Tuning Electrical Conductivity of CNT-PDMS Nanocomposites for Flexible Electronic Applications

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***Abstract*— This paper presents a study into the electrical conductivity of multi-wall carbon nanotube–polydimethylsiloxane (MWNT-PDMS) nanocomposite and their dependence on the filler concentration. It is observed that the electrical conductivity of the composites can be tailored by altering the filler concentration. Accordingly, the nanocomposites with filler weight ratio ranging from 1% to 8% were prepared and tested. Finally, the significance of results presented here for flexible pressure sensors and stretchable interconnects for electronic skin applications have been discussed.**

Keywords— Carbon nanotube (CNT)-PDMS composite, multi-wall carbon nanotube (MWNT), electrical conductivity.

I. INTRODUCTION

Nanocomposites developed through integration of nanomaterials within the polymers have long been heralded as a class of material with a huge potential in various future engineering applications. Among various applications, the nanocomposites are attractive candidate for the development of large area flexible electronics and touch sensors due to improved mechanical and electrical properties [1]. Indeed, the introduction of nanomaterials within polymers often enriches their mechanical and electrical properties. Though polymer composites have long been investigated since 1960s, their use was primarily limited by higher filler concentration. Unlike in common polymer composites, the required properties can be achieved at a low filler concentration in nanocomposites [2]. Some of the widely used nanomaterials for the development of nanocomposites includes metal nanoparticles [3], nanowire [4], carbon black [5], CNT [6] and graphene [2].

CNTs are sp^2 allotrope of carbon, whose atoms are arranged in graphenes layers resulting in a hollow cylindrical shaped molecule. CNTs have received significant attention by scientific community owing to its excellent intrinsic material properties such as high electrical, mechanical and thermal properties. CNTs can be classified as either as single wall CNTs (SWNTs) or MWNTs depending on the number of graphene layers in the structure. SWNTs can be either metallic or semiconducting depending on its chirality and diameter. Whereas, MWNTs are in general only metallic. In fact, the discrimination of their electrical properties is difficult to determine because of the presence of walls with different chiral vectors [6]. Ajayan and his coworkers [7] reported the development of first CNT based nanocomposite. Since then, rapid progress has been made in development of composites for various applications such as reinforcement of materials, thermal management materials [8] and flexible electronic applications [9].

The high aspect ratio, excellent electrical conductivity and longitudinal polarizability of CNT are some of its defining features, which results in a significant enhancement of electrical conductivity of the composite at a very low electrical percolation threshold [10]. Percolation threshold determines the minimum volume fraction of filler required to form the conductive path within the polymer to transfer from its insulating nature to its conductive nature [11]. In contrast to other nanomaterials like carbon black and metal nanoparticles, CNTs exhibit a very low percolation threshold ranging from 0.0025% [12] to 5% weight percentage (wt.%). The huge variation observed in the electrical percolation threshold of CNT is attributed to several factors such as quality, dimension, dispersion and functionalization of CNTs [6]. Furthermore, other factors like aggregation of CNT, twisting and curling of tubes within the polymer further degrades the CNT properties. Hence, the excellent properties of CNTs are lost in the transition of polymer development.

Over last two decades, tremendous effort has been invested in improving composite performance by retaining the fundamental properties of the nanofillers. A key criterion for such requisite is to achieve a homogenous distribution of the CNTs along the polymer. However, the van der Waals force between the individual CNTs causes aggregation of CNTs often leading to poor dispersion. Dispersion of CNTs within the polymer has been achieved by chemical modification of CNTs dispersion, such as surfactant assisted process [13] and by physical mechanisms. Some of physical dispersion techniques are sonication [7], manual stirring, sheer mixing [14] and bead milling [15].

In the present study we investigate the development of MWNT-PDMS composite. During the study we investigate the dependence of electrical conductivity on filler concentration. Based on the electrical conductivity, the composites were used for the development of flexible pressure sensors and stretchable interconnects for electronic skin. The paper is organised as follows: The materials and methodology used for the development of composite is presented in section II. Experimental evaluation on the conductivity of CNT-PDMS composite with different filler concentration is presented in Section III. Finally, Section IV present conclusion of the paper.

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II. Materials and Methods

A. Materials

Polymers are a key component in the development of nanocomposites. Various polymers such as poly(methyl methacrylate) (PMMA) [16], polycarbonate (PC) [17], poly(ethylene) (PE), have been used in development of flexible sensors. Among various polymers reported in the literature, polydimethylsiloxane (PDMS) exhibit a superior mechanical strength, biocompatibility and chemical inertness and has been widely used in the development of stretchable and flexible electronics [18]. The PDMS kit (Sylgard 184, from Dow Corning) comprising of pre-polymer resin and curing agent were used in the development of the composite in the ratio of 10:1.

