



## The Effect of MWCNT on the Mechanical and Electrical Properties of HDPE/MWCNT Nanocomposite

Mohammad Ghalenovi<sup>1</sup>, Mahdi Pourafshari Chenar<sup>1,\*</sup>, Seyed Abbas Mousavi<sup>2</sup>, Hamid Afshoun<sup>1,3</sup>, Seyed Reza Ghafarian<sup>3</sup>

<sup>1</sup> Chemical Engineerin Department, Faculty of Engineering, Ferdowsi Univercity of Mashhad, Mashhad, Iran

<sup>2</sup> Chemical & Petroleum Engineering Department, Sharif University of Technology, Tehran, Iran

<sup>3</sup> Khorasan Razavi Gas Co., Mashhad, Iran

\*[pourafshari@um.ac.ir](mailto:pourafshari@um.ac.ir)

### Abstract

In this study the developmnet of a method for the preparation of multiwalled carbon nanotube (MWCNT) reinforced high density polyethylene (HDPE) nanocomposites based on high energy ball milling (HEBM) with consequent improvement of the electrical and mechanical properties of the samples was aimed. In this regard, HEBM was used as an innovative process to incorporate MWCNTs into the HDPE matrix at room temperature without any solvents, ultrasonication, chemical modification or physical treatment of the nanotubes. HDPE/MWCNT nanocomposites with 1, 2, 3, 5, and 10 wt% of MWCNTs were prepared. After that, the effect of MWCNT loading on the mechanical and electrical properties of the nanocomposites was investigated.

MWCNT/HDPE nanocomposites showed a significant increase in electrical conductivity with increasing MWCNT loading and a percolation threshold of about 3 wt% was obtained. The volume resistance of HDPE was decreased 8 orders of magnitude, from  $10^{17}$  to  $10^9$   $\Omega$ .cm. Tensile test also showed 48% increase in the Young's modulus (from 722.19 MPa to 1066.4 MPa), increase in yield stress from 8.65 to 9.13 MPa and ultimate tensile strength from 19.67 to 22.1 MPa due to 5-10 wt% addition of MWCNT into the HDPE.

**Keywords:** Polyethylene, Multiwalled carbon nanotubes, High energy ball milling

### Introduction

Carbon nanotubes (CNTs) are being used in various fields such as chemistry, physics, material science, and electrical engineering. The inherent very high electrical and thermal conductivity, capacity to storage hydrogen, selectively permeable membranes and use as sensors for gas detection and also use as reinforcement in composites has been reported [1]. CNTs are hardly participate in any chemical reaction. They are insoluble in any solvents and can not be melted or fused at any temperature before decomposing [2].

Multiwalled carbon nanotubes (MWCNTs) comprise of many concentric cylinders around a common central hollow with a constant separation between the layers. The interlayer spacing is about 0.34 nm. Length of each cylinder is several microns and its diamater is in the range of 2 to 25 nm. Each cylinder can be explained by a different helical angle. The graphitic nature of the nanotube lattice results in a fibre with high stiffness, strength and conductivity [3].



As mentioned, CNTs have superior mechanical, electrical and thermal properties. CNTs have very high Young's modulus ( $\sim 1$  TPa), comparable to that of diamond (1.2 TPa) and the tensile strength is in the range of 10-50 GPa [3,4]. The excellent mechanical properties of CNTs is due to the high strength of the C-C bonds and their complete lattice structure. In addition, depending on CNTs atomic structure, CNTs can be either electrically conductive or semi-conductive. They demonstrate electrical conductivity as high as  $10^5$ – $10^7$  S/m (1000 times higher than that of copper wire) and thermal conductivity equal to 3000  $\text{Wm}^{-1}\text{K}^{-1}$  (twice of that of diamond) [1]. Therefore, composites which contain CNTs as filler have chance to get electrical conductivity in very low filler contents compared to other used conductive fillers, such as carbon blacks, metallic powders and other nanoparticles. It means that CNTs are cost effective and have high performance. So, many of current researches are focused on the manufacturing of nanotube reinforced polymer matrix composites. The main purposes of researches are following this goals: improvement of the mechanical properties, enhancement of thermal properties and electrical conductivity of the composites. CNTs reinforced polymer matrix composites which their electrical resistivity have been reduced, are using in applications where static electrical dissipation is needed, such as in antistatic panels, protections or packages of electronic components, exterior automotive parts, gas transmission pipelines and so forth [5].

