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DC electrical conductivity studies on copolymer/carbon black composites

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Abstract
The direct current (DC) conductivity of carbon black (CB) filled EAB composite material was measured in the temperature range from 130 to 290 K ($T_g \approx 198$ K). That conductivity data was analyzed and interpreted in order to identify the conduction mechanisms and to observe the doping effect of CB particles on the EAB matrix. It shows that the conduction, in the high temperature region ($T > T_g$), is due to thermally activated tunneling of charge carriers in the band, and, in the low temperature range ($T < T_g$), conduction takes place through variable range hopping in the localized states near the Fermi level.

Keywords: Composite; DC conductivity; Glass temperature; VRH model; Activation energy.

1. Introduction
The inclusion of conducting charges in insulating copolymers creates new polymeric materials composites, with particular mechanical and electrical properties [1-3]. The electrical conductivity of these composites arises from the conducting polymers inclusions dispersed in the insulating matrix. Several conducting polymers are the subject of technological and scientific works, as carbon black-filled epoxy polymer composites [4], polypyrrole-polymethylmethacrylate [5] and carbon black filled poly(ethylene-co-alkyl acrylate) [6]. The charge carriers produced in conducting copolymers are polarons and bipolarons [7-8], participating in the electrical conductivity by phonon assisted hopping or tunneling effect [9-10]. The analysis of the conduction mechanisms in the polymeric composites demands the study of the total electrical conductivity dependencies on temperature and frequency. El Hasnaoui et al. [11] have exploited the alternating current (AC) conductivity spectrum for the temperature near the melting point T_m and Costa et. al. [12] have analyzed the complex impedance Z^* spectrum using the Cole-Cole model of this materials at room temperature.

In this paper we purpose to study the mechanisms of electrical transport of charge using direct current (DC) conductivity in the temperature range from 130 to 290 K, and the effect of the volume fraction of CB powder dispersed in the insulating matrix of EAB, above the critical percolation threshold $\Phi_c \approx 11\%$ [11].

2. Experimental details

2.1. Materials

Three samples of carbon black filled ethylene butylacrylate (EBA) used in this investigation were prepared from Borealis AB (Sweden). The butylacrylate monomer contains butylester side groups, providing a certain polarity and a relatively low crystallinity (about 20% in volume). The neat EBA matrix has a density of 1.19 g.cm^{-3} and a glass transition temperature, $T_g \approx 198$ K [13]. The average size of the carbon black particles was about 30 nm, the mean size of the primary aggregates was of the order of 150 nm, the density of the CB particles 1.89 g.cm^{-3} and the specific surface area (NSA) 639 m^2.g^{-1}.

2.2. Electrical measurements

For the electrical measurements, the samples were prepared as discs with a thickness of about 1 mm. Aluminum electrodes of 10 mm diameter were deposited on the opposite sides of the samples. The electrical leads were fixed by silver paint. The DC conductivity measurements were made using a Keithley 617 programmable electrometer, inside a cryostat, in the temperature range from 130 to 290 K, in a helium atmosphere. The stabilization of temperature was better than 0.1 K over the period of the measurement of current.

3. Results and discussion

Fig 1 shows the variation of $\ln(\sigma_{DC}.T)$ versus the inverse of temperature for three different volume fractions of CB. From the straight-line fits, it has been observed that the plots are linear, but a change in the slope was observed at about T_g. This behavior shows that the conduction mode in the high temperature range (domain I) seems to be a thermally activated conduction mechanism, and, in the low temperature (domain II) all the curves decrease very slowly with the inverse of temperature, which implies that conduction occurs via Mott's variable range hopping (VRH) of the charge carriers in the localized states near the Fermi level.

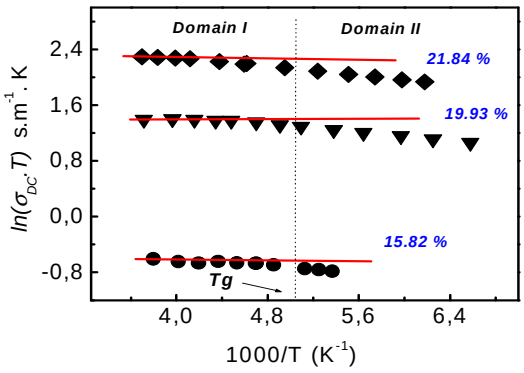

Fig 1: Linear dependence of DC conductivity on temperature for three concentrations of CB loaded in EAB matrix.

Fig. 2 shows the Arrhenius plots of three samples, in the high temperature range, from T_g to 290 K (domain I). According to the Arrhenius relationship:

$$\sigma_{DC}(\omega) = \frac{A_o}{T}\exp\left(-\frac{E_a}{k\,T}\right) \quad (1)$$

where A_o and E_a represent the pre-exponential factor and activation energy respectively, and k the Boltzmann's constant ($k \approx 8.617\ 10^{-5}$ eV.K^{-1}) . The calculated values of activation energies and pre-exponential factors are given in table 1. We suggest that low difference in the activation energies and the high increase of the pre-exponential factors of the three samples investigated are an indication of the dynamically heterogeneous nature of the CB aggregates within the polymer matrix.

