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LETTER

Electrical conduction of graphite filled high density polyethylene composites; experiment and theory

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Introduction

Disordered conductor–insulator composites exhibit a variety of phenomena, some of which have important commercial applications. Among large number of composite materials, conductive polymer composites have been extensively used in resistors, self regulating heaters, over current and over temperature circuit protection devices, antistatic materials, and materials for electromagnetic interference shielding. In order to analyze the conducting behavior in such systems on microscopic scale, several models have been proposed, such as percolation theory [1], effective media theory as projected by Bruggeman [2], aggregate structure model which overcome the disadvantage of effective media theory [3], and McLachlan's general effective medial (GEM) theory which combines most of the features of both percolation and effective media theory [4]. GEM equation is an interpolation between Bruggeman's symmetric and asymmetric theories. The format of equation is in the same mathematical form as of the percolation equation of conductivity when the ratio of conductivities of the two components is infinitely large. While introducing this equation it has been supposed that the binary system is microscopically homogeneous, the particle size distributions are infinitely wide and the particles are in contact with each other with no voids. This equation is applicable to all volume fractions and not only near the insulator–conductor transition as in percolation theory.

In the past few decades, some works on effective media theory on polymer composites filled with carbon black particles have been reported [3, 5], but the use of graphite as filler is almost unavailable in literature. The experimental studies in which the critical behavior of polymer composites have been investigated using effective media theory are so far concerned with system of sphere-like conducting particles embedded in an insulating matrix. A reasonable agreement between the experimental results and theoretically predicted critical behavior of conductivity was found [5].

This work presents the study of decisive behavior of percolation process using general effective media theory in a composite in which the conducting particles localized in an insulating matrix are better described as flakes, than spheres. Previous experimental studies reported by this group for graphite/polymer composites are concerned with the qualitative features of conductivity [6] and the theoretical studies are confined only to the percolation theory [7]. No attempt has been made to explain the conductivity behavior using GEM theory. In the present work, conducting behavior of a series of graphite/HDPE composites has been studied experimentally. A comparative analysis of applicability of GEM equation for expressing of conductivity behavior of HDPE composites filled with different fillers has been made. The effect of processing methods besides shape and size of filler particles has been discussed.

Experimental

Commercial grade of high density polyethylene used in this work was procured from Reliance industry, India. Flake shaped graphite powder [7] supplied by Graphite India was selected as filler. The particle size was ranging from 10 to 20 μm with a resistivity of 7.5×10^{-5} Ω cm and density of 1.75 g cm^{-3}. The requisite ratios of two powders were mixed for 200 min at room temperature using tumble

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mixing procedure. The resulting mixture was heated to temperature of 135 °C, brought back to 100 °C and then compressed for 15 min with 75 MPa pressure in a piston cylinder assembly. The thicknesses of the pellets varied between 1 and 2 mm. A series of specimen pellets were prepared with graphite content ranging from 0 wt% to 15 wt%. For electrical measurements, conducting silver paint of SEM grade was used on both surfaces. In order to determine the volume resistivity of composites, a Keithley electrometer was used. The measurements were carried in sandwich geometry through copper electrodes by loaded spring method. For each composition five pellets were formed. The *dc* data of specimens presented here is the mean value.

Result and discussion

Percolation theory gives a phenomenological equation for the conductivity of a system near to insulator–conductor transition. Ideally speaking, percolation theory only applies when the conductivity of polymer matrix and the resistivity of conducting filler are zero, which presents a problem in many real systems. In the present system, HDPE is an insulator with a volume resistivity of the order of 10^{14} Ω cm, where as graphite exhibit a volume resistivity that of the order of 10^{-5} Ω cm. The large difference between the resistivities of conducting and insulating phases has been considered to be a nearest approach to the percolation theory for real systems.

