



# Electrically conducting superhydrophobic microtextured carbon nanotube nanocomposite



Paul O. Caffrey, Mool C. Gupta\*

Department of Electrical & Computer Engineering, University of Virginia, Charlottesville, VA 22904, USA

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## ABSTRACT

We report a simple and inexpensive method of producing an electrically conductive superhydrophobic polymer surface by adding multiwall carbon nanotubes directly into the polymer poly(dimethylsiloxane) (PDMS) matrix and replicating micro/nanotexture using a replication master prepared by ultrafast-laser microtexturing process. No additional coatings on conducting PDMS are required to achieve water contact angles greater than  $161^\circ$ . The conductivity can be controlled by changing the percent MWCNT added to PDMS and at a bulk loading of 4.4 wt% we report a conductivity improvement over pure PDMS by a factor of more than  $10^{11}$  with electrical resistivity  $\rho = 761 \Omega \text{ cm}$ . This combined behavior of a conductive, superhydrophobic nanocomposite has exciting applications for allowing a new class of enclosures providing EMI shielding, water repellency and sensing to provide built-in temperature feedback. The effect of temperature on the nanocomposite was investigated and a negative temperature coefficient of resistance ( $-0.037 \Omega/\text{K}$ ) similar to that of a thermistor was observed.

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## 1. Introduction

With the rapid growth of high-speed electronic devices operating in the 1–10 GHz frequency range, especially computing equipment, there is an ever-increasing need for effective electrical shielding both for and from this sensitive equipment. The Federal Communications Commission (FCC) specifically regulates emissions in the range 30 MHz–5 GHz [1,2] and since space, shape and weight are primary design factors in this class of equipment the enclosures tend to be created from polymer materials [3]. Traditionally EMI shielding is provided to an enclosure by adding a layer of metal foil either inside the enclosure or embedded as a layer in the polymer [4]. Other methods include bulk loading of conductive particles into the polymer matrix or the addition of a conductive finish coating [3,4]. More and more these devices are required to operate in harsh environments where the sensitive devices may be exposed to water. There has been work done on the use of conductive nanomaterials [5–7] for EMI shielding and structural applications [8] but there is a need for a light weight material that is not only electrically conducting, but also has superhydrophobic properties. Recently Wang et al. [9,10] and Madeani et al. [11] demonstrated the addition of MWCNTs in

PDMS to produce a superhydrophobic nanocomposite. Zhao et al. [12], Talaemashhadi et al. [13] and Bayer et al. [14] have also reported electrically conductive superhydrophobic materials based on MWCNTs embedded in copolymers. Yao et al. [15] reported electrically conductive superhydrophobic films based on functionalized MWCNTs. Park et al. [16] demonstrated replication of a complex surface using PDMS-MWCNT nanocomposite with superhydrophobic and conductive properties.

Conductive polymer materials typically have a positive temperature coefficient (PTC) of resistance and there has been interest in these materials due to the potential for self-regulation of temperature [17]; however the nanocomposites demonstrated in this work displays a negative temperature coefficient (NTC) of resistance similar to that of a thermistor. A thermistor is a thermally sensitive resistor [18] and can be fabricated from PTC materials such as platinum film, metals such as platinum being used because of their linear temperature coefficient of resistance over a wide temperature range [18]. It is more typical to fabricate thermistors from NTC semiconductor based materials [19] as these typically have a larger temperature coefficient of resistance and can be made at very low cost. These NTC devices find uses in many circuits where temperature compensation is required [19]. The operating premise of a NTC thermistor [18,20] is that as temperature rises more electrons are promoted into the conduction band and the resistance to current flow decreases. Little or no suitable explanation for NTC [21] nanocomposites materials has been suggested especially where the

\* Corresponding author.

E-mail address: [mgupta@virginia.edu](mailto:mgupta@virginia.edu) (M.C. Gupta).

**Table 1**  
MWCNT products.

Product	Length ( $\mu\text{m}$ )	Diameter (nm)	Structure	Packing Density ( $\text{g}/\text{cm}^3$ )	Resistivity at 1 wt% ( $\Omega\text{ cm}$ )
PD15L15-20	15–20	15	Hollow	0.032	$7 \times 10^4$
BPD30	20	30	Bamboo	0.025	$3 \times 10^4$
PD30	20	30	Hollow	0.070	$>2 \times 10^{16}$
PD15L1-5	1–5	15	Hollow	0.100	$>2 \times 10^{16}$

NTC occurs below or in absence of a PTC region as nanocomposites have been shown to have a NTC area at high temperature beyond their normal operating region [21].

