Effects of Charge Trapping on the Electrical Conductivity of Low-Density Polyethylene–Carbon Black Composites

D. Dudić,[1] B. Škipina,[2] J. Dojčilović,[1] L. Novaković,[1] D. Kostoski[1]

[1]*Faculty of Physics, University of Belgrade, 11001 Belgrade, Serbia*
[2]*Faculty of Technology, University of Banja Luka, Vojvode Stepe Stepanovića 73, 78 000 Banja Luka, Bosnia and Herzegovina*

ABSTRACT: Electrical conductivities of low-density polyethylene (LDPE)–carbon black (CB) composites were studied using high resistance meter at room temperature (DC conductivity) and dielectric spectroscopy (AC conductivity) in the frequency range between 90 kHz and 13 MHz and temperature range from 120 to 355 K. DC measurements revealed a percolation threshold at about 20 wt % of CB content, whereas AC measurements show two conductivity peaks at about 15% and 23% of CB content. The presence of two percolation thresholds was attributed to different dispersions of CB particles in structural inhomogeneities of LDPE. The experimental data were analyzed using the model of Efros and Shklovskii, which describes the critical behavior of a complex conductivity using critical indexes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 138–143, 2011

Key words: polyethylene (PE); carbon black; composites; dielectric properties; percolation

INTRODUCTION

The electrical conductivity and dielectric constant, or complex conductivity, of metal insulator mixtures are the most widely investigated physical property of percolation systems. Many review articles include sections on the complex conductivity.[1–3]

Carbon black (CB), graphite, and carbon fibers are typical conducting fillers used in the preparation of conductive polymer composites.[4–6] In the composites of a polymer matrix with CB filler material, the conductivity often increases by many orders of magnitude when the filler concentration becomes higher than a critical value. This percolation threshold is usually of the order of 0.1–0.2 in volume fraction.[7] The level of conductivity of the polymer–CB composite can be varied by over 10 orders of magnitude depending on several factors. Among these we can mention CB content, specific conductive properties of CB, surface free energy and morphological properties of the polymer, processing conditions which mainly affect the degree of CB dispersion in the polymer matrix.[8]

The low-density polyethylene (LDPE) is often selected as the matrix because of its good dielectric and mechanical properties, low cost, and relatively simple processing with carbon particles.[9] However, LDPE is a crystalline branched polymer with special lamellar thickness distribution where the presence of CB particles and agglomerates can induce changes in the structure of the amorphous phase and lamellae distribution.[10,11] On the other hand, in some of our previous studies, we investigated the effects of charge trapping and their release in crystalline LDPE.[12,13] Among other mechanisms of electrical transport (hopping, tunneling, and percolation), their release can have some influences on the DC and AC conductivities of CB–LDPE composites. Because of that, in this work, we have studied the effects of morphology on the DC and particularly on the complex AC conductivity of CB–LDPE composites, using DC conductivity measurements as a function of composition at room temperature and measurements of complex AC conductivity as a function of frequency, composition, and temperature.

EXPERIMENTAL

LDPE (PE552, HIP Pancevo, Serbia, $M_w = 110,000$, and $\rho = 0.922$ g/cm^3) was used as a polymer matrix. Producer of carbon-black fillers (ellipsoidal shape, diameter 3–5 μm, and conductivity 7×10^4 S/m) is Laboratory for Thermal Engineering and Energy, INN "Vinča" Serbia. Different mass
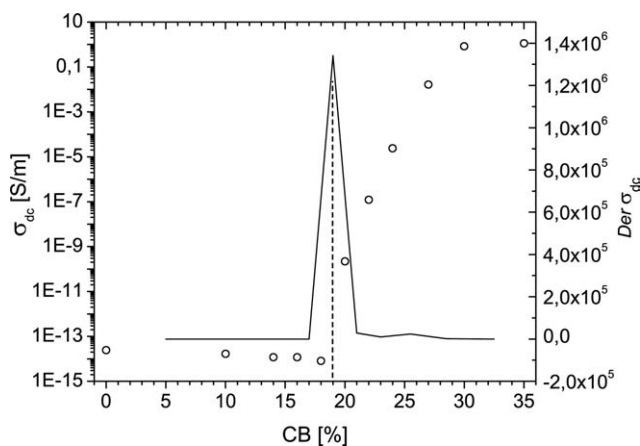
Figure 1 DC conductivity versus CB weight content (circle, left axis) and function Der σ_{dc} (line, right axis).

concentrations (0–35%) of carbon-black fillers were mixed with polymer matrix in a *Haake* rheometer at 433 K for 10 min. Isotropic sheets were obtained by compression moulding at 460 K and pressure of 1.75 MPa for 5 min, followed by quenching in water at room temperature. The samples in the form of discs ($D = 13$ mm, $d = 1$ mm) were cut from the middle of the sheets.

