Nanoparticle-doped Electrically-conducting Polymers for Flexible Nano-Micro Systems

by Ajit Khosla

Polymers—primarily polydimethyl-siloxane (PDMS), a silicone-based elastomer—are chosen as substrate materials for creating new flexible microsystems because of numerous benefits of PDMS including flexibility, biocompatibility, low cost, low toxicity, high oxidative and thermal stability, optical transparency, low permeability to water, low electrical conductivity, and ease of micropatterning.[1] Many stand-alone NEMS-MEMS and microfluidic devices have been fabricated by micromolding PDMS against SU-8 photopolymer masters (called soft lithography), including micromixers, nano and microchannels, cell sorters, valves, pumps, microlenses, and interconnect structures for a wide variety of applications for Nano and Micro Systems. However, most devices to date based on PDMS are passive, as making active devices out of PDMS is extremely challenging. When PDMS is bonded to substrates with conventionally-realized active components like electrodes, heaters, sensors, actuators, antennas, etc., it is rendered inflexible—defeating one of its key benefits. For example, the common method of bonding PDMS with glass renders the resulting devices completely inflexible. This is because it has proven difficult to integrate, embed, or pattern conducting lines on PDMS because of the weak adhesion between PDMS and metals.[2]

Integration of functional material (electrically-conductive) structures in and/or on bulk PDMS is extremely important for signal routing, interfacing to signal processing electronics, for powering active devices, heating elements, electrostatic, stretchable antennas, and actuation purposes. It has proven difficult to integrate, embed, or pattern conducting lines on PDMS because of the weak adhesion between PDMS and metals.[2] In the case of metal/metal-alloys deposition and nano-micromachining, microcracks appear on the surface of the patterned conductive lines on being flexed, bent, or twisted, leading to electrical disconnection and device failure. Microcracks appear because there is a materials mismatch between flexible nonconductive polymers like PDMS and metals/alloys or less flexible conductive polymers (such as PDOT, polyaniline, etc.). Hence, in order to alleviate the problem of microcracks appearing on sputtered metals on PDMS surfaces, it is important to develop PDMS-based active materials of similar flexibility to the undoped and insulating PDMS, so that they can also be easily micromolded using similar soft lithography techniques in order to provide robust system electrical routing.

While PDMS is inherently electrically-insulating, this property can be modified by introducing conducting nanoparticles in the polymer matrix.[3] Most commonly used nanoparticles are derived from graphene, carbon nanotubes (CNTs), and silver nanowires. Such electrically-conductive polymers are of great interest to nano-microelectronics, microfluidics, and lab-on-a-chip communities for packaging, microsensor, and other related applications,[3] which may lead to the ultimate development of fully integrated flexible polymer systems.

Before we begin discussing fabrication and nano-micro-patterning of electrically-conducting PDMS based nanocomposite polymers, a few key concepts, with respect to the theme of this article are briefly reviewed, namely: what are nanoparticles, nanocomposite polymers, percolation threshold, and various dispersion mechanisms of nanoparticles in polymers.[4,5]

Defining Nanoparticles

There is no accepted international definition of a nanoparticle, but one given in the new Publicly Available Specification 71 (PAS71) document developed in the United Kingdom is as follows: "A particle having one or more dimensions of the order of 100 nm or less." However, a note associated with this definition further refers to the characteristics of such particles: "Novel properties that differentiate nanoparticles from the bulk material typically develop at a critical length scale of under 100 nm."[6] A nanopowder is "an agglomeration of non-crystalline nanostructural subunits with at least one dimension less than 100 nm."

Effect of Nanoparticle Shape and Size

Nanoparticles come in different shapes: spheres, flakes, rods, tubes, fibers, wires, and random assortments that may contain all of these shapes. Nanoparticles can have a very high aspect ratio of 1:1000000, or they can be simple spheres. These shapes and sizes play an important role in determining the percolation threshold (discussed below), the ability to uniformly mix particles, and calculating mechanical changes (*e.g.*, Young's modulus) to the polymer matrix after addition of nanoparticles. Aspect ratio (length to width ratio) is thought to play a large role in percolation threshold, as it appears that conductive percolation paths are, in general, more easily set up between long and thin nanoparticles.

