

Study of the Conductive Paths of Carbon-Black-Filled Polyethylene Composites by the Alternating-Current Impedance Method

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ABSTRACT: Conductive carbon-black (CB)-filled polyethylene composites were prepared after irradiation with a cobalt 60 source. The conductive composites were characterized by alternating-current impedance spectroscopy, and the conductive mechanism of the conductive composites was analyzed in terms of a mathematical model. The values of the conductive ability, conductive style, sum of the electrical resistance of the continuous CB chains, electrical resistivity of the CB chains with one gap or a few small gaps, room-temperature resistance, and slopes of the

conductive composites were calculated. The investigation indicated that there existed continuous (contacting)-path CB chains, small-gap chains, and larger gap CB chains in the composites, and the conductive paths in the composites were considered to be a three-dimensional network. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3748–3752, 2008

Key words: annealing; composites; conducting polymers; extrusion

INTRODUCTION

One of the most common additives used in conductive semicrystalline polymers is carbon black (CB). The CB initially forms isolated structures within the matrix, then isolated clusters form, and finally contacting paths arise. A *contacting path* is a continuous network of conductive particles in sufficiently close proximity to allow electrons to flow throughout a specimen. The critical amount of CB necessary to form a conductive network is referred to the *percolation threshold*.^{1,2} The dispersion of CB particles in semicrystalline polymers, where the CB is localized in the amorphous regions and covers the surface of the matrix to establish conductive paths, results in a percolation threshold decrease.^{3,4} The kind of CB-filled semicrystalline polymer composites with positive temperature coefficient traits used for intelligent applications has been investigated in great detail for their capabilities in self-regulating heaters, sensors, current limiters, microswitches, overcurrent protectors, thick films, printed circuit boards, laminated multichip module techniques, and so forth.^{5–8} It is useful in power stations, in the petrochemical profession to defend piping, and in precise apparatus to become viscous or freeze.

Electron transport mechanisms have been examined in a number of *ex situ* formed polymer composite systems.⁹ The field-dependant temperature coefficient of resistance of CB–polyethylene (PE) was explained by fluctuation-induced tunneling conduction, which incorporated the effect of thermal expansion on the tunneling gap.^{10,11} In graphite–polyimide films, the conduction mechanism was attributed to phonon-assisted variable range hopping.^{12,13} Other hopping mechanisms invoked include nearest neighbor hopping, one- and three-dimensional variable range hopping,¹⁴ and the hopping of charge carriers between conducting islands across the soft gap generated by the Coulombic repulsion of electrons within a dielectric matrix.¹⁵ A model comprising comprehensive percolation-tunneling behavior has also been invoked to explain complex behavior in some of these composites.¹⁶ Voet¹⁷ suggested that this effect results from an increase of the average gaps of conductive particles. Medalia¹⁸ tabled every kind of conductive mechanisms related to the CB concentration, width of gaps in the CB chains, temperature, electric field intensity, and so on, but he did not give cogent evidence, and the conductive model has not been identified widely. Many models are largely based on the motion of CB particles and their redistribution during crystallite matrix melting, volume expansion, which occurs when the crystalline melting zones are reached and entered. The most common explanation for the positive temperature coefficient effect is that as the melting temperature is approached, conductive paths are broken due to the

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volume expansion of the semicrystalline polymer matrix compared with the amorphous matrices.^{19–26}

Although there are many theories that try to describe the conductive mechanism,^{9–26} few have been sufficiently accepted.²

Many researchers have tried to study the conductive mechanism of the composites by morphological properties, and some cloudlike aggregates or wire-like paths of CB particles in the polymer matrix are clearly seen from the scanning electron micrographs of CB/polymer composite samples.^{2,27–31} Li et al.²⁸ gave the morphology of *s*-CB/poly(ethylene terephthalate)/PE composites with 7.5 and 15 phr CB, in which the PE matrix was etched away by hot xylene; well-defined microfibers of the CB/poly(ethylene terephthalate) compound were apparently generated. From rough measurements, the diameter of the microfibers was 8–10 μm . Because of the limit of the visible region, it was hard to evaluate the length of the microfibers. On the basis of the morphology micrographs, we know there were aggregates of CB particles contacting or even entangling each other to construct a filled composite with a three-dimensional, electrically conductive network. A difficulty is that one could not see the conductive style of the conductive network in the CB/polymer composite with the positive temperature coefficient effect, so the conductive mode of the conductive paths in the composites has been disputed until now.^{32–36}

The aim of this study was mainly to study the electrical properties of CB/PE composites by alternating-current impedance spectroscopy. To the best of our knowledge, this study represents the first reported attempt to use an alternating-current impedance apparatus to investigate the electrical conductivity of CB/PE composites. In addition, the results of this study may stimulate a better understanding of the conductive network of CB/PE composites.