High density polyethylene (HDPE) is a commodity polymer, cheap and with different applications in many fields and commercial uses in a variety of forms and ease of availability. In addition, HDPE supplies superior chemical resistance, high impact strength, good fatigue and abrasive wear resistance, low coefficient of friction, moderate stiffness and rigidity [3]. Currently, different methodes have been used to improve the mechanical and physical properties of HDPE. These include cross-linking, reinforcement with carbon fibers and carbon black, reinforcement with nanoparticles and reinforcement with carbon nanotubes [6]. It should be mentioned that, if the expansion of HDPE application fields and enhancment of HDPE properties are the object, suitable dispersion and alignment of CNTs in the polymer matrix are desirable.

The properties of CNT reinforced polymer composites depend on different factors such as the purity of carbon nanotube, diameter, length, aspect ratio and type of carbon nanotube, orientation, dispersion and distribution of carbon nanotube in the polymer matrix and so on [6]. Because of small size and large surface area of CNTs, they are powerfully affected by van der Waals forces. These forces lead to the formation of aggregates, which make the dispersion of CNTs in polymers difficult, so overcoming this clumping of nanotubes in the manufacturing of CNTs/polymer nanocomposites should be done. To obtaine the highest performances of nanocomposite, a uniform dispersion of nanotubes in the polymer matrix, and so strong interfacial interaction between the polymer and the nanotubes, which is very important for load transfer from the polymer matrix to the nanoparticles, is required. Any load applied to the polymer matrix should be transferred to the nanotube particles. This load countes on the strong and effective interfacial stress transfer at the polymer–nanotube interface. The homogeneous dispersion of carbon nanotubes is not easy to achieve, especially in nonpolar polymers such as polyolefines.

Currently, there are many commonly used methods for better mixing and incorporation of CNTs into the polymer matrix: direct mixing, high power ultrasonic mixers, surfactants, in-situ polymerization, solution method and melt processing. These techniques may have many limitations, for example they may not be commercially viable and are environmentally arguable. Recently, reaserchers found a new method relies on solid-state mixing at ambient temperature, which can be a very good alternative and efficient procedure for mixing two or



more species by mechanical milling, without need to high temperatures or solvents. Mechanical milling and mechanical alloying are techniques originally developed in the late 1960's for the solid state processing of metals [7]. Nowadays, mechanical alloying is widely used in the metal industry for producing powders from metal composites with very fine microstructures. High energy ball milling (HEBM) is also a new effective unconventional method currently used in material synthesis and processing. This technique may support the more conventional and utilized techniques for producing nanocomposites, mainly based on in-situ polymerization and melt extrusion [5].

There are only a few studies on CNTs reinforced polyethylene. Tang et al. [8] prepared composite films of HDPE/MWNT containing up to 5 wt% MWCNTs by melt processing. They found an increase in the stiffness and work to failure of 7.88% and 4.95%, respectively, for the 5 wt% composite. Ruan et al. [9] reported an increase in the ductility by addition of 1 wt% MWNTs to UHMWPE films processed by solution casting. Wang et al. [10] also prepared UHMWPE fibers reinforced with MWNTs by gel spinning. They reported very small increase in the tensile strength and modulus by addition of 3 wt% MWCNTs.

In this paper the preparation of HDPE/MWCNT nanocomposites using HEBM at room temperature in the dry state with no chemical or physical treatment or functionalising of the nanotubes was investigated. The morphology of prepared nanocomposites and dispersion of MWCNTs in the HDPE matrix were also studied. The effect of loading of nanotubes was analyzed as function of the mechanical and electrical properties to determine the percolation threshold for this system.

### **Experimental**

Multi walled carbon nanotubes (MWCNT) were purchased by Neutrino (Iran). They were synthesized by chemical vapor deposition (CVD) process. The carbon purity was found higher than 95% (reported by manufacturer). The specific surface area (SSA) was higher than 250 m<sup>2</sup>/g. According to the specifications of the manufacturer, the samples of nanotubes were 10-20 nm in outer diameter (OD), 5-10 nm in inner diameter (ID) and about 10-30 μm in length. The density of MWCNTs was about 2.1 gr/cm<sup>3</sup> and the electric conductivity (EC) was higher than 100 S/cm.

