Impedance Spectra of Carbon Black Filled High-Density Polyethylene Composites

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ABSTRACT: Carbon black (CB) filled high-density polyethylene (HDPE) composites are prepared by ordinary blending for use as an electrical conductive polymer composite. The composite changes from an electrical insulator to a conductor as the CB content is increased from 10 to 20 wt %, which is called the percolation region. For explanatory purposes, three models, namely, "conduction via nonohmic contacting chain," "conduction via ohmic contacting chain," and a mixture of them corresponding to the conductions in the percolation region, high CB loading region, and limiting high CB loading are proposed by the reasonable configurations of aggregate resistance, contact resistance, gap capacitance, and joining aggregates induction. The characters of the impedance spectra based on the three models are theoretically analyzed. In order to find some link between the electrical conductivity and the CB dispersion manner in the composites, the impedance spectra of three samples, HDPE/15 wt % CB (the center of the percolation region), HDPE/25 wt % CB (a typical point in the high CB loading region), and HDPE/19 wt % CB (the limiting high CB loading region), are measured by plotting the impedance modulus and phase angle against the frequency and by drawing the Cole–Cole circle of the imaginary part and real part of the impedance modulus of each sample. The modeled approached spectra and the spectra measured on the three samples are compared and the following results are found: the measured impedance spectrum of HDPE/15 wt % CB (percolation region) is quite close to the model of conduction via nonohmic contacting chain. The character of the measured spectrum of HDPE/25 wt % CB consists of the form of the model of conduction via ohmic contacting chain. The impedance behavior of HDPE/19 wt % CB exhibits a mixture of the two models. From the comparisons, it is concluded that the electrical conducting network in the percolation region of the CB filled HDPE composite is composed of aggregate resistance, nonohmic contact resistance, and gap capacitance, and that of the high CB loading region consists of continuously joined CB aggregate chains, which are possibly wound and assume helix-like (not straight lines) conductive chains, acting as electrical inductions as the current passes through. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1344–1350, 2005

Key words: composites; polyethylene; modulus; chain

INTRODUCTION

Carbon black (CB) filled polymer composites are some of the most extensively studied composites because of their adjustable electrical conductivity and wide applications as thermistors (positive temperature coefficient resistance), self-limited electrical heaters, electrical screening materials, and so forth in industry.[1–3] Various mechanisms have been proposed concerning the physical processes involved in electrical conduction. The electrical conduction of these composites is realized not only by the conductive CB particles but also by the manner of contacting and joining between them, within which ohmic and nonohmic contacts, field electron emission, and tunneling are possibly operated,[4–7] and consequently by the CB loading level, degree of aggregation, measurement conditions, and so forth.[8–10]

Impedance spectroscopy was employed here to study the conduction mechanism and CB conducting network structure in CB filled high-density polyethylene (HDPE). The key parameters, which reflect the network structure and electron conduction mechanism of the composite, are aggregate resistance, nonohmic or ohmic contact resistance, effective gap capacitance, and effective electrical inductance of joining CB chains. Corresponding to two typical CB loading levels (the percolation region and the high loading region), two effective electrical circuits containing these parameters for "conduction via nonohmic contacting chain" and "conduction via ohmic contacting chain" were modeled and the modeled impedance spectra were analyzed. In addition, the impedance spectra of three samples, HDPE/15 wt % CB (the percolation region, a typical composition for positive temperature coefficient resistance), HDPE/25 wt % CB (the high loading region, a typical composition for electrical screening polymer composites), and HDPE/19 wt %

