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Physical Properties of Polymers

Preparation, Micro-Patterning and Electrical Characterization of Functionalized Carbon-Nanotube Polydimethylsiloxane Nanocomposite Polymer

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Summary: We present the preparation, improved micro-patterning, and electrical property characterization of COOH- functionalized mutli-walled carbon nanotube (MWCNT) and polydimethylsiloxane (PDMS) conductive nanocomposite polymers that can be employed for lab on a chip applications. The nanocomposites are prepared by mixing functionalized MWCNTs into an uncured PDMS matrix and employing high frequency ultrasonics ($\sim$ 42-50 kHz) using a horn tip probe. The prepared nanocomposites are micromolded using soft lithography techniques down to a feature size of 25 μm against a micropatterned SU-8 polymer master. An array of peg like microstructures have been fabricated with a radii of 25 μm and height of 100 μm, that are embedded on a non-conductive PDMS substrate using novel and improved fabrication techniques. The percolation threshold of the prepared nanocomposite is achieved at 1.5 weight percentage (wt.%) of COOH- functionalized MWCNT in the PDMS matrix. Resistivity levels at 2 wt.% of functionalized MWCNTs are 62 Ω-cm or better, which is an improvement over our previously reported nanocomposite resistivity value of 100 Ω-cm at 2 wt.% of nonfunctionalized MWCNT's in a PDMS matrix. The nanocomposites also have fairly uniform dispersion and no agglomeration of COOH- functionalized MWCNT as shown by SEM analysis. Furthermore, the nanocomposites show a negative temperature coefficient of resistivity (NTCR), making them ideal candidates for micropatternable temperature microsensors for lab on a chip systems.

Keywords: conducting polymers; elastomers; functionalized carbon nanotubes; high frequency ultrasonics; nanocomposite; soft lithography

Introduction

Polymer materials that exhibit high electrical conductivity and/or negative temperature coefficient are of great interest to the microelectronic, microelectromechanical systems (MEMS), and lab-on-a-chip (LOC) communities for packaging, microsensor, and microactuator applications. The integration of conductive tracks or structures in bulk polymers is extremely important for signal routing, interfacing to signal processing electronics, and to power active devices.[1] One polymer of particular interest is polydimethylsiloxane (PDMS). PDMS is a non-conductive silicone based elastomer that has been under special focus for microdevices and systems for over a decade due to its flexibility and ease of micromolding for prototyping. While many passive microfluidic devices have been fabricated by micromolding non-conductive PDMS against SU-8 photopolymer

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masters, including micromixers, microchannels, and interconnect structures for a wide variety of applications for LOC systems,[2,3] the addition of electronic functionality to PDMS-based MEMS and microfluidic systems has lagged behind. It has proven exceptionally difficult to integrate, embed or pattern conducting lines on non-conducting PDMS because of the weak adhesion between PDMS and metals or other conducting polymers.[4] Thus, there is a need to develop PDMS-based micropatternable nanocomposite polymers to alleviate these compatibility problems. Furthermore, characterization of the temperature coefficient of these materials is important for temperature sensing applications, as temperature sensing is extremely important for many LOC applications such as polymerase chain reaction (PCR)[5] and other temperature sensing applications where mechanical flexibility is essential, such as for wearable microsystems, foldable electronics and no-coplanar surface temperature measurements.[6]

Carbon nanotubes dispersed in an insulating polymer matrix are well known to exhibit exceptionally high physical and electrical properties because of quantum size effects.[7] The small size of carbon nanotubes, their high aspect ratio (length to radius ratio), high conductivity, and lower percolation threshold compared to spherical fillers, make them an excellent choice for electrically conducting nanocomposite polymers.

