Volume 11, Number 1, 2018. pp. 35-43

Jordan Journal of Physics

ARTICLE

Modeling the Electrical Impedance of Epoxy Polymer/Carbon Black Composite Materials

Z. Samir[a], **R. Belhimria**[a], **S. Boukheir**[a,b], **M. E. Achour**[a] and **L. C. Costa**[c]

[a] *LASTID Laboratory, Department of Physics, Faculty of Sciences, Ibn Tofail University, BP 133, 14000 Kenitra, Morocco.*

[b] *LNEE Laboratory, Department of Physics, Faculty of Sciences, Cadi Ayyad University, B.P. 2390, 40000 Marrakech Morocco.*

[c] *I3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal.*

Received on: 24/7/2017; *Accepted on: 17/10/2017*

Abstract: The effect of filler aspect ratio on the dielectric properties of epoxy resin reinforced with carbon black (CB) is here investigated. The composites change from an electrical insulator to a conductor as the CB content is increased from 1.5% to 4.5%, which is called the percolation region. Complex impedance spectra and Bode diagrams of these composites were carefully analyzed and the corresponding equivalent circuits (EC) under different concentrations of CB were also provided. Furthermore, the correlation between the shape of Bode diagrams and the equivalent circuits was discussed. Finally, the Cole–Cole representation was used to interpret the impedance spectra of all the samples.

Keywords: Carbon black, Percolation, Complex impedance, Bode diagram, Cole-Cole.

Introduction

Dielectric properties of composites have been the focus point of extensive studies during the last decades [1]. This general interest in the dielectric properties of these composites is due to both interesting features of the electricity flow through these composites and wide range of applications in many fields, such as thermistors, electrical screening materials, self-limited electrical heaters and so forth in industry [2–4]. One of the most important studied composites of this type is carbon black (CB) polymer composite [5]. Electrical properties of CB polymer composites can be remarkably enhanced with small CB concentrations. Epoxy/carbon black (epoxy/CB) system is one of the widely used organic/reinforcing filler composites [6–8]. Epoxy resins have high strength, good stiffness, excellent heat, good thermal stability and chemical resistance; therefore, they are applied in the field of coatings, adhesives, casting, composites, laminates and encapsulation of semiconductor devices [9–12]. However, the development of polymers with high electrical conductivity has opened up the possibility of new applications for polymers [13].

In this paper, we report on the dielectric properties of the dispersion of CB particles in epoxy polymer composites. In order to study the influence of the volume fraction of CB on the dielectric properties of these materials, the impedance spectra of the epoxy/CB composites for different CB concentrations, below and above the threshold concentration, are measured by plotting the complex impedance spectra, the corresponding equivalent circuits and Bode diagrams and also by drawing the Cole–Cole plots of the imaginary part and real part of the impedance of each sample.

Corresponding Author: M. E. Achour **Email**: achour.me@univ-ibntofail.ac.ma

Experimental

The samples investigated in this study consist of small carbon black particles (produced by Cabot Co.) embedded in an insulating epoxy matrix DGEBF: Diglycidylic Ether of Bisphenol F (from Ciba Geigy Co.). The mixture of CB particles and DGEBF was processed with an amine curing agent (diaminodiphenyl-sulfone; DDS). The average size of carbon black particles is 11 nm, density 1.89 $g.(cm)^{-3}$, dc conductivity 350 $(\Omega.m)^{-1}$ and specific surface area 639 $m^{-2}.g^{-1}$. The neat DGEBF has a dc conductivity of 1.4 10^{-14} $(\Omega.m)^{-1}$ and a density of 1.19 $g.(cm)^{-3}$. The ratio, by weight, of the mixture of the CB particles and DGEBF to the amine curing agent was adjusted to achieve stoichiometry [14-16]. The mechanical mixing operation that was used to fabricate samples with specific CB volume concentration ϕ has been previously described in detail elsewhere [17-18]. The samples were cured at room temperature for 24 h. The CB loading was varied from 0 to 6.5 %. Impedance spectroscopy measurements were carried out in the frequency range from 180 Hz to 15 MHz, using an Agilent 4294A precision impedance analyzer, in the $C_P - R_P$ configuration.