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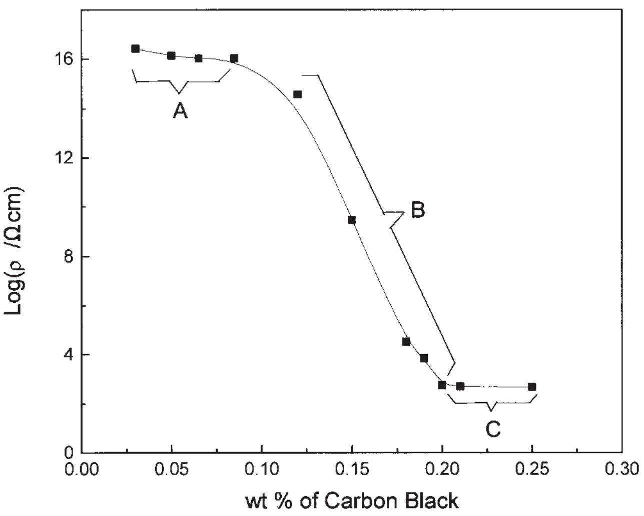

Figure 1 The resistivity as a function of the weight fraction for carbon black filled high-density polyethylene.

CB (the limited high loading region, a typical composition for self-limited electrical heaters), made by ordinary blending were measured and illustrated by plotting the impedance modulus ($|Z|$) and phase angle (ϕ) against the frequency (f) and by drawing the Cole–Cole circle of the real part (Z_2) versus the imaginary part (Z_1) of the impedance (Z). The experimental data were then fitted by the effective circuit functions to obtain those parameters including aggregate resistance, contact resistance, gap capacitance, and electrical induction of joining CB chains. On the basis of deriving and fitting the effective electrical circuit functions with experimental data, the conduction mechanism and network structure of the composites were analyzed and discussed.

THEORETICAL

The evolution of the resistivity as a function of the CB loading is shown in Figure 1 for the CB filled HDPE composites under study. At low loadings of CB, the gap between CB aggregates, where the electrons are transmitted, is very large and the resistivity of the composite is approximately that of the polymer matrix. As the loading rises, a percolation threshold or critical loading is reached where the resistivity starts to decrease abruptly as a function of CB loading. The entire dramatic resistivity decreasing region is called the percolation region. In this region, the gap between CB aggregates is close but not touching. As a result, the electron must conquer a potential barrier to get out of the CB aggregate and across the gap [see Fig. 2(a)]. Early researchers[11,12] proposed that the electrons "jump" across this gap, with an exponential dependence on the gap width. However, most researchers considered that the electron passage between the aggregates is due to tunneling.[11] Tunneling is a quantum mechanical process in which the wave function of the electron is not confined entirely within a potential box, but has a small tail extending beyond the potential barrier. At the same time, tunneling takes place only between very closely neighboring CB aggregates.

Regardless of the transport mechanism of electrons across the gap,[13] there must be a certain contact resistance (R_c), the so-called nonohmic resistance for the passage of electrons through the gap or junction in the composite being studied. At the same time, the gap can be approximated by a parallel plate capacitor with an area (A), separation distance (w), and capacitance (C) $= \varepsilon A/w$, where ε is the dielectric constant of the polymer. Each CB aggregate has a resistance (R_a), the resistance within the aggregate. An equivalent circuit of the microarea is schematically shown in Figure 2(b). The impedance can be written as

$$Z = R_a + \frac{1}{\dfrac{1}{R_c} + j\omega C} = R_a + \frac{R_c}{1 + \omega^2 R_c^2 C^2} - j\frac{\omega R_c^2 C}{1 + \omega^2 R_c^2 C^2} \tag{1}$$

where ω ($=2\pi f$) is the angular frequency. In macroscale, a whole composite may also be regarded as a similar equivalent circuit in which, instead of C, R_c, and R_a, equivalent series components of capacitance (C_s), contact resistance (R_{cs}), and aggregate resistance (R_{as}) are used to model the situation of conduction via nonohmic contacting chain [see Fig. 2(c)]. The overall impedance of the composite is given by

$$Z = R_{as} + \frac{R_{cs}}{1 + \omega^2 R_{cs}^2 C_s^2} - j\frac{\omega R_{cs}^2 C_s}{1 + \omega^2 R_{cs}^2 C_s^2} \tag{2}$$

The respective real and imaginary parts of the impedance can now be simply expressed as