Other researchers have examined conductive nanocomposite polymers of MWCNTs in PDMS for soft (flexible) MEMS applications. However, the percolation thresholds achieved were at weight percentages (wt.%) of 8 wt.%[8] and 10 wt.%,[9,10] which are significantly higher than our reported value of 1.5 wt.%. Until now, very little work has been reported on dispersion techniques, practical microfabrication techniques, and negative temperature coefficient of resistivity of MWCNT-PDMS nanocomposite polymers. In this paper we discuss preparation, novel hybrid microfabrication, dispersion mechanism, and negative temperature coefficient properties of COOH- functionalized MWCNT PDMS nanocomposites.

Previously we have reported the preparation, basic micromolding, and electrical characterization of MWCNT in a PDMS matrix.[11] However, the non-functionalized MWCNTs tended toward agglomeration, which resulted in difficulty in uniform dispersion of MWCNTs in the PDMS matrix. In this work we instead employ COOH- functionalized MWCNTs, which are well known to disperse more easily in a polymer matrix.[12] Although the purchased MWCNTs were COOH- functionalized, some amount clumping or bundling was still observed on initial mixing with PDMS base, and hence, we additionally employed high frequency ultrasonic dispersion method in order to achieve de-agglomeration,[13] leading to better uniformity in dispersion. We also demonstrate an improved micropatterning process than has not been previously reported: hybrid systems composed of micromolded combinations of both conductive nanocomposites with non-conductive PDMS. This improved micropatterning processes enables patterning of conductive nanocomposite structures such as electronic lines or electrodes on a non-conductive flexible substrate. Finally, we examine the temperature coefficient of our materials for potential employment as temperature sensors.

Experimental Part

Materials

Polydimethylsiloxane (Sylgard 184 Elastomer Kit), consisting of a base elastomer and curing agent, were purchased from Dow Corning, USA. Multiwalled carbon nanotubes (MWCNTs) with an average outer diameter of 10nm and length of 30 μm, with COOH- functionalized surfaces, were purchased from Cheap Tubes Inc, USA. SU-8 100 and SU-8 developer were bought from Microchem^{TM}, USA. All the materials were used as purchased.

Fabrication of Conducting Nanocomposite

The electrically conducting MWCNT-PDMS nanocomposites were prepared by first manually stirring and then ultrasonically dispersing COOH- functionalized MWCNTs in the PDMS base elastomer in varying weight percentages (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 and 4.5 wt.%) by using a horn tip VC 750 (Sonics Inc, USA.) programmable ultrasonic processor. The operating frequency was 42 kHz and the ultrasonic processor was operated in pulse mode (10 seconds on and 15 seconds off cycle), which provided mixing by repeatedly allowing the sample to settle back under the probe after each burst. The high frequency ultrasonication process was carried out for 2 minutes, which is much shorter than previous times of several hours needed for non-functionalized MWCNTs.[11] We observed that we needed longer relaxation time than sonication time, as it took approximately 12 to 15 seconds for the sample to settle back after each burst. The curing or crosslinking agent was then added after the ultrasonication process was completed so as not to thermally set the polymer with the heat produced as a result of the the ultrasonication process. The base elastomer and curing agent ratio were 10:1 as recommended by the supplier.[14] Each nanocomposite (of varying wt.%) was then manually stirred for one minute. Calculation of weight percentage takes in to account the curing agent which is added. The prepared nanocomposite samples were each placed into a vacuum chamber to remove air bubbles for 30 minutes.

