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Research paper

# Simple fabrication of a multiwall carbon nanotube – elastomer composite with a rough surface and its application in force sensing

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ABSTRACT

A simple method based on solution casting on a template is presented which allows one to create rough conductive elastomer surfaces incorporating carbon nanotubes. The electrical contact mechanism between the rough elastomer and a hard and smooth conductor is studied in detail with the aim of understanding its increased force sensitivity compared to a flat conductive elastomer surface. For the samples investigated here, the contact area increases in a nonlinear fashion before it saturates at large applied forces, while the electrical resistance decreases nonlinearly with force before saturating. The resistance is found to decrease inversely proportional to the contact area, and changes highly nonlinearly with applied force even in a relatively small dynamic range, which is attributed to the nonlinear dependence of contact area on force. The conductive elastomer can be mounted on a flat or a curved surface, such as a glove, to function as a force-sensitive resistor.

## 1. Introduction

Conductive elastomers composed of a mixture of a polymer matrix and a conductive filler hold promise as multifunctional materials in electronic systems which require stretchable sensors or soft interfaces [1, 2]. Carbon nanotubes [2–5], liquid metal [6] conductive phases have in recent years been investigated intensively as fillers in dielectric elastomers to facilitate low resistivity in systems with different mechanical compliance requirements. Carbon nanotubes have been used extensively as fillers in structured and unstructured elastomer matrices to obtain piezoresistive strain sensors with a range of sensitivities [7–10]. While the properties of long carbon treads have been studied for a long time [11], an enhanced interest in carbon nanotubes occurred after a report published in 1991 [12]. Carbon nanotubes have been proposed for use in environmental monitoring [13], desalination of salt water [14–16], solar cells [17] and as probes for atomic force microscopy [18, 19], to mention a few applications. Multi-walled carbon nanotubes (MWCNTs) exhibit typical conductivities in the range $10^5$–$10^6$ S/m and therefore a metallic character. Their large aspect ratio results in a low percolation threshold when mixed in polymeric matrices [20, 21].

When electrically connecting a conductive elastomer to a traditional hard conductor, one has to take into account both mismatch in mechanical compliance and the contact electrical resistance. Traditionally, the contact resistance is attempted minimized by using an intermediate connection matrix, e.g. a metal paste or a metal, or large pressure. In order to decrease the contact resistance, several techniques such as mechanical polishing [22], plasma treatment [23], acid etching [24] or metallization have been used. Metallization of elastomers is nontrivial, as the metal film may form wrinkles on flat elastomers and tends to form cracks as the strain increases [25]. Considerable progress has been made through control of texture of metal films [26]. Moreover, the detrimental effects of these crack on stretching-dependent conduction to some extent can be relieved using rough dielectric elastomeric surfaces [27], but it is not clear whether the problem can be solved for hard metallic surfaces docking onto soft elastomeric surfaces. Furthermore, in the case that metallic layers are coated onto elastomeric conductors, they may contribute to the observed electrical noise characteristics as cracking occurs. More research is needed to understand and optimize the docking of conducting elastomers and hard conductors.

Elastomers such as polydimethylsiloxane (PDMS), have a range of favorable properties, which have allowed them to be used as waterproof covers for crack-based strain sensors [28], as capacitive oil spill sensors [29] and optical sensor components [30–32], to name a few. For energy harvesting purposes, triboelectric nanogenerators have benefited from the use of soft polymeric surfaces [33–40]. Soft triboelectric generators and sensors may be mounted in shoes or clothes [41–44], and may function as smart skin [34–36]. Conducting solid nanoparticles embedded in an elastomer matrix allow one to form

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stretchable nanocomposites for harvesting energy [45, 46]. Well-defined [47] and randomly structured [48] elastomer surfaces have found use as triboelectric generators for harvesting energy upon contact.

The contact mechanics between insulating elastomers of microstructured surfaces and hard solid surfaces has been reported with the aim of developing skin mountable pressure sensors. Utilizing the entire bulk, through microporous structures, has been found to allow enhanced sensitivity [49]. Also pure surface structuring is of interest. By casting a thin layer of intrinsically conducting polymer [50] or nanotube-protubing [51] PDMS on a regular pyramidal array, highly sensitive pressure-induced changes when pressed against a counter electrode were found [52, 53]. In some cases, it is more economical and simpler to produce rough surfaces [54], leading to wearable piezoresistive sensors [55]. Embedding carbon nanotubes in PDMS allowed a more direct and sensitive surface responsive system for sensitive pressure detection [52]. Such advances demonstrate the applicability of rough-surfaced conducting elastomers in sensing. However, it is also of interest to understand in more detail the contact area and electrical resistance when conducting elastomers dock onto hard conductors, and how this can be used in force sensors.

On the nanoscale, the interaction between surfaces can be obtained using the Surface Force Apparatus [56, 57]. Atomic Force Microscopy can be used to study both the molecular interactions and surface topography on nanoscopic level for a range of materials [58], where considerable research has been done on precise calibration methods required for optimal performance [59, 60]. Furthermore, optical imaging of surface topography and contact area has a long history [61], where recent modern experimental setups have allowed one to study contact mechanics [62] and frictional behavior of rough rubber spheres and glass contacts [63, 64]. Experimental studies of microrough surfaces typically rely on obtaining the surface topology before and after electrical resistance measurements are made, since the electrodes might block the contact area measurements. The author is not aware of studies where one has measured both the contact area and the electrical resistance simultaneously. Here we will attempt to do just that for a conducting elastomer. The surface facing the rough surface elastomer is a hard, transparent indium tin oxide (ITO) electrode that has a surface which is flat on the macroscopic scale (i.e. $> 1$ μm). This allows convenient observation of surface roughness of the conducting elastomer, but not the electrode, using conventional optical reflection microscopy. When the two surfaces come in contact, it is possible to observe how the surface roughness of the soft elastomer complies with the hard ITO surface.