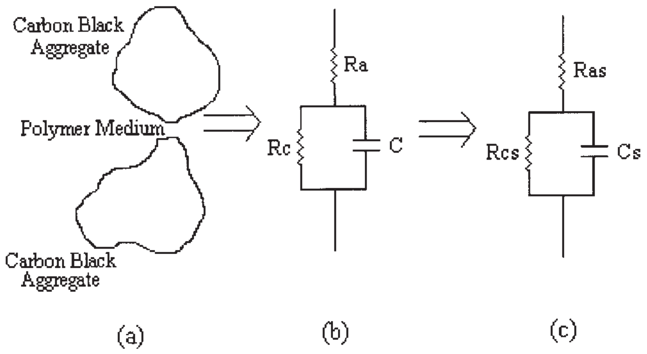

Figure 2 The equivalent resistor–capacitor series for carbon black filled high-density polyethylene in the percolation region.

$$Z_1 = R_{as} + \frac{R_{cs}}{1 + \omega^2 R_{cs}^2 C_s^2} \tag{3a}$$

$$Z_2 = -\frac{\omega R_{cs}^2 C_s}{1 + \omega^2 R_{cs}^2 C_s^2} \tag{3b}$$

We can also obtain the respective impedance modulus and phase angle:

$$|Z| = \left(R_{as}^2 + \frac{R_{cs}^2 + 2R_{cs}R_{as}}{1 + \omega^2 R_{cs}^2 C_s^2} \right)^{1/2} \tag{4}$$

and

$$\tan\varphi = \frac{Z_2}{Z_1} = \frac{-\omega R_{cs}^2 C_s}{R_{as} + R_{cs} + \omega^2 R_{cs}^2 R_{as} C_s^2} \tag{5}$$

Comparing eqs. (3a) and (3b), the relation between Z_1 and Z_2 is

$$\left(Z_1 - \frac{2R_{as} + R_{cs}}{2} \right)^2 + Z_2^2 = \left(\frac{R_{cs}}{2} \right)^2 \tag{6}$$

Therefore, plotting Z_2 against Z_1 can give a half-circle, which has the circle center at $((2R_{as} + R_{cs})/2, 0)$ and a radius of $R_{cs}/2$. Because the circular curve of the Z_2 versus Z_1 curve occurs only for the parallel resistor–capacitor circuit, it can be used to confirm the existence of the capacitor effect, that is, the gaps between the CB aggregates controlling the electron conduction via nonohmic contacting chain in the percolation region.

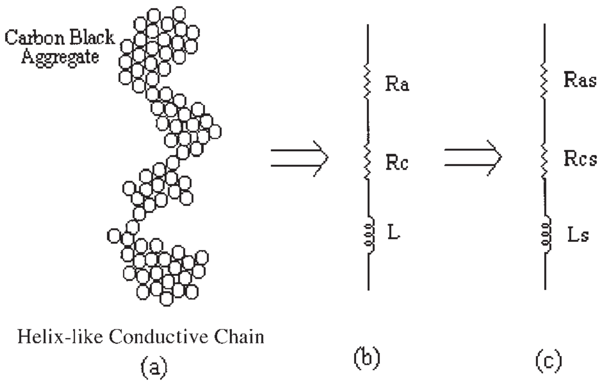

Figure 3 The equivalent resistor–inductor series for carbon black filled high-density polyethylene at high loading.

When the loading keeps rising, however, the gap between the aggregates is further reduced. According to El-Tantawy et al., the gap between two neighbor aggregates can be as small as 17 Å,[14] and the conductive mechanism between aggregates may be by a wave function overlap. As a result, the aggregates in the composite with a high loading level would be in strong contact just as within CB aggregates, and the classical conduction via ohmic contacting chain becomes the leading mechanism of conduction instead of tunneling in the percolation region where conduction via nonohmic contacting chain dominates. In this situation, the R_c becomes much lower than the R_a and the net resistance (R) is thus approximately equal to R_a. However, the CB usually does not disperse exactly uniformly in the polymer matrix for many reasons, such as the presence of PE spherocrystals within which the CB aggregates cannot stay and the chain cannot go through, the limit of processing conditions, and so forth. In addition, the electrical conductive network is very likely composed of bunches of winding CB aggregate chains. When alternating current of some fixed frequency passes through the composite, these chains may act as an electrical inductor in addition to an electron passageway. Overall, the electrical conduction network may be modeled as a series circuit of R_{as}, R_{cs}, and electrical inductance (L_s) and an equivalent "screwlike conductive chain" joining neighboring CB aggregates instead of a 3-dimensional regular array is assumed based on L_s (see Fig. 3). The impedance for a single chain can be described as