Micromold Fabrication

SU-8 is a negative tone epoxy-based photoresist that can be photopatterned using deep UV light. SU-8-100 was the chosen material for micromold fabrication as it can be patterned in very thick films (up to 1 mm thick or more)[15] and makes an excellent mold for PDMS. Glass slides 3"x 3" square and 1 mm thick were used as substrates which were first cleaned in 100% Micro 90 Detergent (purchased from International Products Corporation, USA) using ultrasonic agitation for 5 minutes and then rinsed with de-ionized (DI) water, acetone, isopropyl alcohol (IPA) and DI water. Substrates were blow dried using nitrogen followed by dehydration baking for 20 minutes at 120 °C in a convection oven and cooling to room temperature. A 25 nm thick chrome layer was sputtered on each glass substrate which acts as an adhesion promoter for the SU-8 100.[16] A 100 μm thick layer of SU-8 100 was spin coated (at 2250 RPM) on top of the adhesion layer of each substrate, followed by soft baking at 90 °C for 80 minutes and cooling to room temperature. Hole structures were patterned using photolithographic UV exposure through a photomask for 60 seconds. Full crosslinking of the SU-8 100 was achieved by a post-exposure bake at a temperature of 60 °C for 65 minutes (ramp rate: 300 °C/hr) followed by cooling to room temperature. The structural layer on each substrate was then developed in SU-8 Developer (Microchem™) for 90 seconds in an ultrasonic bath. Figure 1 outlines the fabrication steps.

Micromolding

Micromolding was accomplished using standard soft lithography methods as are typically utilized for non-conductive (undoped) PDMS[17] and as we have previously employed for PDMS-based nanocomposites with non-functionalized MWCNTs.[11] However, we now introduce a modified process that enables hybrid systems with combined micropatterned nanocomposite polymers and undoped substrates (Figure 2). The MWCNT-PDMS nanocomposites with different doping levels (i.e., different weight percentages of MWCNTs in the PDMS matrix) were prepared as defined previously in "Fabrication of Conducting Nanocomposite", and poured onto the SU-8 micromolds (a,b) prepared as discussed in the "Micromold Fabrication" section. For each weight-percentage of MWCNTs, the excess PDMS on the SU-8 mold was scraped off using the Damascene-like process with a surgical knife, and then de-gassed to remove air bubbles for 30 minutes (c). The samples

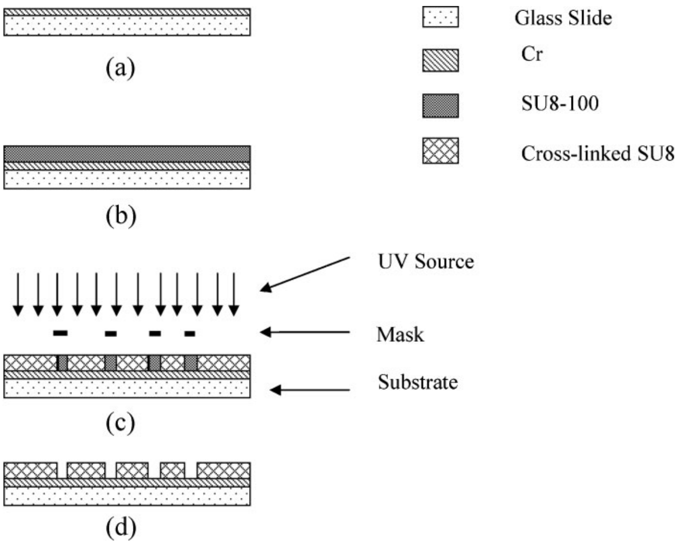

Figure 1.
Fabrication process steps for SU-8 micromold preparation via photopatterning of SU-8 100 epoxy-based photopolymer.

were baked on a hot plate at a temperature of 75 °C for 1 h followed by cooling to room temperature. Undoped PDMS polymer was then poured onto the surfaces of the samples, de-gassed for 20 minutes, and then baked on a hotplate at 75 °C for 1 hour (d). The resulting hybrid structures composed of micropatterned nanocomposite on non-conductive PDMS were then peeled off from the mold and were ready for testing (e). Figure 3 shows example structures of functionalized MWCNT-PDMS microfabricated peg structures on a non-conductive PDMS substrate.

