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A model-based approach to electrical percolation behavior of CB-HDPE composites

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The electric conductivity of CB-HDPE composites has been studied by investigation of the dependence of resistivity upon filler volume fraction after irradiation or at different ambient temperatures. The experimental data can be well fitted to the GEM equation. The parameters, ϕ_C and t in the corresponding GEM equations obtained by fitting and L_ϕ and L_f derived after fitting are analyzed in combination with the dispersion of the components in the composites. SEM study on morphology of the composites find those parameters are closely related to the structure of filler's conductive network and the configuration of the network with polymer matrix. © *2000 Kluwer Academic Publishers*

1. Introduction

Conductive polymer composites (CPC) are usually prepared by incorporation of conductive fillers such as carbon black (CB) and metal particles into insulating polymer matrices. In the electrical properties of CPCs two switching phenomena have been observed. First, as the content of conductive filler is varied, the resistivity of the composite is changed and the composite experiences an insulator-to-conductor transition at a critical content of the filler. This is usually defined as percolation transition, and the critical volume fraction of the filler is the threshold dividing the composite into insulator and conductor. Second, when the temperature of the composite is raised into the melting region of the polymer, the resistivity of the composite shows an anomalous increase (Positive-Temperature-Coefficient effect, PTC effect) and the composite is changed from a conductor to a semi-insulator or insulator within a narrow temperature range. Moreover, if the temperature of the composite is further elevated, the PTC resistivity effect is sometimes followed by a declination in resistivity, exhibiting a negative temperature coefficient (NTC) effect of the composite. The NTC effect is usually not desirable and efforts have been made to eliminate it [1–4]. One of the effective methods to eliminate NTC and to improve the stability of electric properties and PTC transition is crosslinking of the composites by either irradiation or by adding chemical crosslinking agents.

It is commonly believed that both percolation transition and PTC effect are closely linked to the structure of filler's conductive network and the configuration of the network with polymer matrix. Unfortunately, direct characterizations of network structures and configurations of the network with polymer matrices are difficult. In studying the attribution of percolation behavior, some models have been proposed to indirectly assess the structures and the configurations. These models are mainly based on some general equations relating the electric conductivity of composites to volume fraction of conductive filler and, on the other hand, containing some parameters describing network structures and configurations between fillers and matrices. The models often used include many, in which the general-effective-media (GEM) equation proposed by Mclachlan [5] is most universal because other equations are just the GEM equation rearranged under special boundary conditions. The GEM equation has been proved to be able to fit the percolation data for a various composite media [5–10] such as W-Al_2O_3, Fe_2O_3-epoxy, and V_2O_3-HDPE. In a previous report, Pan *et al.* [9, 10] applied the GEM equation to fit the room-temperature percolation data of V_2O_3-polymer composites without crosslinking, and showed that the spatial arrangements of both the filler and the polymer described by the parameters in GEM equation after fitting were consistent with SEM observations.

Carbon black filled polyethylene is an important category of conductive polymer composites, which has been widely used as self-heater and over-current protector. In the present study, the percolation behavior of the composites of carbon black and high-density polyethylene (CB-HDPE) is investigated by fitting GEM equation to the volume fraction dependence of conductivity. The computer fittings have been not only performed for room temperature and as-prepared composites but also for the composites in high temperature range covering PTC transitions and for the composites crosslinked by different dose of electron-beam irradiation. The computer fitting for each case generates a set of parameters,

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which can be used to describe the network structure and the configuration of the network and the polymer matrix.

2. GEM equation

Substantial work has been done to study how the volume fraction and the morphology of conductive components affect the electrical behavior of CPCs. The GEM equation proposed by Mclachlan has been the one that provides a method to model real binary systems without strict assumption [5]. The GEM equation may also be used for other physical properties (such as Young's modulus, thermal conductivity and static permeability) of composites besides electrical conductivity. As far as the electrical conductivity is concerned, the GEM equation is written as

$$\frac{(1-\phi)\left(\sigma_1^{1/t}-\sigma_{\mathrm{m}}^{1/t}\right)}{\sigma_1^{1/t}+A\sigma_{\mathrm{m}}^{1/t}}+\frac{\phi\left(\sigma_{\mathrm{h}}^{1/t}-\sigma_{\mathrm{m}}^{1/t}\right)}{\sigma_{\mathrm{h}}^{1/t}+A\sigma_{\mathrm{m}}^{1/t}}=0 \quad (1)$$