Theoretical Models

Percolation theory defines an insulator-conductor transition and a corresponding threshold of the conductive filler concentration, *via* the percolation model [19-20]:

$$\sigma_{dc} \sim (\phi - \phi_c)^t \text{ for } \phi > \phi_c, \quad (1)$$

where σ_{dc} is the dc conductivity of the composite, ϕ_c is the percolation threshold and t is the conductivity exponent.

The relaxation phenomenon in materials has been the subject of extensive study [19]. In most cases, the single relaxation time does not describe the dynamic response of the material [20] and several empirical models were used to fit that response. Between them, the Cole-Cole model [21] is frequently used:

$$Z^*(\omega) = (Z' + iZ'') = Z_\infty + \frac{Z_S - Z_\infty}{1+(i\omega\tau)^\alpha}. \quad (2)$$

In this equation, Z' and Z'' are the real and imaginary parts of the complex impedance (Z^*), respectively. Z_S and Z_∞ are the high and low frequency resistance, respectively, τ is the relaxation time, α is empirical exponent and ω is angular frequency ($\omega = 2\pi f$, f is frequency).

CPE is the abbreviation of ‘constant phase element’ in electromagnetics. A constant phase element is an equivalent circuit component that describes the behaviour of a double layer, which is an imperfect capacitor. The impedance module of a CPE can be calculated by the following equation [22]:

$$|Z_{CPE}| = \sqrt{(Z')^2 + (Z'')^2} = \omega^{-N}/A \quad (3)$$

$$\varphi = \tan^{-1}(Z''/Z'). \quad (4)$$

The constant phase φ is always $-(90 \times N)°$, with N from 0 to 1 and A is a real parameter expressed in $F.s^{(N-1)}$. The case $N = 1$ describes an ideal capacitor, while the case $N = 0$ describes a pure resistor [23]. When the value of N is between 0 and 1, then it describes a constant phase element.

Results and Discussion

DC Electrical Conductivity

The evolution of conductivity as a function of CB concentration is shown in Fig. 1 for the epoxy/CB composites under study. At low filler concentrations, the gap between CB aggregates, where the electrons are transmitted, is very large and the conductivity of the composites is approximately that of the insulating matrix. As the concentration of conductive fillers rises, a critical concentration is reached, where the conductivity starts to increase abruptly from 1.5% to 4.5%, which is called the percolation region. By using a least-square fit (see the inset of Fig. 1), we found the value of the percolation threshold ϕ_c = 2.75 % and the critical conductivity exponent t=1.89 *via* Eq. (1). The value obtained of the exponent t is slightly smaller than the universal value of three-dimensional percolating systems that is equal to 2 [24].

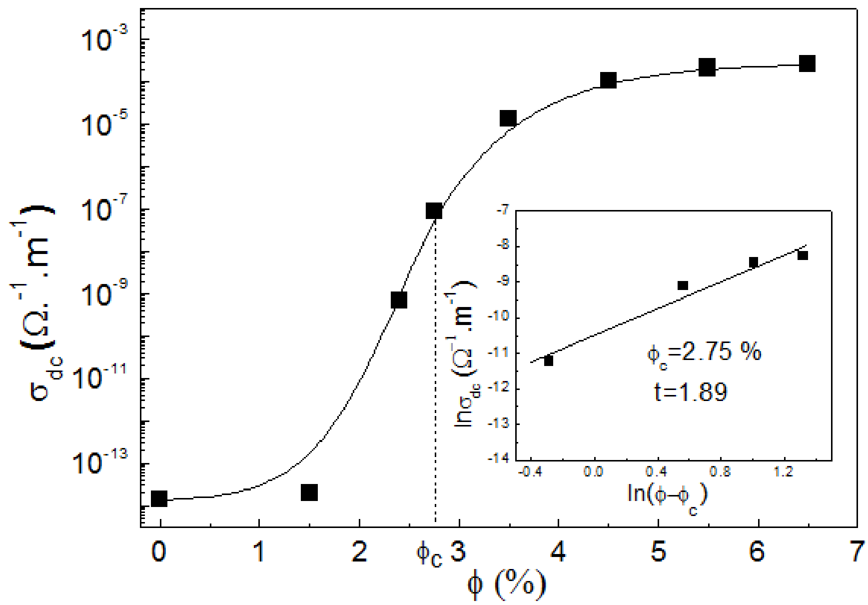

FIG. 1. Variation in dc conductivity (σ_{dc}) with filler loading in CB.

