

Experimental Study and Analysis of Defragmented Carbon Nanotubes in Polyacrylonitrile Matrix



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Abstract The aim of this research is to elucidate the change in electrical properties of polyacrylonitrile (PAN) polymer when reinforced with defragmented multiwall carbon nanotubes. In conventional chopped fiber-reinforced polymer composites, uniform distributions of fibers throughout the matrix are critical for producing materials with superior physical and electrical properties. The previous methods have dispersed carbon nanotubes by aggressive chemical modification of the nanotubes or by the use of a surfactant prior to dispersion. Here, ultrasonic energy was used to uniformly disperse and defragment the multiwall nanotubes (MWNTs) in solutions and to incorporate them into composites without chemical pretreatment. A common solvent dimethylformamide (DMF) is used for the dissolution process. The film is formed by solvent casting method which involves evaporation of the homogeneous solution of CNT and polymer. Electrical characteristic studies were done on the film samples. The electrical properties such as conductivity and resistivities were found and compared to the original polymer matrix.

Keywords Carbon nanotubes (CNT) · Dimethylformamide (DMF) · Nanocomposite · Single-wall carbon nanotubes (SWNTs) · Multiwall carbon nanotubes (MWNTs) · Polyacrylonitrile (PAN) · Chemical vapor deposition (CVD)

1 Introduction

Recent theoretical and experimental studies suggest that carbon nanotubes have remarkable mechanical and electrical properties [1–4]. In this article, the electrical properties of carbon nanotubes [5] are applied to enhance the conducting property

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of a poor conductor [6]. The previous study indicated that most polymers are poor conductors [7]. Our broad objectives were to explore the development of advanced composites in which carbon nanotubes serve as the reinforcing element in a polymer matrix. Although several studies have focused on producing polymer nanotube composites, many practical challenges remain before their potential can be fully realized. Dispersing the nanotubes individually and uniformly into the matrix seems to be fundamental in producing composites with reproducible and optimal properties [8, 9]. The article focuses on dispersing defragmented MWNTs into the polymer matrix using solvent casting process [10, 11] and analyzing the change in the electrical properties of the nanocomposite material. Polyacrylonitrile (PAN) was chosen as the matrix material because its properties are well known; it is soluble in a broad range of solvents; and its clarity allows dispersion of MWNTs to be observed at the micron scale [12]. DMF (dimethylformamide) was chosen as a common solvent. MWNTs were prepared without any aggressive chemical pretreatment, purification, or modification using CVD method [13]. MWNTs and the polymer (PAN) solutions were dispersed and defragmented using a probe sonication process. The solution samples were evaporated to form a film using solvent casting process [14] which was later characterized by scanning electron microscopy (SEM) to determine dispersion and orientation of MWNTs within the PAN matrix. Composite samples were tested for its electrical properties such as conductivity and resistivity, and the results were plotted and tabulated.

2 Experimental

2.1 Synthesis of CNT (CVD Method)

See Fig. 1.

2.2 Process

The catalyst employed was a 1:1 mixture of misch metal-based alloy ($MmNi_3$) and graphene oxide (GO). Hydrogen decrepitation was employed for powdering the ingot of $MmNi_3$, and a modified Hummer's method [15] was used for preparing GO as described by the authors [16, 17]. The catalysts were grinded together in a mortar for a few minutes and then loaded into the center of a horizontal quartz tubular reactor, and hydrogen was allowed to enter at 240 °C for 30 min. Hydrogen reduction of GO to graphene has been observed under these conditions. The sample was heated further at 700 °C, before introducing a burst of acetylene (C_2H_2) as the carbon containing precursor, in addition to the argon (Ar) flow. The as grown samples were purified by refluxing in conc. HNO_3 at 60 °C for 6 h where the end hemispherical distorted