The CB filler aggregation for all samples was controlled by optical microscope (Carl Zeiss Jena 354726, magnification 200×). The aggregation of CB filler is exhibited for the samples with 20% CB and more. For DC and AC conductivity measurements, we used samples with the following wt % CB contents: 0, 10, 14, 16, 18, 20, 22, 24, 27, 30, and 35% (35% only for DC measurements). Electrical DC conductivity measurements were performed in a shielded cell using an Agilent 4339B high resistance meter at room temperature. Electrodes were made on the major faces, using silver contact paste. To provide the samples of the same thermal history, all of them were annealed at 400 K for 5 min and after that cooled down to room temperature at a rate of 2 K min^{-1}. Before measurement, the samples were conditioned for 2 days at room temperature in a desiccator at humidity of 50 $\pm$ 2%. The DC conductivity was measured in electric field in the range from 1 to 4000 V cm^{-1}. Each conductivity value was obtained after 15 s application of a certain voltage.

Dielectric spectroscopy measurements were performed on an Agilent 4285A instrument in the frequency range between 90 kHz and 13 MHz and temperature range from 120 to 355 K, using Temperature Controller Lake Shore 340. The heating rate was 3 K min^{-1}, and acquisition step was 5 K with 1.5 V applied voltage. The preparation and conditioning of the samples were the same, except the samples without silver electrodes. Conductance (G) and susceptance (B) were measured using the C_p model of the instrument, while the AC conductivity (σ_{ac}) was calculated as $\sigma_{ac} = \sqrt{B^2 + G^2}$. All results were checked on at least two samples.

Both instruments (Agilent 4339B and Agilent 4285A) were calibrated against Keithley 5155 standards (10^8–10^{13} Ω, $\Delta R/\Delta V = -0.03\%/V$) at all voltage ranges.

RESULTS AND DISCUSSION

DC conductivity

Figure 1 shows the results of DC conductivity measurements at room temperature for LDPE–CB composites filled with different contents of CB. A sharp rise of conductivity is evident. The level of conductivity of the LDPE–CB composites can be varied by over 10 orders of magnitude, depending on several factors, among which the CB content, specific conductive properties of CB, surface free energy and morphological properties of LDPE, processing conditions that affect the degree of CB dispersion in the polymer matrix. The percolation threshold in our measurements was about 20 wt % of the CB content, whereas the saturation of conductivity occurred at about 30% of the CB content. The percolation range is about 10% of the CB weight content. Good percolation systems are characterized by a smooth and rapid change of the DC electrical conductivity in a narrow range of the CB weight content. This behavior of DC conductivity of the composites was attributed to the insulator-conductor transition in polymer–CB composites, which depends on the aggregation, structure, porosity, average size, and size distribution of the conducting particles.[8] For CB-filled polymer, the polarity of the polymer matrix has a significant influence on the CB distribution.[9] Some authors have shown that the increase of the CB agglomerates can be related to the increase of the critical CB weight content and makes narrow percolation range.[7–9] A certain effect of morphology on the electrical behavior of composites was shown for the composites of polymer blends and CB.[7–9] Patnaik et al. have studied electrical conductivity of HDPE–CB composites using Positron Annihilation Lifetime Spectroscopy and suggested existence of three different morphological domains with different free volumes.[14] In our experiments, LDPE as a crystalline branched polymer has a morphology with the possibility of formation of structural parts in percolation range. Also, there is a possibility of formation of "cavity" traps because of structural defects in LDPE, which can have effects on the mechanisms of conductivity.[12,13]