$$Z = R_c + R_a + j\omega L \approx R_a + j\omega L \tag{7}$$

where L is the induction of the chain and R_c is negligible compared to R_a because of perfect ohmic contact between CB aggregates. Similarly, for a large piece of composite material, the inductance and resistance [Fig. 3(c)] and the impedance of the composite can be rewritten as the following:

$$Z = R_{as} + j\omega L_s \tag{8}$$

The respective real and imaginary parts of the impedance are then given by

$$Z_1 = R_{as} \tag{9a}$$

$$Z_2 = \omega L_s \tag{9b}$$

The respective impedance modulus and phase angle can thus be easily calculated as

$$|Z| = (R_{as}^2 + \omega^2 L_s^2)^{1/2} \tag{10}$$

and

$$\tan\varphi = \frac{\omega L_s}{R_{as}} \tag{11}$$

From eqs. (9a) and (9b), one can conclude that the Z_2 versus Z_1 curve is a straight line perpendicular to the Z_1 axis. The particular behavior of resistor–inductor

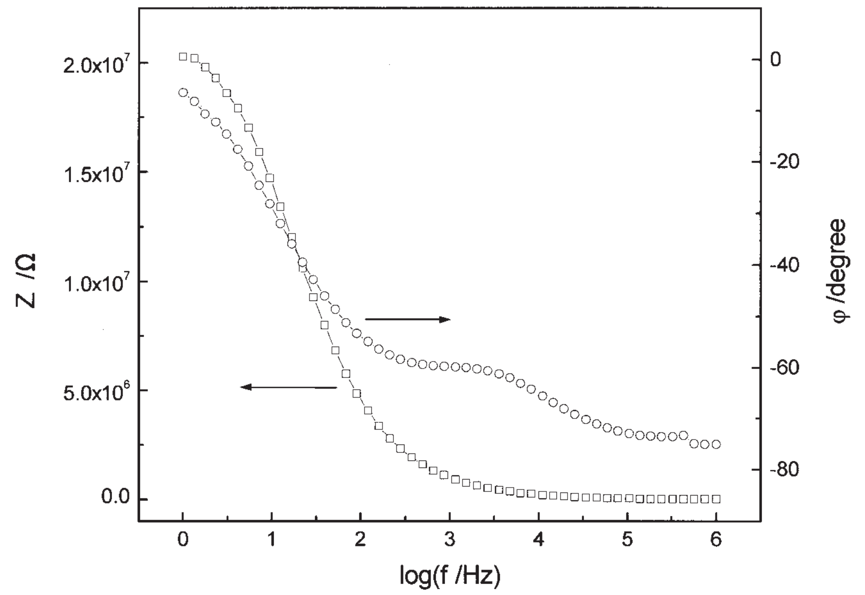

Figure 4 The frequency dependence of the (□) impedance modulus (|Z|) and (○) phase angle (ϕ) for the composite of polyethylene with 15 wt % carbon black.

series can be used to confirm the formation of conduction via ohmic contacting chain in the composites.

If the loading does not reach an adequate high level that only pure inductance effect exists, say limiting the high loading level, both the capacitance effect and inductance effect could coexist. A model based on a resistor–capacitor–inductor series is then used to represent the composite, and the impedance can be written as

$$Z = R_{as} + \frac{1}{\dfrac{1}{R_{cs}} + j\omega C_s} + j\omega L_s \tag{12}$$

$$= R_{as} + \frac{R_{cs}}{1 + \omega^2 R_{cs}^2 C_s^2} + \left(\omega L - \frac{\omega R_{cs}^2 C_s}{1 + \omega^2 R_{cs}^2 C_s^2} \right) j$$

In other words, the impedance of the composites can be displayed by different functions at different loading levels and those functions correspond to various equivalent electrical series, suggesting different conduction mechanisms and network structures of the composites. Therefore, impedance spectroscopy can be a useful tool to study the electron transport mechanism and investigate the network structure of conductive filler loaded polymer composites.