Lee et al. [21] explores the effect of adding multi walled carbon nanotubes (MWCNT) to a polyethylene Carbon Black (CB) nanocomposite concluding that the addition of 0.5% MWCNT stabilized the positive temperature coefficient (PTC) response of the nanocomposites. Indeed the response seen by Lee et al. [21] shows a marked flattening of the response up to the PTC threshold indicating a negative temperature coefficient component added by the addition of the MWCNT. Zhang et al. [22] surveys the literature for explanations for both PTC and NTC phenomena concluding that although there is no conclusive theory that the most widely accepted explanation is based on the tunneling effect where electron tunneling occurs across the gaps between the nanotubes and the changes in resistivity occur due to the different thermal coefficients of expansion between the polymer matrix and the nanotubes. The polymer material we have used, PDMS and nanomaterial, MWCNTs, have a large difference in the coefficient of thermal expansion (CTE), PDMS CTE is given as 310 ppm/K [23,24], the CTE for MWCNT is in the range 16–26 ppm/K [25–27]. This difference in CTE of over an order of magnitude may indeed account for the strange behavior of NTC when compared with other polymer nanocomposites. Looking again at Zhang et al. [22] the polymer is polyethylene with a CTE of 180–200 ppm/K and the nanoparticles used are Carbon black nanoparticles which have a low aspect ratio. In fact, Wei et al. [28] found using molecular dynamics (MD) simulations that the addition of CNT to the polymer matrix caused an increase of 18% to the CTE. Yi et al. [29] presents a method for eliminating the NTC and discusses an operating theory for explaining the NTC where it is seen in a nanocomposites after the PTC. In another paper [30] Yi et al. show that polyethylene composites of vanadium suboxides ( $\text{V}_2\text{O}_3$  and  $\text{VO}_2$ ) exhibit strong NTC effects over a wide range of temperatures.

Recently poly(dimethylsiloxane) (PDMS) as a material for manufacturing devices on the micron scale has attracted much attention [31–33] due to the simplicity of the fabrication processes. The addition of carbon nanotubes as a filler for PDMS had become popular in the field of micro-electromechanical systems (MEMS) [33,34]. Our earlier work [35] explored the superhydrophobic properties of PDMS with replicated surface microtexture [36]. The use of other polymers combined with carbon nanotubes has also been investigated for their use in producing superhydrophobic conductive nanocomposites. Luo et al. [37] constructed a nanocomposite using nafion and carbon nanotubes that exhibits a high contact angle ( $\text{CA} = 165^\circ$ ) and high electrical conductivity ( $1600\text{ S m}^{-1}$ ). Nafion is a perfluorosulfonated polymer with similar properties to Teflon [37,38]. The highest contact angle Luo et al. reported was at a loading of 90.2% CNT with the polymer nafion accounting for 9.8% of the weight. Luo et al. also found that increasing the nafion content above 9.8% decreased the contact angle and that the nanocomposite was no longer superhydrophobic, with a contact angle of  $149.5^\circ$  at a nafion loading of 21.0 wt%. It should be considered that Luo et al. are producing a thin film rather than a bulk material. Comparing the process above to our earlier superhydrophobic work [35] from a practical perspective, nafion is special polymer

currently used in the production of fuel cells and is relatively expensive [39] compared to PDMS [40]. Also, loading levels in Luo et al. [37] require greater than 41 wt% CNT. We now build on our earlier work [35] to encompass PDMS composites with various amounts of MWCNT loading to provide electrical conductivity along with superhydrophobic properties. This will fill the need outlined above for a superhydrophobic conductive nanocomposite with low loading of CNT ( $\sim 5$  wt%) that will have wide applications in many industries.

## 2. Experimental

### 2.1. Materials

PDMS was obtained from Ellsworth Adhesives (Dow Corning Sylgard 184 Silicone Encapsulant). Carbon nanotubes of dimensions outlined in Table 1 were obtained from NanoLab Inc. (PD15L15-20, BPD30, PD30, and PD15L1-5). Agitation was accomplished using an ultrasonic processor (Qsonica Q500) and a small 3.8 V dc motor. Volume and surface resistivity measurements were made using a Keithley 6105 Resistivity Adapter and for current measurements either a Keithley 616 Digital Electrometer (p-Ammeter) or a UNI-T UT803 Multi-meter ( $\mu$ -Ammeter). Voltage measurements were made using a Fluke 8012A Multi-meter. Voltage was applied using either a Keithley model 240 High voltage DC supply for voltages over 30 V and for less than 30 V, a Mwtech HY3005A DC Power supply was used. For replication of the microtextured surface, a Ti master was fabricated. The self-assembled microtexture was obtained through the direct laser processing method, and the details and the novelty of this self-assembled technique and the fabrication process can be found in the following Refs. [41–43].

### 2.2. Preparation of MWCNT-PDMS nanocomposites

The PDMS used is a two-part polymer comprised of a base and a hardener and is mixed together at a 10:1 ratio. The MWCNTs are added to the base and must be mixed such that the MWCNT are distributed uniformly. Several methods of agitation were investigated; agitation using an ultrasonic agitator was first attempted but it was found that the solution mixture heated up significantly and became viscous resulting in premature curing. Hand mixing using a glass rod was also attempted but the resulting electrical resistances of the samples were not sufficiently low due to the fact that we were unable to increase the bulk loading to more than 3 wt%. In another method MWCNTs were mixed in toluene, and then added the resulting suspension to a toluene diluted PDMS solution similar to Liu et al. [34] a bulk loading of 2 wt% was the limit for this method. The method that was found to be most effective was simple mechanical stirring with a low RPM dc motor and using this method we were able to reach a bulk loading of 4.4 wt% and relatively high electrical conductivity.

For the fabrication of the nanocomposite, 20 g PDMS base was measured in a 50 ml flask. MWCNT was added to achieve the desired weight percent bulk loading and the resulting mixture was agitated for one hour to achieve a uniform mixture. Two grams of PDMS hardener was then added and stirred for five minutes. Ten grams

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