Impedance Spectroscopy Properties

The frequency dependence of the impedance modulus, |Z| and the impedance phase, φ, for different CB concentrations below and above ϕ_c are presented in Figs. 2 and 3 with the frequency changing from 180 Hz to 15 MHz. Below ϕ_c, as can be seen from Figs. 2 and 3, |Z| is a straight line with a negative slope coefficient and φ is nearly constant (near to, but less than $-90°$). Above ϕ_c, the impedance modulus curves may be divided into two distinct regions (Fig. 2): at low frequencies, |Z| is frequency independent, which suggests that the ohmic resistance plays an important role, while the capacitive effects can be neglected [25]. With increasing frequency further, the impedance decreases, which defines the character of an R-C network. Similar behaviour has been reported in our previous work [26]. It is obvious from Fig. 3 that for $\phi > \phi_c$, the phase angle increases with frequency and approaches $-90°$ (capacitive dominated) at high frequency region.

Nyquist (Z'' $vs.$ Z') plot of 1.5 % of CB composites and corresponding |Z| and φ are shown in Fig. 4-a and Fig. 4-b. As can be seen from Fig. 4-a, the complex impedance spectrum is a straight line, suggesting that at low CB concentration the response is purely capacitive and the dielectric properties of the polymer dominate the composite dialectical characteristics. As shown in Fig. 4-b, φ is nearly constant (close to $-90°$) and |Z| is a straight line with a negative slope coefficient. So, the equivalent circuit can be described by a CPE (see Section: Theoretical Models) as shown in the inset of Fig. 4-a. Replacing ω with $2\pi f$ in Eq. (3) and then taking the logarithm on both sides of the equation, we obtain: $\log|Z| = \log|Z_{CPE}| = -N\log f + \log\frac{1}{(2\pi)^N A}$. Obviously, the plot should be a straight line with a slope coefficient of $-N$, which is in line with the experimental results illustrated in Fig. 4-b. We make the linear fit based on the experimental data at 1.5% CB. As can be seen, the experimental data strongly agreed with the fit result and the slope of this straight line equals -0.96 (in the inset of Fig. 4-b). Table 1 summarizes the obtained fitting parameters N and A for all concentrations below ϕ_c. One can clearly see that the values of N decrease with increasing concentrations of CB, in contrary to the parameter A which increases considerably with CB.

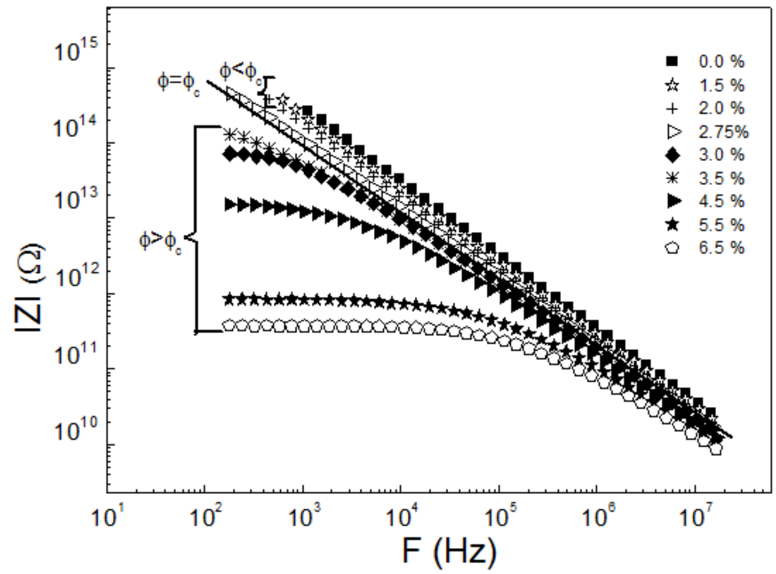

FIG. 2. Frequency dependence of the impedance modulus, |Z|, of epoxy/CB composites, for concentrations below and above ϕ_c.

