PREPARATION AND PROPERTIES OF POLYSTYRENE/MW-CNT COMPOSITES

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Abstract
Polystyrene/MWCNT (Multi-walled Carbon-Nanotube) composites were fabricated by direct melt mixing method. The electrical and structural properties of the composite with different weight percentages (0.01, 0.10, 0.15, 0.20, 0.50, 1.00 and 3.00) wt % of dopant was studied using Keithley two-point probe and GBC EMMA X-ray diffractormeter respectively. The dimension of the samples is 100mmx100mmx3mm. At room temperature, the results showed significant increase in electrical conductivity value from $0.03x10^{-6}$ - $1.7x10^{-6}(\Omega m)^{-1}$ when the filler weight percentage is increase from 0.01% to 3.00%. The conductivity of the composites was also observed to increase as temperature increases. The percolation threshold was observed to occur at a very low loading of 0.10%. The structural result showed that the amorphous structure of polystyrene was converted to crystalline nature as the different weight % of filler is added. It was also observed that the crystallite size of the composites decreased as the filler weight% is increased.
Keywords: polystyrene, multiwalled carbon nanotube, composite

1. Introduction

Polymers are one of the most used materials in the modern world and have attracted a lot of attention due to its easy solution processing and low materials cost. Most polymers contain a very low concentration of free charge carriers and thus they are non-conductive and hence are not capable of being used in the fabrication of electronic components. Inorganic materials which dominates the electronic industry is very expensive and needs to be replaced with more affordable, light weight and flexible organic conducting and semiconducting polymers. The significant developments in synthetic polymer have seen the emergency of electrical conductivity as a valued property in polymers (Netravali and Chabba, 2003). Polymer electronics is an emerging technology that focuses on the development of electronic devices incorporating electrically conductive and semiconductive organic materials especially polymers.

Most polymers are electrical insulators but its electrical properties can be suitably enhanced by the addition of conductive fillers (dopants). The presence of conductive particles in an insulating polymer is known to change the composite system's electrical conductivity. The conductivity remains at the level of the undoped insulating matrix for lower filler content but with increase filler content, there is a sudden but significant increase in its conductivity. This critical concentration which is called the percolation threshold determines the insulator to semiconductor/conductor transition.

Polymer nanocomposite which are made up of polymer matrices and carbon nanotubes are a class of advanced materials with great application (Tyagi and Tyagi , 2014). A lot of research has been done on conductive polymer composites based on insulating polymer matrices using conductive fillers as dopants (stankovich et al., 2006, Arun et al., 2007, Hamed et al., 2012, kelechi and Eboatu,2014).

The polymer used in this study is the polystyrene while multiwall carbon nanotube (MWCNT) is used as the conductive filler. Polystyrene is one of most widely used plastics. It is chemically inert and does not react with most substances. It is highly flammable and burns with an orange yellow flame, giving

off carbon particles or soot. Multiwalled carbon nanotubes are zero gap metals and their high electrical conductivity makes them an excellent additive to impart electrical conductivity in an insulating polymer. They have high aspect ratio which means that a very low loading is what is needed to form a connecting network in an insulating polymer.

2. Method/Experiment

2.1: Materials

The polystyrene (with an average diameter of pellet ≈2.35mm and length ≈2.70nm) was supplied by British Drug House (BDH) chemical limited. The MWCNT (with a diameter of 6.9nm and length of 5μm), acetone and poly Vinyl Alcohol (PVA) was procured from sigma-Aldrich Inc. Canada

2.2: Method/Sample Preparation

The method employ is the melt mixing method and it is most suitable because the polymer is a thermoplastic. This technique uses high temperature to make substrate less vicious and high shear forces to disrupt the nanotube bundles.

First, the injection moulding machine was rinsed with acetone to remove any contaminants and then coated with mould releasing agent (polyvinylalcohol), PVA for easy removal of samples after formation. Then one hundred gram of polystyrene pellet (100g) was measured using a precision measuring machine and poured into the injection moulding machine and heated up. The polystyrene melted at a temperature of 240^{o}C. The melt was injected into a square Teflon mould which solidifies within 5mins. This serves as the control sample.