EXPERIMENTAL

Materials

Low-density PE (2102TN26), a commercial product from China Petroleum & Chemical Corp., was used as the matrix polymer of the composites prepared for this study. The low-density PE material had a melting temperature of 110°C, a density of 950 kg/m³, and a melt-flow index of 0.4 g/10 min. CB was adopted as the electrically conductive filler of the composites. The CB was acetylene black, a commercial product from Longkou Carbon Black Factory (Shandong, China), with an average 46-nm-diameter particle size and a surface area of 63 m²/g. The anti-oxidant and nucleator were added to the recipes to raise the life and modify mechanical properties of the conductive composites.

TABLE I
Designation and Composition of the CB/PE Composite Samples

Designation	CB content (wt %)	PE content (wt %)	Content of other additives (wt %)
CB/PE composites	11.3	86.7	2.0

Preparation of the conductive composites

The CB/PE conductive composite samples were prepared via two steps of processing. First, PE, CB, and other additives were mixed according to the recipes in Table I. The compounding process was performed in a double-roll mixing mill at 160°C for 30 min. In the second step, the composite was extruded by a single-screw extruder. During the extrusion, two parallel bronze leads were embedded in the extrude bars. The bronze leads, which were used as electrodes, were coated with CB powder before extrusion to ensure better contact between the composite and the electrodes. Subsequently, the extrudate was immediately quenched in cold water after stretching. Finally, a conductive thin ribbon was obtained, with a thickness of about 0.2 mm and a width of 1.0 cm.

The conductive thin ribbon was sectioned for the purpose of electrical parameter measurement. Radiation crosslinking was carried out for the section at room temperature with γ rays with a cobalt 60 source. The dosage of radiation was 250 kgy.

Measurement

The resistivity of the CB/PE composite samples was measured on Hewlett Packed HP4192-LF impedance analyzer in the frequency range 5 Hz–13 MHz at room temperature.

The gel content of the composites after radiation was measured by the Soxhlet extraction method with xylene as a solvent. The extraction was carried out for 40 h.

RESULTS AND DISCUSSION

Electrical conductive mode of the CB/PE composites

The CB used as the conductive filler was composed of the aggregates of numbers of fine particles. The number and the linking condition of the aggregates had significant effects on the conductive levels of the CB/PE composites. The elongated aggregates were in favor of better conductive levels.^{2,3} Crosslinking by irradiation with a cobalt 60 source at room temperature in air eliminated the undesired negative temperature coefficient of the composites. The extraction experiments showed that when the dosage

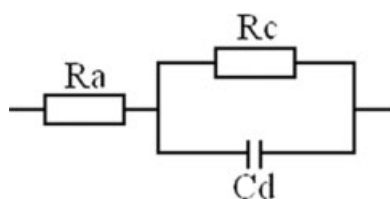


Figure 1 Equivalent circuit model of the CB/PE composite.

of radiation was above 220 kgy, the gel content of the composites could exceed 75% and the negative temperature coefficient could be eliminated. Electron conduction in the CB-filled composites occurred along CB particles contacting each other or CB particles separated by very small gaps in the composites. The gaps could be considered as potential barriers for electrons to hop by the tunneling effect. Reducing the numbers or widths of gaps in the CB chains could enhance the flow of electrons and decrease the macroscopic electrical volume resistivity. The average distance was affected by many factors, such as concentration, structure, size, shape of the CB aggregates, size distribution of CB, mixing efficiency, and temperature. The composites became conductive only if the content of CB reached the threshold concentration, which was called the *critical percolation threshold*. The critical percolation threshold represented a condition in which continuous CB chains had been first formed.^{3,13} Under these conditions, the conductive CB chains were either contacting each other or were separated by very small gaps through which electrons could tunnel. So the conductivity of the CB/PE composites relied on both of them.³⁷

A mathematic model of conductive composites is used to describe the relationship between the electrical current (I) and electrical voltage (U):

$$I = AU^B \quad (1)$$

where A represents the conductive ability and B represents the conductive style of the conductive com-

posites. According to the theory of conductive network,^{3,31} there were continuous CB chains and discontinuous CB chains in the CB/PE composites. The gaps between the CB particles could also be conductive due to the tunneling effect. The results of the alternating-current impedance spectroscopy implied that the alternating-current conductive mode of the composites fit the parallel connecting equivalent circuit model,^{4,37} as shown in Figure 1.