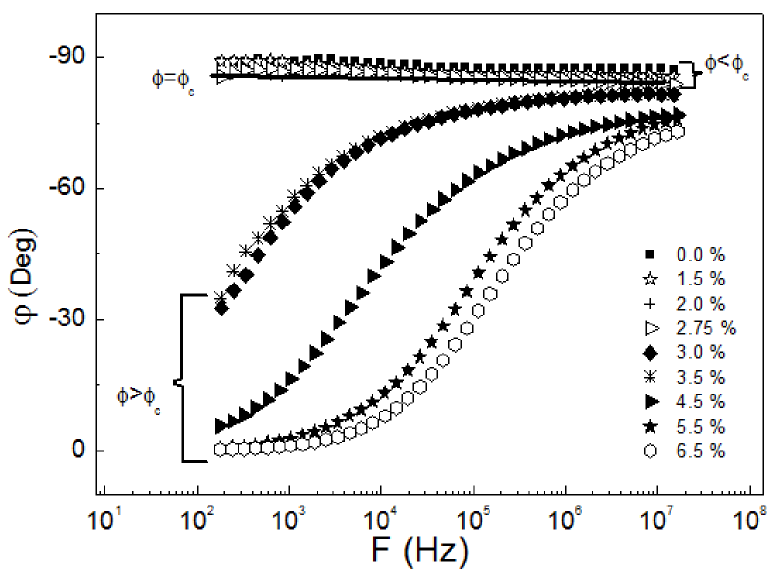

FIG. 3. Frequency dependence of the impedance phase (φ) of epoxy/CB composites, for concentrations below and above ϕ_c.