Another one hundred gram (100g) of polystyrene poured into injection moulding machine was heated which liquidified at a temperature of 240^{o}C after which 0.01% of MWCNT which represents 0.01% of the mass of polystyrene was measured and added into the melt. A uniform composite was achieved by the application of high shear force by the table top injection moulding machine. The composite was ejected into the Teflon mould which took about 5mins to solidify. The sample was removed and labelled X1.

The same process was repeated for the MWCNT of known different weight percentage (0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00%). and were labeled X2, X3, X4, X5, X6, and X7 respectively. A uniform thickness of 3mm was used for all the samples and a total number of 8 samples were formed. The dimension of the samples is 100mm × 100mm × 3mm which is the dimension of the Teflon mould

2.3: The characterization of the sample

The composite samples were characterized for their electrical and structural properties using two-point probe and X-ray diffractometer respectively.

Electrical analysis of the samples was carried out at room temperature (27^{0}C). The samples were also analyzed at different temperatures, 60^{0}C, 80^{0}C and 100^{0}C. These temperatures were achieved by heating the samples in an oven. The oven and the Keithley two-point probes were placed very close to each other. The heated samples were immediately transferred to the two-point probe to avoid loss of heat.

The structural characterization of the samples was done using X-ray diffractometer, GBC EMMA, CuKα radiation (kα = 1.54178 Å), with an acceleration voltage of 25 kV and current of 400 μA. The diffraction angle 2θ was scanned from 10 ^{o} to 50^{o} step size of 0.05^{o}, and rate of 2.00 ^{o}/min. This instrument determines the type of crystal lattice and intensities of the diffraction peaks.

The percentage Crystallinity calculations were carried out using Topaz Rietvel Refinement software from Bruker. The crystallite size was determine using the Debye Sherrer's formula,

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1.0)$$

Where D is the particle size (Å),

K = constant (usually k = 0.89)

λ = wavelength of the incident X-ray beam ($\lambda_{CuK\alpha}$ = 1.5418 Å),

β = full width at half maximum of the X-ray diffraction peaks (rad)

θ = Bragg angle of X-ray diffraction peak

Where percentage crystallinity [X*c*], is determined using equation 1.1, the percentage crystallinity is calculated by dividing the total area of crystalline peak by total area under the diffraction curve (crystalline plus amorphous peaks).

$$X_c = \left[\frac{I_{crystalline}}{I_{crystalline}+I_{amorphous}}\right] \times 100 \quad (1.1)$$

3. Results and Discussion

The resistivity of the samples was determined by the two-point probe. The conductivity of the sample was calculated using the relationship between resistivity and conductivity, ($\sigma = \frac{1}{\rho} = \frac{L}{R.A}$).

Figure 1 shows the plot of the conductivity of the composite against MWCNT weight % at different temperatures, it was observed that at room temperature (27^{o}C) the conductivity of the control sample is $0.03x10^{-6}(\Omega m)^{-1}$, on addition of 0.01% filler concentration there was no significant change in the conductivity. Further increase in MWCNT filler concentration to 0.10% 0.15%, 0.20%, 0.5%, 1.00% and 3.00%, the conductivity of the sample were increased to $0.86x10^{-6}(\Omega m)^{-1}$, $0.93x10^{-6}(\Omega m)^{-1}$, $0.99x10^{-6}(\Omega m)^{-1}$, $1.20x10^{-6}(\Omega m)^{-1}$, $1.61x10^{-6}(\Omega m)^{-1}$ and $1.80x10^{-6}(\Omega m)^{-1}$ respectively. The swift increase in conductivity of the sample as the filler concentration is increased **could** be attributed to increase in ion charge carriers (Raya and Majeed, 2013). Also considering the significant change in conductivity of the sample as the weight% of MWCNT is increased from 0.01% to 0.10%. It can be deduced that the percolation threshold is at 0.10% weight concentration which is in agreement with Sandler *et al.*, 2003. At this point the filler concentration becomes sufficient to provide continuous electrical paths through the polystyrene which are either making physical contact between them or separated by very small distance across which electrons can tunnel.