where σ_{m}, σ_1, and σ_{h} are the conductivities of medium, low- and high-conductivity components, respectively and ϕ is the volume fraction of the high-conductivity component. Constant A is defined as

$$A=\frac{1-\phi_{\mathrm{C}}}{\phi_{\mathrm{C}}} \quad (2)$$

where ϕ_{C} is the critical volume fraction of the high-conductivity component at which the percolation transition occurs. ϕ_{C} and the exponent t are related to the geometry and orientations of both components according to the following equations:

$$\phi_{\mathrm{C}}=L_\phi(1-L_{\mathrm{f}}+L_\phi) \quad \text{(oriented ellipsoids)} \quad (3a)$$

$$\phi_{\mathrm{C}}=m_{\mathrm{f}}/(m_{\mathrm{f}}+m_\phi) \quad \text{(random ellipsoids)} \quad (3b)$$

$$t=1/(1-L_{\mathrm{f}}+L_\phi) \quad \text{(oriented ellipsoids)} \quad (4a)$$

$$t=(m_{\mathrm{f}}m_\phi)/(m_{\mathrm{f}}+m_\phi) \quad \text{(random ellipsoids)} \quad (4b)$$

in which L_ϕ and L_{f} are demagnetization constants of high- and low-conductivity component particles, respectively. L represents the combination of shape and orientation in the applied electric field. For the case that the component is fiber- or layer-shaped, $L=0$ if the component is oriented in the direction of the electric current across the medium and $L=1$ if the component is perpendicular to the electric current. For the case that the component is sphere-shaped, $L=1/3$. m_{f} and m_ϕ are parameters for description of random orientations of the particles. The details of derivation and interpretation of the GEM equation can be found in the reports of Mclachlan and Pan [5–10].

3. Experiments and computer fitting

3.1. Starting materials

The conductive filler used was commercial acetylene black with an average particle size of 42 nm, BET (determination method developed by Brunauer, Emmet and Teller) of 63 m^2/g, and DBP (dibutyl phthalate absorption measurement method) of 3.3 ml/g measured using a particle size analyzer.

The matrix polymer was high-density polyethylene (QiLu 2480) with melting range from 94 to 134 °C, melt flow rate (MFR) of 0.14 g/10 min, and density of 0.943 g/cm^3. To make the composites similar to those used in engineering applications, all the investigated composites had a additive content of 15 wt% in total, including stabilizers, antioxidants and processing aids.

3.2. Sample preparation

Composites were prepared using a Bandury. When the polymer with additives was melted at 170 °C, the CB powder was gradually added and then mixed in the Bandury for 15 min at a mixing rate of 50 rpm. The samples were compression-molded to approximately 20 mm thick sheets at 170 °C. Some samples were irradiated using an electron-beam source in air at room temperature to get crosslinked. Before the measurements all samples experienced a treatment of heating above the melting region of the polymer and then cooling to room temperature in 3 hours. The volume fraction was determined by simple weighing before blending and comparing the density of the composite to that of the bare matrix material processed under the same conditions.

3.3. Resistivity measurements

Electrical resistivity was measured in thickness direction of the sheet sample. Room-temperature resistivities of $10^8 \sim 10^{17}$ Ω·cm were measured using a ZC36, a high-resistance electrometer. Lower resistivities were determined using an ordinary electrometer (M890D Digital Electrometer). Resistivity as a function of temperature was directly obtained on a computer-controlled apparatus developed in our laboratory. The resistivity versus volume fraction of composite crosslinked with different doses of low energy electron beams and at different ambient temperatures is shown in Fig. 1 and Fig. 3, respectively.

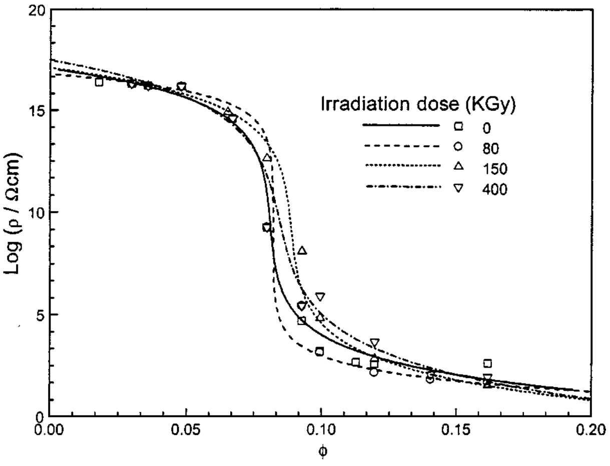


Figure 1 Resistivity as a function of volume fraction of CB-HDPE composites with different electron-beam irradiation doses. The scattered symbols represent experimental data and the lines represent computer-fitting results.

