofeatures introduced by the presence of the sub-100-nm ZnO particles (see Figure 2i). Whereas such hierarchical morphology has been produced previously (11), the objective of the present study was to achieve high liquid repellency without compromising adhesion. This was achieved by means of our new PVDF/PECA polymer blending procedure, which allowed good adhesion and flexibility (12).

The wettability of the resulting composite coatings was tested with pure water or a water + IPA mixture (90/10 wt %) to determine the degree of liquid repellency. The water + IPA mixture (surface tension of 40.42 mN/m (13)) serves as a stringent measure of the liquid repellency of coatings intended for use in the medical or clean-room fabrics industry. Achieving liquid repellency for such a low-surface-tension liquid is a more severe test for the surface energy of the coating and, in general, is very challenging to achieve in large-area-coating applications (3b). It should be mentioned here that our coatings consist of biocompatible components, which combined with their alcohol repellency could be especially well suited for medical applications.

Figure 3 shows the contact angles of coatings containing different particle fillers and their variation with the filler content. Contact angles were measured with water (Figure 3a) and water + IPA (Figure 3b) droplets. The three curves within each of these figures represent coatings prepared using only PTFE particles, only ZnO particles, or both PTFE + ZnO particles in a 50/50 wt % proportion.

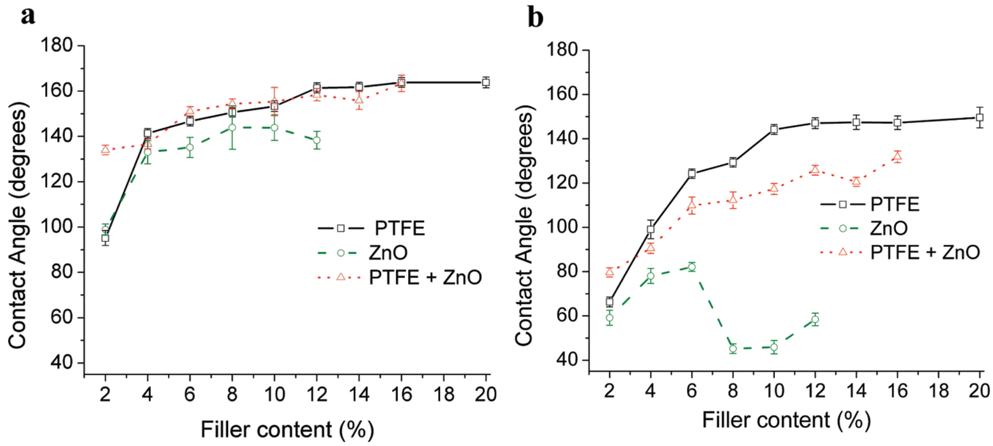

FIGURE 3. Sessile droplet contact angle change with the filler particle content for coatings containing different fillers. The measurements were performed with two different liquids: (a) water; (b) a water + IPA mixture (9:1 weight ratio).

The addition of filler particles is expected to influence the wettability of the coatings by two different mechanisms. On the one hand, filler particles change the surface roughness as shown in the SEM images of Figure 2. On the other hand, particles change the surface energy of the coatings, depending on whether the particles are hydrophilic or hydrophobic. Both of these mechanisms can affect the contact angle of the liquid droplets on the coated surface and are described by either the Wenzel (14) or Cassie–Baxter models (15), depending on the contact state of the liquid droplet on the surface. Recently, the validity of the Wenzel and Cassie–Baxter equations has been challenged (16) for specially designed surfaces with differing roughness near the droplet contact line compared to the roughness under the bulk of the droplet. However, for the self-organized cellular morphology, which extends throughout the surface of our composite coatings (see Figure 2), the improvements in the liquid repellency with roughness (manipulated by the filler content) can still be interpreted under the framework of these equations (17). For each type of filler particle used, the particle concentrations in the sprayed solution were varied up to the highest possible limit in order to attain the widest range of wettability possible.

The addition of hydrophobic PTFE particles individually in the coating increases the surface roughness and should also reduce the overall surface energy of the coating. Both of these effects lead to increased liquid repellency. Figure 3 shows a gradual increase in the contact angle of both water and water + IPA mixture droplets, reaching maxima of 164 and 150° (see Figure 3a,b), respectively, up to the maximum PTFE content (20%). These results clearly show the additive effect of PTFE on the wettability of the coating surface. The addition of only hydrophilic ZnO nanoparticles in the coating increases the surface roughness but should also increase the surface energy. These two effects of the ZnO particles are then expected to have competing effects on wettability. In this case, the results of Figure 3 show an increase in the contact angle for both liquids with increasing ZnO content up to 4%; however, at higher particle concentrations, the increase in the contact angle diminishes. For water, the contact angle levels off to ∼145°, whereas in the more severe case of water + IPA, the contact angle actually decreases when the ZnO content is increased from 6% to 8%. These results suggest that at low ZnO content the increase in the surface roughness dominates, but at higher ZnO content, the contribution of higher surface energy from the added ZnO particles dominates the overall effect on the liquid repellency.