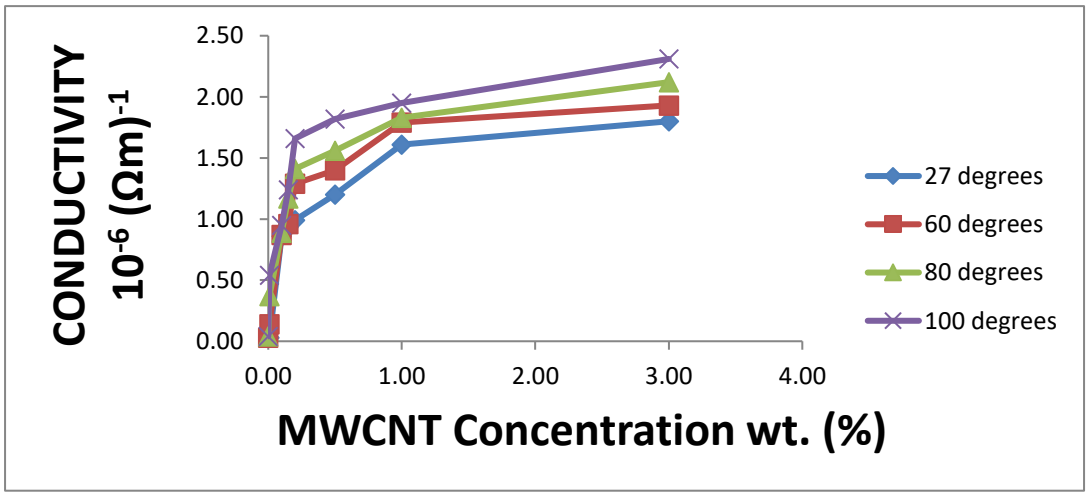


Figure 1: Graph of the conductivity of the composite against MWCNT weight % at different temperatures:

It could also be seen from the graph that as the temperature of the composites increases there is a corresponding increase in the conductivity but there was no increase in the conductivity of the control sample.
At 100 ^{o}C, the conductivity of composite at different weight % (0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00%) increases to $0.54x10^{-6}(\Omega m)^{-1}$, $0.95x10^{-6}(\Omega m)^{-1}$, $1.24x10^{-6}(\Omega m)^{-1}$, $1.66x10^{-6}(\Omega m)^{-1}$, $1.82x10^{-6}(\Omega m)^{-}1$, $1.95x10^{-6}(\Omega m)^{-1}$ and $2.31x10^{-6}(\Omega m)^{-1}$ respectively. At this temperature, it was demonstrated in figure 1 that the percolation threshold is attained faster at 0.01% filler concentration. This could be attributed to the particles gaining higher energy which increases the mobility of the ion charge carriers thereby forming conductive path faster at low filler concentration. It can also be attributed to the movement of the ion charge carriers by hopping process which is an incoherent temperature activated process in which an electron moves from one site to another which increases with increase in temperature. The results obtained compares well with the work of Guohua *et al.*, 2003 and Kelechi and Eboatu, 2014.

This increase in conductivity as a result of increase in the temperature of the composite samples shows that the doped polystyrene has negative temperature coefficient of resistance, which is a property of semiconductors.

For the structural properties, the X-ray diffraction pattern of polystyrene is shown in Figure 2. The largest specific diffraction peak at 2θ between 15^{o} - 20^{o} indicates that pure polystyrene is amorphous in nature. The X-ray diffraction pattern of MWCNT in figure 3 shows prominent peak at angle 2θ = 26.22^{o} and 44.68^{o}. The peaks correspond to (002) and (100) planes of reflection. The crystallite size of MWCNT calculated using Debye Sherrer's formula is 111.28Å.