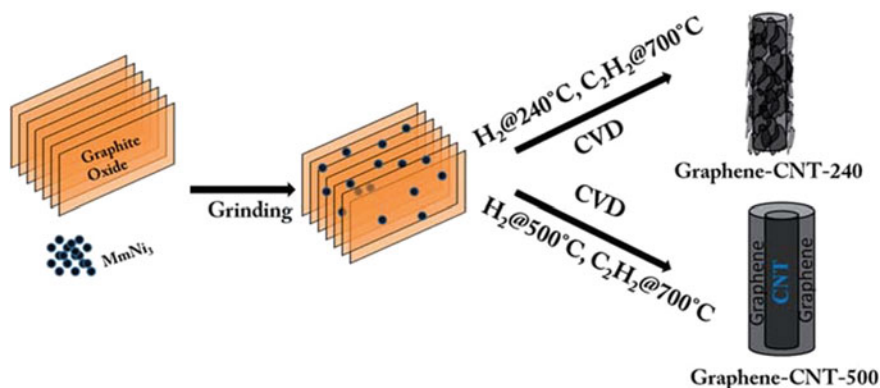


Fig. 1 Schematic illustration of the synthesis of graphene-coated CNT composites

carbon layers were removed. Acid-treated samples were washed with deionized water until pH 7, filtered using a 0.2 micron polytetrafluoroethylene (PTFE) membrane, and dried at 60 °C in a vacuum. The graphene-wrapped CNT samples grown at 240 °C and 500 °C of H₂ flow were labeled as graphene-CNT-240 and graphene-CNT-500, respectively. The growth mechanism of the graphene-wrapped CNT is now considered. At 500 °C, GO exfoliated into graphene sheets in the presence of hydrogen gas. The reaction was further carried out by allowing acetylene at 700 °C. When the catalyst particle (MmNi₃) is saturated with carbon, carbon leaves the particle in another form. Saturated carbon atoms nucleate into six membered rings and finally lead to CNT formation which is described in Fig. 1. The magnified images using FESEM and TEM are described in Fig. 2. This is the well-reported vapor liquid solid (VLS) mechanism for the growth of carbon nanotubes by chemical vapor deposition. The graphene nanosheets located at a distance of ≥ 0.35 nm from a nanotube get affixed to the surface of the nanotube by van der Waals interaction.

2.3 Observation and Inferences

The catalyst (MmNi₃) must be crushed into very fine powder. The growth of the carbon nanotubes takes place on the surface of the catalyst. Hence, finer the particles of the catalyst more surface area is formed for nanotube growth. The tubular structure of CNTs depends upon the insertion of gases at optimal temperature. Hydrogen is passed at 2400 °C to reduce the graphene oxide into graphene. The oxide group reacts with hydrogen and leaves as water vapor from the furnace. Graphene is the main source of carbon to form the carbon nanotubes. Acetylene is passed at 7000 °C to separate the carbon nanotubes from the misch metal catalyst.