Figure 1 depicts *dc* volume resistivity of composites versus graphite concentration and identifies the critical percolation threshold at a filler loading of 0.0113 volume fraction (2 wt%). At percolation threshold, a drastic increase in conductivity by six orders of magnitude with

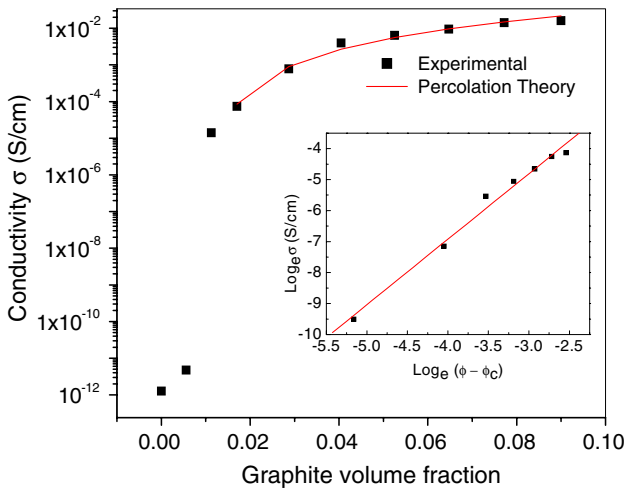

Fig. 1 Volume resistivity of composites versus graphite concentration for graphite/HDPE composites

the increase in graphite content by 0.0056_5 volume fraction (1 wt%) has been recorded. This phenomena is endorsed to the formation of a network of conductive pathways and quantum mechanical tunneling of electrons therein [8]. These conductive pathways consist of graphite particles. The electrical conduction is believed to take place by inter-particle contacts, besides electrons hopping/tunneling across the gaps or through energy barriers between conducting particles in polymer matrix. When the distance between conductive components within the polymer matrix are close to a threshold value usually a few nanometers, quantum mechanical tunneling is expected to take place.

The behavior of conductivity σ with ϕ can be analyzed using power law model

$$\sigma \propto (\phi - \phi_c)^t$$

$$\sigma = \sigma_h(\phi - \phi_c)^t \quad (1)$$

where ϕ, ϕ_c, and t are the volume fraction of filler, critical volume fraction of filler and critical exponent, respectively. The σ_h, the constant proportionality, is equivalent to the conductivity of the filler.

Inset in Fig. 1 shows a relationship between electrical conductivity of composite and $\phi - \phi_c$ of graphite. The best linear fit with minimum standard deviation of ±0.24 has been obtained with $\phi_c = 0.0113$ volume fraction of graphite. The value of t has been estimated from the slope of the line and is found to be 2.11. The value of t is in proximity to the widely accepted value of $t = 2.0$ in literature [9]. The value of σ_h was found to be 4.6323 S/cm from the equation. There is a good quantitative correspondence between the experiment and theory (Fig. 1). The maximum rms deviation between the calculated and experimental values is found to be 2.2×10^{-3}. It is desirable to point out that the estimated value σ_h does not match with the electrical conductivity of filler graphite (1.33×10^4 S/cm). This discrepancy has also been mentioned by other investigators and in case of PVC/graphite composites too [10]. The reason is yet unclear. Normally, the researchers have considered σ_h as a pre-factor that depends on the details of transport process [11]. In case of ultra high molecular weight polyethylene (UHMWPE) filled with multi-walled carbon nano tube (MWCNT) composites, this inconsistency has been referred to the dependence of electrical conductivity of MWCNTs on their diameters, helicity degree, and presence of defects [12, 13].

A comparison between ϕ_c, and t for HDPE/graphite [this work], HDPE/carbon black [14], and UHMWPE/MWCNT [12] composites has been made in Table 1. The value of t for all composites is closer to the widely accepted value of ~2.0. The ϕ_c for composites with MWCNT, graphite and carbon black (CB) are 0.00036, 0.0113, and 0.082 volume fraction, respectively. Lowest ϕ_c in case of MWCNT is

Table 1 Fitting parameters of GEM equation

Sample	Shape and size of filler	σ_l (S/cm)	σ_h (S/cm)	t	ϕ_c
HDPE/Gr	Flake shape particles 10–20 μm	1.27×10^{-12}	4.632	2.11 ± 0.11	0.0113
UHMWPE/MWCNT	Cylindrical asp. ratio 10^2–10^3	$\sim 4.523 \times 10^{-16}$	10.00	2.07 ± 0.09	0.0003_6
HDPE/CB	Spherical particle diam. ~60 nm	1.68×10^{-17}	4.412	2.06 ± 0.11	0.0820

assumed to be due to its nanostructure having high aspect ratio (10^2–10^3). Low percolation threshold often corresponds to the use of filler particles with elongated geometry, or high demagnetization coefficient (rods or discs) [15]. The geometry of MWCNT and graphite can be correlated to that of elongated geometry, which favors the formation of conducting paths at lower percolation concentration compared to CB filler which is spherical in shape [8]. In case of CB filled polymers, it has been accepted [16] that low percolation threshold ascribe to the small particle size of the filler. But as shown in Table 1, the percolation threshold for CB filled polymer obtained is large, though the filler size is small compared to graphite. This difference may be endorsed to the processing method. The processing techniques for composites with graphite and MWCNT are more or less similar. Since particle size of MWCNT is smaller compared to graphite the percolation threshold of MWCNT/UHMWPE composites is low in contrast to graphite/HDPE. Hence from the correlation of size, geometry, and processing technique, MWCNT favors the conducting paths/channels at low percolation threshold.