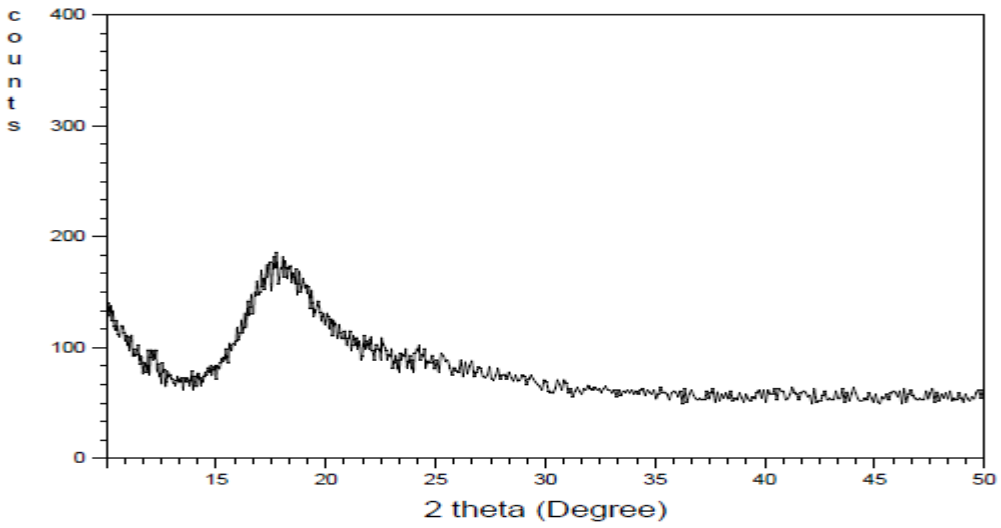


Figure 2: XRD Pattern of Polystyrene

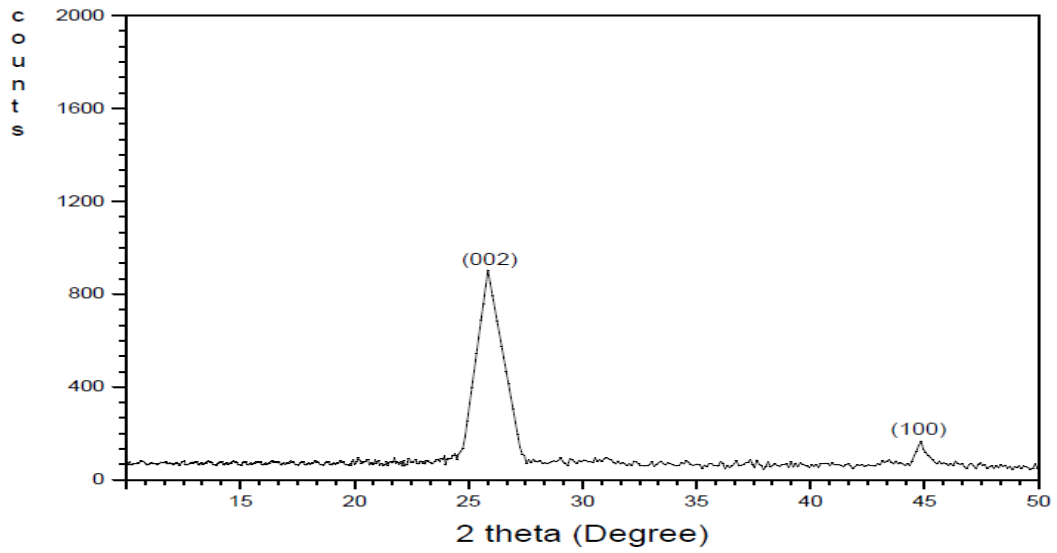


Figure 3: XRD Pattern of MWCNT

At the filler weight of 0.01%, 0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00%, the prominent peaks are observed at 2Θ = 26.25° and 43.17°, 26.20° and 43.17°, 26.20° and 43.17°, 26.20° and 43.17°, 26.30° and 43.17°, 26.20° and 43.17°, 26.34° and 43.17°, with varying intensites which increases as the weight percent of the filler increases. Figure 4 shows the diffraction pattern of MWCNT doped polystyrene at different MWCNT weight of 0.01%, 0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00% respectively.