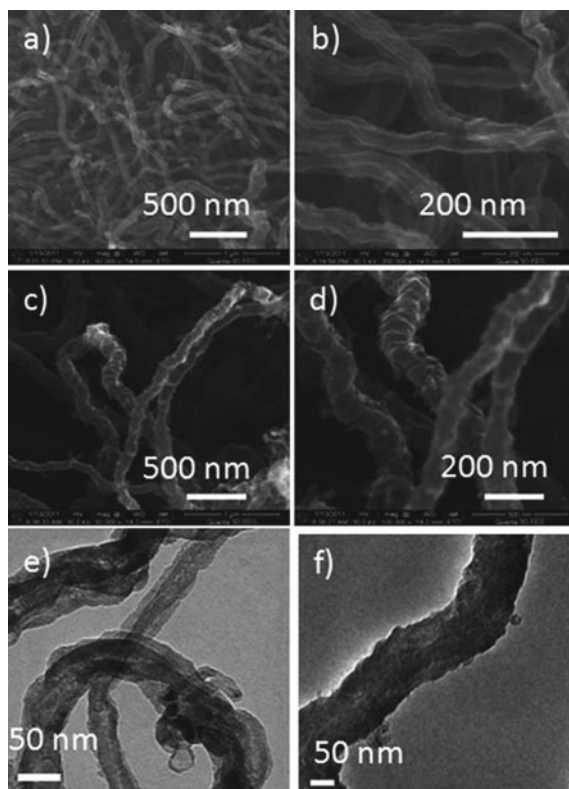


Fig. 2 **a** Low, **b** high-magnification FESEM images and **e** TEM images of graphene-CNT-500; and **c** low, **d** high-magnification FESEM images **f** TEM images of graphene-CNT-240

2.4 FESEM and TEM Images of Purified CNT

The CNTs formed by CVD method were checked for morphology using field electron scanning electron microscope (FESEM) and transmission electron microscope (TEM) at different magnifications. The tubular structures are the carbon nanotubes indicated in Fig. 2.

2.5 Carbon Nanotube Production Device by Chemical Vapor Deposition

Three independent temperature adjusters are applied to control the temperature at different positions of quartz tube furnace to gain high temperature balance so that the created carbon tube has high crystallizability. Various carbon nanotubes or nano-coil,

micro-carbon coil, and hexagonal crystal lattice may be created and form film. Put silicon, quartz, porcelain, oxide, and other carriers in the external import device with catalyzer precursor which is prepared at advance, catalyst and carbon nanotube will be created at the same time, without the necessity to prepare catalyzer separately. The device can easily prepare highly dispersed CNT compound with CNT lamella structure/core structure of compound material. The catalyst is placed in the center of the furnace to ensure that there is uniform heating and uniform chemical vapor deposition. The gases and other chemicals are passed as mentioned earlier, and various formation processes of the carbon nanotubes take place at their respective temperatures.

2.6 Preparation of Polyacrylonitrile Polymer (PAN)

The polymer used in this research was purchased from Sigma-Aldrich. The polymer has 99% purity and a molecular weight ranging from 1,50,000 to 2,00,000 mol. Preparation method adopted to prepare this polymer is described by the authors of [18] in Fig. 3.