For electrical conductivity of binary system GEM equation has been postulated [16] after studying and summarizing various previous works.

$$\left[f\left(\sigma_l^{1/t} - \sigma_m^{1/t}\right) \Big/ \left(\sigma_l^{1/t} + A\,\sigma_m^{1/t}\right)\right] + \left[\phi\left(\sigma_h^{1/t} - \sigma_m^{1/t}\right) \Big/ \left(\sigma_h^{1/t} + A\,\sigma_m^{1/t}\right)\right] = 0 \quad (2)$$

where f is the volume fraction of HDPE and the subscripts m, l and h stands for medium, low, and high conductivity components.

$$f + \phi = 1$$

A is defined as

$$A = (1 - \phi_c)/\phi_c$$

The fitting parameters of GEM equation for present work and for others are illustrated in Table 1. The values of σ_l are the experimental values of conductivity of HDPE (specimen compact), UHMWPE as read from graph [12] and HDPE as mentioned in literature [14]. The σ_h and t are as obtained through fitting of power law model.

Figure 2 shows the experimental and theoretical data (using GEM equation) for graphite/HDPE, HDPE/CB, and MWCNT/UHMWPE. Qualitatively the character of curves

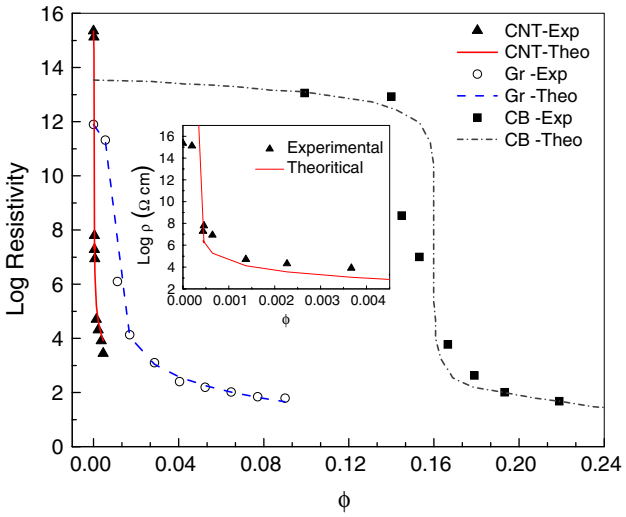

Fig. 2 Resistivity versus ϕ for MWCNT/UHMWPE, graphite/HDPE, and CB/HDPE; Inset-figure for MWCNT/UHMWPE (on magnified scale)

is identical. Quantitatively, the rms deviations between experiment and theory for composites with graphite, carbon black, and MWCNT are 0.502, 2.845, and 0.41, respectively. In case of graphite and MWCNT composites there is a good agreement between the experiment and theory as compared to the CB composites. The concurrence between experiment and theory for HDPE/graphite and UHMWPE/MWCNT is comparable because of the similarity in processing methods.

Conclusion

Conductivity measurements on compacts of graphite/HDPE specimens reveal the behavior that is manifested by a sudden change in conduction at percolation threshold near 0.0113 volume fraction of graphite content. The conductivity has been explained in terms of percolation theory. There is good agreement between experimental and theoretical values above percolation threshold. A comparative analysis with previously reported work on CB/HDPE composites shows that graphite/HDPE composites exhibit percolative behavior at low value of percolation threshold which suggest the segregation of graphite particles inside the HDPE matrix besides higher aspect ratio due to

elongated flake shape of graphite particles. Consistency of experimental values with GEM equation for these composites using diverse fillers has also been tested. Difference in percolation threshold for graphite and CB can be attributed to the shape and size of the filler particles besides use of processing methods. The accord between experimental and theoretical values for graphite/HDPE and MWCNT/UHMWPE is comparable. MWCNT favors the conducting paths at low percolation threshold as a result of their size and geometry as well as processing technique.

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