Superhydrophobic and conductive carbon nanofiber/PTFE composite coatings for EMI shielding

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This paper presents a solvent-based, mild method to prepare superhydrophobic, carbon nanofiber/PTFE-filled polymer composite coatings with high electrical conductivity and reports the first data on the effectiveness of such coatings as electromagnetic interference (EMI) shielding materials. The coatings are fabricated by spraying dispersions of carbon nanofibers and sub-micron PTFE particles in a polymer blend solution of poly(vinylidene fluoride) and poly(methyl methacrylate) on cellulosic substrates. Upon drying, coatings display static water contact angles as high as 158° (superhydrophobic) and droplet roll-off angles of 10° indicating self-cleaning ability along with high electrical conductivities (up to 309 S/m). 100 μm-thick coatings are characterized in terms of their EMI shielding effectiveness in the X-band (8.2–12.4 GHz). Results show up to 25 dB of shielding effectiveness, which changed little with frequency at a fixed composition, thus indicating the potential of these coatings for EMI shielding applications and other technologies requiring both extreme liquid repellency and high electrical conductivity.

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1. Introduction

Electrostatic dissipation, microwave absorption and electromagnetic interference (EMI) shielding of sensitive electrical/electronic circuitry and devices, antenna systems, aerospace and military equipment (e.g. lightning-protection aircraft composite panels), stealth technology, radar absorbing materials, avionics line replaceable unit (LRU) enclosures, etc., are just few of many technologies where metal-based materials have been considered almost exclusively to this date. Flexible and lightweight, electrically-conducting, polymer-based coatings have tremendous potential for such technologies, as recent studies indicate [1–6]. Added functionalities, such as chemical inertness and water repellency, further contribute to the value of polymer-based coatings by preventing contamination and corrosion when exposed to outdoor conditions.

The first report of superhydrophobic, conductive, polymer-based coatings was made by Zhu et al. [7] who electrosprun stable, polyaniline/polystyrene, large-area films well suited for corrosive environments. The conductivities of these films are too low (10–2 S/m) for EMI shielding. Han et al. [8] created transparent, conductive and superhydrophobic films using carbon nanotube/silane sol solutions. Their high-quality nanotubes (3–5 nm dia.) raise the cost of these coatings. Luo et al. [9] used solution processing and vacuum filtering to produce superhydrophobic carbon nanotube/nanofiber composite films with conductivities up to 1700 S/m, which were maintained even after 1000 bending cycles. However, since the films were formed on the filtration membranes, their transfer and adherence to other surfaces might pose challenges. Meng and Park [10] applied transparent, conductive, superhydrophobic films on glass using fluoropolymer grafted multiwall carbon nanotubes. The high quality of the carbon nanotubes does not classify their process as low-cost. Zou et al. [11] synthesized polymer-based superhydrophobic coatings with very high conductivities in the range 3 × 10−3 – 104 S/m (as compared to 6 × 10−3 S/m for Ag); these coatings were created by a one-step solution casting process that involved a carbon-nanotube-conjugated block copolymer dispersion. Attractive features of this method included the ability to apply on various substrates ranging from glass and silica wafers, to metals, fabrics or even paper. However, the higher cost of the carbon nanotubes (10–20 nm dia.) hinders scale-up to large-area applications.