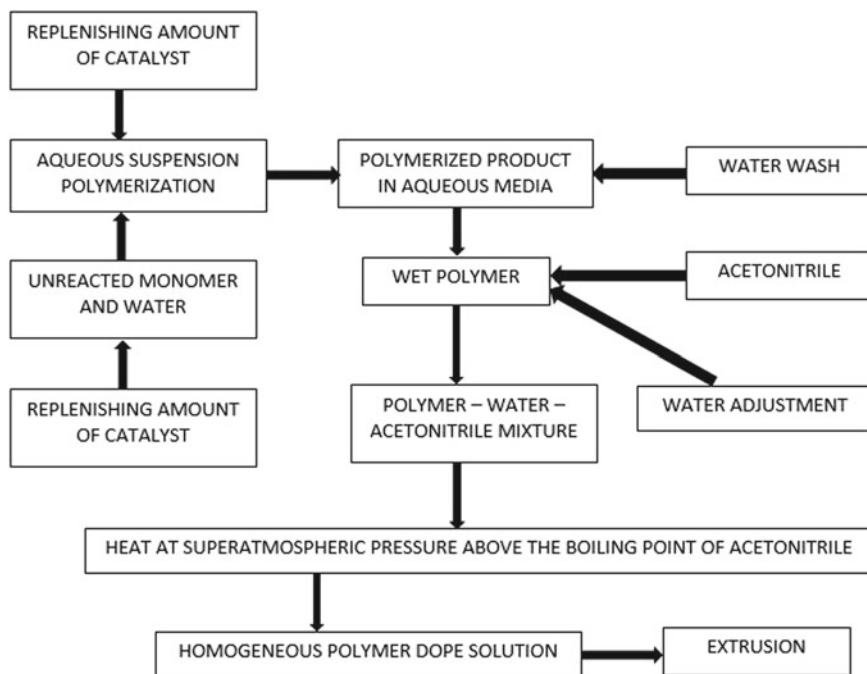


Fig. 3 Flowchart of the preparation process of polyacrylonitrile

2.7 *Preparing the Polymer Solution*

Polyacrylonitrile (PAN) powder was first weighed and placed in the beaker described in Fig. 4. It is then dissolved in DMF using a probe sonicator which produces ultrasonic waves to form a homogeneous polymer solution described in Fig. 5. The time used for obtaining a complete homogeneous solution of PAN is about 12 min having an OFF and ON cycle of 5 s and with a pulse of 50 Hz.

Fig. 4 Polyacrylonitrile polymer (PAN) weighed in a beaker before preparation of PAN solution

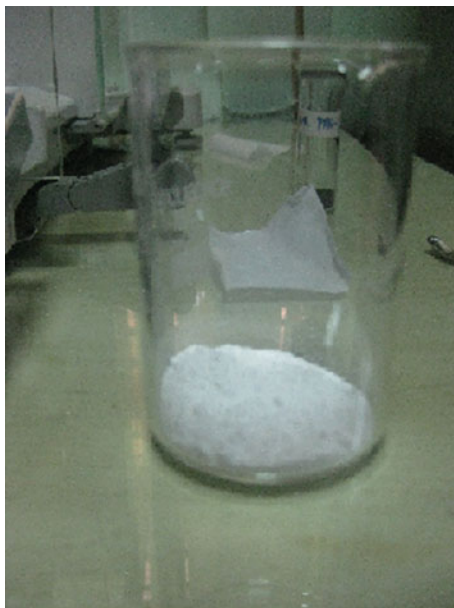
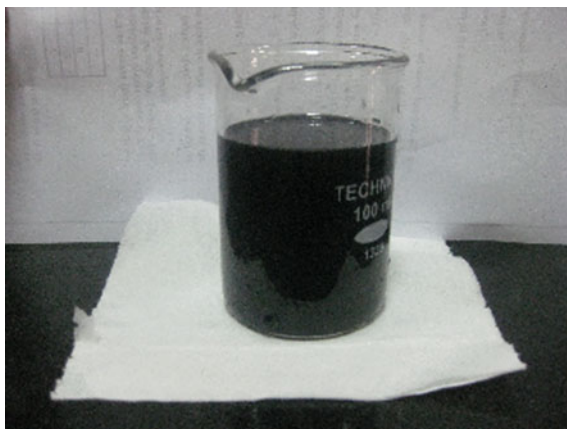


Fig. 5 Prepared PAN solution after probe sonication process



Fig. 6 Prepared CNT solution after probe sonication process



2.8 Preparing the Carbon Nanotube Solution

The multiwall carbon nanotubes were weighed using the electronic weighing balance. Solutions were created with wt% varying from 1 to 10. The solvent used in this application is the same dimethylformamide (DMF). 60 ml of the solvent was taken in 100 ml beaker, and the carbon nanotubes were added. The amount of carbon nanotubes added for every sample preparation varies from 10 to 100 mg, respectively. A total of 10 samples were created with weight percentage 1–10 %wt. The probe sonicator was used to disperse and defragment the carbon nanotubes in DMF. The complete dispersion takes place in 20 min and having an ON cycle of 15 s and OFF cycle of 5 s and with a pulse of 50 Hz. The final homogeneous solution of defragmented CNT and DMF is shown in Fig. 6.

2.9 Mixing the Polymer and Carbon Nanotubes Solutions

It was ensured that the solvent chosen (DMF) would be a common solvent for both PAN and CNTs, thereby assuring no chemical reactivity between solvents. The two solutions formed in 2.7 and 2.8 were mixed using a probe sonicator for about 30 min with a pulse of 50 Hz and an ON and OFF cycle of 5 s. A homogeneous solution of defragmented CNT and PAN was formed which is described in Fig. 7. Evaporation process is carried out by pouring the solution in a 4-inch petri dish and placing it on a hotplate as shown in Fig. 8. The hot plate is maintained at a constant temperature of 90 °C. A vacuum furnace can also be used for evaporation purpose.