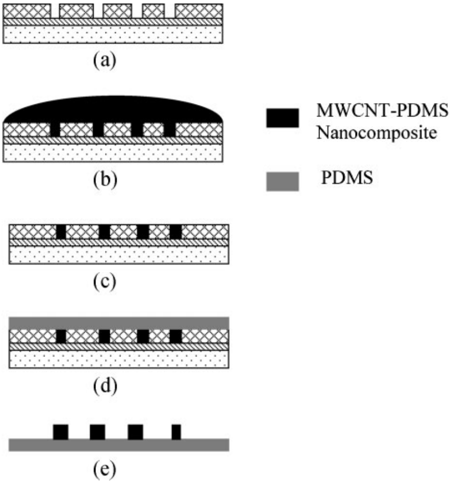

Figure 2.
Hybrid fabrication process for combining micromolded nanocomposite microstructures with nonconductive polymer. a) SU-8 micromold; b) MWCNT-PDMS nanocomposite is poured on the SU-8 micromold; c) excess nanocomposite is scraped off from the surface of the micromold; d) PDMS is poured on the surface of the mold; e) the nanocomposite/nonconductive PDMS is pealed off the mold.

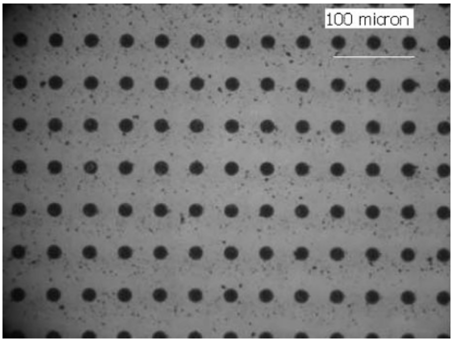

Figure 3.
Example structures micromolded using soft lithography micropatterning of conductive PDMS on a nonconducting PDMS substrate: array of pegs 25 μm in diameter and 100 μm in height.

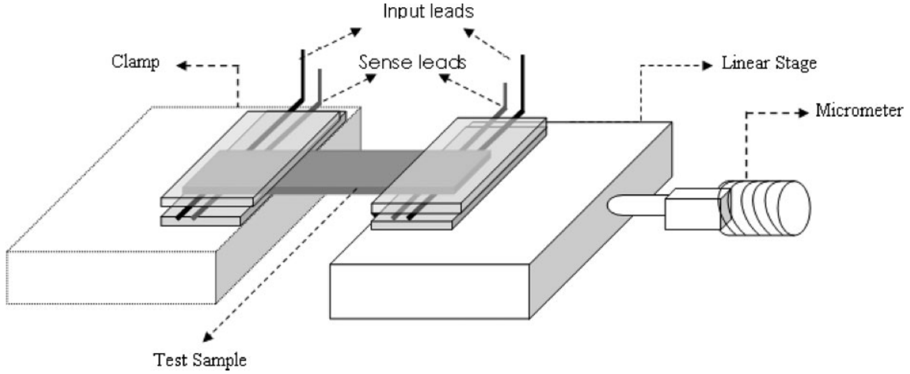

Figure 4.
Test fixture to measure the resistance of MWCNT-PDMS nanocomposite samples.

Resistivity and Temperature Coefficient Measurements

In order to characterize the electrical properties of the nanocomposites, sample films of 3 cm x 1 cm x 0.01cm were prepared with 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 and 4.5 wt.% of MWCNTs in the PDMS matrix. Four point resistance measurements of the samples were made using the illustrated test fixture (Figure 4) with leads connected to an HP-3478A multimeter so as to eliminate contact resistance. To measure the resistance, the multimeter passes a known current through the sample using the ''input'' leads and measures the voltage across the sample using the ''sense'' leads. The resistance between the ''sense'' leads is then calculated using Ohm's Law. Because the sense leads are not drawing any current, the effects of contact resistance are eliminated, thus giving only the resistance of the bulk material. Using the known sample geometry and distance between the leads, the resistivity of the sample can subsequently be calculated. To characterize the temperature coefficient of the samples, characterization of resistance using the fixture was carried out in a thermal chamber.