Figure 3 also shows the effect of the addition of equal amounts of ZnO and PTFE particles on the contact angle of the two liquids. The trend of the water contact angle is similar to the case of only PTFE particles, whereas for water + IPA droplets, the contact angles are intermediate between those obtained by using PTFE or ZnO fillers individually. A key difference to note in the contact angle of water is observed at 2% filler content. The PTFE + ZnO filler has a water contact angle of 134°, whereas the corresponding values for 2% only ZnO and 2% only PTFE are 99 and 95°, respectively (Figure 3a). Here, it is likely that the ZnO nanoparticles combine with the submicrometer-sized PTFE particles to provide an effective hierarchical morphology for increased water repellency. A similar, but less dramatic, effect is seen with the alcohol solution (Figure 3b). The incipient formation of particle clusters and their hierarchical morphology for coatings with 2% PTFE + ZnO is shown in Figure 4. Such a hierarchical structure was absent for coatings with a low concentration of either PTFE or ZnO filler particles.

The influences of the three particle filler types used here become clear by means of roll-off (sliding) angle measurements, which are presented in Table 2. In this table, the errors are calculated from the repeatability of the measurements (3–4 for each coating) and the angle accuracy of the tilt stage. For coatings with PTFE particles only, the sliding angle shows a gradual reduction, reaching minimum values of 2 and 10°, for water and water + IPA, respectively. In the case of water + IPA, a higher content of PTFE is required for a low sliding angle to be observed. This is further testimony of the alcohol solution offering a more stringent test of the liquid repellency due to its much lower surface tension. When the ZnO filler is used by itself, the liquid droplets remain stuck on the plate at all tilt angles no matter

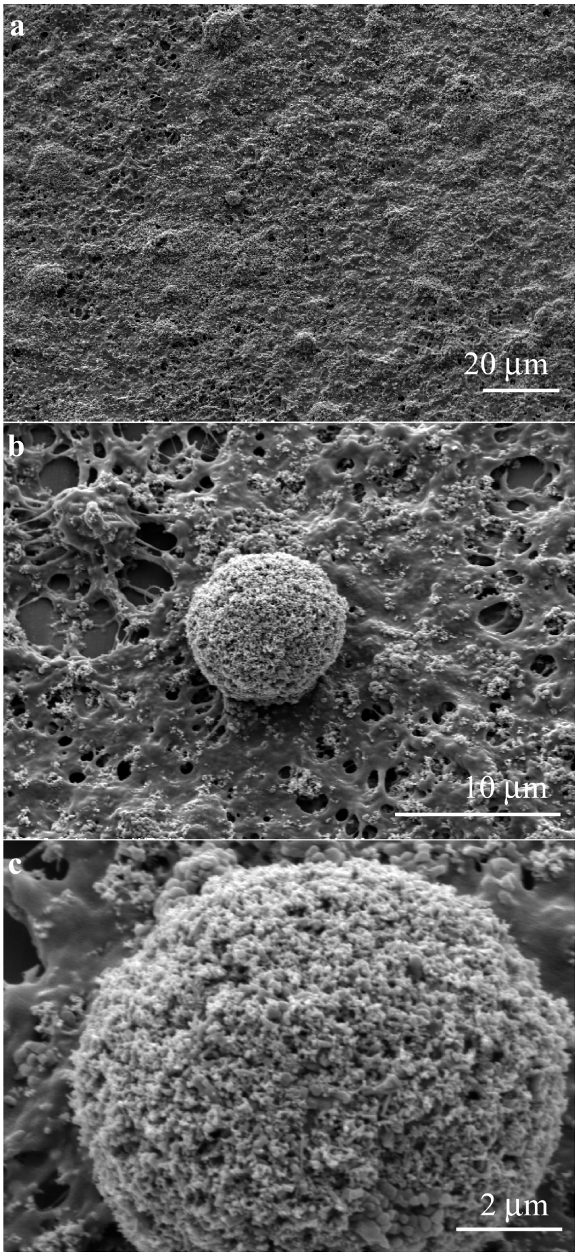

FIGURE 4. Morphology of coatings with 2% ZnO + PTFE (50/50 wt %) filler particles. The SEM micrographs correspond to increasing magnification from top to bottom and show hierarchical morphology on clusters. Such a morphology was found to be absent at 2% filler content when using ZnO or PTFE particles individually (not shown).