The polyethylene (PE) used in this study was high density polyethylene (HDPE) kindly provided by Arak Petrochemical Co. It was in the form of white powder of bulk specific gravity 622 kg/m<sup>3</sup> (HDPE density ρ=940 kg/m<sup>3</sup>) to promote the best mixing during the milling, with a melt flow index (MFI) equal to 10.8 g/10 min (at 190°C, 21.6 kg).

The Planetary Ball Mill, supplied by Ferdowsi University of Mashhad was used to mix MWCNTs and HDPE powder. The Hot Press supplied by Iran Polymer and Petrochemical Institute (IPPI) was used to melt and mold the nanocomposites. AZC-36 Resistance Test Meter (Polymer and Petrochemical Institute, Iran) equipped with ring electrodes was used to measure resistance of the nanocomposites. The tensile strength of the nanocomposites was measured using a Zwick/Z250 tensile testing machine supplied by Ferdowsi University of Mashhad.

Powders of MWCNTs and HDPE were milled in the solid state in the ball mill. Before start milling, 0.1 wt% of calcium stearate, 0.1 wt% of zinc stearate (to increase the processability of the samples) and 0.3 wt% of B215 (to prevent oxidation) were added to the mixture. After that, constant weight ratio of ball/powders (i.e. 10) were added to the ball mill. Samples were milled in a cylindrical steel jar of 50 cm<sup>3</sup> with 20 steel balls with different diameters. Applied rotation speed was 300 rpm and milling time was fixed at 2 hours. During the milling, the carbon nanotube bundles crack, and intimate mixing are promoted.



In these experimental conditions, five HDPE/MWCNT nanocomposites with 1, 2, 3, 5 and 10 wt% of carbon nanotubes were prepared. Pure HDPE sample to be taken as the reference was also milled. The HDPE/MWCNT mixtures and the pure milled HDPE were molded and pressed at  $120 \text{ kg/cm}^2$  pressure and  $190\text{-}200^\circ\text{C}$  for 1-2 minutes by a hot press. After forming films with  $3\text{ mm}$  ( $\pm 0.1\text{ mm}$ ) thickness, samples were quenched with water bath (at  $15^\circ\text{C}$ ). The melting point of HDPE is around  $135^\circ\text{C}$  but it is very viscous at this temperature and consolidation takes a long time if done at the melting point. So it was necessary to perform consolidation at slightly higher temperatures (for example at  $190^\circ\text{C}$ ). The samples will be coded as follows: NX, where  $X = 0, 1, 2, 3, 5$  and  $10$  that indicates the weight percent of CNTs in the samples ( $X=0$  denotes the pure HDPE).

The tensile tests were carried out on the samples using an Zwick/Z250 tensile tester. Each sample was in the shape of a dog bone with a length of  $115 \text{ mm}$ , width of  $19 \text{ mm}$  and a thickness of  $3.2 \text{ mm}$ . The gage length of the sample was  $25 \text{ mm}$ . Tensile tests were performed at ambient temperature at a constant cross-head rate of  $5 \text{ mm/min}$ .

The mechanical properties of the samples were evaluated from obtained stress-strain curves. The Young's modulus, yield stress and ultimate tensile strength of the nanocomposites was determined from tensile testing dumbbell samples.

Volume resistance was measured with a AZC-36 Resistance Test Meter. Small strips of HDPE/MWCNTs nanocomposites ( $\sim 9 \times 9 \times 0.3 \text{ cm}^3$ ), (both sides of the samples were coated by silver paste to ensure an intimate contact with electrodes) were used as resistors between two dedicated holding clamps in a 2-probe resistance measurement set-up. A DC voltage was applied along the length direction of the strips and the corresponding current was measured.

## **Results and Discussion**

### **Morphological analysis**

Figures 1 and 2 show the SEM and TEM images of the as-received MWCNTs.