Why Nanoparticles

Nanoparticles exhibit size-related properties that differ significantly from those observed in micrometer-sized particles or bulk materials. Nanoparticles can be embedded in many different polymer matrices, such as polycarbonate, polystyrene, nylon, PDMS, PMMA, silicone rubbers, polyamide, ABS, polyethylene, etc. From these materials, nanocomposites based on PDMS are of interest to the flexible nano-micro systems community. These nanocomposites exhibit enhanced properties and are mainly due to the high aspect ratio and/or the high surface area of the fillers, since nanoparticulates have extremely high surface area to volume ratios when homogeneous dispersion is achieved. This new class of composite materials show enhanced optical, electrical, magnetic, and dielectric properties compared to microparticle-reinforced polymers.

Percolation Threshold

Silicone-based polymers can be made electrically-conductive by filling them with conductive particles. The particles are called fillers, and the material in which they are embedded is called the matrix; the total of matrix with fillers is called a composite. When the size of the particles is of the order of 10^{-9} m to 10^{-7} m a composite becomes a nanocomposite. When the fillers form a continuous path from one side of the material to the other, the material is above its critical filler fraction/concentration (Fig. 1, indicated by point B) and a direct current (DC) can flow through it. For fewer particles, no continuous path is formed from one side to the other and the material is below its critical filler fraction (Fig. 2, indicated by point A). It is desired to have a critical filler fraction that is as low as possible, in order to have a conductive material already for a low amount of filler. Figure 1 shows resistivity versus mass percentage of nanoparticle filler in a polymer matrix for a conductive nanocomposite polymer. It can be clearly seen that after the percolation threshold (p_c), resistivity drops down drastically. The advantage of such a material is that the properties of the matrix (like transparency, hardness, stiffness, etc.) are largely maintained. Above the critical filler fraction/concentration (Fig. 1, indicated by point C), the resistivity is generally hardly dependent on the amount of filler.
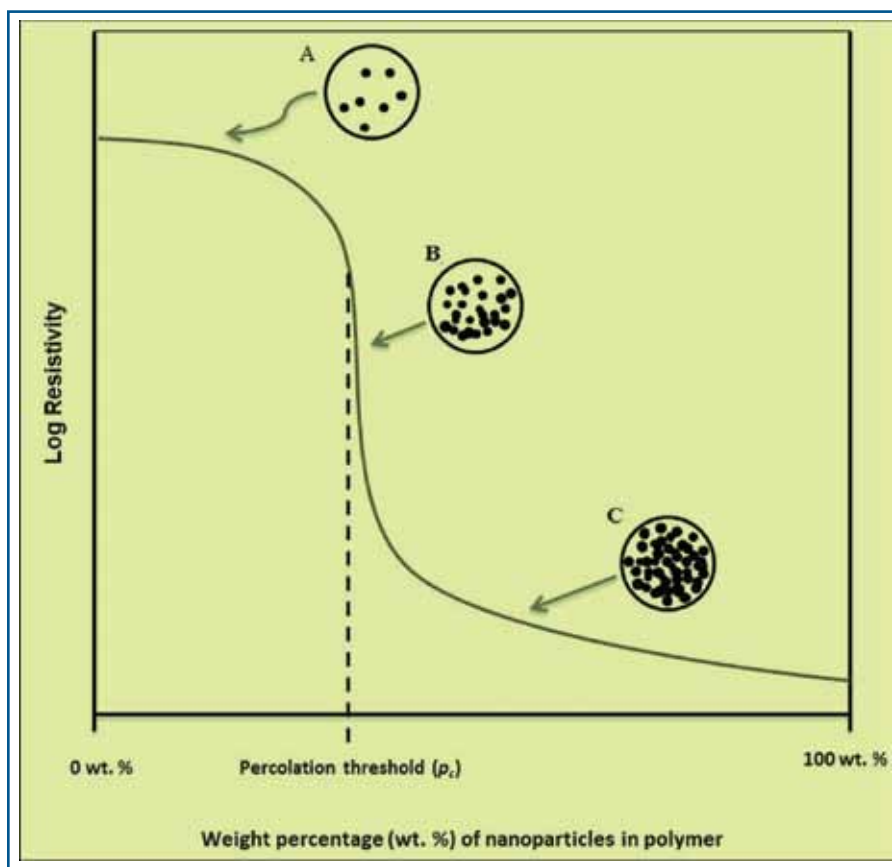
Fig. 1. *Resistivity versus weight percentage of nanoparticle filler in polymer matrix for conductive nanocomposite polymer. The percolation threshold (pc) is labelled.*

