

Electrical Resistivity and Electromagnetic Interference Shielding Effectiveness of Multiwalled Carbon Nanotubes filled Carbon Black-High Density Polyethylene Nanocomposites

Dinesh. P, N. M. Renukappa, Siddaramaiah, Sundara Rajan

Abstract- The polymer based conducting composites are popular in electronics applications due their light weight, low cost, high strength and easy processing. In this paper, conducting nanocomposites were prepared by melt mixing of different wt. % of multiwalled carbon nanotubes (MWNTs) in high density polyethylene (HDPE) and 20 wt. % carbon black (CB). The crystallinity of the nanocomposites were characterized by X-ray diffraction (XRD) and showed a peak at about 21.53° of 2θ . The electrical resistivity was examined by four-probe method at different testing temperatures up to 110°C and PTC behavior of HDPE-CB-MWNT nanocomposites was studied. The result showed that the resistivity decreased with increase in MWNTs loading whereas increased with increase in temperature, leading to the occurrence of PTC effect near T_g of HDPE matrix. The measurements of shielding effectiveness (SE) of the composites were carried out in the frequency range 8–12 GHz (X-band). It has been observed that the shielding effectiveness of the composites is frequency dependent and increases with increasing filler loading. The melting behavior of the composites was determined using a differential scanning calorimeter.

Keywords- Electrical resistivity, Melt mixing, Nanocomposites, Positive temperature coefficient, Shielding effectiveness

I. INTRODUCTION

CARBON NANOTUBES (CNT) possess a variety of useful properties, such as excellent structural, mechanical, electrical properties, much higher conductivities when compared with conventional carbon fillers have attracted many scientists to use them as reinforcements in composite materials [1]. A combination of these carbon nanomaterials with a variety of other reinforcements leads to the development of carbon nanocomposites which can be used in wide range of potential applications. In recent years, many

polymers, such as epoxy [2], poly (methyl methacrylate) (PMMA) [3]-[4], Poly vinyl acetate (PVA) [5], Poly (vinyl chloride) (PVC) [6], polypropylene (PP) [7], Polyethylene (PE) [8] and Polystyrene (PS) [9], have been employed as matrices to prepare CNT/polymer composites.

The temperature-resistivity characteristics of conductive particles filled polymer composites have been widely investigated [10]-[12]. One of the desired properties of these composites lies in its positive temperature coefficient (PTC) behavior characterized by a drastic rise in resistivity when the temperature approaches the melting point of the matrix. According to such a temperature activated switch feature for electricity, polymer based self-regulating heaters, sensors, and microswitches, coupled with excellent formability, moldability, light weight, and flexibility, can be manufactured [13]-[14].

Electromagnetic interference (EMI) shielding refers to the reflection and/or adsorption of electromagnetic radiation by a material, which thereby acts as a shield against the penetration of the radiation through the shield [15]. The shield should be in high conductance, thus metals, such as copper, aluminum, etc., are the most common materials used for EMI shielding. Since metal shielding has shortcomings of heavy weight, corrosion and physical rigidity, polymer composites with carbon conducting fillers are extensively employed in EMI shielding [16]-[18].

II. EXPERIMENTAL DETAILS

A. Materials

The high density polyethylene (HDPE) melt flow is 0.2 g/10 min; density is 0.94 g/cc and melting point is 128°C , was supplied by Honam Petrochemical Corporation, Korea. The carbon black (Hi-Black 420B), with particle size around 24 nm was supplied by Korea Carbon Black Company, Ltd., Korea. The multiwalled carbon nanotubes (MWNTs) with diameter of 10–20 nm and length of 10–50 μm were supplied by Iljin Nanotech Company, Ltd., Korea.