While electrical conductivity of superhydrophobic polymer-based coatings/films has been measured in the sporadic works [7–11] published in this area, and the potential of such materials...
has been mentioned [8,11] in conjunction with EMI shielding, no study exists on EMI shielding properties of super-repellent, polymer-based films. Since the EMI shielding effectiveness of a material depends not only on its conductivity but also its permeability [4], EMI shielding does not correlate directly with conductivity. Furthermore, EMI shielding effectiveness varies with frequency [12], thus requiring EMI measurements to be performed over a frequency range or the entire spectrum, when necessary. In response to the need for defining the EMI shielding effectiveness of novel superhydrophobic and conductive, polymer-based films, the present study examines water repellent, composite coatings comprising of carbon nanofiber/PTFE fillers dispersed in a hydrophobic polymer matrix and applied by spray. The work utilizes only solution-processable, commercially available, raw materials, and is therefore inherently low-cost. Water droplet sessile contact angle, roll-off angle and electrical conductivity measurements are performed on coatings applied on glass microscope slides. EMI shielding measurements are performed over the range 8.2–12.4 GHz (X-band) on identical coatings applied on cellulose paper substrates, which in their uncoated state, have typical thickness of ~100 μm. The underlying hypothesis is that coatings deposited on either glass or paper have similar properties and structure when applied under identical conditions.

2. Experimental

A solution blend of poly (vinylidene fluoride) (PVDF) and acrylic poly (methyl methacrylate) (PMMA) forms the composite polymer matrix, which has a good degree of hydrophobicity and interfacial adhesion properties. PVDF with its environmental durability, hydrophobicity and electroactivity, combined with its chemical inertness, is an ideal choice for the hydrophobic component in the binder polymer, while adhesion and particle dispersion is imparted by the acrylic PMMA. PMMA on its own generally forms brittle coatings with much lower mechanical flexibility and stress bearing capacity [13]. Sub-micron PTFE particles are used as hydrophobic fillers to tune the coating microstructure and reduce surface energy [14], whereas the electrical conductivity is manipulated using heat-treated, vapor-grown carbon nanofibers (CNFs) [15,16].

To prepare the composite coatings, 60/40 wt.% solution blends of PVDF (530 kDa; Sigma–Aldrich, USA) in Dimethylformamide (DMF) and PMMA (996 kDa; Sigma–Aldrich, USA) in acetone were mixed first. CNFs (average fiber dia. 100 nm, PR24 XT-HHT Pyrograft III; Applied Sciences Inc., USA) and sub-micron PTFE particles (average dia. 260 ± 54.2 nm; Sigma–Aldrich, USA) in dispersions were added as fillers to create sprayable solutions which, after application on glass and cellulose substrates, were heat-dried at 90 °C for 1.5 h to remove any residual solvent. The CNFs are free of CVD carbon with highly graphitized structure developed by high temperature treatment, resulting in higher electrical and thermal conductivity compared to as-grown fibers [17]. The composite films were superhydrophobic and had electrical conductivities spanning over six orders of magnitude for the following weight composition range: Polymer matrix/PTFE/CNF 1/576/0.068–1.1. A more detailed description of the suspension preparation and coating application is provided in Supplemental material section.

The dried coating thickness was measured using an optical microscope calibrated for depth measurement (top vs. bottom of the coating). At least three different thickness measurements at different locations were performed on each sample to assess point-to-point thickness uncertainty. Typical coating thickness was near 100 μm. The electrical conductivity of the coatings applied on glass slides was measured using a Keithley 6517 electrometer/ammeter and the two-probe method. The coating areas slanted for contact with the measuring probes were coated with a conductive silver paint to ensure good electrical contact. A Lab-view based program was used to generate I–V curves and extract the electrical resistance of the coatings, which was then used to determine conductivity using the measured values of the coating thickness, width and length. Electrical conductivity of the coatings rose with CNF loading. Water droplet contact and roll-off angle measurements were performed using an in house goniometer-type optical setup described previously [14].

3. Results and discussion

Fig. 1 shows the results of wettability tests and conductivity measurements for composite coatings with different CNF loadings expressed in terms of CNF/polymer weight ratio. As shown in Fig. 1a, static water contact angles for all CNF loadings remained above 150°. At the maximum CNF loading of 1.1, contact angle reached a value of 158°. It is worth noting that the corresponding contact angle for CNF-free coating was 158° (see Fig. S1), which indicates that super-repellency is not contingent on the presence of CNFs. As Fig. 1b indicates, water droplet roll-off angles for all CNF loadings remained close or below 10°, confirming the self-cleaning water repellent nature of these coatings. Self-cleaning is promoted by low roll-off angles when the water droplet carries impurities off the tilted surface.