Dispersion Mechanisms of Nanoparticles in Polymers

In order to fabricate nanocomposites with enhanced properties such as electrical conductivity for their fill percentage or mass percentage (percentage of nanoparticles in the polymer matrix), the nanoparticles must be thoroughly mixed so they are homogeneously and uniformly distributed within the polymer matrix. Dispersion is the key to developing a high quality nanocomposite with uniform properties.

Typical methods of nanoparticle dispersion in polymers fall into two main categories: physical dispersion and chemical dispersion. Physical dispersion involves separating agglomerates of nanoparticles, nanorods, or a bundle of CNTs, which are tied up or clumped up together by van der Waals forces. Three main physical dispersion mechanisms are commonly used: (1.) ultrasonic agitation, (2.) shear mixing, and (3.) ball milling. The most popular technique is ultrasonic agitation, in which the nanoparticles are first manually stirred in a solvent and then exposed to ultrasonic waves/irradiation. There are two different types of ultrasonic waves that can be used. The first type is low-frequency ultrasonics (~ 20-24 kHz), in which the composite is placed in an ultrasonic bath and is agitated

for a specified time depending on the type of nanoparticles. The second type involves using high-frequency ultrasonics (~ 42-50 kHz) in which an ultrasonic probe (a "horn") is immersed into the composite. Usually, the probe is operated in pulse mode, which provides mixing by repeatedly allowing the sample to resettle under the probe after each burst. The shock waves generated by ultrasonic pulses lead to collisions between nanoparticles. Consequently, the agglomerated nanoparticles are eroded and split by the collisions. One of the major problems with ultrasonic agitation is that immense local heat is produced; hence it is recommended to operate the ultrasonic bath or the probe in the pulse mode. In the case of CNTs it has been observed that prolonged exposure to ultrasonic waves can damage them. Thus, other mixing methods may be required, such as prolonged shear mixing for 6 to 7 h.

For viscous monomers/polymers and photoresists (*e.g.*, PDMS, SU8 100, SU8-2050, etc.) shear mixing is the preferred method as it allows direct dispersion of nanoparticles in the polymer matrix. The nanoparticle aggregates are forced apart by high speed shear mixing. The viscosity of the solvent/polymer matrix does not allow the nanoparticles to re-aggregate. One of the most common ways for shear mixing is to use a magnetic stirrer (usually at 1000 to 5000

rpm, depending on the viscosity of polymer or monomer); however, magnetic stirring is, for obvious reasons, not recommended for magnetic nanoparticles such as nickel, iron hexferrites, NdFeB, etc.

Ball milling is another technique used for nanoparticle dispersion and it is usually preferred for CNT dispersion because of the bundle size of CNTs. It consists of a rotary cylinder along with iron or plastic balls to break the clumps of nanotubes. However, this method is not widely used at the research level and tends to break the carbon nanotubes. Bead milling, which is a technique similar to ball milling, has proved efficient for dispersing nanoparticles in which balls of micrometer scale diameter are used to disperse nanoparticles to the primary particle size. Among all the three physical dispersion methods ultrasonic dispersion is preferred because it is quick, easy to use, and the dispersion degree is acceptable as compared with other physical methods.

Chemical dispersion methods are classified as covalent and non-covalent methods. Extensive research is being carried out in chemical dispersion techniques for CNT based polymer nanocomposites. Covalent method consists of functionalizing the surface of CNTs with –OH or –COOH groups and non-covalent method makes use of surfacants which attach to CNTs and prevent them from aggregating. Functionalizing of other nanoparticles dispersion method is still a heavily researched on topic. Chemical dispersion methods are highly promising for fabrication of uniformly dispersed nanoparticle composites. Other functionalization methods include O_2 plasma treatment of nanoparticles.