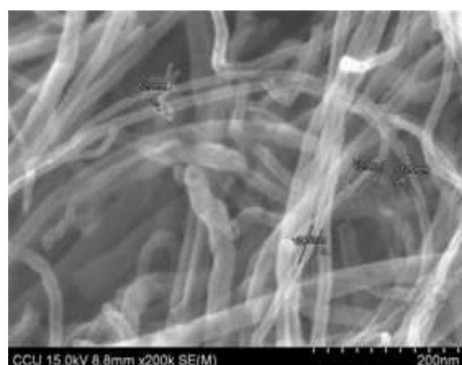


Fig.1. SEM microphotograph of used CNT

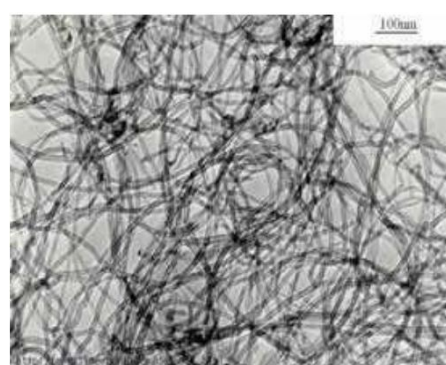


Fig. 2. TEM micrograph of used CNT

As we can see, the tubes have an integrated structure and there are some spiral tubes. Helical structure leads to better anchoring and CNTs attach firmly in the polymer matrix than straight nanotubes. Also, it was appear that the average diameter and length of the tubes are  $10\text{-}20 \text{ nm}$  and up to  $10 \mu\text{m}$ , respectively.

### **Mechanical Properties**

Figure 3 shows a picture of the tensile samples. White sample is pure HDPE and black sample is a HDPE/MWCNT nanocomposite sample. The stress-strain curves of the samples (Fig. 4), show that at the beginning zone (nearly at strain=0.1), according to Hook's law, the stress is



proportional to the deformation. After yield stress, we see a flat zone with constant stress. In this zone samples begin to stretch and its shape is similar to the neck. Following the neck propagation, a zone in which a higher stress is needed for small deformations, up to the breaking of the sample was observed. According to the obtained results, maximum stress attained by the samples or ultimate tensile strength ( $\sigma_{UTS}$ ) of HDPE and HDPE-5wt% MWCNT film was found to be 19.67 MPa and 22.1 MPa, respectively.



Fig. 3. Picture of the tensile samples

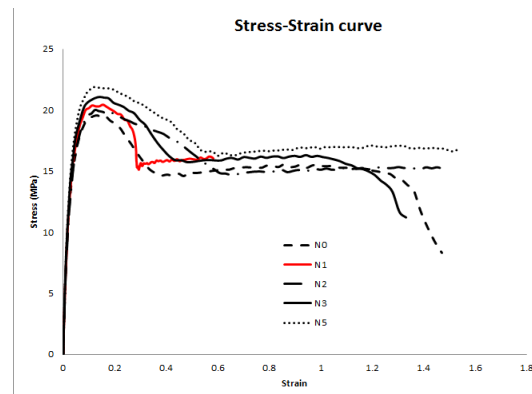


Fig. 4. The stress-strain curves of the samples

The mechanical properties of the nanocomposites were measured as a function of MWCNT loading. Figure 5 shows the Young's modulus curve which derived from the stress-strain curves. As shown, a significant increase of the Young's modulus of the polymer up to 5 wt% of the filler was obtained. The Young's modulus of HDPE and HDPE-5 wt% MWCNT film was found to be 722.19 MPa and 1066.4 MPa, respectively. It can be clearly seen that 48% increasing in Young's modulus due to addition of 5-10 wt% MWCNT to the polymer matrix was obtained. Figure 6 shows the yield stress of nanocomposites as function of MWCNT loading. As shown, the yield stress increases with increasing the CNT (wt%) loading. As seen in Fig. 6, the yield stress ( $\sigma_y$ ) increased slightly as the loading of MWCNTs increased up to 5 wt% (from 8.65 to 9.13 MPa), after that a dramatically increasing in yield stress between 5-10 wt% of MWCNTs was observed and final yield stress became 9.13 MPa at 10 wt% of MWCNT. So, 48% increasing in yield stress was obtained.

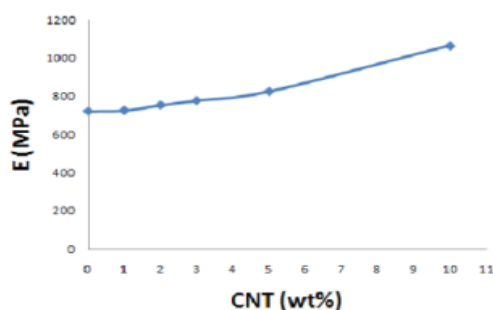


Fig. 5. E (Young's modulus) [MPa] of HDPE/MWCNTs composites as function of MWCNT loading.