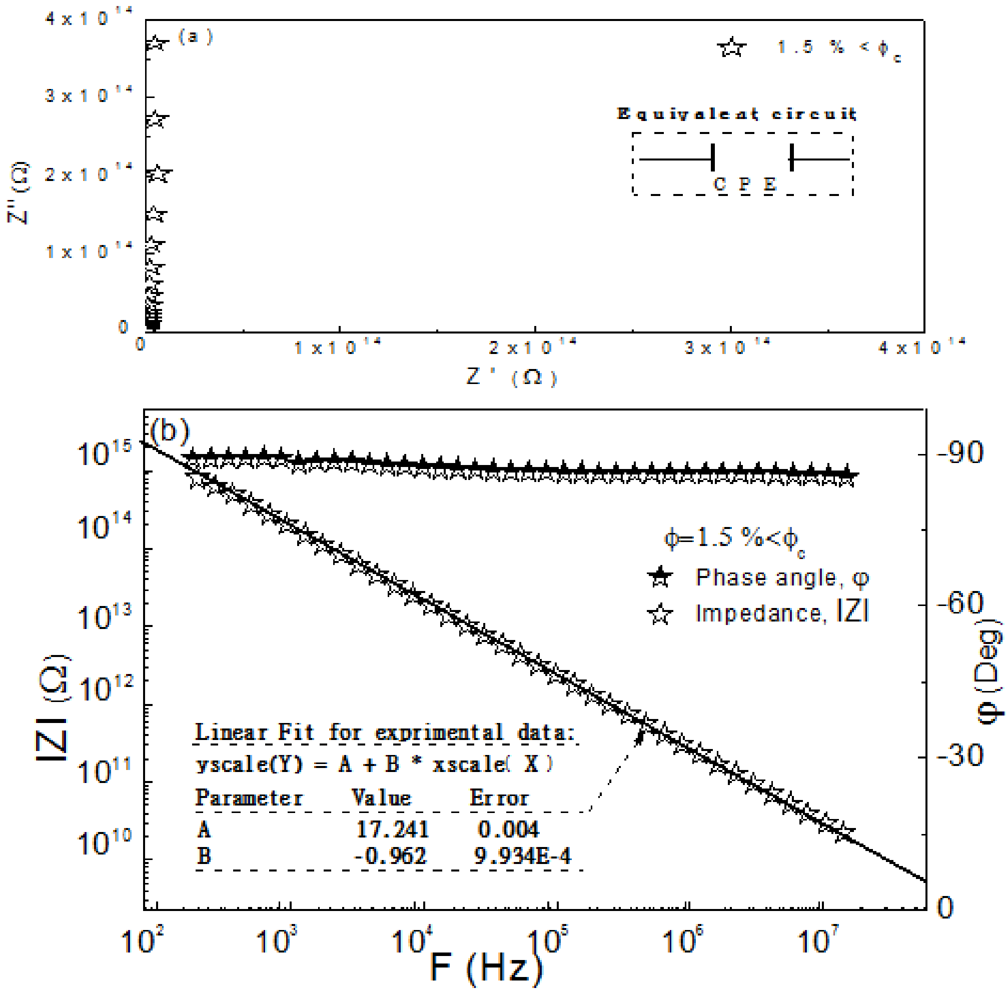

Fig. 4. (a) Z'' *vs*. Z' curve and (b) corresponding |Z| and φ of epoxy/CB at 1.5 % of CB.

TABLE 1. Fitting parameters A and N using the CPE circuit for different CB concentrations below ϕ_c.

ϕ (%)	0.0	1.5	2.0	2.75
N	0.98	0.96	0.95	0.90
$A*(10^{-17})$ $F.s^{(N-1)}$	2.36	3.32	4.62	9.55

At high CB concentration of (5.5%), the shape of the complex impedance spectrum is a semicircle as shown in Fig. 5-a. The complex impedance spectrum at 5.5% CB can be characterized by an equivalent circuit including a resistor (R) and a capacitor (C) connected in parallel as shown in the inset of Fig. 5-a. Fig. 5-b displays |Z| and φ at this high concentration. It is clear that φ increases with frequency and approaches $-90°$ at high frequency region. This could simply be deducted from the following phase angle equation for the above mentioned equivalent circuit: $\varphi = \tan^{-1}(\omega RC)$. As can be seen in this equation, φ increase with frequency and when the frequency tends to infinity, the phase angle must get closer to -90°, which is fully consistent with the results of the experiment. The modulus can be divided into two parts by lines as shown in Fig. 5-b. We make tangents of the first and the second part of the curve, then the two tangents intersect at point f_c, where the corresponding frequency was near 63 kHz. This frequency is compatible with the characteristic frequency in Nyquist plot shown in Fig. 5-a. The obtained fitting parameters are presented in Table 2. This table shows that the parameter N varies between 0.89 and 0.77 and A increases considerably with CB. On the other hand, the last column of this table presents the estimated values of the critical frequency. We note that this critical frequency increases with increasing concentrations of CB.