How to Fabricate Nanoparticle-doped Electrically-conducting Polymers

Fabrication of a PDMS-based electrically-conductive nanocomposite is an easy five-step process.[4] The most commonly used nanoparticles used to fabricate electrically-conductive nanocomposites are: graphene, CNTs, and silver nanoparticles. The five-step process is explained below.

1. The desired quantity of nanoparticles is distributed in an organic solvent, such as heptane or toluene, via high-frequency ultrasonics employing a horn tip probe in pulse mode (10 seconds on and 15 seconds off) for a total time of two minutes.
2. The base elastomer/monomer is added to the nanoparticle-organic solvent emulsion, followed by high-frequency agitation.
3. The polymer curing/crosslinking agent is added in ratio of 10:1; *i.e.*, 10 parts of base elastomer and 1 part of curing agent, as recommended by the supplier (Dow Corning Inc., USA). It

is important to add curing agent after the high-frequency ultrasonic process as a lot of heat is produced during ultrasonication process, which can start to solidify (cure) the nanocomposite during mixing.

4. The prepared PDMS-based nano-composite is shear-mixed until the heptane evaporates. Evaporation of the organic solvent from a PDMS nanocomposite may be determined visually, by weight, or by calculating volume of the nanocomposite.

5. The prepared nanocomposite is placed in a vacuum for 30 minutes to remove air bubbles.

The nanocomposite is now ready to be micropatterened. Figure 2 shows SEM micrographs of nanoparticles dispersed in a PDMS polymer matrix.