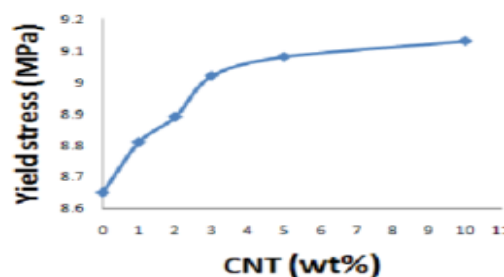


Fig. 6.  $\sigma_y$  (yield stress) [MPa] as function of MWCNT loading.

Strength in composites is a complex issue involving load transfer, stress concentrations and defect distribution, especially in the case of fibers [4]. The obtained data suggest that the



significant property enhancement, up to 5 wt% CNT was observed. The improvement of the mechanical properties of nanocomposites depends on two parameters: a) a high degree of load transfer between polymer matrix and nanotubes because of good adhesion between nanotubes and polymer matrix [5]. If interfacial adhesion between nanotube and polymer matrix is not strong enough, the nanotubes may behave as holes or nanostructured defects, in this case the benefits of the CNTs properties are lost. b) highly dispersed and well aligned nanotubes [4]. Bad dispersion may lead to significant reduction in strength.

### Electrical Properties

As stated before, this research also focuses on the study of the effect of MWCNT loading on the volume resistance and electrical conductivity of produced HDPE/MWCNT nanocomposites. Figure 7 shows the logarithmic volume resistivity ( $\Omega/\text{cm}$ ), as a function of weight fraction of MWCNT in the HDPE matrix.

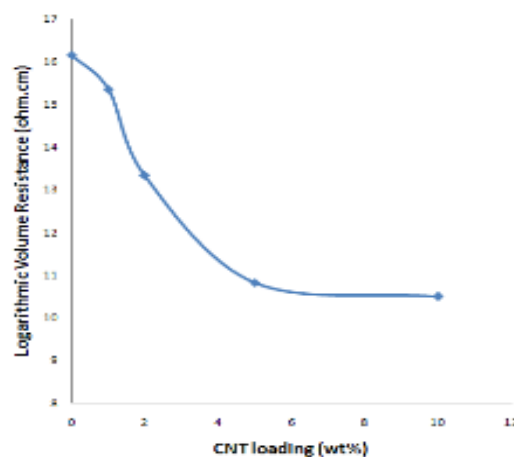


Fig. 7: Plot of the logarithm volume resistance versus the weight content of MWCNTs

From Fig. 7 it can be seen that, increasing the MWCNTs loading resulted in a progressive decrease in resistance. The volume resistivity of the pure PE used in this study was  $10^{17} \Omega/\text{cm}$ . Increasing the MWCNT loading from 1 to 10 wt%, resulted in an almost 8 orders of magnitude reduction in resistivity (increase in conductivity) to about  $10^9 \Omega/\text{cm}$ . The plot exhibited the presence of a conductance threshold between 2 and 3 wt%. According to the obtained results a significant drop in resistivity for a percolation threshold of about 3 wt% was observed. When the concentration of MWCNTs increases in the polymer matrix and supposing the efficient mixing, the average distance between nanotubes decreases until a third interconnectivity of CNTs in the PE matrix is formed. So, a network structure and a facilitated electron transport through tunnelling throughout the polymer is obtainable, where a critical minimum distance between carbon nanotube structures has been attained and electron conduction make easy through a 'hopping' or 'tunnelling' mechanism [1]. Temporary and labile bonding of chains to the filler surface leads to trapped entanglements, which has both near and far-field effects on matrix chain motion, and plays a role of physical cross-linking, thus causing greatly enhanced strength of the matrix [3, 11].

It is considerable that when carbon nanotubes used as filler in the reinforced polymer composites, around 2-5 wt% of CNT to receive a certain amount of electrical conductivity is needed, while in the case of using other conductive fillers such as carbon black and metallic powders and other nanoparticles to increase the conductivity, higher percentage of filler



(around 20–50 wt%) is required. For example, the reduction in electrical resistivity for PE on addition of MWCNTs was at least 5 orders of magnitude greater than that reported for composites of LDPE and nanoscale ZnO.