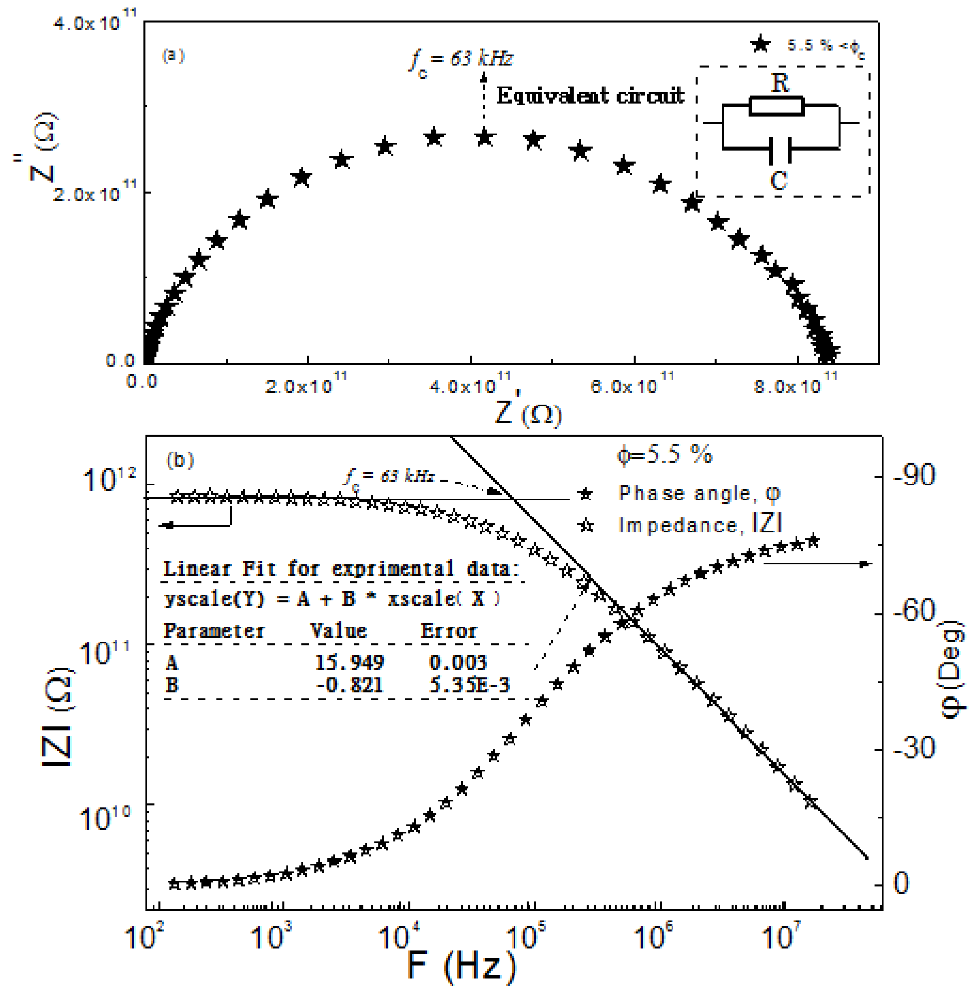

FIG. 5. (a) Z'' *vs*. Z' curve and (b) corresponding |Z| and φ of epoxy/CB at 5.5 % of CB.

TABLE 2. Fitting parameters A, N and f_c using the CPE circuit for different CB concentrations above ϕ_c.

ϕ (%)	3.0	3.5	4.5	5.5	6.5
N	0.89	0.88	0.87	0.82	0.77
A $*(10^{-17})$ $F.s^{(N-1)}$	1.53	1.46	2.00	5.08	11.90
f_c (kHz)	1.20	1.60	3.00	63.00	1140

In order to obtain more detailed information on these composites prepared herein, we used the Cole-Cole representation, as depicted in Fig. 6 for different concentrations of CB. We have analyzed the data with the Cole–Cole function [23], Eq. (2). For determining the parameters τ and α, we first calculated the approximate values from the asymptotic part of the data, then used them as starting values in a non-linear curve fitting algorithm [27]. When α is close to 0, the material is more homogeneous, the dipole interaction is low and the semicircle is practically centered in the Z' axe. For pure epoxy and low CB concentrations, the response is purely capacitive and therefore no semi-circle is observed (Fig. 6-a). From Figs. 6-b, c and d, it can be observed that as CB is added to the epoxy matrix, the introduction of the real component to the impedance leads to the formation of a semi-circle [28]. This semicircle decreases in diameter as the CB concentration increases, which is indicative of the lowering in the electrical resistivity of the composite due to the presence of conduction paths [29]. Indeed, the material is characterized by the formation of an infinite cluster of CB, which allows the displacement of electrons through large distances of the sample. It can also be seen from Table 3 that the strength of resistance, $Z_s - Z_\infty$, decreases with CB concentration, indicating the increase in electrical conductivity. The calculated values of α between 0.216 and 0.419 are responsible for the depressed semicircle in impedance plane, which indicates an increase in heterogeneity with the concentration of the conducting particles [30].