Nano-Micro-Patterning of Electrically-conducting Nanocomposites

The developed PDMS-based electrically-conducting nanocomposite polymers are nano-micro-patterned by employing a novel hybrid fabrication process against a SU-8 mold. SU-8, which is a negative-tone photoresist, has been commonly used as a structural nano-micro mold material for over a decade. This novel hybrid fabrication process enables hybrid systems with combined micro-patterned PDMS-based nanocomposites and undoped PDMS. In this process the nanocomposite is first poured on the SU-8 micro-mold and then degassed to remove air bubbles. The excess composite is scraped off using the Damascene-like process from the surface of the mold using a surgical knife. Undoped PDMS is poured over the substrate, baked, and peeled off from the SU-8 substrate. This results in electrically-conducting nanocomposite structures combined with nonconductive PDMS (the step-by-step fabrication process shown in Fig. 3). Figure 4 shows examples
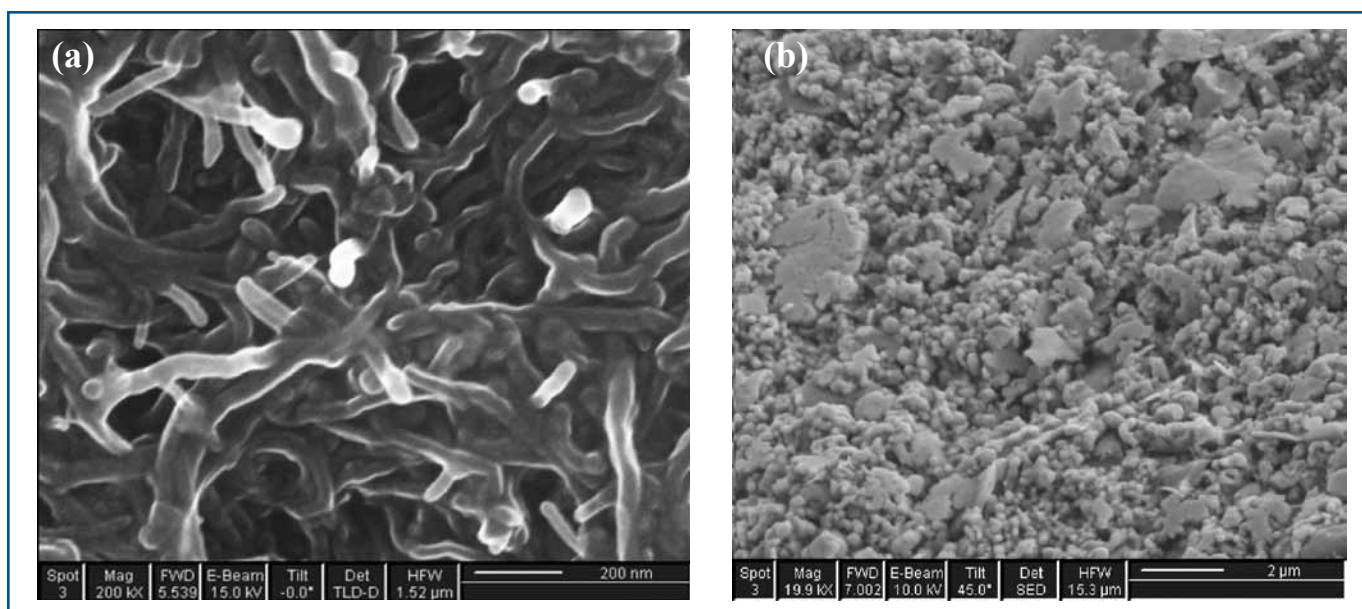
FIG. 2. *SEM photographs of SEM micrographs of nanoparticles dispersed in PDMS polymer matrix: (a) multi-walled carbon nanotubes (scale bar: 200 nm), and (b) silver nanoparticles (scale bar: 2 μm).*
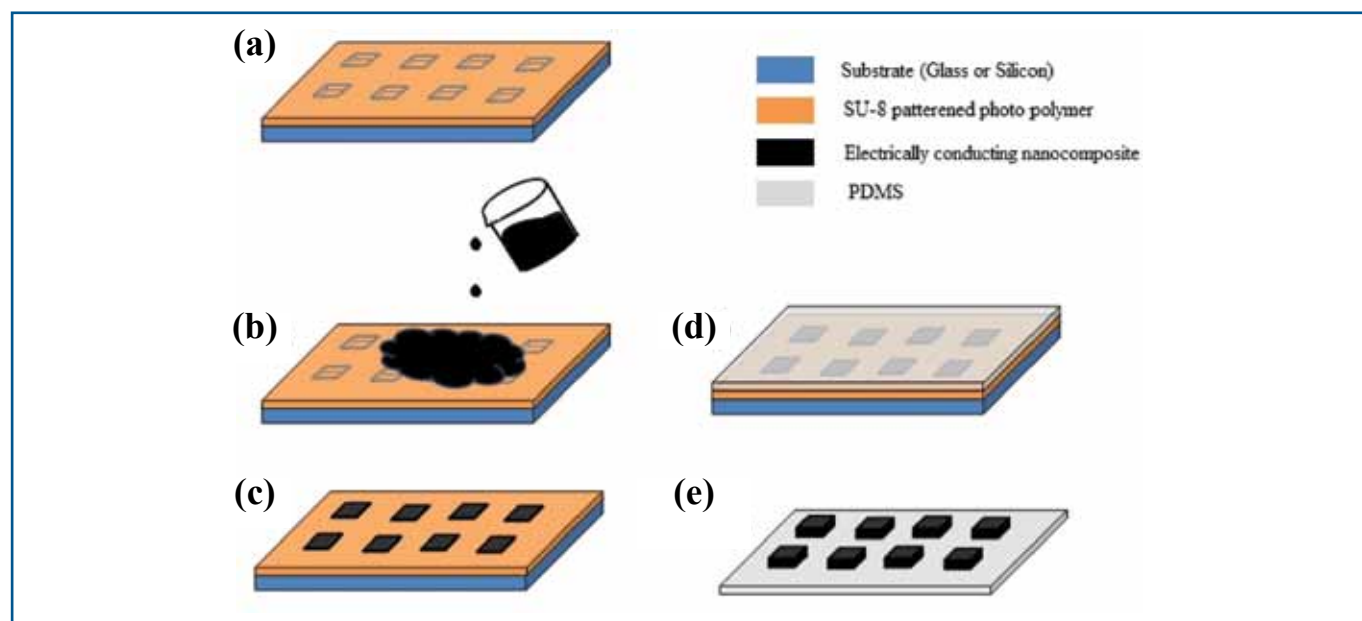