In addition the obtained results and outcomes are in agreement with others found for similar composites obtained by HEBM and also significantly better than others obtained by melt blending for which the percolation threshold is at about 4-7.5wt% [5]. The percolation threshold was reported to be 2 wt% for the MWCNT/HDPE composites prepared by solution-precipitation and 3.1 wt.% for those by solution casting-drawing using mixed-solvents [3, 5, 11 and 12].

Volume resistivity measurements of the PE-MWCNT nanocomposites also showed that the efficient dispersion, good distribution and interconnectivity of MWCNTs in PE was obtained. The complex viscosity increases as the concentration of MWCNT increases given the high aspect ratio of CNTs [1].

### **Conclusions**

In this study MWCNTs dispersion was achieved into a high density polyethylene matrix through high energy ball milling technique. Films from composite powders were obtained on a laboratory scale by hot-pressing. The obtained results are summarized below:

- Remarkably, the volume resistance of PE (the most electrically insulating of polymers), was increased by 8 orders of magnitude (from  $10^{17}$  to  $10^9$   $\Omega/\text{cm}$ ) by addition of 5 wt% MWCNTs into the polymer matrix.
- Tensile test showed 48% increase in Young's modulus due to addition of 5-10 wt% MWCNTs into the polymer matrix, 48% increasing in yield stress and ultimate tensile strength.

### **Acknowledgements**

The authors highly appreciate Khorasan Razavi Gas Co. for their technical and financial support of this research.

### **References**

- [1] T. McNally, P.P. Tschke, P. Halley, M. Murphy, D. Martin, S.E.J. Bell, G.P. Brennan, D. Bein, P. Lemoine and J.P. Quinn, Polyethylene multiwalled carbon nanotube composites, *Polymer* 46 (2005) 8222–8232.
- [2] L.M. Jian, W.X. Bao, T. Rong, W. Li, L.S. Qing and L. Qin, Carbon nanotubes periodically decorated by high-density polyethylene crystalline using solution crystallization, *Sci. China Ser B-Chem.* 52 (2009) 905-910.
- [3] D. Zhao, Q. Lei, C. Qin and X. Bai, Melt process and performance of multi-walled carbon nanotubes reinforced LDPE composites, *Pigm. Resin Technol.* 35 ( 2006 ) 341–345.
- [4] G. Gorrasi, R.D. Lieto, G. Patimo, S.D. Pasquale and A. Sorrentino, Structure-property relationships on uniaxially oriented carbon nanotube/polyethylene composites, *Polymer* 52 (2011) 1124-1132.
- [5] G. Gorrasi, M. Sarno, A.D. Bartolomeo, D. Sannino, P. Ciambelli and V. Vittoria, Incorporation of carbon nanotubes into polyethylene by high energy ball milling: morphology and physical properties, *J. Polym. Sci. Part B Polym. Phys.* 45 (2007) 597-606.
- [6] S.R. Bakshi and J.E. Tercero, Synthesis and characterization of multiwalled carbon nanotube reinforced ultra high molecular weight polyethylene composite by electrostatic spraying technique, *Composites: Part A* 38 (2007) 2493–2499.



- [7] S.M. Zebarjad and M. Noroozi, Production of polyethylene/carbon nanotube nanocomposite using mechanical milling process and investigation of its microstructure, Fibre Reinforced Composites Conference, South Africa, 2007.
- [8] W. Tang, M.H. Santare and S.G. Advani, Melt processing and mechanical property characterization of multi-walled carbon nanotube/high density polyethylene (MWNT/HDPE) composite films, Carbon 41 (2003) 2779–2785.
- [9] S.L. Ruan, P. Gao, X.G. Yang and T.X. Yu, Toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes, Polymer 44 (2003) 5643–5654.
- [10] Y. Wang, R. Cheng, L. Liang and Y. Wang, Study on the preparation and characterization of ultra-high molecular weight polyethylene–carbon nanotubes composite fiber, Compos. Sci. Technol. 65 (2005) 793–797.
- [11] E. Kymakis, I. Alexandou and G.A.J. Amaratunga, Single-walled carbon nanotube-polymer composites: electrical, optical and structural investigation, Synth. Met. 127 (2002) 59-62.
- [12] J. Du, L. Zhao, Y. Zeng, L. Zhang, F. Li, P. Liu and C. Liu, Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure, Carbon 49 (2011) 1094–1100.