In Figure 1, R_a is the electrical resistance of continuous CB chains, R_c is the electrical resistivity of CB chains with one gap or a few small gaps, and C_d is the capacitive resistivity of the larger gap CB chains. When a conductive composite has more larger gap chains, its B value will become bigger, and the CB chains in it will be less uniform. Because the heat produced by the high electrical voltage influences accuracy of the testing, the testing electrical voltage was set to 0.5 V to eliminate the influence of heat. We chose five CB/PE composite sections (length = 10 cm each) with different values of B and measured their conductive parameters. As shown in Table II and Figure 2, the electrical resistances of the samples were not influenced by frequency in the range 10–10⁴ Hz.

The parameter values A , B , and $R_a + R_c$ of conductive composites is inherent, and the A and B value can be calculated with the formula $I = AU^B$. For a sample, there will be a current in a voltage; when the voltage is changed, another current can be obtained. When the equations are joined, one can determine the A and B values of a sample. They could not be obtained from Table I. The slopes of the quasi-straight lines reflected the B value of the composites; the bigger of the B value was, the bigger the pure value of the slopes was. The A value is the ohm resistivity of a sample in direct current or at a low frequency; it reflects the conductive conditions of the continuous CB chains and accords with the value of $R_a + R_c$. The value $R_a + R_c$ is the resistivity of a sample in low frequency on the alternating-current impedance spectroscopy. At a low frequency, C_d (Fig. 1) cannot be conductive; its value is infinity, so

TABLE II
Heat Treatment of the Electric Parameters of the CB/PE Composite Samples

		Sample				
		1	2	3	4	5
Before heat treatment	A	418	1.09×10^3	898	3.22×10^3	1.86×10^4
	B	1.02	1.26	1.42	1.55	1.75
	$R_a + R_c$	400	1.03×10^3	810	2.42×10^3	1.33×10^4
	Slope of the quasi-straight line	-0.27	-0.36	-0.39	-0.43	-0.92
After heat treatment	A	323	1.15×10^3	448	846	1.17×10^4
	B	1.01	1.11	1.28	1.29	1.34
	$R_a + R_c$	350	1.43×10^3	423	870	3.20×10^4
	Slope of the quasi-straight line	-0.065	-0.26	-0.30	-0.45	-0.50

The slope of the fitting line came from linear regression.

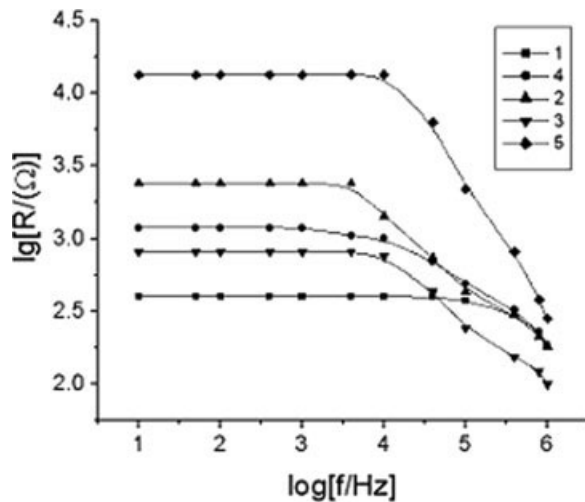


Figure 2 Room-temperature resistance (R) of the CB/PE composite versus the frequency (f).

the resistivity of a sample is $R_a + R_c$. When the frequency high enough, the value of C_d change is small, and the total resistivity of a sample change is small (Figs. 2–4).

Although the frequency was in the range 10^4 – 10^6 Hz, the electrical resistivity decreased with increasing frequency. As shown in Figure 2, when the B value became larger, the resistivity decreased more quickly. That is, with increasing B value, the distribution of the CB chains were not be uniform, and there were more gaps or more capacitance compositions in the conductive CB/PE composites. This was because the CB gap chains were not conductive in low-frequency scope or direct current. When the frequency was high enough, some gaps in the CB chains became conductive, and the CB chains with small gaps became conductive first. The conductive modes include tunneling, field shoot, or hopping,¹⁸

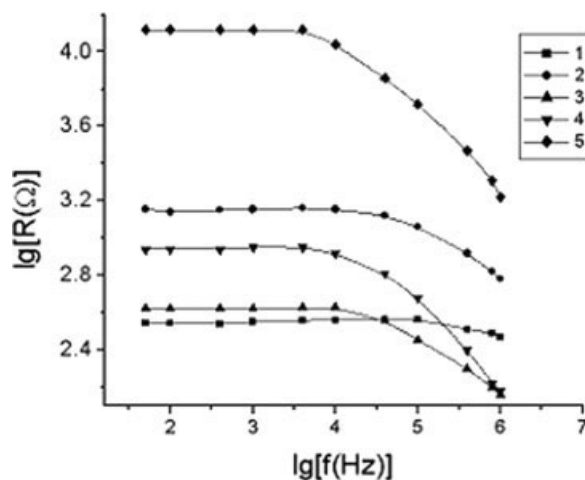


Figure 3 Room-temperature resistance (R) of heat-treated CB/PE composite samples versus the frequency (f).