FIG. 3. *Hybrid fabrication process for combining micromolded nanocomposite microstructures with nonconductive polymer: (a) SU-8 micro-mold, (b) electrically-conductive-PDMS nanocomposite is poured on the SU-8 micro-mold, (c) excess nanocomposite is scraped off the surface of the micro-mold, (d) PDMS is poured on the surface of the mold, and (e) the nanocomposite+nonconductive PDMS is peeled off the mold.*
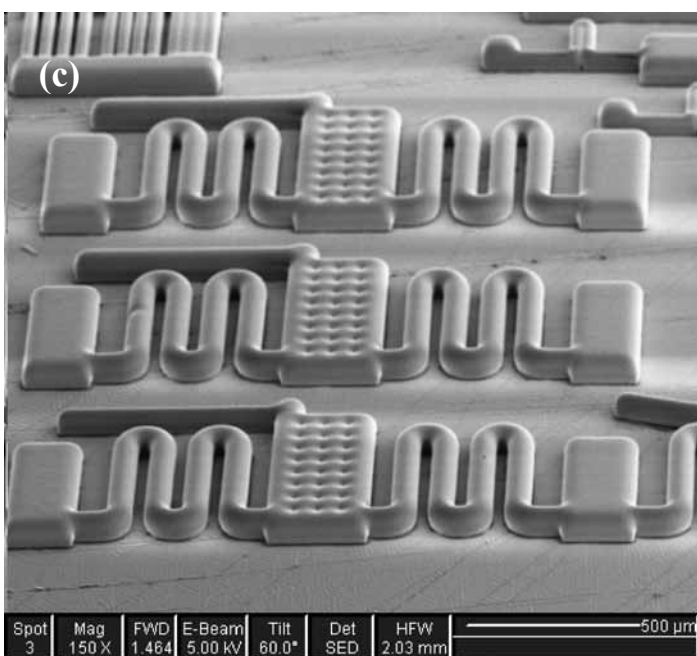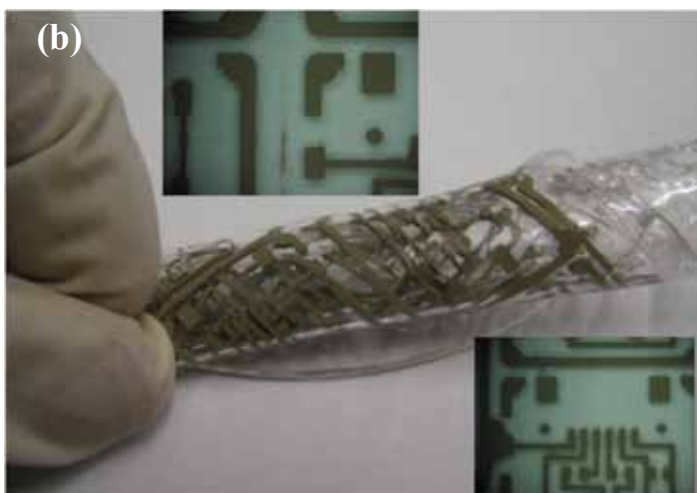
of different PDMS-based electrically-conductive nanocomposite polymers thus fabricated on flexible undoped PDMS.

In summary, electrically-conducting nanocomposite polymers and hybrid fabrication process alleviates problems with materials mismatch between flexible nonconductive polymers and metals/alloys or less flexible conductive polymers for soft (polymer) (N)-M-EMS and flexible lab-on-chip systems.

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FIG. 4. *Optical micrographs of fabricated conductive microstructures on non-conducting PDMS: (a) MWCNT-PDMS nanocomposite array of microribbon cables with a height of 30 µm and width of 100 µm, (b) silver PDMS rolled up flexible circuit board height of 30 µm and width of 100 µm, and (c) SEM micrograph of electrically-conducting and soft magnetic nickel-PDMS nanocomposite bridges.*