The evaporation process takes place till all the solvent has evaporated and a thin film (50 μm thick) of composite material is formed in the petri dish as depicted in Fig. 9. The film was then peeled from the petri dish carefully without tearing as shown in Fig. 10. This method adopted for preparing a thin film by evaporating

Fig. 7 Prepared homogeneous solution of CNT and PAN by probe sonication process

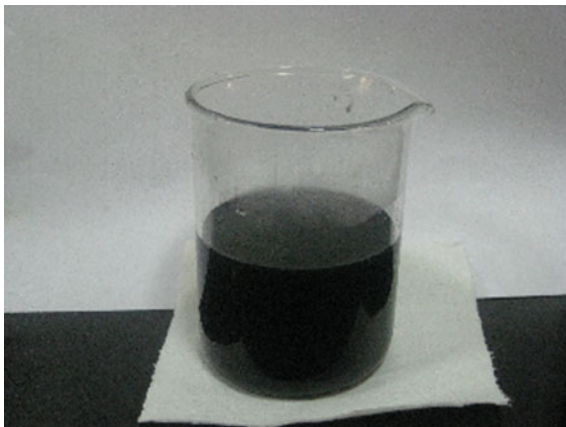


Fig. 8 Homogeneous composite solution placed on a hot plate for evaporation process



Fig. 9 Nanocomposite films which is formed after evaporation (solvent casting process)

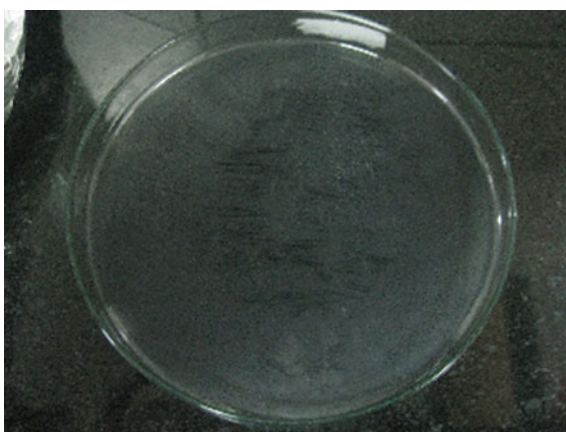


Fig. 10 Composite films when taken out from petri dish



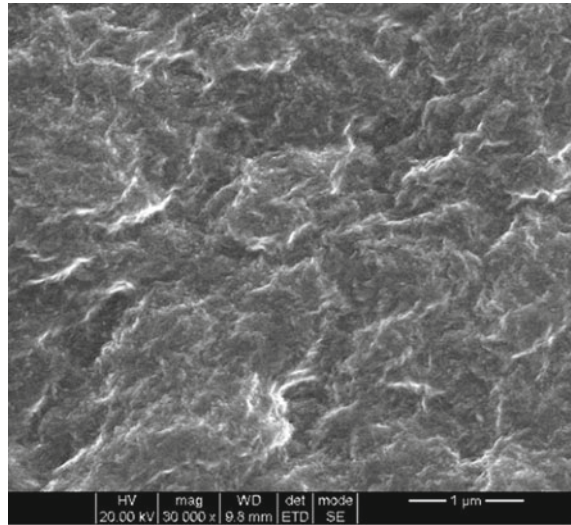
the common solvent is known as solvent casting process explained in detail with an example by the authors of [19, 20]. The concentration of the nanotubes was varied with respect to the polymer concentration. The same process was repeated for all the samples and was checked for its morphology using a scanning electron microscope. SEM observations at low resolution were used to assess the degree of dispersion of the defragmented carbon nanotubes in the polymer matrix.