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B. Preparation of Composites

The MWNTs were first oxidized using nitric acid to yield the o-MWNT, then nanocomposites were prepared by solution-melt mixing process. The MWNTs of 0.25, 0.5, 0.75 and 1.0 wt.% were mixed with the HDPE for precursor master batch by solution method using xylene as solvent, prior to the melt mixing. The prepared master batches were melt mixed with HDPE with 20 wt. % of CB using internal Haake mixer at 180°C with 60 rpm for 30 min. mixing time. Further, the blended mixtures were hot pressed at 180°C into sheets with a thickness of ~0.35 mm. The prepared samples are designated as follows

Samples	Designation
HDPE + 20 wt.% CB	a
HDPE + 20 wt.% CB + 0.25 wt.% MWNTs	b
HDPE + 20 wt.% CB + 0.5 wt.% MWNTs	c
HDPE + 20 wt.% CB + 0.75 wt.% MWNTs	d
HDPE + 20 wt.% CB + 1 wt.% MWNTs	e

C. Measurements

A four-probe resistance measurement was carried out for determining the resistance. The electromagnetic interference measurements were carried out using the network analyzer N 5230A (Agilent Technologies) in the frequency range 8-12 GHz. The X-ray diffraction pattern of the samples were recorded in the range 20-80° of 2θ with the scan speed of 2°/min. using Rigaku Corporation Kyoglas-XA diffractometer using CuK_α ($\lambda = 1.54\text{\AA}$) radiation as the source. The melting behavior of the composites was determined using a differential scanning calorimeter (DSC-Q200). The samples weighing 6 mg were heated from ambient to 180°C at a heating rate of 10°C/min under a nitrogen atmosphere.

III. RESULTS AND DISCUSSION

XRD studies have been carried out in order to monitor the formation of the nanocomposites. The XRD patterns of different weight percent of MWNTs filled HDPE-CB nanocomposites samples are shown in Fig.1. All the composites showed two characteristic peaks for the crystalline phase of the polymer matrix. There is an intense peak at $2\theta = 21.53^\circ$ ($d = 4.124 \text{ \AA}$) and another less intense peak at $2\theta = 23.89^\circ$ ($d = 3.72 \text{ \AA}$) for the sample HDPE-20 wt. % CB. The peak intensities decreased when MWNTs were added to the HDPE-CB. The decrease in peak intensity after the incorporation of MWNTs is due to a decrease in the amount of crystalline phase HDPE in the composites. The intensities of the HDPE-20 wt. % CB composite were 36563 and 12647 for the first and second peaks, respectively. For HDPE-20 wt. % CB-0.25 wt. % MWNTs, the first and second peaks intensities were 25323 and 8340, respectively, which are lower than that of the HDPE-20 wt. % CB composite.

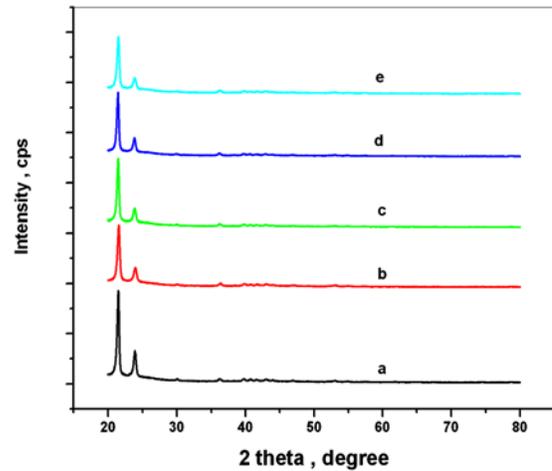


Fig.1 X-ray diffraction patterns of the HDPE-CB-MWNT nanocomposites

To reveal the PTC mechanism of the composites, a differential scanning calorimeter was used to study the melting behaviors of the varying wt. % of MWNTs filled HDPE-20 wt. % CB nanocomposites. From the DSC plots, the values of onset temperatures (T_o), peak temperatures (T_p) and area under the melt curve (enthalpy, ΔH) were measured and values are tabulated in Table I.