AC conductivity

The results of the temperature dependences of AC conductivity (σ_{ac}), conductance (G), and susceptance
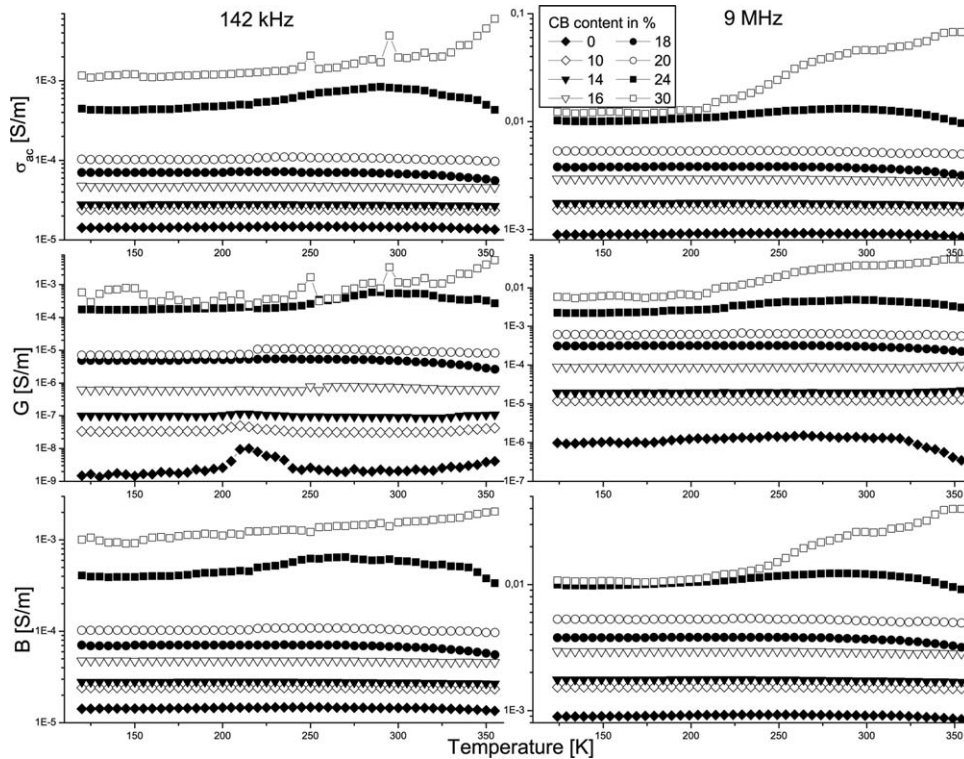
Figure 2 AC conductivity (σ_{ac}), conductance (G), and susceptance (B) versus temperature for two frequencies 142 kHz and 9 MHz.

(B) for two frequencies, 142 kHz and 9 MHz, are presented in Figure 2. Contrary to DC measurements, the results of the temperature and frequency dependences show the absence of the sharp rises of AC conductivity (σ_{ac}), conductance (G), and susceptance (B) with an increase of the CB weight content. A permanent increase of σ_{ac} and its components with the increasing CB weight content is evident from Figure 2. The increase of the weight content of the conducting CB increases the number of continuous paths through the composite, thus allowing the conduction of charge carriers yielding for the conductivity of the LDPE–CB composite. Figure 2 also shows the increase of susceptance (B) with increasing CB content, which can be related to the formation of capacitive gapes in the composites.

Figure 2 reveals different rises of conductance and susceptance with an increase of the CB content of up to 30%, at 142 kHz and 9 MHz.

To observe the experimental results in more detail, we introduced numerical derivation of the conductivity Der σ in eq. (1), which represents the rate of the conductivity change with the increasing CB weight content. This method of observation is very convenient to use in analyzing experimental data and relating them to percolation theory.

$$Der\sigma_i\left(\frac{C_{i+1} + C_i}{2}, f, T\right) = \frac{\sigma_{i+1}(f, T) - \sigma_i(f, T)}{(C_{i+1} + C_i)}\frac{100}{\sigma_i(f, T)},$$
$$i = 1, \ldots N - 1. \quad (1)$$

where N is the number of samples with different CB weight content, C_i ($C_{i+1} > C_i$), $\sigma_i(f,T)$ is the measured value of conductivity, f is the frequency, and T is the temperature. Maximum values of this function can be related to the percolation threshold. Frequency and temperature dependences of AC percolation were analyzed using the conductivity function defined in eq. (1). Equation 1 was also used to observe the sharp rise of the DC conductivity, as shown in Figure 1.