Results and Discussion

Resistivity Measurement Results

The evolution of the electrical resistivity of COOH- functionalized MWCNTs in PDMS as a function of weight percentage and temperature has been determined using the set up illustrated in Figure 4. As can be seen from Figure 5, it is observed that the resistivity increases slowly up to 1.5 wt-%. However, after this point the conductivity increases rapidly, which corresponds to the resisitivity decreasing. This behavior of conductivity variation can be explained in terms of the percolation theory:[18] at lower concentrations of functionalized MWCNTs, the percolation paths are not completely set up by the MWCNT network. As the concentration of MWCNTs in the composite increases, the percolation paths via conducting MWCNTs are set up, and the MWCNTs control the conductivity of the nanocomposite matrix. The concentration of MWCNTs required for insulator conductor-transition is referred as threshold concentration or percolation limit,[19] which was 1.5 wt-% for the functionalized MWCNT-PDMS nanocomposite. The resistivity level achieved at 2 wt-% was approximately 62 Ω-cm.

Negative Temperature Coefficient of Resistivity Results

It is observed that the MWCNT-PDMS nanocomposites show a negative temperature coefficient of resistivity (NTCR), which has been characterized for three different weight percentages (1.5, 2 and 2.5 wt.%) as shown in Figure 6. The

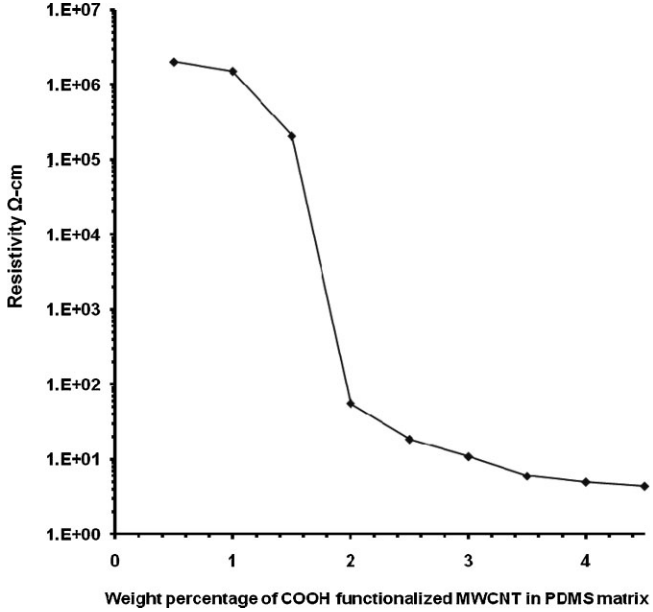

Figure 5.
Resistivity verses COOH- functionalized MWCNT wt.% in the PDMS matrix.

functionalized MWCNT-PDMS nanocomposite samples were loaded onto the four probe test fixture (Figure 4) and placed in the thermal chamber. The temperature was increased in steps of 20 °C up to a maximum temperature of 300 °C and the corresponding value of resistance was recorded at each temperature. A clear trend is observed from the values obtained and shown in Figure 6: for every 20 °C rise in temperature, a predictable trend is that there is a decrease in resistivity with an increase in temperature, thus showing a negative temperature coefficient of resistivity. Negative temperature coefficients are of interest because they can be exploited for on-chip

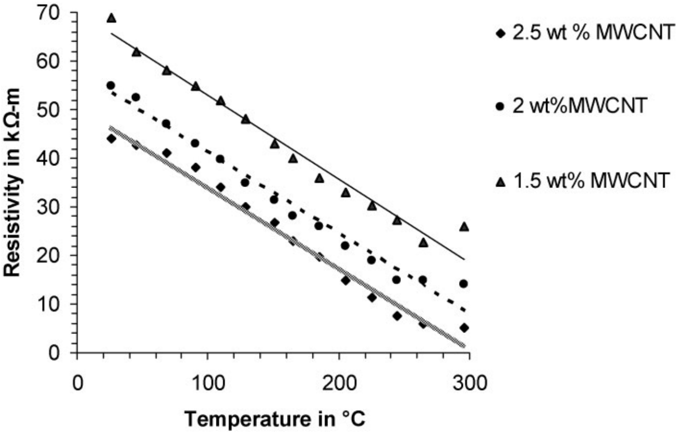

Figure 6.
Negative temperature coefficient of resistivity of COOH- functionalized MWCNT in PDMS for different weight percentages of nanotubes.

temperature sensors[20] for, e.g., measuring local temperature during on-chip chemical reactions for lab on a chip devices.