3.4. Computer fitting

The experimental data for each composite system were fitted to the GEM equation by computer programming using a method shown below. For those composites with high room-temperature resistivities ($>10^8$ Ω·cm), their resistivities at elevated temperatures were approximated by the corresponding room-temperature resistivities of samples. The GEM equation (Equation 1) can be rearranged to be a direct function of ϕ. That is

$$\phi = \alpha + \beta P_{\mathrm{m}} + \gamma / P_{\mathrm{m}} \tag{5}$$

where $P_x = \sigma_x^{1/t}$ (x represents l, h or m) and α, β, and γ are functions of ρ_1, ρ_{h} and ϕ_{C}:

$$\alpha = 1/(1+A) \tag{5a}$$

$$\beta = A/[P_{\mathrm{h}}(1+A)] \tag{5b}$$

$$\gamma = (-P_{\mathrm{h}}P_1)/[P_{\mathrm{h}}(1+A)] \tag{5c}$$

where A is defined by Equation 2.

Define a function S as

$$S = \sum^{n} (\phi - \phi_{\mathrm{E}})^2 \tag{6}$$

in which n is the number of data points and ϕ_{E} is the experimental volume fraction. To find the best fit, the parameters ϕ_{c}, t, ρ_1, ρ_{h} were varied until S reaches its minimum, or

$$\frac{\partial S}{\partial a_i} = 0 \tag{7}$$

where a_i represents α, β or γ. The error of the four-parameter fitting was evaluated by

$$\delta = [S/(n-p)]^{1/2} \tag{8}$$

Here S and n were defined as previously. p is the number of fitting parameters. The whole fitting process has been described in detail in reference 10.