Frequency dependence of AC percolation

Figure 3 shows the frequency dependences of Der G and Der B at room temperature. Evidently, there are two sharp rises with increasing weight content of CB. The first percolation point (low percolation point) is at about 15–16% of CB, and the second one (higher percolation point) is at about 23% of CB. The observed changes of conductance in Figure 3 are about 10 times higher than susceptance with increasing CB content in the measured frequency range.

The maximum of Der B at 27% CB content is temperature dependent and shifts to higher frequencies
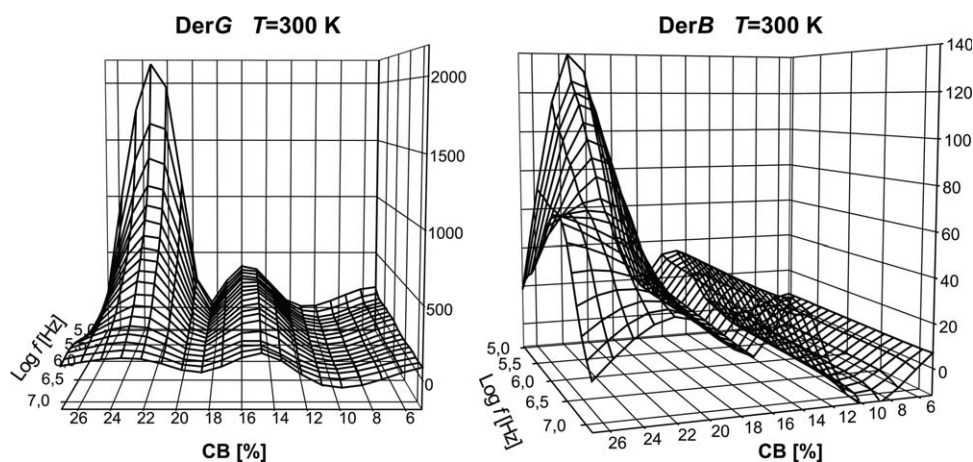
Figure 3 Frequency dependences of functions Der G and Der B at 300 K.

with increasing temperature. The change rates of conductance and susceptance at the higher percolation point are more frequency dependent. Their values decrease with increasing frequency.

If we compare the results in Figures 2 and 3, we notice in Figure 2 the absence of a clear percolation threshold, whereas Figure 3 shows clear increases of conductivity at the low (15% CB) and higher (23% CB) percolation points. If we take into consideration the results of Patnaik et al.[14] about structural inhomogeneity in HDPE–CB composites and our previous results of the effects of charge trapping in crystalline LDPE,[12,13] the presence of two peaks on the graphs in Figure 3 can be attributed to different dispersions of CB particles in structural inhomogeneities and micro defects of LDPE. A more significant frequency dependence at the higher percolation peak than at the low one can be related to different surroundings of CB fillers. Namely, the contributions to the AC conductivity at these critical concentrations of CB are different because of the differences between the filler–filler and filler–LDPE interactions.