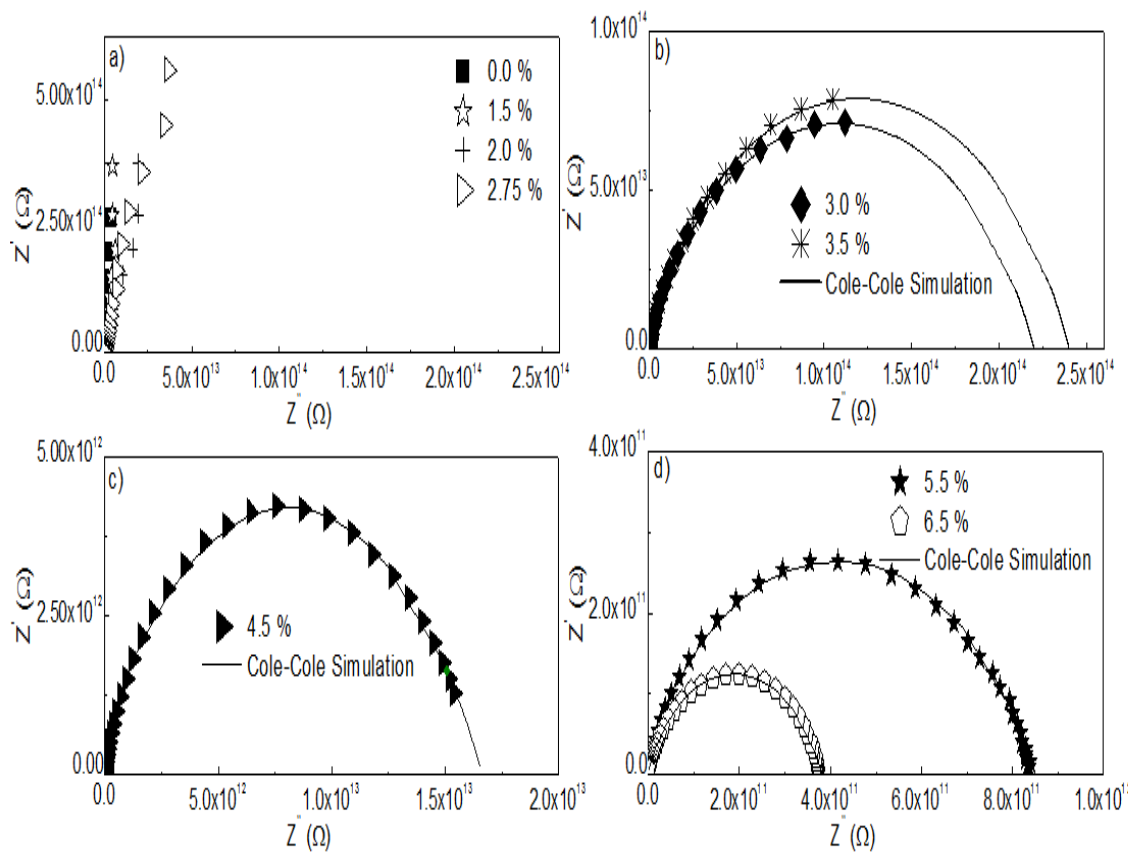

FIG. 6. Cole-Cole plot for different concentrations of CB below and above ϕ_c.

TABLE 3. Dielectric relaxation parameters obtained by simulation of the Cole-Cole equation at different CB concentrations above ϕ_c.

ϕ (%)	$(Z_s - Z_\infty)$ (Ω)	τ (s^{-1})	α
3.0	$2.20*10^{14}$	$12.10*10^{-4}$	0.27
3.5	$2.40*10^{14}$	$9.90*10^{-4}$	0.26
4.5	$16.64*10^{12}$	$4.70*10^{-5}$	0.42
5.5	$0.85*10^{12}$	$2.28*10^{-6}$	0.30
6.5	$0.38*10^{12}$	$1.42*10^{-6}$	0.26

Conclusion

In summary, the influence of the volume fraction of CB on the dielectric properties of epoxy/CB composites was studied. It was found that these composites change from an electrical insulator to a conductor as the CB content is increased from 1.5% to 4.5%, which is linked to the percolation region. Complex impedance spectra and Bode diagrams of these composites were carefully analyzed and the corresponding equivalent circuits were also provided. At the end, the Cole–Cole representation was used to interpret the impedance spectra of all the samples.

References

[1] Sichenko, M.B., Rev. Mod. Phys., 64 (1992) 961.

[2] Klason, K. and Kubat, J., Int. J. Polym. Mater., 10 (1984) 259.