3 Result and Discussion

The tubular structure of carbon nanotubes has been distorted into flake-like structures during probe sonication. According to references [1–4], carbon nanotubes have excellent electrical conducting properties. Our discussion focused on using this property of CNTs to enhance the electrical conductivity of insulators, namely polymers by incorporating CNTs into them. Polymers have two major drawbacks which restrict its usage. One being its mechanical strength and other its electrical and thermal properties. By overcoming its drawbacks and with addition to its advantages (light in weight, high corrosion resistant, etc.), it would have a huge impact in replacing conventional materials in structural and electrical domains.

The samples were observed under a scanning electron microscope, and images of the morphology were obtained. The following are the SEM images for a few samples of the nanocomposite film. It is evident that the carbon nanotubes are completely defragmented into carbon layers or strands of carbon. This carbon is represented by the dark shaded area in the image. The lighter strands represent the polymer polyacrylonitrile strands which are spread throughout the matrix. Fig. 11 is the SEM image of 4 %wt CNT (which is 40 mg of CNT in 960 mg of polymer). The magnification was taken to 1 μm , and the analysis was conducted. While the defragmentation process using the probe sonicator, it is noticed that complete defragmentation into

Fig. 11 Low-resolution SEM images of composite films prepared using the probe sonicator



pure carbon will occur only during extensive use of the device. Figure 11, 12, and 13 indicate a lesser level of defragmentation of the CNTs which can be noticed by the flake-like structure indicating the graphene distorted rings merged with polymer. Hence, longer the sonication process, more the defragmentation of CNTs occurs. The flake-like structure indicated in Fig. 12 has graphene layers fused with the polymer which was the result of defragmenting the CNTs during solvent casting it with the polymer. The magnification was taken at 500 nm. Partial flakes and dispersion of PAN and defragmented CNTs are noticed in Fig. 13. The sample consisted of

Fig. 12 SEM image of nanocomposite containing 5% wt CNT

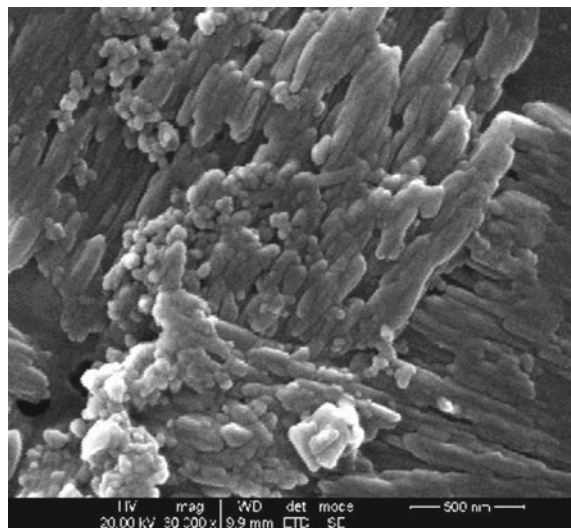
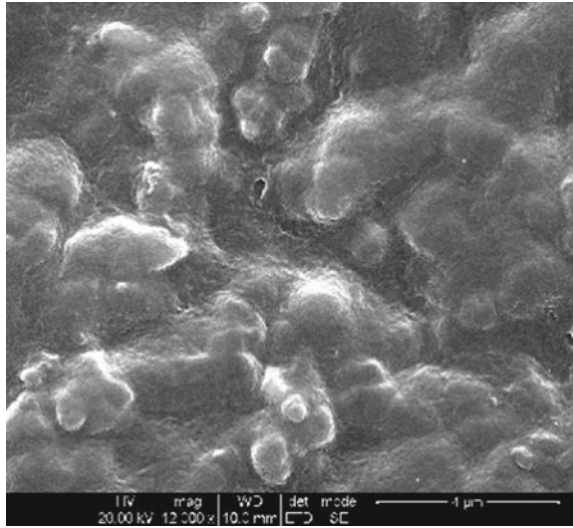


Fig. 13 SEM image of nanocomposite containing 8 %wt CNT



8 %wt CNT and was magnified at 1 μm . The broad flake-like structure represents the carbon/graphene structure merged with the polymer which is similar to Figs. 11 and 12 (Fig. 14 and Table 1).