CNTs were used as nanofillers for the development of nanocomposite owing to aforementioned properties. MWNT (synthesized via CVD, with an outer diameter in the range of 6-9*nm*, length ~5μm) purchased from Sigma Aldrich (Product Number - 724769) is used as the nanofillers for the development of the composite. The choice of MWNT over SWCNT is attributed to superior electrical conductivity of MWNT and for cost effectiveness

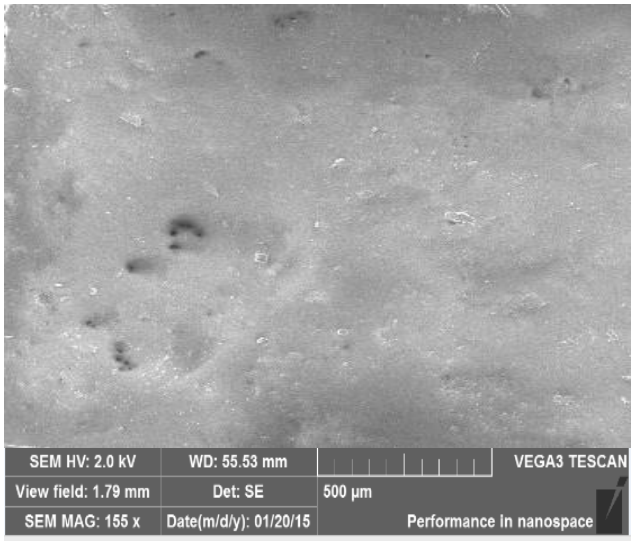
B. Prepration of MWNT-PDMS composite

Production of CNT composites have primarily focused on achieving uniform dispersion of CNT within the polymer matrix, as poor dispersion has a detrimental effect on the eventual properties of composite. However, intermolecular van der Waals force between the CNT causes agglomeration of the nanotubes affecting its dispersion within the polymer [19]. To avoid agglomeration and to promote uniform dispersion of MWNTs within the PDMS, the composites were prepared via a combination of mechanical stirring and sonication. In addition, dispersion can also be enhanced via use of a solvent common to both PDMS and MWNTs. Chloroform was used as the common solvent to enhance the dispersion of MWNTs. MWNT-PDMS composites of varying MWNT weight ratio ranging from 1 wt.% to 8 wt.% were prepared. Keeping a lower percolation threshold in in good agreement with sustaining the mechanical stretchability as well as keeping the conductivity in acceptable ranges.

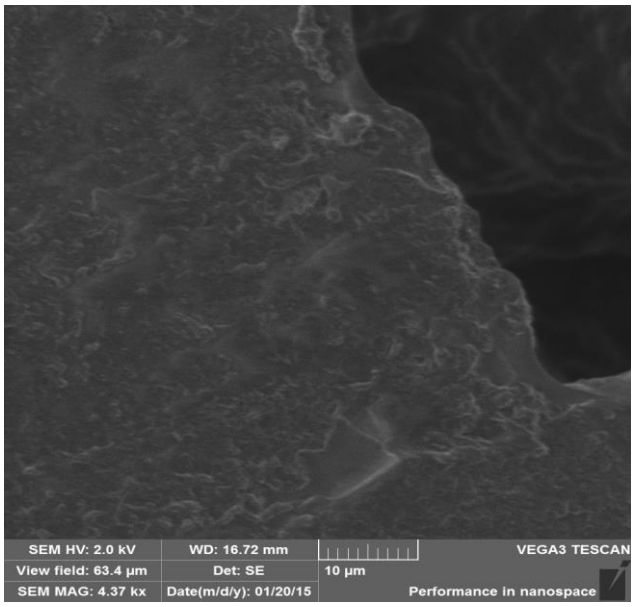
For each composite with different MWNT wt.%, the MWNTs were dispersed in chloroform solution by mechanical stirring followed by sonication treatment for 30 minutes at 42 *kHz*. Polymer resin component of PDMS kit was added into the MWNTs- chloroform dispersion and sonicated for a further 30 minutes. The samples were degassed in a vacuum desiccator to remove any trapped air bubbles. The samples were then placed in an oven at 70^oC for 2h to evaporate the solvent. Finally, the curing agent was added to the sample at the above-mentioned ratio. The direct current (DC) electrical conductivity of the samples was studied to determine the dependence of conductivity on filler concentration.

III. Results and Discussion.

Though a uniform dispersion of CNTs has been the key criteria during the synthesis of composite, it still remains a challenge to reliably evaluate the dispersion of MWNTs within the polymer matrix. The dispersion of fillers within the composite has been primarily studied via the use of optical and electron microscopy. The use of optical microscopy to study dispersion of CNT within the nanocomposite is limited owing to opaque nature of final composite. Scanning electron microscopy (SEM) was used to study the dispersion of CNT within the bulk composite. Fig 1 shows the SEM image composite of 4 wt.% and 8 wt. % of MWNTs respectively. SEM image shows the dispersion of CNT within the composite along with formation of CNT bundles within the composite.