Figure 4 represents frequency dependences of Der G and Der B at the low percolation point and shows
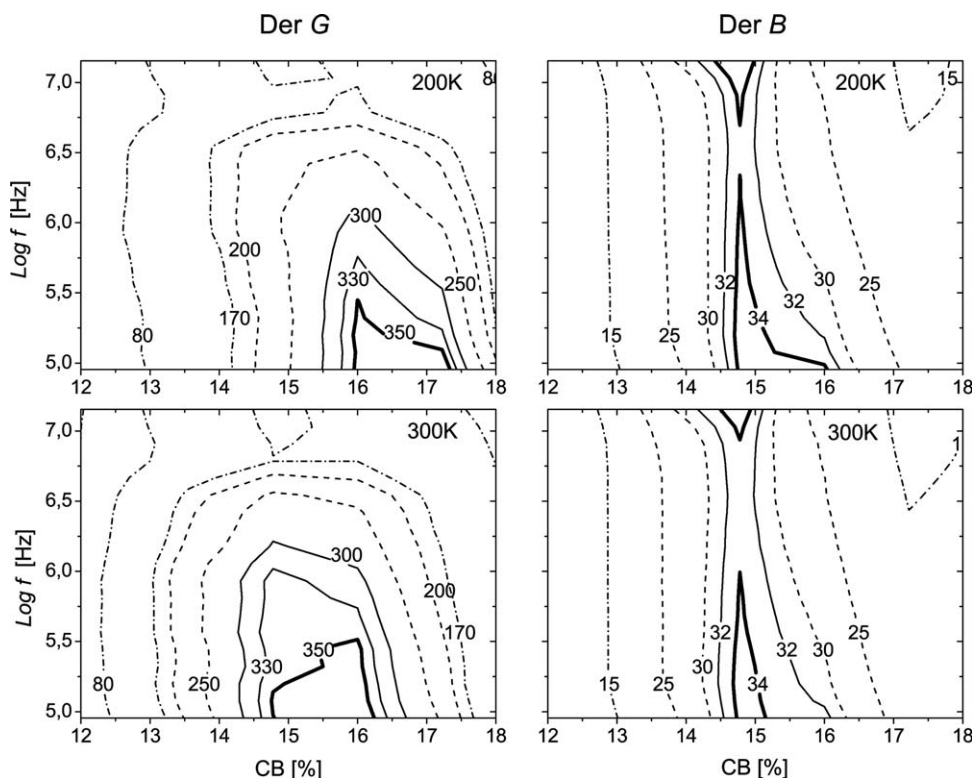

Figure 4 Frequency dependences of Der G and Der B near low percolation peak at two temperatures (200 K up and 300 K down).
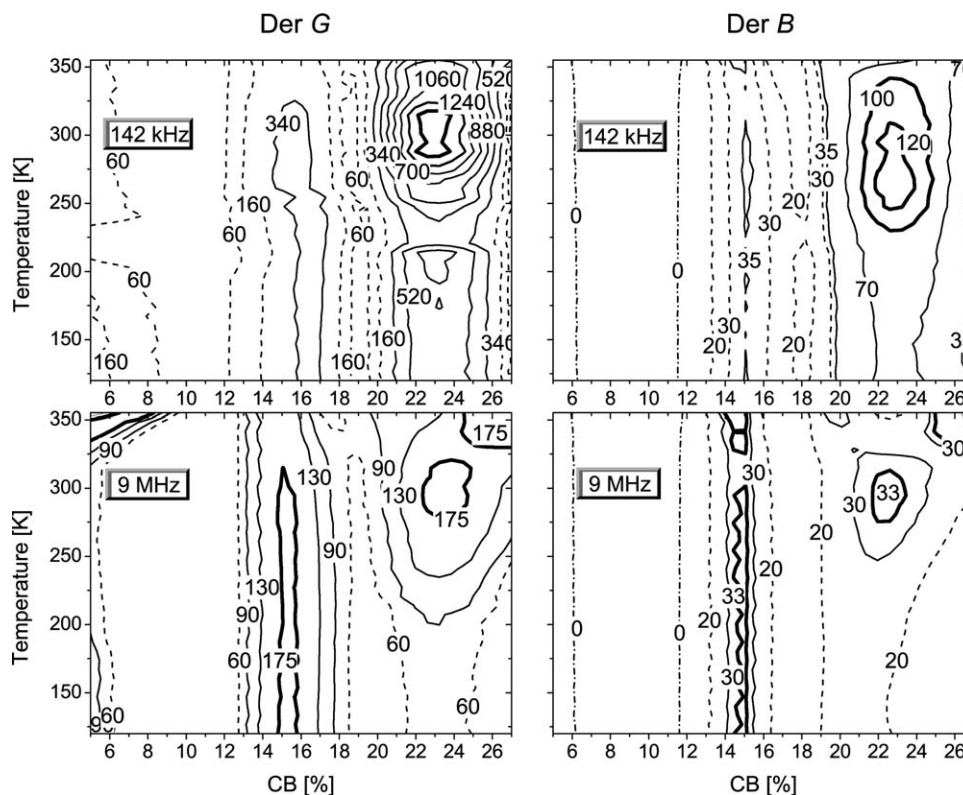
Figure 5 Temperature dependences of Der *G* and Der *B* at two frequencies, 142 kHz and 9 MHz.

different behaviors of Der *G* and Der *B*. The change of the rate of susceptance is practically negligible except for some shifting to higher concentrations of CB with decreasing frequency. On the other hand, the change of the rate of conductance decreases with frequency, as at the higher percolation point.