As expected, Fig. 1a shows an increase in conductivity of the composite coatings with rising content of conductive CNFs. It can be seen that the electrical percolation threshold for the coatings falls within the 0.068–0.138 CNF loading range, which corresponds to CNF content of 1–2 wt.%. This range is well below the theoretical values calculated for spherical particle fillers [18]. The reason for this difference is the high aspect ratio of CNFs [19]. This figure also delineates the required electrical conductivities for three different applications of conductive coatings using two horizontal lines [20]. EMI shielding requires the highest conductivity (top) band. Various electronic products require protection of their internal circuitry and magnetic memory based components (microchips or ICs) from interference of outside electromagnetic fields. Materials with higher values of conductivity can block incoming EM waves more effectively. On the other hand, for electrostatic dissipation (lowest band in Fig. 1a), lower conductivities suffice to reduce charge accumulation on insulator surfaces to avoid damage through electrostatic discharge. As far as electrostatic painting is concerned, this is a process in which materials of moderate to high conductivity (middle band in Fig. 1a) are deposited on substrates by electrostatic attraction. Corrosion resistant and conductive lightweight polymer coatings in the automobile industry offer one such example. The conductivity values achieved by these coatings are above the electrostatic dissipation range and can reach into the EMI shielding range; metals can be painted using this process.

It is clear from Fig. 1a that CNF loading can be used as a tuning parameter to vary conductivity of the coatings by more than five orders of magnitude without compromising superhydrophobicity. A maximum conductivity value of 309 S/m was obtained for coatings with CNF loadings around 1. This underscores the potential of such coatings for numerous applications, and especially EMI shielding.

Fig. 2 shows scanning electron micrographs of the surface morphology of the composite coatings for the two extreme CNF loadings studied (a–b 0.068, c–d 1.1). In both cases, good dispersion of PTFE particles and CNF was achieved within the polymer blend matrix. As mentioned earlier, more than 15-fold increase in CNF loading did not alter the degree of superhydrophobicity of the coatings (see Fig. 1a), although their surface morphology was altered from predominantly PTFE clustered spheres with some CNF...
strands to a mix of PTFE spheres and nanofibers (compare Fig. 2b and d). No phase separation or segregation of the particles is observed even for the highest CNF loading. Moreover, micro to nanoscale surface features are preserved in both cases. The main factor responsible for the good dispersion of PTFE and CNF, as well as the preservation of the rough surface features responsible for water repellency is the existence of the PVDF/PMMA polymer blend matrix. Individually, PVDF is a low-interfacial-energy inert polymer, hence particle dispersion within PVDF is rather challenging. Use of pristine PMMA polymer, on the other hand, can result in coatings with brittle and flaky structure and morphology [21] although PMMA is compatible with the filler particles due to its high interfacial energy. To this end, the 60/40 PVDF/PMMA blend was found to be optimal for maintaining a good degree of filler dispersion and high hydrophobicity.

The EMI shielding effectiveness of the coatings was measured through S parameter measurements in a two-port configuration [22] (see Fig. S2) using an HP 8719D vector network analyzer (VNA) with operating range 50–13.5 GHz. An in house assembly consisting of two opposing WR-90 waveguides coupled together to fully encase one coated sample at a time was used to evaluate the EMI shielding performance of the coatings (Fig. S3). The capability of a thin planar barrier (coating in the present case) to shield from electromagnetic waves is measured in terms of its signal attenuation, defined [23] as

\[ 10 \log \left( \frac{P_i}{P_r} \right) = 20 \log \left( \frac{E_i}{E_r} \right) \text{[dB]}, \]