EXPERIMENTAL

The CB used was acetylene black with an average 42-nm diameter particle size, a Brunauer–Emmett–Teller (determination method) value of 63 m^2/g, and a dibutyl phthalate absorption (measurement method) value of 3.3 mL/g. The polymer used was HDPE (2480) with a melting temperature of 130°C, a melt flow rate of 0.14 g/10 min, and density of 0.943 g/cm^3. Samples were fabricated by mixing the polymer and CB for 15 min in a two-roll mill at 170°C and then hot pressing the mixture in a matched metal die at 170°C for 20 min.

The room temperature resistivity of the samples varied over a wide range from 1 to 10^{18} Ω cm. High resistivity samples were measured on a ZC36 high resistance electrometer using the two-probe technique, whereas the low resistivity samples were measured on a M890D digital electrometer with the four-probe technique.

The impedance spectra of the samples were measured at room temperature with electrochemical impedance spectroscopy using a frequency response analyzer (Solartron model 1255) with a Solartron model 1287 electrochemical interface over the frequency range from 1 Hz to 1 MHz. All samples had the same disk shape with a 30-mm diameter and 2.5-mm thickness. Contact resistances were reduced to a minimum by coating the surfaces of the samples with conductive silver pastern.

RESULTS AND DISCUSSION

Impedance spectra in percolation region

Figure 4 contains the plots of the $|Z|$ and ϕ of the sample of HDPE/15 wt % CB (the center of the percolation region) versus the f from 0 to 10^6 Hz. It can be seen that both the impedance modulus and phase

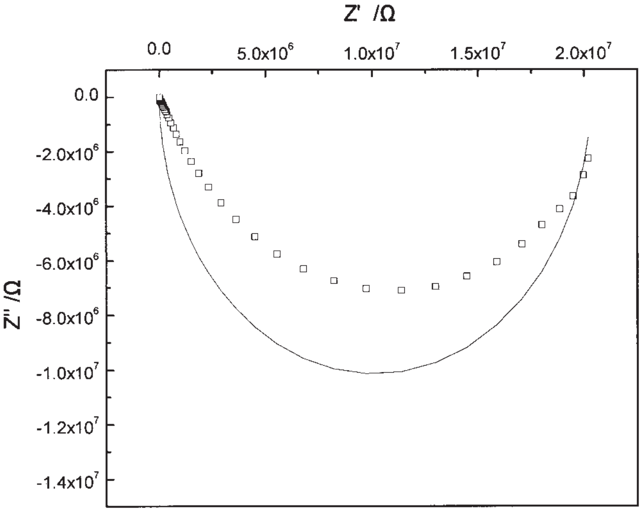

Figure 5 The Z_1–Z_2 curve for the composite of polyethylene with 15 wt % carbon black: (□) experimental data and (—) calculated curve.

angle decrease with the increase of the frequency. Because the loading level of HDPE/15 wt % CB was in the percolation region, gaps exist between the CB aggregates; and the parallel resistor–capacitor series (Fig. 2) can be applied to represent the composite based on the analyses above. At low frequencies ($\omega \approx 0$) the current flows through the nonohmic contact resistance because it is encumbered at the contact capacitance (see Fig. 2), and the impedance is the summation of R_{as} and R_{cs}, according to eq. (4). At high frequencies, however, the reactance of the contact capacitance $(\omega\ C_s)^{-1}$ is much lower than the R_{cs} and the current prefers to flow through the contact capacitance. Furthermore, because the reactance of the capacitance is also much lower than the R_{as}, the net resistance at high frequencies is approximately equal to R_{as}, which is much lower than the net resistance ($R_{as} + R_{cs}$) for low frequencies. As a result, the impedance modulus decreases with the increasing frequency. The reason why the phase angle also decreases with the increasing frequency is similar to that of the impedance modulus. From Figure 4 it can also be calculated that the R_{as}, R_{cs}, and C_s of the HDPE/15 wt % CB composite are about 4990 Ω, 2.03×10^7 Ω, and 6.68×10^{-11} F, respectively, according to eq. (4).