Temperature dependence of AC percolation

As it is assumed above, differential contributions to AC conductivity can be related to the structural inhomogeneity of LDPE. The results in Figure 5 confirm this assumption. The values of the functions Der *G* and Der *B* at the high percolation point (23% CB) in Figure 5 show enhanced temperature dependences. This fact suggests that the CB particles that contribute to the AC conductivity are located in the amorphous phase of LDPE. On the other hand, the lower percolation peaks (15% CB) are generally temperature independent and because of that these peaks can be related to the crystal domains in LDPE. Namely, it is possible that the CB particles are captured between

crystal lamellae.[14] The lower percolation threshold can be explained by a better definition of conducting paths in the interlamellar regions. At the higher percolation point, the maximum changes of conductance and susceptance are at room temperature.

Critical exponent of DC and AC percolations

Some previous works using computer simulations of randomly distributed metallic and dielectric regions in composites succeeded in describing the critical behavior of a complex conductivity using critical indexes.[4,5] To describe our experimental results for conductivity near the critical CB contents, we used the model of Efros and Shklovskii and their relation for DC percolation:[15]

$$\sigma_{DC}(C_c) = \sigma_{CB}\left(\frac{\sigma_P}{\sigma_{CB}}\right)^s \qquad (2)$$

where conductivities of homopolymer and CB are σ_P and σ_{CB}, respectively. C_c is the critical concentration,

TABLE I
Calculated DC and Fitted AC Values of Exponents *s* and Coefficients K_{CB}

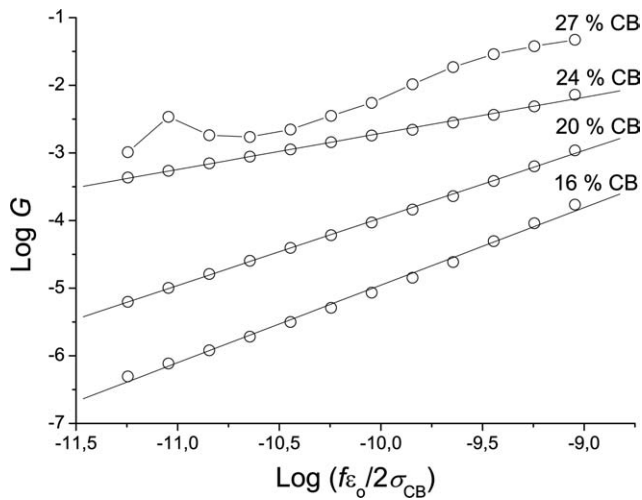| CB (%)	14	16	18	20	22	24	27
Sdc	1.02	1.02	1.03	0.77	0.62	0.49	0.33
Sac	1.28	1.15	0.99	0.99	0.95	0.53	–
K_{CB}	1.3×10^7	3.1×10^6	4.3×10^5	3.3×10^5	10^4	7×10^{-4}	–

Figure 6 Log G versus log f (circles, measured values; straight lines, fitted values).

and s is the critical exponent. Numerical simulation shows that for the two-dimensional system with symmetrical distribution of particles $s = 1/2$, but for the 3D sites or bond model the values of s are in the range from 0.72 to 0.83.[16] The calculations of s_{dc} values from our experimental results for the DC conductivity for several weight contents of CB are presented in Table I.