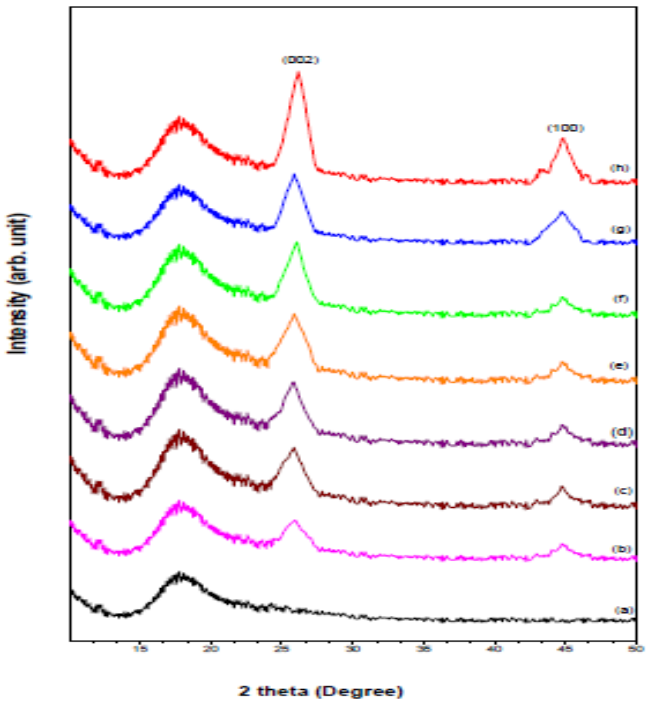


Fig. 4: XRD Pattern of polystyrene/MWCNT at different weight% (a = 0%, b = 0.01%, c = 0.1%, d = 0.15%, e = 0.2%, f = 0.5%, g = 1.0%, h = 3.0%)

This figure shows a change in the structure of the polystyrene, which was evidence in the intensities of the peaks and in the d spacing (interplanar spacing) as the volume of MWCNT increases from 0.01% to 3.00%. The pattern of the doped polystyrene indicates that the addition of MWCNT in the polystyrene samples modified the structure of polystyrene. This modification **could** be observed by the prominent peaks that appeared in the XRD pattern of MWCNT doped polystyrene. This modification changed the structure of the pure polystyrene from amorphous to crystalline. As the weight percent of MWCNT increases, the intensities increases, indicating a structural modification by the addition of MWCNT to the polystyrene.

Figure 5 shows that the crystallite sizes of MWCNT doped polystyrene decreases as the weight% of filler content increases.