Table 2 indicates the values which have been measured using a multimeter. This multimeter has a very high sensitivity of measuring resistivity of sample. The resistance and conductivity have been calculated using basic formula of electrical resistance and resistivity formula. The graph shows the variation of various electric properties of the nanocomposite with the variation of carbon nanotube weight percentage.

Fig. 14 SEM image of nanocomposite containing 9 %wt CNT

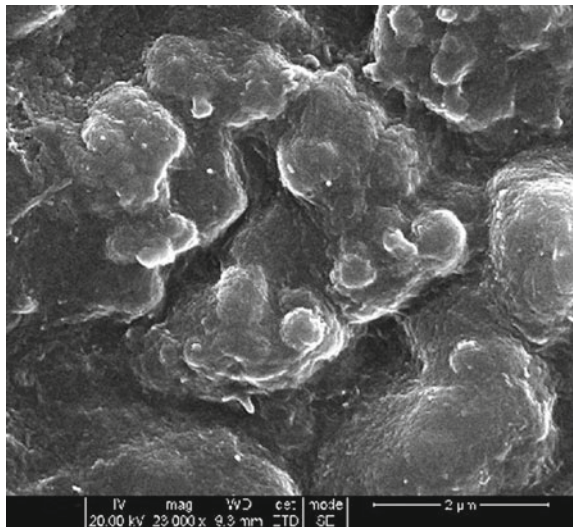


Table 1 Concentration of various samples

S. No.	Percentage of CNT (%)	Weight of CNT added (mg)	Weight of polyacrylonitile (mg)
1	2	20	980
2	3	30	970
3	4	40	960
4	5	50	950
5	6	60	940
6	7	70	930
7	8	80	920
8	9	90	910

Table 2 Electrical characteristics measured

S. No.	CNT (wt%)	Resistivity (Ωm)	Resistance (Ω)	Conductivity (S/m)
1	2	210.17	2526.45	3.96×10^{-4}
2	3	87.16	1045.43	9.57×10^{-4}
3	4	33.26	399.12	2.50×10^{-3}
4	5	8.66	103.92	9.62×10^{-3}
5	6	3.75	45	0.022
6	7	1.51	18.12	0.055
7	8	0.57	6.84	0.146
8	9	0.16	1.92	0.52

The electrical resistivity of the material decreases gradually with increase in concentration of CNT as shown in Fig. 15. Similarly, resistance decreases by a large extent with increase in CNT as shown in the graph. Conductance increases drastically with the increase in CNT as shown in the graph. Resistivity is measured in Ωm (ohm

Fig. 15 Resistivity, resistance, and conductivity versus CNT concentration

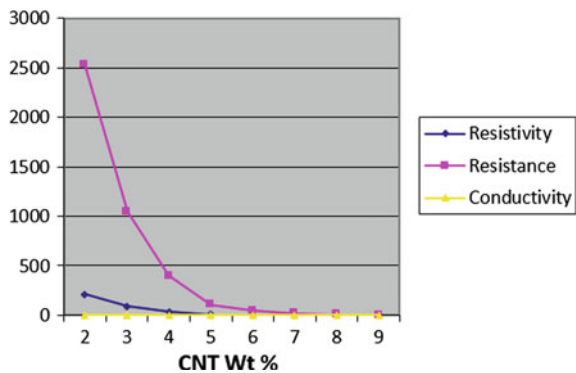
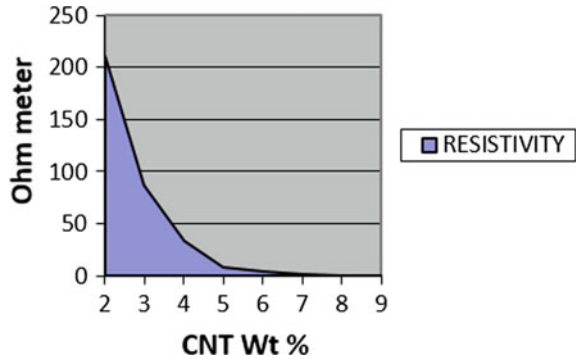