4. Results and discussion

4.1. Percolation behavior of CB-HDPE after irradiation

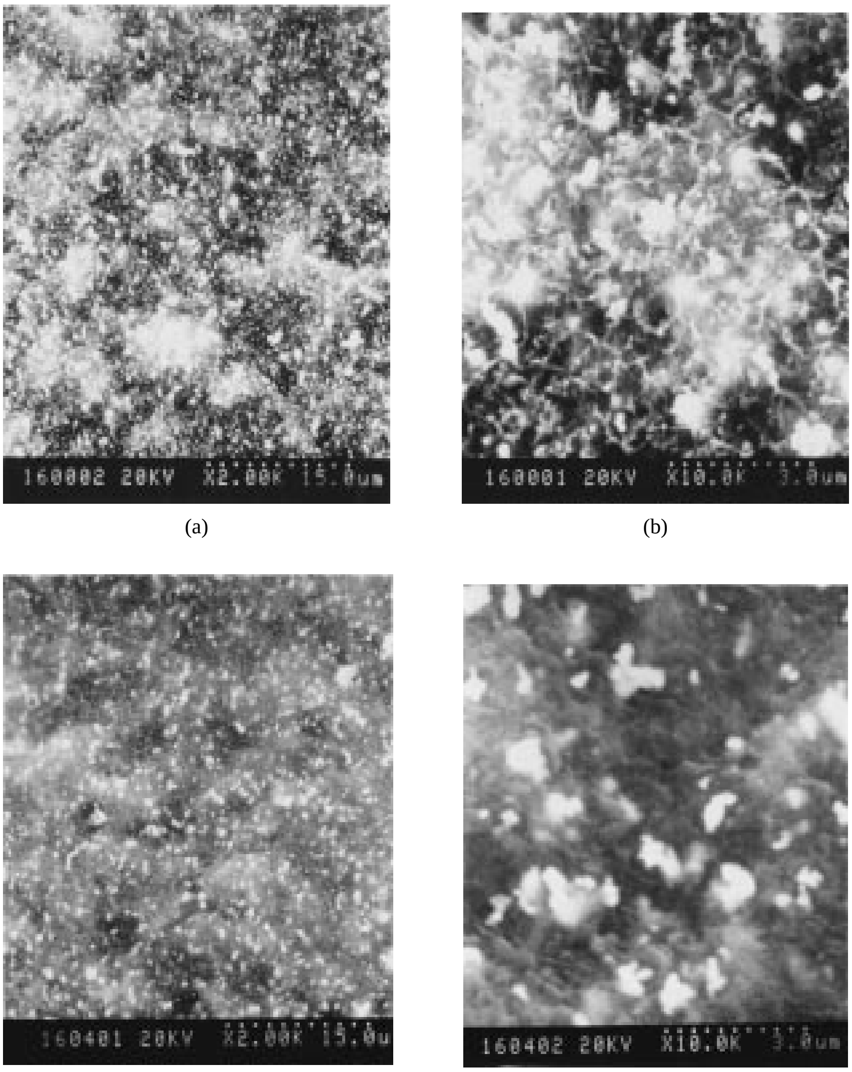
The room temperature resistivity of the CB-HDPE composite as a function of the volume fraction of CB with different irradiation doses is shown in Fig. 1. The parameters, ϕ_{c}, t, ρ_1, ρ_{h} in the corresponding GEM equations and L_ϕ and L_{f} derived after the computer fitting are listed in Table I. The resistivity of the CB-HDPE composite without irradiation (zero dosage) falls abruptly from 10^{15} to 10^4 Ω·cm around a carbon volume fraction of 0.082. Such a volume fraction is defined as the critical volume fraction ϕ_{c} for this case. Previous studies on metal-filled polymer composites [11] have shown that ϕ_{c} is related to the ratio of the particle sizes of the two components. The larger the particle size ratio of polymer to conductive filler, the smaller the value of ϕ_{c} will be. The use of Kusy's equation [12] that is based on cubic packing of particles of the two components gives the value (0.082) of ϕ_{c} for the particle size ratio of 14.8. Table I also shows that ϕ_{C} increases as the irradiation dose increases (except 150 KGy). This result suggests that the irradiation-induced crosslinking of the polymer may slightly change the particle size ratio. SEM micrograph of the composite samples without golden or carbon coatings shown in Fig. 2a, b, c and d provide further information. Fig. 2a is the typical morphology of the CB/HDPE composite without irradiation. Cloud-like CB particle aggregates distributed in the polymer matrix are clearly seen. With a larger magnification in Fig. 2b, among those cloud-like CB aggregates, there are many branch-like CB conductive paths. These paths run from one CB aggregate to another, forming a conductive network throughout the media. The conductive network is sometime called percolation network or "segregated network" according to Malliaris and Turner [13]. It is also found from the micrographs that either the size of the cloud-like CB aggregates or the size of the branch-like conductive paths are much larger than the size of the individual CB particles with an average diameter of 42 nm. The above results indicate that aggregations of the CB particles occur in the polymer matrix. The smallest unit that forms a percolation network is the close-packed aggregates rather than the individual particles. The particle size ratio mentioned above should be the ratio of polymer domain size to the size of CB aggregates. Fig. 2b also shows that the size of the aggregates is not uniform and the dispersion of the aggregates is not microscopically even in the matrix. In the composites with the same CB content as in Fig. 2a and b but after electron-beam irradiation of 400 kGy (see Fig. 2c and d), the CB particles disperse more uniformly in the matrix and the aggregation of CB particles is less pronounced. As a result, the conductive paths in Fig. 2d are not as obvious as in Fig. 2b. This result may be explained by the difficulty of the movements of the CB particles in the melted matrix during the heat treatment and the reduction of the crystallinity of HDPE, both of which are due to crosslinking induced by irradiation.

TABLE I Computer-fitting results of the percolation behavior of CB-HDPE with different irradiation doses

Irradiation Dose	δ (%)	ϕ_{C}	t	L_ϕ	L_{f}	ρ_1 (Ω cm)	ρ_{h} (10^{17} Ω cm)
0	0.78	0.082	2.055	0.040	0.553	0.227	0.594
80 KGy	0.77	0.082	2.125	0.039	0.568	0.212	0.622
150 KGy	0.45	0.089	3.768	0.024	0.758	0.002	1.267
400 KGy	0.80	0.095	4.783	0.018	0.809	0.0004	2.982

Table I indicates that the values of L_ϕ (effective demagnetization constant of CB) with different irradiation doses are all much less than 1/3, the typical value of L for spherical particles. This result suggests that the dimension of the CB aggregates in the direction of the electric current (parallel to the pressing direction during preparation of the composite) is longer than that in other directions. This is in agreement with the conductive paths observed in the SEM micrograph (Fig. 2b). Table I also indicates that the greater the irradiation dose the smaller the L_ϕ value should be. L_ϕ is reduced from 0.040 for the composite without irradiation to 0.018 after an application of electron-beam irradiation of 400 kGy.