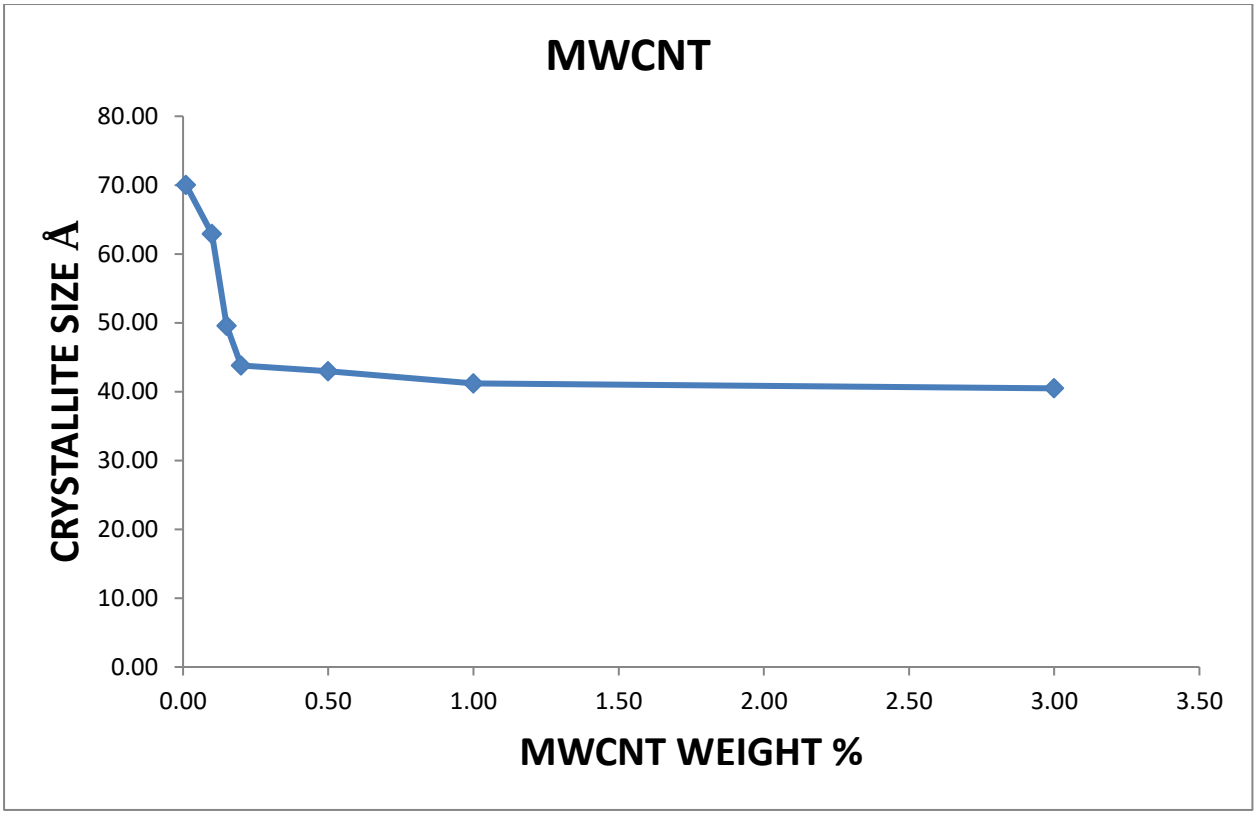


Fig. 5: Plot of crystallite size against weight of polystyrene/MWCNT

The crystallite sizes are 70.04Å, 62.93Å, 49.57Å, 43.78Å, 42.96Å, 41.20 Å and 40.48 Å for 0.01%, 0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00% respectively.

Figure 6 demonstrates that the degree of crystallinity increases as the weight concentration increases from 0.01% to 3.00%. At 0.01%, 0.10%, 0.15%, 0.20%, 0.50%, 1.00% and 3.00% , their degree of crystallization is 22.70, 24.44, 25.63, 28.17, 27.77, 33.15 and 35.17 respectively.