Results presented in Table I are in agreement with function Der σ_{DC} (Fig. 1), as shown above. The maximum of Der σ_{DC} occurs between 18 and 20% of the CB content. The conductivity of the sample with 20% of CB content ($s = 0.77$) is in agreement with the model used.[15] The model used for describing the AC conductivity at the critical contents of CB suggests limited divergence of the imaginary part of conductivity and frequency dependence of the real part of conductivity, which is described by the following relation (f, frequency and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m):

$$G(f, C_c) = \sigma_{CB}\left(\frac{f\varepsilon_o}{2\sigma_{CB}}\right)^s \quad (3)$$

We succeeded in getting the best fit using the coefficient K_{CB} (C_i) for multplication of the right hand side of the relation (3). The exponential coefficient s was determined as the slope of the function described by relation (4). The relative errors of the fitted values of s and K_{CB} are less than 2%.

$$\log G(f, C_i) = s \cdot \log\left(\frac{f\varepsilon_o}{2\sigma_{CB}}\right) + \log[K_{CB}(C_i)\sigma_{CB}] \quad (4)$$

The graphs of log G versus log f at room temperature, fitted by relation (4), are presented in Figure 6. Figure 6 shows that for 27% of CB content there is very complex frequency dependence.

Table I also presents the coefficients s_{ac} and K_{CB}, which are the results of numerical fitting of the real part of the AC conductivity at 295 K. The obtained values of the coefficient K_{CB} decrease with increasing CB content. The decreasing trend of K_{CB} confirms the expected values of $K_{CB} = 1$ and $0.53 < s_{ac} < 0.95$ at the high percolation peak for about 23% of CB content.

CONCLUSIONS

The analysis of DC conductivity measurements as a function of composition at room temperature shows a sharp rise of conductivity of the LDPE–CB composites by over 10 orders of magnitude. The percolation threshold was about 20% of CB content, whereas the saturation of conductivity occurred at about 30% of CB content. Contrary to the results of DC measurements, temperature and frequency dependences show the absence of sharp rises of AC conductivity (σ_{ac}), conductance (G), and susceptance (B) as the CB content increases. Numerical derivation of AC conductivities (80 kHz–13 MHz) showed higher increases of conductivities at 15% and 23% of the CB weight content, which are related to different dispersions of CB particles in structural inhomogeneities of LDPE and to some possibility of formation of "cavity" traps because of structural defects in LDPE which can have effects on the mechanisms of conductivity. DC percolation threshold and behavior of the real part of AC conductivity confirm the expected values of critical exponents from the model of Efros and Shklovskii.[15]

References

1. Kirkpatrick, S. Rev Mod Phys 1973, 45, 574.
2. Bergman, D. J.; Stroud, D. In Solid State Physics; Ehrenreich, H., Ed.; Academic: San Diego, 1992; Vol. 46. p.147.
3. Ce-Wen, N. Phys Rev B 1994, 49, 12619.
4. McLachlan, S. D.; Heaney, M. B. H. Phys Rev B 1999, 60, 12746.
5. Dai, K.; Xu, X. B.; Li, Z. M. Polymer 2007, 48, 849.
6. Hindermann, B. M.; Ehrburger, D. F. Carbon 2001, 39, 375.
7. Jager, K. M.; McQueen, H. D.; Tchmutin, A. I.; Ryvkina, G. N.; Kluppel, M. J. J Phys D: Appl Phys 2001, 34, 2699.
8. Brosseau, C.; Boulic, F.; Queffelec, V.; Bourbigot, C.; Le Mest, Y.; Loaec, J.; Beroual, A. J Appl Phys 1997, 81, 882.
9. Beaucage, G.; Rane, S.; Schefer, W.; Long, G.; Fisher, D. J Polym Sci Part B: Polym Phys 1999, 37, 1105.
10. Gal, O.; Kostoski, D.; Babić, D.; Stannett, T. V. Rad Phys Chem 1986, 28, 259.
11. Djoković, V.; Kostoski, D.; Dramićanin, D. M. J Polym Sci Part B: Polym Phys 2000, 38, 3239.
12. Suljovrujić, E.; Kostoski, D.; Dojčilović, J. Polym Degrad Stab 2001, 74, 167.
13. Kostoski, D.; Dojčilović, J.; Novaković, L.; Suljovrujić, E. Polym Degrad Stab 2006, 91, 2229.
14. Patnaik, A.; Zhu, Z.; Yang, G.; Sun, Y. Phys Stat Sol 1998, 169, 115.
15. Efros, A. I.; Shklovskii, B. I. Phys Stat Sol B 1976, 76, 475.
16. Straley, P. J. Phys Rev B 1977, 15, 5733.