The values of L_{f} (effective demagnetization constant of polymer matrix) listed in Table I are all greater than 1/3 either with or without irradiation. According to the



(a) (b)

(c) (d)

Figure 2 SEM micrographs of CB-HDPE composite samples without golden or carbon coatings. (a) aggregates of CB particle in CB-HDPE composite (without irradiation) (b) conductive network of CB aggregates in CB-HDPE composite (without irradiation) (c) aggregates of CB particles in CB-HDPE composite (with electron-beam irradiation of 400 KGy) (d) conductive network of CB aggregates in CB-HDPE composite (with electron-beam irradiation of 400 KGy).

effective media model, such values of L_f represent elliptical polymer particles perpendicular to the electric current plane. This structure may be referred to polymer matrices forming a three-dimensional network that hinders the CB aggregates from contacting each other. The increase in L_f with increasing irradiation doses indicates increasing hinderance of the matrix network to electrical current passing through the conductive chains of CB aggregates.

The value of t of the composite without irradiation is 2.055 and it increases as the irradiation dose goes up (Table I). According to the classic percolation theory based on the conductivity mechanism of touching-particle model, t is determined by the microstructure of both components in the media and is between 1.65 and 2 [14, 15]. The value of 2.055 obtained without irradiation is approximately equal to the upper limit of the above range. We need then to understand why the conductivity of composite upon irradiation deviates from the typical percolation behavior. It has been observed that the aggregates of CB particles are separated by the insulating polymer in CB-polymer composites [16–18]. The larger the CB content, the shorter the distance between CB aggregates. However, even in the composite with a CB content much larger than the critical value, CB particles do not merge and a thin polymer layer of about 2 nm is maintained between neighboring particles. Balberg [19] suggested that CB-polymer composites are composed of percolation networks in which the values of the local resistance are determined by a tunneling mechanism and the value of exponent t is affected by the type of CB. In Balberg's report, the value of t of highly structured CB-filled composite is 2, and the values of t of intermediately structured CB and no structured CB are 2.8 and 4.0, respectively. Balberg's study further showed that less structured CB results in larger distances between CB particles (aggregates) and thus more difficult tunneling through the polymer layer between CB particles. It is this effect that causes greater deviation of the exponent t from the value for typical percolation behavior. The conductive filler used in this work is acetylene black, a type of highly structured CB. The t value of 2.055 in our system without irradiation is thus consistent with Balberg's results and also with the touching-particle model of the classic percolation theory [14, 15]. After an application of irradiation, the increase in t may be interpreted by the more dominant tunneling mechanism due to the crosslinking. The irradiation crosslinked polymer matrix hinders the movements of CB aggregates and the development of conductive network during heat treatment. This effect causes a larger distance between carbon particles and thus reduces the tunneling current of electrons. Therefore, the tunneling effect becomes more determinative to the whole electric conductivity.

4.2. Percolation behavior of CB-HDPE at different ambient temperatures

The resistivity versus volume fraction for the CB-HDPE composites at different ambient temperatures is shown in Fig. 3. The computer fitting results are given in Table II. The pre-set ambient temperatures of 20, 90, 110, 125, and 133 °C are at different stages of the PTC effect of the composite, as illustrated in Fig. 4.

The mechanism of the PTC effect of the CB-polymer composites has been studied for a long time. Although this effect has been considered to arise from the so-called associated effects of the two main components, it has not been well understood yet. The values of L_ϕ under different ambient temperatures shown in Table II are all less than 1/3, suggesting that the CB aggregates are arranged in such a way that they form conductive chains along the direction of the applied electric field. The decrease of L_ϕ with the elevated temperature is probably caused by thermally activated disaggregation of CB particles. Table II also shows that higher ambient temperatures result in larger values of L_f. This result suggests that the hindrance of the insulating matrix to the electron current is more pronounced as the ambient temperature increases.