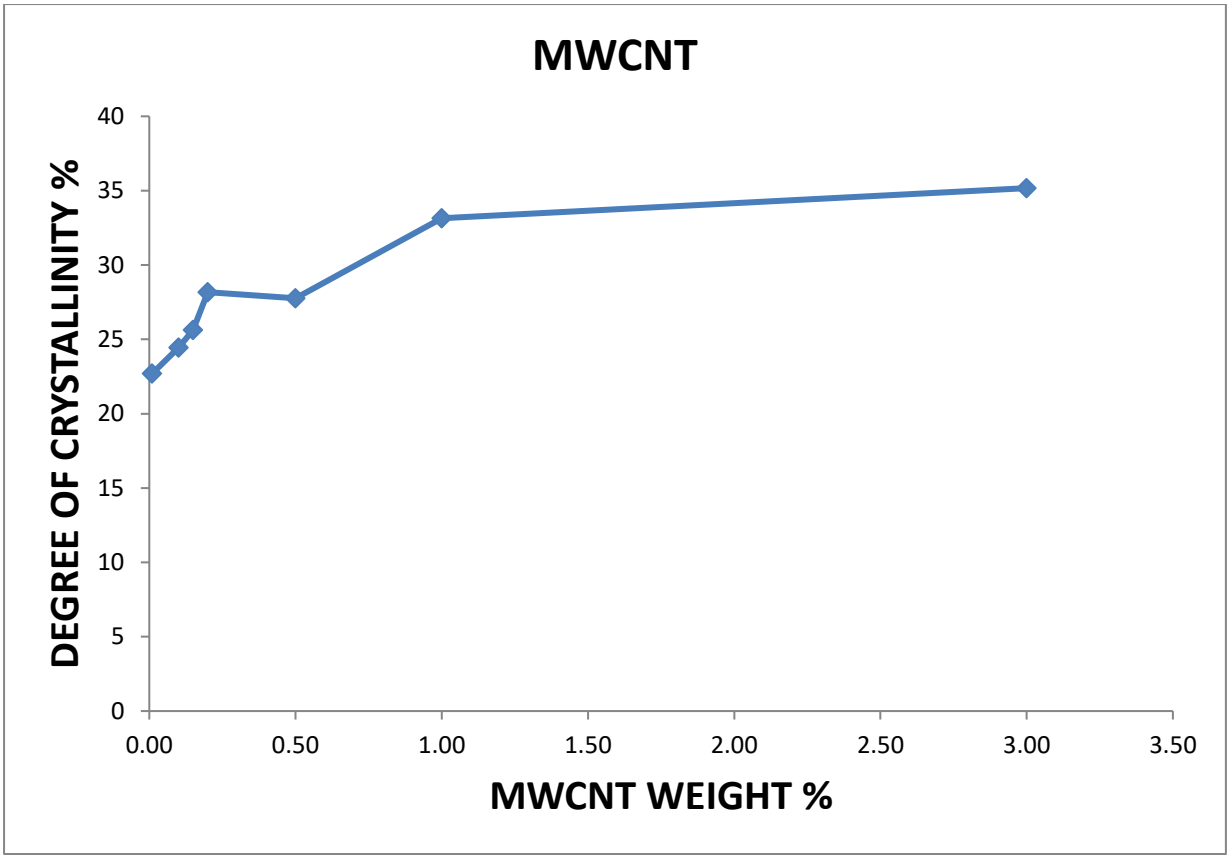


Fig. 6: Plot of degree of crystallinity against weight percent of MWCNT

4. Conclusions

We have demonstrated that polystyrene/MWCNT composite **could** be fabricated by direct mixing method. The conductivity of pure polystyrene is found to be $0.03x10^{-6}(\Omega cm)^{-1}$. It was observed that the electrical conductivity of the composites was improved as the weight percentage of the conductive filler increases. This increase in the electrical conductivity of the composites could be attributed to the intrinsic properties of the dopants. The temperature at which the electrical characterization was performed also affected the conductivity of the composite samples but has no effect on the conductivity of the pure polystyrene. The percolation threshold of the composite was observed at 0.10% MWCNT weight except for composite at $100^{o}C$ where a very low percolation threshold was obtained at 0.01% and once percolation threshold is reached, any further addition to the conductive filler only contribute to small improvement in electrical properties. It **could** be deduced that the enhancement of electrical conductivity of insulating polystyrene by several orders of magnitude has been achieved with a very small loading (low percolation threshold) of MWCNT.

From the XRD results, it was observed that the introduction of MWCNT changed the structure of polystyrene from amorphous to crystalline composite with enhanced properties. This is evidence in the intensities of the peaks and in the d spacing (interplanar spacing) as the weight% of MWCNT increases. The degree of crystallinity increases as the weight% of MWCNT

increases from 0.01% to 3.00% while the crystallite sizes of the composite decreases as the weight % of MWCNT increases.

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