where \( P_i \) is the incident power on one side of the barrier and \( P_r \) is the power transmitted through the barrier to the other side. The power ratio may also be expressed in terms of the ratio of the magnitudes of the incident electric field \( E_i \) and transmitted electric field \( E_r \) by assuming that the fields are plane waves. Moreover, this same ratio can be expressed in terms of the ratio of voltages associated with the ports of an appropriate network, and thus be determined through S parameter measurements [24]. In general, systems that carry electromagnetic waves may be given a simpler description by treating them as networks and focusing only on the exchange of electromagnetic energy at their ports. According to Eq. (1), which
is specific to transmission, the lower the value in decibels, the higher the signal attenuation, and in turn, the higher the shielding effectiveness of the barrier. A similar expression to Eq. (1) can be defined for signal reflection, which is also studied in this work.

The S parameter measurements for coatings with different CNF loadings were made as described in Supplementary material section (Figs. S2 and S3) and are shown in Fig. 3. $S_{11}$ quantifies reflection from the coatings, while $S_{21}$ quantifies transmission through them. Through these measurements, it was observed that the 2-port network under test is reciprocal, i.e., $S_{11} = S_{22}$ and $S_{12} = S_{21}$, which means that the EMI shielding effect of the present composite coatings is similar at their front or back side. In order to confirm the repeatability of the tests, S parameter values were measured for different coated samples (batches) prepared with the same CNF loading. Batch-to-batch variations for S were found to be within 10% (see Fig. S4).

S parameter values can be used to calculate the transmitted and reflected power as a percentage of input wave power in the two-port configuration. The average reflected and transmitted power output (percent of input power) for different coatings with varying CNF loading are thus plotted in Fig. 4, which indicates that as CNF loading rises, the reflected power output rises, hence the absolute value of $S_{11}$ decreases. This is evident from the values of $S_{11}$ in Fig. 3a–f. When reflected power increases, it automatically lowers transmission, as absorption by these very thin coatings is expected to be negligible. This is confirmed by the increasing absolute value of transmission parameter $S_{21}$ at higher CNF loadings in Fig. 3.

$S_{21}$ (in dB) is the negative shielding effectiveness of the coatings and increases in absolute value with increasing CNF loading, see Fig. 3. The maximum attenuation achieved through the present coatings is ~25 dB in the measured frequency range of 8.2–12.4 GHz (used by many radar systems) for coatings with CNF loading of 1.1 (highest). The percentage transmitted power drops from nearly 100% to 0.5% as CNF loading is increased from 0.068...
An important outcome of the measurements drawn in Fig. 3 is that both transmission and reflection parameters $S_{11}$ and $S_{21}$ remain fairly flat in the frequency range 8.2–12.4 GHz. This indicates that the present coatings are equally effective in shielding over this entire frequency range.

### 4. Conclusion

We describe fabrication and characterization of superhydrophobic, carbon nanofiber/PTFE-filled polymer composite coatings with high electrical conductivity. The polymer matrix was a PVDF/PMMA blend, which, even in the absence of particle fillers displayed a good degree of hydrophobicity, interfacial adhesion and flexibility. The electrical conductivity of the coatings was tuned by varying CNF loading, and reached up to 309 S/m without sacrificing self-cleaning water repellent ability. We report the first measurements on EMI shielding effectiveness of superhydrophobic, conductive polymer-based coatings over the X-band (8.2–12.4 GHz). Shielding values as high as $\frac{C24}{25}$ dB (with a corresponding transmission power of only $\frac{C24}{62}$%) were obtained for coating thickness under $\frac{C24}{256}$ lm. For fixed coating composition, the shielding level remained relatively flat over the entire frequency range considered herein. Our results indicate the potential of the present coatings not only for EMI shielding applications, but also for other technologies requiring extreme liquid repellency and high electrical conductivity simultaneously. The synthesis method is attractive because it allows additional functionalities, as required by specific applications, without sacrificing superhydrophobicity.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.09.017.

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