Table 2. Roll-off Angle for Coatings Measured with Water and a Water + IPA Mixture (90/10 wt %) Droplets[a]

	roll-off angle (deg) for the indicated filler type					
	PTFE		ZnO		PTFE + ZnO (50/50 wt %)	
filler content (%)	water	water + IPA	water	water + IPA	water	water + IPA
2	S	S	S	S	S	S
4	35 ± 6	S	S	S	S	S
6	9 ± 3	S	S	S	6 ± 1	S
8	7 ± 2	S	S	S	5 ± 2	S
10	3 ± 2	69 ± 12	S	S	11 ± 2	S
12	2 ± 1	21 ± 2	S	S	7 ± 2	S
14	2 ± 1	13 ± 4			8 ± 3	S
16	2 ± 1	14 ± 3			3 ± 2	S
20	2 ± 1	10 ± 3				

[a] S indicates that droplets remained stuck to the coated surface at all tilting angles up to 180°.

how much ZnO filler is used. For coatings with the combined PTFE + ZnO filler, the drops of water + IPA remain stuck to the surface at all angles, whereas water droplets with higher surface energy slide at 6% or higher particle content, further confirming that lower surface tension liquids provide a more stringent liquid repellency test.

The clear distinction between the roll-off angles of water + IPA droplets for coatings with PTFE filler alone from the coatings with PTFE + ZnO filler can be rationalized in terms of a transition between the Cassie–Baxter state (droplet supported on the asperities of the rough surface with air trapped underneath) and the Wenzel state (liquid penetrates the asperities of the substrate). The transition from the Wenzel to the Cassie–Baxter state should be observed if the true (Young's) contact angle satisfies the condition (3a, 18)

$$\theta > \theta_c, \quad \text{with } \cos\theta_c = -\frac{1-\phi_s}{r-\phi_s} \qquad (1)$$

The symbol r denotes the surface roughness factor, defined as the ratio of the rough surface area to its smooth projection (naturally $r > 1$), while ϕ_s denotes the fraction of the solid surface upon which the droplet rests ($\phi_s < 1$). For very rough surfaces, $r \gg \phi_s$; therefore, eq 1 indicates that the cosine of the critical angle scales as $-1/r$. For hydrophobic surfaces ($\theta > 90°$), as roughness r increases, the critical angle θ_c is reduced, which makes the Cassie–Baxter state the most probable at these conditions (causing a transition from the Wenzel to the Cassie–Baxter state). However, for a given roughness r (i.e., fixed $\cos\theta_c$), if we reduce Young's angle of a liquid on a substrate by either increasing the surface energy of the solid (by adding hydrophilic particles, e.g., ZnO) or decreasing the surface tension of the liquid (by adding IPA to water), we could observe a transition from the Cassie–Baxter to the Wenzel state with an associated loss of roll-off (as the data in Table 2 indicate). The reverse is also true; i.e., an increase in the liquid surface tension or a decrease in the solid surface energy may result in a transition from the Wenzel to the Cassie–Baxter state, with an associated decrease in the roll-off angle. The above argument is consistent with the lack of sliding of water + IPA droplets on coatings containing PTFE + ZnO fillers, which should have a relatively higher surface energy compared to coatings with only PTFE.

The above interpretation could also explain the sudden decrease in the water + IPA contact angle for coatings with pure ZnO fillers when particle concentrations are increased from 6% to 8% (Figure 3b). With increased ZnO content, the roughness r should go up, as should the surface energy of the coated substrate. Increased roughness reduces the value of θ_c (eq 1). Simultaneously, increased solid surface energy reduces the value of Young's angle. As manifested through the reduction in the contact angle from 6% to 8% ZnO in Figure 3b, it seems that the reduction in Young's angle under these circumstances is more severe than the reduction in θ_c, which according to eq 1 indicates a transition from the Cassie–Baxter to the Wenzel state. This does not allow droplets to roll down the inclined substrates, as indicated by the ZnO data in Table 2.

The durability of the present coatings was tested by a manual peeling of a high tack 3M tape (3M 396 Super Bond Film Tape) applied on the coatings. The video included with the Supporting information is for a coating containing 12 wt % PTFE + ZnO filler particles and demonstrates that the peeled tape removed only a small fraction of the coating. The superhydrophobic property was not lost after repeated tape-peeling tests. This outcome provides empirical confirmation of the durability of the present coatings. The video also shows that peeling of a layer of the nanocomposite coating only slightly affects the roll-off angle, changing it from ~2° to ~8°. This clearly demonstrates the high adhesion of the present coatings, in addition to their self-cleaning ability and superhydrophobicity. The video also shows some coated fabric samples, which confirms the versatility of the present method in terms of not being substrate-limited. In principle, any substrate that is not attacked by the organic solvents (DMF and acetone) can be coated with the formulation presented here.