In order to further confirm the reasonableness of the use of the parallel resistor–capacitor series for the composites in the percolation region, the experimental data of Z_2 and Z_1 obtained at different frequencies are displayed as a Z_2 versus Z_1 curve in Figure 5. Note that the Z_2 versus Z_1 curve is nearly semicircular, which agrees with the prediction of eq. (6). The values of R_{as}, R_{cs}, and C_s obtained from Figure 4 are used in eq. (6), and the calculated circular curve is also drawn as a solid line in Figure 5. The calculated curve does not exactly fit the experimental values because the capacitor used in the equivalent circuit is treated as a perfect capacitor (constant), which is not true because the dielectric constant of the polymer (HDPE) between CB aggregates is a function of the frequency and the capacitance is thus dependent upon the frequency. Furthermore, the polarization of the CB dispersed in the polymer matrix cannot be ignored. Therefore, the experimental curve departs from the predicted curve (solid line) but still retains the approximate semicircular shape.

In summary, because a capacitance effect exists in the composite whose loading level is in the percolation region, it appears that the electron transport in this composite is limited by the potential barrier of the gap. At low frequencies the transport of the electron across the gap is a controlling mechanism for the conduction. In addition, at high frequencies the electron conduction in the composite is controlled by the intrinsic conductivity of the CB, that is, the resistance within the CB aggregates.

Impedance spectra at high loadings

Figure 6 presents the plots of the $|Z|$ and ϕ as functions of the frequency for the composite filled with 25 wt % CB, which was a very high CB loading level among the composites. Both the impedance modulus and phase angle are stable until f reaches $10^{5.5}$ and $10^{4.5}$ Hz, respectively, and both abruptly increase with further increase of the frequency, indicating that the band-type conduction of the electron, that is, the conduction through-going chain, takes place. Here, the conduction through-going chain is the same as the conduction via ohmic contacting chain being formed.

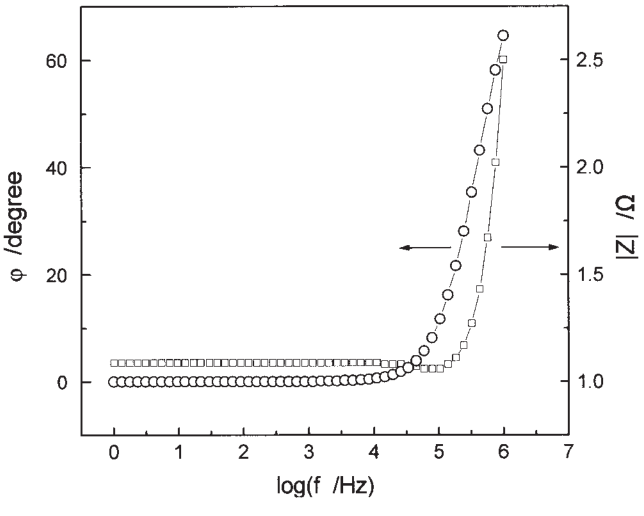

Figure 6 The frequency dependence of the (□) impedance modulus ($|Z|$) and (○) phase angle (ϕ) for the composite of polyethylene with 25 wt % carbon black.