Fig. 16 Resistivity versus CNT concentrations



meter). Weight of the CNT in the composite is measured in mg. Figure 16 shows that with the increase in carbon nanotubes in the polymer matrix, the resistivity decreases. This happens because the free electrons travel through a defined path along the carbon nanotubes. Therefore, there is less opposition to the flow of electrons. Hence, there is decrease in resistivity with more number of CNTs added in the polymer matrix. Resistance is measured in ohms (Ω). Concentration of the CNT is measured in mg. Resistance is defined as the opposition to the flow of electric current. This opposition involves protons which oppose the flow of electric current by creating a barrier. When CNTs are added to the polymer matrix, the potential barrier space is reduced drastically and the concentration of current along the carbon nanotubes increases; hence, the opposition is less. Therefore, there is a decrease in resistance with more number of CNTs added in the polymer matrix as shown in Fig. 17. Conductivity is measured in siemens/meter. The concentration of the CNTs is measured in mg. Conductivity is defined as the flow of electrons through a material for a specified area of cross section and length. The conductivity of the material increases drastically with the increase in CNT concentration as depicted in Fig. 18. Hence, conductance also increases. The flow of electrons is aligned along the carbon nanotube walls and acts as a carrier of current which is present all through the polymer matrix.

Fig. 17 Resistance versus CNT concentrations

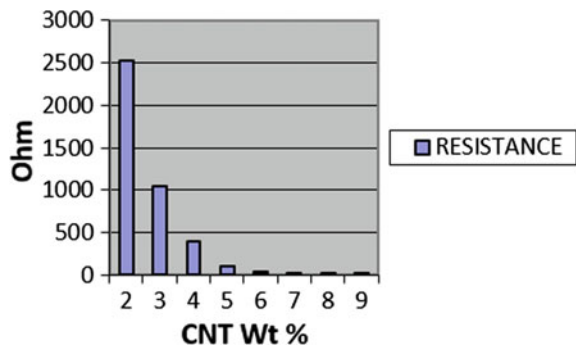
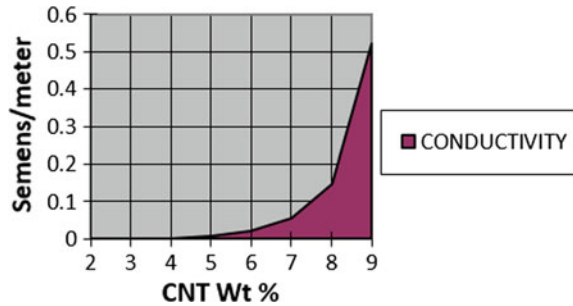


Fig. 18 Conductivity versus CNT concentrations



4 Conclusion

It has been experimentally proved that by inserting the carbon nanotubes into the polymer matrix, the electric properties of the polymer are improved drastically. The original resistance of the polymer was found to be in the range of $10^{16} \Omega$. After adding carbon nanotubes into the matrix, it was found to be in the range of 10 to $10^3 \Omega$. This proves that a significant increase in the electrical properties of a polymer can be improved by addition of carbon nanotubes. With further doping of carbon nanotubes, the conductance can be compared with the present materials which are used for electrical purposes such as copper and silver. The PAN nanocomposite is a unique material which consists of good electrical properties, high tensile strength which is inherited from the carbon nanotubes and also good corrosion resistant which is inherited from the polymer polyacrylonitrile.

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