IV. CONCLUSION

A wet-processed synthetic approach has been developed to deposit liquid-repellent PVDF/PECA coatings with self-cleaning ability and high adhesion on metal substrates; the approach is scalable to large-area applications. The technique incorporates polymer blends in solution along with particle fillers that contribute to liquid repellency by lowering the surface energy and imparting hierarchical micro/nanoscale texture, a necessary requirement for high liquid repellency. The composite coatings were applied on aluminum foil by spray-casting PVDF/PECA blend solutions in DMF/acetone containing submicrometer-sized PTFE (hydrophobic), nanosized ZnO (hydrophilic), or their combinations. The sprayed films were heat treated at 125 °C for less than 1 h to eliminate the liquid organic content. Contact angles and roll-off angles were reported for droplets of pure water and water with IPA (9:1 weight ratio) mixtures. The coating wettability ranged from partially hydrophilic to superhydrophobic. The coatings sustained their repellent ability even after been subjected to tape-peeling tests.

The present results clearly show that coating morphology, hydrophobicity, and self-cleaning ability are tunable by adjusting the particle filler composition in the sprayed solution. Furthermore, extreme liquid repellency in the present method results from low-cost wet-processing steps (spraying and drying) in the absence of costly instrumentation (e.g., lithographic, plasma processing, vacuum technology, etc.). To this end, the present results have important ramifications for practical applications where large-area super-repellent coatings are required.

Supporting Information Available: Video demonstrating the spray application of a coating containing both PTFE and ZnO filler particles on an aluminum substrate, the heat cured coating undergoing peel tests to show its durability, roll-off of water droplets on inclining coated and uncoated surfaces, and the same coating also applied on a hydrophilic woven fabric, which becomes super-repellent after coating. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Koo, J. H. *Polymer Nanocomposites Processing, Characterization, and Applications*; McGraw-Hill Co., Inc.: New York, 2006.

(2) Koch, K.; Bhushan, B.; Barthlott, W. *Prog. Mater. Sci.* **2009**, *54*, 137–178.

(3) (a) Quere, D. *Rep. Prog. Phys.* **2005**, *68* (11), 2495–2532. (b) Li, X. M.; Reinhoudt, D.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 1529–1529. (c) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. *Soft Matter* **2008**, *4*, 224–240.

(4) (a) Tuteja, A.; Choi, W.; Ma, M. L.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* **2007**, *318* (5856), 1618–1622. (b) Steele, A.; Bayer, I.; Loth, E. *Nano Lett.* **2009**, *9*, 501–505.

(5) (a) Soeno, T.; Inokuchi, K.; Shiratori, S. *Appl. Surf. Sci.* **2004**, *237*, 543–547. (b) Zhai, L.; Berg, M. C.; Cebeci, F. C.; Kim, Y.; Milwid, J. M.; Rubner, M. F.; Cohen, R. E. *Nano Lett.* **2006**, *6*, 1213–1217.

(6) Xia, F.; Jiang, L. *Adv. Mater.* **2008**, *20*, 2842–2858.

(7) Tiwari, M. K.; Bayer, I. S.; Jursich, G. M.; Schutzius, T. M.; Megaridis, C. M. *Macromol. Mater. Eng.* **2009**, *294*, 775–780.

(8) Kim, S. H. *J. Adhes. Sci. Technol.* **2008**, *22*, 235–250.

(9) Bayer, I. S.; Megaridis, C. M. *J. Fluid Mech.* **2006**, *558*, 415–449.

(10) Pierce, E.; Carmona, F. J.; Amirfazli, A. *Colloids Surf., A* **2008**, *323*, 73–82.

(11) Manoudis, P. N.; Karapanagiotis, I.; Tsakalof, A.; Zuburtikudis, I.; Panayiotou, C. *Langmuir* **2008**, *24*, 11225–11232.

(12) Bayer, I. S.; Tiwari, M. K.; Megaridis, C. M. *Appl. Phys. Lett.* **2008**, *93*, 173902.

(13) *CRC Handbook of Chemistry and Physics*, 86th ed.; Taylor & Francis: New York, 2005.

(14) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–995.

(15) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546–551.

(16) Gao, L. C.; McCarthy, T. J. *Langmuir* **2007**, *23*, 3762–3765.

(17) (a) Nosonovsky, M. *Langmuir* **2007**, *23*, 9919–9920. (b) Marmur, A.; Bittoun, E. *Langmuir* **2009**, *25*, 1277–1281.

(18) (a) Bico, J.; Thiele, U.; Quere, D. *Colloids Surf., A* **2002**, *206*, 41–46. (b) Patankar, N. A. *Langmuir* **2004**, *20*, 7097–7102.

AM900894N