[3] Miyasaka, K., Watanabe, K., Yogima, E., Aida, H., Sumita, M. and Ishikawa, K., J. Mater. Sci., 17 (1982) 1610.

[4] Gardiner, K., Calvert, I.A., van Tongeren, M.J.A. and Harrington, J.M., Ann. Occup. Hyg., 40 (1996) 65.

[5] Sichel, E.K., Gittleman, J.I. and Sheng, P., Journal of Electronic Materials, 11(4) (1982) 699.

[6] Hosaka, H., Ohnabe, H. and Saikawa, T., Proc. Yonezawa Conference, Tohoku Branch, (JSME), Japan, (1999) 13.

[7] El- Tantawy, F. and Deghaidy, F.S., Polym. Int., 49 (2000) 1371.

[8] Park, D.M., Hong, W.H., Kim, S.G. and Kim, H.J., Eur. Polym. J., 36 (2000) 2429.

[9] El-Tantawy, F. and Deghaidy, F.S., Polym. Int., 49 (2000) 1371.

[10] Park, D.M. and Hi, H.W., Eur. Polym. J., 36 (2000) 2429.

[11] Kang, S., Hong, S., Choe, C.R., Park, M., Rim, S. and Kim, J., Polymer, 42 (2001) 879.

[12] Punchaipetch, P., Ambrogi, V., Giamberini, M., Brostow, W., Carfagna, C. and D'Souza, N.A., Polymer, 42(5) (2001) 2067.

[13] Wilson, A. and De Paoli, M., Eur. Polym. J., 35 (1999) 35.

[14] Essone Mezeme, M., El-Bouazzaoui, S., Achour, M.E. and Brosseau, C., J. Appl. Phys., 074107 (2011) 109.

[15] Brosseau, C. and Achour, M.E., J. Appl. Phys., 124102 (2009) 105.

[16] El-Bouazzaoui, S., Droussi A., Achour, M.E. and Brosseau, C., J. Appl. Phys., 104107 (2009) 106.

[17] Achour, M.E., El-Malhi, M. and Carmona, F., J. Appl. Polym. Sci., 61 (1996) 2009.

[18] Achour, M.E., El-Malhi, M., Miane, J.L., Carmona, F. and Lahjomri, F., J. Appl. Polym. Sci., 73 (1999) 969 3.

[19] Feldman, Y, Gusev, Y.A. and Vasilyeva, M.A., Tutorial, Kazan Federal University, Institute of Physics (2012) 134.

[20] Frohlich, H., "Theory of dielectrics: Dielectric constant and dielectric loss (Monographs on the physics and chemistry of materials)", (Clarendon Press Oxford, 1958) 192.

[21] Samir, Z., El-Merabet, Y., Graça, M.P.F., Teixeira, S.S., Achour, M.E. and Costa, L.C., Compos. Mater., 51(13) (2016) 1831.

[22] Macdonald, J.R. and Johanson, W.B., "Theory in Impedance Spectroscopy", (John Wiley & Sons, New York, 1987).

[23] Diard, J.P., Gorrec, B.L. and Montella, C., J. Electroanal. Chem., 471 (1999) 126.

[24] Zen, J.M., Ilangovan, G. and Jou, J.J., Anal. Chem., 71 (1999) 2797.

[25] Grimaldi, C. and Balberg, I., Phys. Rev. Lett., 96(14) (2006) 066602.

[26] Vivo, B.D., Lamberti, P., Spinelli, G., Tucci, V., Guadagno, L. and Raimondo, M., J. Appl. Phys., 118 (2015) 064302.

[27] Costa, L.C. and Mendiratta, S.J., Non-Cryst. Sol., 172–174 (1994) 1324.

[28] Bowen, C.R., Buschhorn, S. and Adamaki, V., Pure Appl. Chem., 86 (2014) 765.

[29] Shrivastava, N.K., Maiti, S., Suin, S. and Khatua, B.B., Express Polym. Lett., 8 (2014) 15.

[30] Costa, L.C., Achour, M.E., Graça, M.P.F., El-Hasnaoui, M., Outzourhit, A. and Oueriagli, A., Non-Cryst. Solids, 356 (2010) 270.