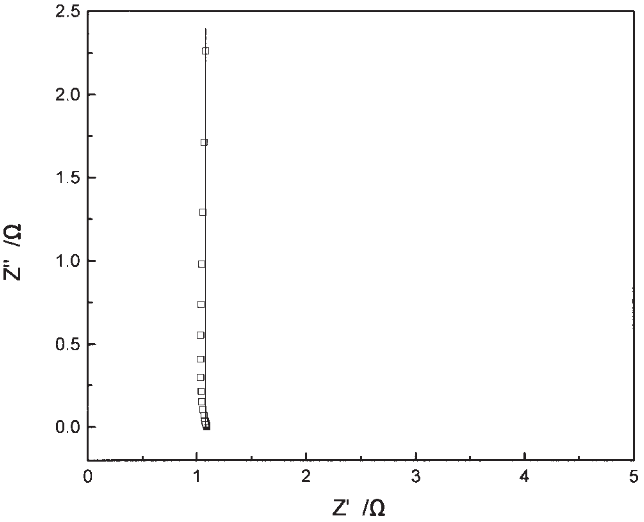

Figure 7 The Z_1–Z_2 curve for the composite of polyethylene with 25 wt % carbon black: (□) experimental data and (—) calculated curve.

Because the loading level is very high, the aggregates are more tightly packed and pressed against each other. The conduction via through-going chain is thus formed, and the resistor–inductor series can be used to represent the composite. At low frequencies the current flows through the inductance easily, and the R_s can be determined by the sum of R_{cs} and R_{as}. At high loading level the processing procedure might lead the aggregates to be tightly squeezed but without so much disturbance inside the aggregates. Therefore, the contact resistance became much lower than the aggregate resistance, and the net resistance could be replaced by R_{as}. However, when the frequency rises, the inductance begins to block the current and the impedance combining the two resistances and the reactance of the induction increases. As a result, the impedance modulus increases with the increasing frequency. Figure 6 does exhibit such a character. From Figure 6 it can also be calculated that the R_{as} value of the HDPE/25 wt % CB composite is about 1.08 Ω and the L_s value is 3.60×10^{-7} H, according to eq. (10).

As the net resistance of the composite is about R_{as} at low frequency and increases with the increasing frequency, it can be concluded that the conduction is controlled by the intrinsic conductivity of the CB at low frequency, but influenced by the CB dispersion in the polymer matrix at higher frequency.

The experimental Z_2 versus Z_1 curve of the HDPE/25 wt % CB composite is shown in Figure 7. It can be seen that the Z_1–Z_2 curve is indeed a perpendicular straight line of the Z_1 axis, characteristic of the resistor–inductor series from eq. (9). Equation (9) also predicts that the intersection of the straight line at the Z_1 axis is R_{as}, which is also plotted in Figure 7 (solid line), which agrees with the value of R_{as} obtained from Figure 6. Therefore, the model of the resistor–inductor series can be used to represent the conduction behavior of the composites at high loading and it is the inductance effect that determines the frequency dependence of the electrical property for the composites at high loadings. It can also be seen that, because there is L_s, the assumption of the so-called equivalent helix-like conductive chain is reasonable when the conduction via through-going chain is formed at high loading.

Impedance spectra at limiting high loadings

The impedance spectra for CB filled PE composites both in the percolation region and at high loadings were studied, and important results were obtained. However, the loading level of these composites for many applications (e.g., some thermistors) is between the percolation region and high loading, that is, a limiting high loading. It is conceivable that the impedance spectra of the composites at limiting high loading have both the characteristics in the percolation region and at high loadings. Figure 8 demonstrates the variation of the impedance modulus of HDPE/19 wt % CB with frequencies from 0 to 10^6 Hz. The impedance modulus first decreases with the increase of the frequency until $10^{5.2}$ Hz, which is similar to the composites in the percolation region. The gaps between the CB aggregates strongly affected the electron transport below the frequency of $10^{5.2}$ Hz, and the equivalent series used to represent that composite must contain a parallel plate capacitor. We also found that the impedance modulus increases with increasing frequency beyond $10^{5.2}$ Hz, which is similar to the behavior of the composites with very high CB loading. It indicates