(a)



(b)

Fig.1. SEM image of bulk MWNT-PDMS composite with wt. % of (a) 4 wt. % (b) 8 wt. %.

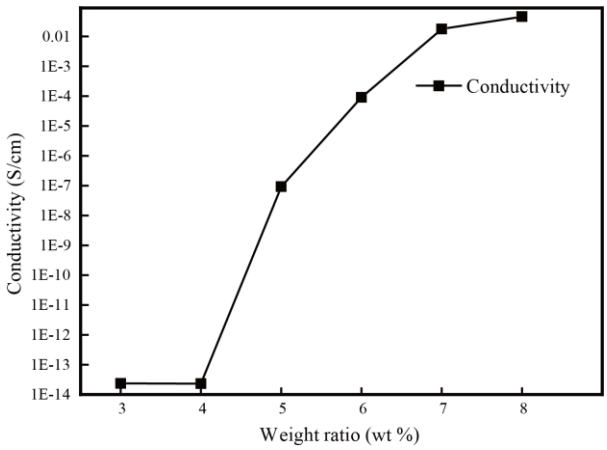


Fig. 2. Conductivity of CNT-PDMS composite as a function of wt. % of MWNT.

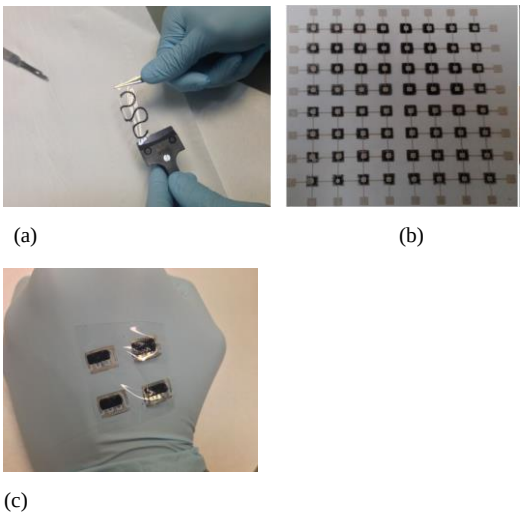
The introduction of CNT into PDMS changes an electrically insulating polymer into a conductive material when the filler concentration exceeds the percolation threshold. This observed change is due to the formation of CNT conductive path within the polymer matrix. The increase in sample's electrical conductivity at higher MWNT wt.% can be explained by the percolation scaling law

$$\sigma = \sigma_0(p - p_c)^t \qquad p > p_c \qquad (1)$$

Where σ_0 is a constant, t is the critical exponent, p and p_c are weight fraction of nanotube and critical filler concentration respectively [20]. As it can be observed from Fig 2, the percolation threshold of the sample is attained at 5 wt.%, where an abrupt change in the composite's conductivity is observed. The sudden increase in the composite conductivity indicates the formation of conduction path within polymer. The constant σ_0 was found to be 1.25×10^{-4} *S/cm*. The higher percolation threshold in comparison to values reported in the literature [12] [21] can be attributed to coating of the CNT by polymer which affects its conductivity [21].

The piezoresistive behavior of CNT-PDMS composite has been extensively exploited for tactile sensing applications. Piezoresistive behavior of the composite is influenced by two factors: (1) CNT filler concentration; (2) Deterioration and reformation of the CNT network. Relying on this behavior, pressure sensors have been developed by integrating, the composites into the active area of the devices.

The electrical conductivity of the MWNT-PDMS composite can be tuned by altering the filler concentration as depicted in Fig 2. Nanocomposites with different electrical conductivity was used for the development of flexible electronic applications. Stretchable pressure sensor [22] and interconnects required MWNT-PDMS composite with higher MWNT wt.% (6 wt.%, 7wt. % and 8 wt. %). On the contrary, for a flexible pressure sensor based on parallel plate configuration, lower wt.% of MWNT-PDMS composites were used [23]. The developed devices are depicted by Fig. 3. Application of force causes the disruption of CNT conductive



(a) (b)

(c)

Fig 3: (a) Stretchable interconnects developed from CNT-PDMS composite on PDMS substrate (b) Pressure sensor consisting of CNT-PDMS composite as dielectric layer (c) Stretchable pressure/strain sensors based on the piezoresistive mechanism of CNT-PDMS composites.

path within the polymer leading to change in the conductivity of the composite. This property has been exploited in the development of sensors.

IV. Conclusion

In summary, we have reported the development of MWNT-PDMS composite for flexible electronic applications. The dispersion of nanotube was achieved via a combination of a solvent assisted and physical dispersion process. An investigative study on relationship between the electrical conductivity and MWNT wt.% is presented. It was observed the electrical percolation threshold of the composite was attained at 5 wt.% of MWNT. The study provided an overview of conductivity of the composite at different MWNT weight ratio, which was used for the development of MWNT composite based flexible sensor pressure devices.

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