Dispersion of MWCNT's in PDMS Matrix

Typical methods of MWCNT dispersion in polymers are classified into two main categories: physical dispersion and chemical dispersion. Physical dispersion methods involve physically separating agglomerates or bundles of MWCNT's which are tied up or clumped up together by van der Waals forces. There are four main physical dispersion mechanisms which are commonly used: ultrasonic agitation,[21] shear mixing,[22] ball milling[23] and micro-bead milling.[24] The most popular technique is ultrasonic agitation in which the MWCNTs are first manually stirred in a solvent and then exposed to ultrasonic waves. There are two different types of ultrasonic waves which can be used: 1) low frequency ultrasonic (~ 20-24 kHz); and 2) high frequency ultrasonic (~ 42-50 kHz).

Chemical dispersion methods involve changing the surface chemistry of the of MWCNTs, and can be done in two ways: covalent and non-covalent methods. Covalent methods involve functionalizing the surface of nanoparticles (e.g., with -OH or -COOH groups for MWCNTs.[25] It is thought that the production of robust nanocomposite materials may require strong covalent chemical bonding between the filler particles and the polymer matrix, rather than the much weaker van der Waals physical bonds which occur if the particles are not functionalized. Non covalent

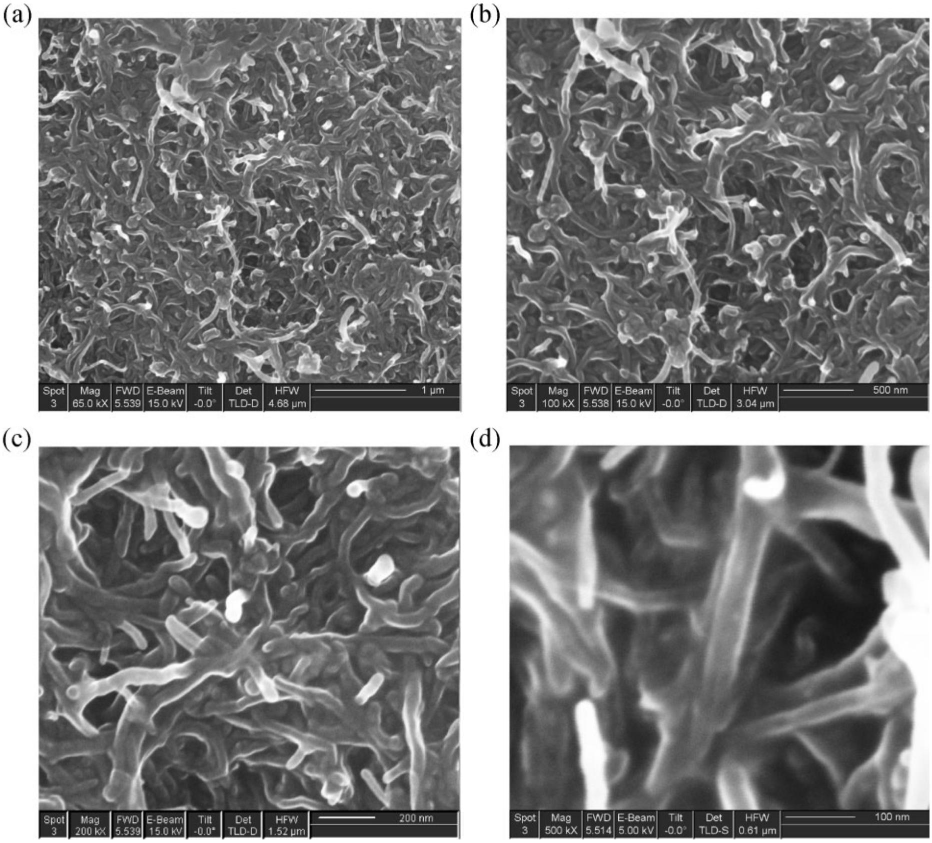

Figure 7.