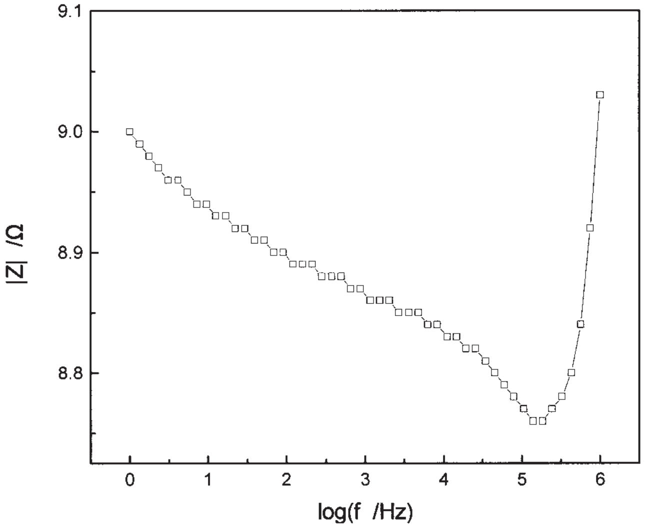

Figure 8 The frequency dependence of the impedance modulus for the composite of polyethylene with 19 wt % carbon black.

TABLE I
Aggregate Resistance, Contact Resistance, Gap Capacitance, and Induction of CB-Filled HDPE Composites with Different CB Loading Levels

CB loading	R_{as} (Ω)	R_{cs} (Ω)	C_s (F)	L_s (H)
HDPE/15 wt % CB	4990	2.03×10^{7}	6.68×10^{-11}	
HDPE/25 wt % CB	1.08			3.60×10^{-7}
HDPE/19 wt % CB	8.76	0.24 Ω	2.57×10^{-9}	3.51×10^{-7}

that, at limiting high loading, the conduction via through-going chain also formed to some extent and the electrical induction effect generated by the helix-like conductive chain came into effect only at high frequencies. Therefore, the equivalent electrical circuit should contain both C_s and L_s in addition to R_{as} and R_{cs}, as described in the previous section. As a result, the resistor–capacitor–inductor series can be applied to represent the composite under study and eq. (12) can thus be used to calculate the impedance. From Figure 8 it is calculated that the R_{as} of the HDPE/19 wt % CB is about 8.76 Ω, R_{cs} is 0.24 Ω, C_s is 2.57×10^{-9} F, and L_s is 3.51×10^{-7} H. In other words, the conduction via nonohmic contacting chain and the conduction via ohmic contacting chain coexisted in the composites at limiting high loading at the same time. At low frequencies the conduction via nonohmic contacting chain model is dominant, and at high frequencies the conduction via ohmic contacting chain is dominant.

The evaluated values of R_{as}, R_{cs}, C_s, and L_s for three typical CB loading levels are summarized in Table I. Note that R_{as} and C_s increase and R_{cs} decreases with increasing CB loading. This is reasonable because the CB aggregates were densely packed during processing and R_{as} was thus reduced because the CB loading level was high. The same reason made R_{cs} small and C_s large when the CB loading was high. The values of R_{as}, R_{cs}, C_s, and L_s obtained by fitting the experimental data to the three models are directly related to the structural character of the electrical network made by CB aggregates.

CONCLUSION

Three models characterizing the CB aggregate configurations in the conductive network of HDPE/CB composites were proposed for the percolation region, high loading region, and limiting high loading region. In the percolation region, the electrical conduction is through nonohmic contact chains formed by CB aggregates, and the aggregate resistance, contact resistance, and gap capacitance in the nonohmic contact are taken into consideration in the model. In the high loading region, the conduction is through ohmic contact chains and the model assumes aggregate resistance, contact resistance, and effective induction as a series. In the limiting high region, the model mixes the two models. The impedance spectra measured on HDPE/15 wt % CB (percolation center), HDPE/25 wt % CB (high CB loading), and HDPE/19 wt % CB (limiting high loading) were found to match the three models well, suggesting that impedance spectroscopy is a tool to characterize CB network structures. The effective aggregate resistance, contact resistance, gap capacitance, as well as the effective electrical induction were obtained by fitting the measured spectra to the models. Their values can be used to describe the CB aggregate compacting degree and the contacting manner at different loading levels and to suggest helix-like CB aggregate chains in the high CB loading composite.

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