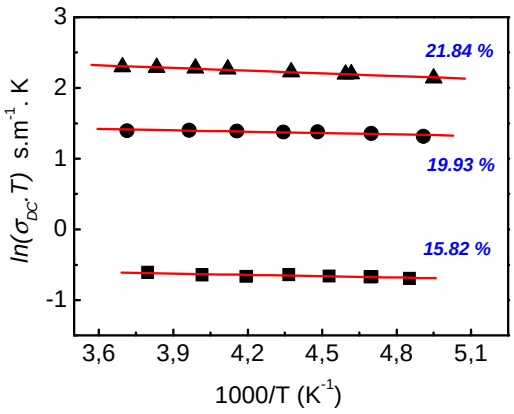

Fig 2: Arrhenius plots at three concentrations of CB loaded in EAB matrix. The solid lines represent the best linear fits to the data.

Table 1: Electrical parameters of Arrhenius's relation in the temperature range from Tg to 290K

Φ (%)	15.82	19.93	21.84
A_o (S.m^{-1}.K)	0.68±0.04	5.24±0.32	16.08±0.57
E_a (meV)	5.24±1.12	5.51±1.21	10.09±0.71

At lower temperature range (domain II), Mott [14] has proposed that the charges transport take place beyond nearest neighbor by the VRH. The DC conductivity in this case is given by [14-16]:

$$\sigma_{DC}(\omega) = \frac{B_o}{T^{2\gamma}} \exp\left[-\left(\frac{T_o}{T}\right)^{\gamma}\right] \qquad (2)$$

where B_o is high temperature limit of conductivity, T_0 is a characteristic barrier associated with degree of localization of the electronic wave function and the exponent γ determines the hopping space dimensionality of the charge transport in conducting medium. The values of γ are ½, ⅓ and ¼ for one, two and three dimensional hopping transport respectively. In order to evaluate the dimensionality of the conduction process in EAB/CB, semi logarithmic plot of conductivity as a function of $T^{-\gamma}$ should follow a straight line according to equation 2. The experimental curves of data have been plotted for three cases (not shown here), and the values of their quality factor R^2 are listed in table 2. It is clear that R^2 closer to unity, for γ = ½, rather than γ = ⅓ and γ = ¼, indicates that the transport mechanisms corresponds to a quasi-one-dimensional process. In Fig 3, we show $\ln(\sigma_{DC}T)$ versus $T^{-1/2}$ plots, for different volume fractions. The numerical values of the pre-exponential, B_o, and the degree of disorder, T_o, are presented in table 3. Joo et. al. [17] have established, by studying polyaniline composite in the case of a quasi-one-dimensional hopping process, that kT_o can be considered as the effective energy separation between localized states and that this value represents a measure of the degree of disorder in an amorphous region. From table 3, the lower values of T_o, i.e., the lower kT_o, the more coherently the polymer chains are organized, and a change in conducting mechanisms at low temperatures is usually observed. This behaviour can be explained by the decrease of the free charges concentration at low temperatures, and then, the temperature approaches to the transition temperature of the compound.

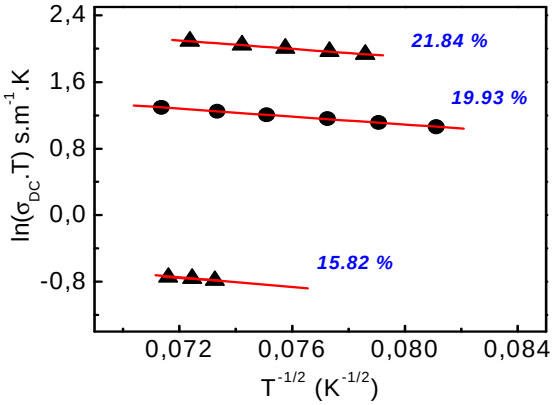

Fig 3: Dependence of the DC conductivity according to equation 2, with γ = ½, corresponding to the one-dimensional transport mechanism in the polymer composite EAB/CB. The solid lines represent the best linear fits to the data.

Table 2: Quality factor R^2 of the best fit for γ = ½ (D1), γ = ⅓ (D2) and γ = ¼(D3).

Φ (%)		D1	D2	D3
R^2	**15.82**	0.9930	0.9799	0.9546
	19.93	0.9997	0.9989	0.9975
	21.84	0.9999	0.9998	0.9995

Table 3: Electrical parameters of Mott's model in the temperature range from 130K to T_g.

Φ (%)	15.82	19.93	21.84
B_o (s.m^{-1}.K)	2.39±0.46	19.98±0.44	49.21±0.30
T_o (K)	510.94±121.14	568.25±13.99	623.39±4.05

Conclusion

A study on the charge transport properties of EAB doped with CB particles, in the temperature range from 130 to 290 K, was carried out. Electrical conductivity was found to be temperature dependent, indicating that there is more than one mechanism involved in charge transfer in EAB/CB, depending on the temperature range. The charge conduction is found to be dominated by thermally activated hopping in the high temperature range, and by variable range hopping (VRH) at low temperatures with the one-dimensional hopping transport.

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