SEM photographs of COOH- functionalized MWCNTs at different (increasing) magnifications in PDMS. Scale bar: a) 1 µm ; b) 500 nm; c) 200 nm; d) 100 nm.

methods make use of surfactants which attach to the MWCNTs and prevent them from aggregating.[25] Functionalizing of other nanoparticles is still a heavy researched topic, with chemical dispersion methods showing great promise for fabrication of uniformly dispersed nanoparticles composites.[26]

Although the purchased MWCNTs were COOH- functionalized, some amount clumping or bundling was still observed, so we additionally employed manual stirring, followed up with high frequency ultrasonic dispersion which is a much faster process as compared to low frequency dispersion, shear mixing, ball milling or bead milling. As recommended by the supplier,[13] an ultrasonic probe was immersed into the uncured nanocomposite and operated at 42 kHz. We operated the probe in pulse mode (i.e., 10 seconds on and 15 seconds off cycle), which provided mixing by repeatedly allowing the sample to settle back under the probe after each burst. We operated the probe in such a burst mode to minimize damage to the fragile CNTs, as it has been observed that prolonged exposure to ultrasonics can damage CNTs,[27–29] which the pulse mode avoids. We also minimized ultrasonication by employing functionalized MWCNTs, with the mixing time cut down from several hours previously reported with non-functionalized MWCNTs[11] to only a few minutes with the functionalized MWCNTs.

By employing these methods, good uniformity of COOH- functionalized MWCNT dispersion in the PDMS matrix can be seen, which is shown in Figure 7. From these SEM micrographs, individual COOH- functionalized MWCNTs can be observed indicating that the clumping of COOH- fucntionalized MWCNTs has been minimized in the PDMS matrix.

Conclusion

We have presented the preparation, improved micropatterning, nanoparticle dispersion analysis, and electrical property characterization of COOH- functionalized mutli-walled carbon nanotube (MWCNT) and polydimethylsiloxane (PDMS) conductive nanocomposite polymers that can be employed for lab on a chip applications. SEM analysis shows that COOH- functionalized MWCNT are well dispersed with little observable agglomeration. This problem of some amount clumping or bundling cab be easily overcome by additionally employing 42 kHz high frequency ultrasonic dispersion method, leading to fairly uniform dispersion and improved resistivity. It is observed that a percolation threshold occurs at approximately 1.5 wt.% and show lower resistivity (62 Ω-cm or better) at 2 wt.% than our previously reported value of 100 Ω-cm at 2 wt.% of MWCNT's in PDMS matrix.[11] Improved micropatterning has been demonstrated, with micromolded MWCNT-PDMS nanocomposite structures combined with non-conductive PDMS. This process alleviates problems with materials mismatch between flexible nonconductive polymers and metals or less flexible conductive polymers for soft (polymer) MEMS and flexible lab-on-chip systems. The negative temperature coefficient of resistivity (NTCR) of samples at 1.5, 2 and 2.5 wt.% have been characterized, and a predictable trend of a decrease in resistivity is observed with an increase in temperature from 20 °C to 300 °C. Thus, the micropatternable nanocomposites should make good candidates for micro- temperature sensor applications in addition to conductive lines and other structures for lab on a chip systems and other MEMS applications.

However, further experimentation is needed to characterize the smallest feature size, aspect ratio, resolution, etc., although unfilled PDMS has been micromolded with features smaller than 670 nm.[30]

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