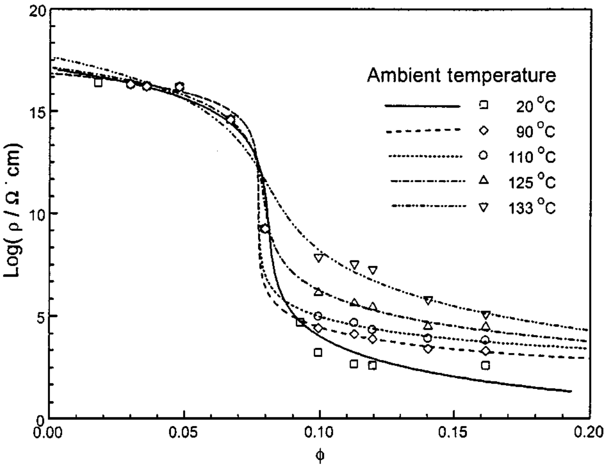


Figure 3 Resistivity as a function of volume fraction of CB-HDPE composites at different ambient temperatures. The scattered symbols represent experimental data and the lines represent computer-fitting results.

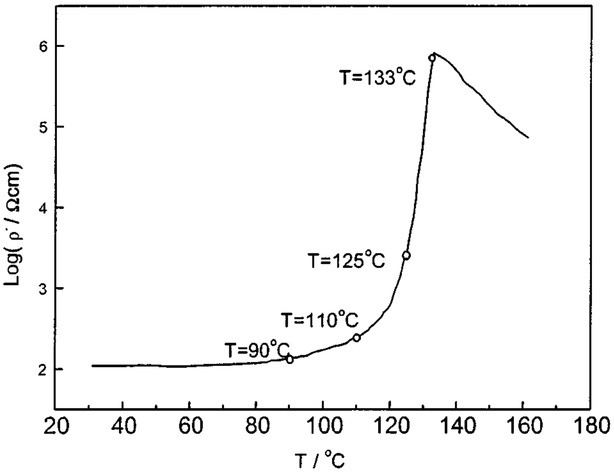


Figure 4 Typical resistivity versus ambient temperatures of a CB-HDPE composite without irradiation.

As discussed above, the value of the exponent t may provide information about the conductance mechanism of the composite. At room temperature (20 °C), the dominant mechanism of the conductance of highly structured CB-filled composites is the classic percolation theory. With the increase of the ambient temperature from 90 to 133 °C, t increases from 2.098 to 5.767. This result can be interpreted by the fact that at higher temperatures the tunneling mechanism plays a more important role in the conductance of the composite. As the temperature increases, the average distance between CB particles becomes longer and thus the tunneling of electrons is suppressed. This mechanism may give a microscopic explanation to the effect of thermal volume expansion on the PTC phenomenon.

It is also noticed that increasing the irradiation dose before heat treatment and elevating the temperature of the composite without irradiation had similar influences on the values of L_f, L_ϕ, and t. This result again supports the segregation effect of crosslinking on the conductive network, as the segregation effect of elevated temperatures on the conductive network has been well-known [20].

5. Conclusions

1. The experimental data of volume fraction-dependence of the room temperature resistivity of the CB-HDPE composite after irradiation of different doses

TABLE II Computer-fitting results of the percolation behavior of CB-HDPE without irradiation at different ambient temperatures

Ambient Temperature (°C)	δ(%)	ϕ_C	t	L_ϕ	L_f	ρ_l (Ω cm)	ρ_h (10^{17} Ω cm)
20	0.78	0.082	2.055	0.040	0.553	0.227	0.594
90	0.58	0.077	2.098	0.037	0.560	11.51	0.693
110	0.62	0.077	2.123	0.036	0.565	33.73	0.701
125	0.76	0.079	3.208	0.025	0.713	5847	1.367
133	0.83	0.080	5.767	0.016	0.819	19400	4.323

and at different ambient temperatures were well fitted to the GEM equation. The parameters in the GEM equation, corresponding to the dispersion characters of CB in HDPE matrix, were determined through the programmed fitting.

2. The values of the characteristic parameters and the SEM micrographs indicate that aggregates of carbon black particles (rather than individual particles) that construct a three-dimensional conductive network are oriented along the direction of the electrical field, also the thickness direction of the samples. The polymer matrix, however, is statistically vertical to the electrical current and hinders conductive particles (aggregates) from contacting each other. The hindering effect is more pronounced with higher irradiation doses or at higher ambient temperatures.

3. While the electrical conductivity of the highly structured CB-filled HDPE composite is dominated by percolation mechanism based on particle-touching model, crosslinking induced by irradiation or increase of the ambient temperature causes longer distance between the conductive particles and tunneling mechanism is more appropriate in interpretation of the conductivity under those conditions.

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