## 2. Materials and experimental setup

The multiwalled carbon nanotubes used here had length 5–9 μm and diameters 110–170 nm (Sigma-Aldrich, 659,258-2 g). Upon mixing with PDMS (Sylgaard 184), a conductive elastomer could be formed. The percolation limit was found experimentally to between 3 and 4%, in agreement with other studies [65]. The conducting elastomer used in this study was made by mixing 6 g Sylgaard 184 (10:1 elastomer to curing agent ratio) with 1 g multiwalled carbon nanotubes. High carbon nanotube content (about 17%) was chosen to ensure that the composite had low resistivity. The mixture of polymer and carbon nanotubes was stirred mildly with a stick for a short period to ensure that it appeared homogeneous. The mixture was cast on Silicon Carbide (SiC) abrasive paper of grit size P180 [66]. The process is shown in Fig. 1a and b. In this manner, we could create flat surfaces (i.e. flat as observed in an optical microscope) or surfaces with well-defined roughness. The surface roughness is defined by the roughness of the abrasive paper used as a template. The elastomer was degassed in vacuum until no air bubbles could be observed ($> 1$ h), and subsequently cured at 110° Celsius for 30 min, obtaining a thickness of 0.8 mm. The solid elastomer was carefully peeled off the abrasive paper. A sharp knife was used to cut sections of the samples into pieces. The cross-section of one of the conducting elastomer samples, as observed by conventional optical microscopy, is shown in Fig. 1c and d. The height variations are typically $< 50$ μm with a standard deviation of 17 μm. Note that Fig. 1 only shows the length scale generated by templating on P180 abrasive paper, and that the nanometer variations associated with the carbon nanotube dimensions are not considered here. That is, only properties on microscale or larger are visualized by conventional optical microscopy.

More detailed images of how the carbon nanotubes are located at the elastomer surface can be seen in Fig. 2. Here, the surface topography was imaged using the InLens of a Scanning Electron Microscopy (Raith eLine) at an acceleration voltage 10 kV and working distance 9.4 mm. A detailed description of microscope adjustment and charging effects using this particular electron microscope has been detailed in Ref. [67]. While, some nanotubes are aligned parallel to the elastomer surface, others are protruding it as seen in Fig. 2b.

While the images in Fig. 2 provide a view of the protruding carbon nanotubes, it was found that the images could not provide reliable information about the roughness statistics. The samples exhibit large variations in length-scale and elasticity. While the elastomer roughness are soft and show length scale variations on the microscale, the carbon nanotubes are hard and feature dimensions from a few nanometers and up to many micrometers. Considerable technical efforts are required to obtain Atomic Force Microscopy images of these very rough and at the same time fine variations exhibiting such large variations in elasticity, and it is not certain whether such data could provide accurate information about the roughness statistics. The profile images taken by scanning electron microscopy could follow some of the individual carbon nanotubes. However, when zooming out to obtain not only the nanoscale, but also the micronscale variations, the build-up of charge increases due to the nonconducting elastomer, thus introducing systematic and nonremovable errors when attempting to do roughness statistics including both conducting and nonconducting areas. The profile optical microscopy images do not provide resolution below the micron scale, but also do not suffer from similar issues as discussed above, and were here selected for their ability to accurately picture the elastomer roughness on the micron scale. Further characterization of the multiwalled carbon nanotubes in order to determine their defects or disorder under stress could be undertaken using Raman spectroscopy [68, 69]. However, such a study is outside the scope of the current work.

Here, the correlation between the electrical properties and the contact area between conducting elastomer and the hard conductor is of interest. Therefore, a novel experimental setup for finding the contact area and resistance was constructed, see Fig. 3. The conducting elastomer sample (3), containing one rough surface (facing P180 while being cured) and one flat surface (facing air while being cured) was mounted on aluminum electrode (2) using adhesive carbon glue. The electrode was mounted on a plastic holder (not shown) for support. The rough surface of the sample was facing a glass slide coated with transparent Indium Tin Oxide (ITO, Sigma-Aldrich 578,274-25PAK) (4).

The surface facing the rough surface elastomer is a hard, transparent indium tin oxide (ITO) electrode that has a surface which is flat on the macroscopic scale (i.e. $> 1$ μm). This allows convenient observation of surface roughness of the conducting elastomer (but not the electrode roughness), using conventional optical reflection microscopy. When the two surfaces come in contact, it is possible to observe how the surface roughness of the soft elastomer complies with the hard ITO surface.

The electrical resistance between the aluminum and the transparent ITO electrodes were measured using a H8118 LCR bridge (5) equipped with HZ184 4-terminal Kelvin test cables. The measurements were taken at a frequency of 1 kHz with an applied voltage of 1 V. It was found that the resistance did not change within the experimental uncertainty from 20 Hz and up to 1 kHz. The voltage was kept low in order to have a low current and no excessive heating of the polymer matrix. Direct contact between the aluminum and the ITO electrodes resulted in