TABLE I.
DATA OBTAINED FROM DSC CURVES OF HDPE-CB-MWNT NANOCOMPOSITES

Samples	Transition temperature (°C)				ΔH (J/g)
	T_o	T_p	T_c	T_g	
a	82	130	137	62	177
b	82	127	135	60	143
c	77	128	135	60	140
d	76	128	135	58	136
e	78	128	135	64	126

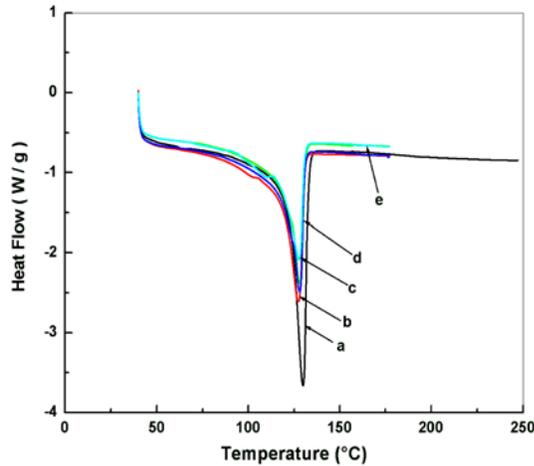


Fig.2 DSC curves of the HDPE-CB-MWNT nanocomposites

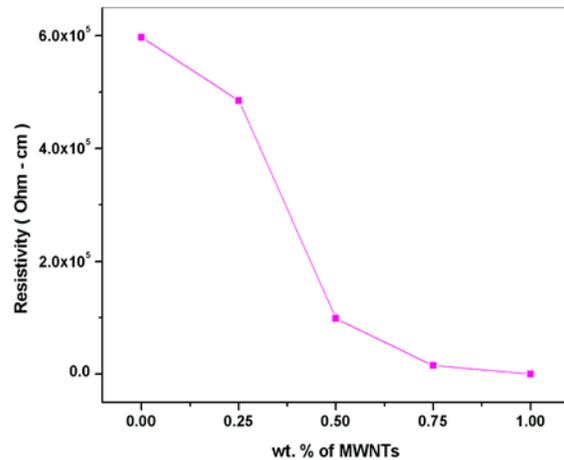


Fig.3 Effect of MWNTs on the resistivity of the HDPE- CB-MWNTs nanocomposite at room temperature

A. Effect of Filler Loading On the Resistivity of the Composites.

HDPE is highly insulating in nature. Its inherent resistivity is in the range of $10^{15} \Omega \text{ cm}$. However, on incorporation of 20 wt. % carbon black the resistivity of the insulating matrix decreases rapidly by 10 orders of magnitude i.e. $6 \times 10^5 \Omega \text{ cm}$. Fig. 3 shows the change of resistivity as a function of MWNTs loading on the HDPE-CB matrix. The resistivity of the composites depends strongly upon the MWNTs loading. By varying 0-1 wt. % of MWNTs the resistivity decreases further as shown in Fig.2. When the amount of loading is increased in the polymer matrix a discrete chain structure is formed in the small gaps, and electrical conductivity begins to be observed. On further increase of loading, a continuous conductive network forms by physical contact of the filler through which the charge species can move from one end to the other end under an electrical field, and it shows a stable electrical conductivity. So, at higher concentration, at or above the percolation limit (when continuous conductive networks are already formed), the conductivity of the composite mainly depends on the conductivity of the filler rather than on their ability to form a continuous conductive network through aggregation.

B. Effect of Temperature on the Resistivity of the Composites

The dependency of electrical resistivity on temperature for conductive polymer composites is quite a complex phenomenon. The temperature coefficient of resistance may be positive (PTC), negative (NTC), or zero, depending on the concentration of filler and the nature of the polymer and the filler [19]. The variation of electrical resistivity with temperature for the HDPE-CB-MWNT nanocomposites is shown in Fig.4. From Fig.4, it can be seen that the resistivities of all the composites at different MWNT loading increased with temperature. The resistivity increased steadily as temperature increase from room temperature, and it increased very rapidly after 60°C till 105°C indicating the PTC effect. Different MWNT filled composites did not show exactly the same PTC behavior. In the lower MWNT loading (0, 0.25 and 0.5 wt. %) the resistivity decreases after 105°C with increase in temperature but not in the samples with 0.75 and 1 wt. %. The resistivity increases with increase in temperature can be explained based on conductive network rearrangement, tunneling effect, and electric field radiation. [20] In fact, the actual conduction seems to be the net result of the combined effect of different mechanisms described in these theories. The PTC mechanism of HDPE-CB-MWNT nanocomposites can be explained by the predominant breakdown of the conducting network structure attributed to differential thermal expansion of matrix.[21] Because of an increased gap between conducting elements with the increase in temperature the resistivity increases; also the probability of electron tunneling and electric field radiation is reduced in this condition.