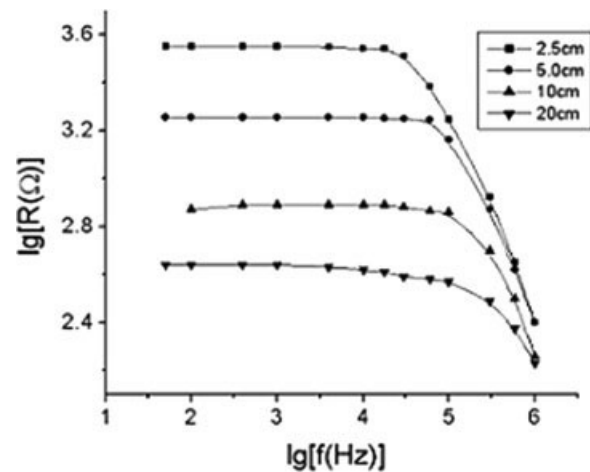


Figure 4 Room-temperature resistance (R) of CB/PE samples of different lengths versus the frequency (f).

and the conductive mechanism of the CB/PE samples showed a non-Ohm style; the relationship of the room-temperature resistance (R) versus U is $R = A^{-1} \cdot U^{1-B}$. So when the frequency was elevated, the capacitive reactance became larger, and the macroscopic electrical resistivity of the CB/PE sample was diminished.

Heat treatment of the CB/PE composites

It is known that heat treatment can loosen the stress and reorganize CB chains to a certain degree, even though the composites are crosslinked enough. The five samples of the CB/PE composites shown in Table II were heated to 98°C in an oven and held at that temperature for 3 h; then, they were slowly cooled to room temperature. Table II shows the values of A , B , and $R_a + R_c$ before and after heat treatment.

As shown by Table II and Figure 3, the electric parameters A , B , and $R_a + R_c$ of the CB/PE composites became smaller after heat treatment. This was because heat treatment caused CB redistribution, and more CB gap chains began to contact CB chains, so the resistances and B values of the samples became smaller.^{39–43}

The electrical resistivity of the samples after heat treatment, which were maintained constant in low-frequency scope (50 to 10^4 Hz) and decreased in the higher frequency scope ($>10^4$ Hz), showed the same changing trend as those before heat treatment. The difference between the before heat treatment and after heat treatment samples (Figs. 2 and 3) was that the electrical resistivity's decreasing percentage of the heat-treated samples became smaller when the frequency went up in a high-frequency scope ($>10^4$ Hz). This was because heat treatment loosened the CB chains to some extent, and the organization of

CB particles became more uniform and orderly in the heat-treated composites, the continuous CB chains increased, and the CB chains with gaps decreased, so the B value and the slope of line fitting in the high-frequency scope ($>10^4$ Hz) became smaller. This could have made the macroscopic electrical resistivity become smaller after heat treatment in the same frequency for a sample.

Conductive mode of CB/PE composites of different lengths

Another five CB/PE composite samples of different length were cut from a long stable sample of CB/PE composite, and R_a and R_c values were measured under different frequencies with alternating-current impedance spectroscopy. As shown in Figure 4, the slopes for samples of different length (20, 10, 5, and 2.5 cm) were -0.56 , -0.58 , -0.70 , and -0.72 , respectively, and their electrical capacities were 7.12, 4.58, 1.60, and 0.82×10^{-12} F, respectively. Figure 4 indicates that a shorter sample had a higher macroscopic electrical resistivity, and the slope of line fitting in the high-frequency scope ($>10^4$ Hz) became smaller than that in the low-frequency scope.

The reason was that the connection mode of the CB chains were in parallel connection in the CB/PE composite. A shorter sample had less continuous and few small gaps in the CB chains, its R_a and R_c were bigger, and the macroscopic electrical resistivity was bigger in the same frequency.

When the frequency was high enough, the electrical capacitance of a shorter sample made a higher contribution to the conductivity. The CB gap chains gave a larger conductive ratio on alternating current in the same frequency. Therefore, when the frequency increased, the decreasing rate of a shorter samples' electrical resistivity became larger, and the numerical value of the slope became larger. It is reasonable to believe that the CB/PE composites had a network conductive mode.

CONCLUSIONS

There were three kinds of CB chains in the CB/PE composites, where the CB chains were continuous with small gaps and with large gaps. The three-dimensional network conductive mode was believed to be the conductive mode of the CB/PE composites, as determined by the study with alternating-current impedance spectroscopy. In the lower frequency range, the continuous CB chains and the small gaps between CB particles made a contribution to the conductivity, although in the higher frequency range, the large gaps could participate in the conduction of the composites.

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