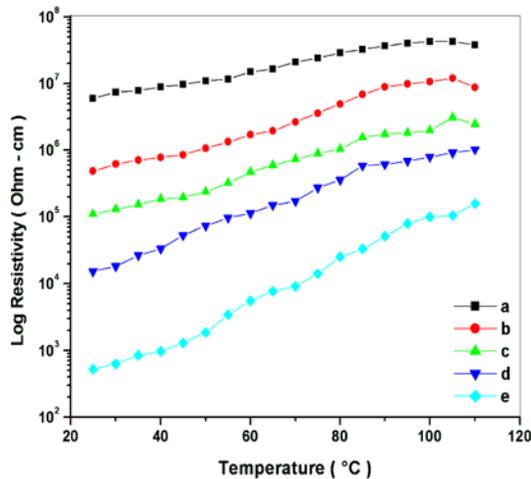


Fig.4 Effect of temperature on the resistivity of the HDPE-CB-MWNT nanocomposites

C. EMI Shielding Effectiveness of the HDPE-CB-MWNTs Nanocomposites

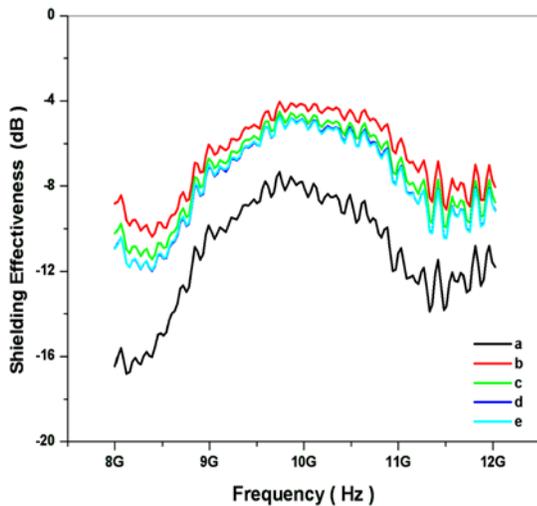


Fig.5 Effect of MWNT content on the EMI shielding effectiveness of HDPE-CB-MWNT nanocomposites

Fig. 5 shows the EMI shielding effectiveness over the frequency range of 8-12 GHz for HDPE-CB-MWNT nanocomposites with various MWNTs loadings. It has been observed that the shielding effectiveness of the composites is frequency dependent and increases with increasing filler loading. The slight decrease in SE is observed for all the nanocomposites and the maximum of -4 dB were achieved at 10 GHz. MWNT is more effective than CB to provide higher EMI shielding.

IV. CONCLUSIONS

- The XRD results show the reduction in peak intensity indicating there is a decrease in the crystallinity with the addition of MWNTs in to the HDPE-CB.
- DSC thermograms shows the addition of 0.25 to 0.75 wt. % MWNTs, T_g values decreased by 4 °C whereas addition of 1 wt. % MWNT increased by 6°C.
- Addition of 20 wt. % CB in HDPE drastically reduced the ρ_{dc} by 10 orders of magnitude (10^{15} to $6 \times 10^5 \Omega \text{ cm}$). Further, addition of 1 wt. % MWNTs to HDPE-20 wt. % CB reduces the ρ_{dc} by 3 orders of magnitude.
- The HDPE-CB-MWNTs nanocomposites showed the PTC effect in the range 60-105°C. It indicates the PTC effect occurs around T_g of the nanocomposites.

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