

Hopping conduction on carbon black/styrene–butadiene–styrene composites

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Abstract This study describes the preparation and electrical characterisation of conducting carbon black-filled/styrene–butadiene–styrene tri-block copolymer. Composites containing 5 and 10 vol% of carbon black were studied. The carbon black distribution, conductive mechanism and electrical properties of the composites were investigated from 8 to 304 K. For the first time, an analysis of the differential activation energy is carried out for carbon black composites, allowing the classification of the variable range hopping as one-dimensional for composite containing 5% of carbon black and as three-dimensional for the composite containing 10% of carbon black. Such results are found to be determined by two factors: the concentration of carbon black in the filler-rich phase and by the structural continuity of this phase. Increasing the carbon black content induces structural transition that results in variable range hopping conduction changing from one-dimensional to three-dimensional. From the hopping parameters, the mean hopping distance, the density of active centres and the energy associated with it were obtained.

Introduction

Conducting polymeric composites, constituted by conducting filler dispersed inside an insulating polymer matrix, has important applications in antistatic materials, electrostatic discharge, dissipation, electromagnetic interference [1–4], temperature, pressure and gas sensors [5]. These composites are usually characterised by a sharp insulator–conductor transition at a specific volume fraction of the filler. At this point, known as percolation threshold, a continuous conducting network of conducting particles is formed inside the insulating matrix [6]. Among the available fillers, carbon black (CB) has been extensively employed because of its ability to impart high electrical conductivity to an insulating polymer at relatively low filler content [6]. These systems usually present a sharp insulator–conductor transition characterised by a critical CB loading, that is, the percolation threshold concentration. This behaviour is mainly due to the unique elongated aggregate structure and the tendency to agglomerate [7, 8].

The filler content must be as low as possible in order to optimise processing and the mechanical properties of the final composite.

To obtain the low percolation threshold value, some researchers had even tried to achieve preferred dispersion of CB in polymer blends by using two or more polymers with different affinity with CB [4, 5, 8–15]. This is due to the uneven distribution of the filler in a polymer blend matrix [8–15]. In such cases, the electrical conductivity depends on two factors: the concentration of CB in the filler-rich phase and the structural continuity of this phase. This double percolation affects the conductivity of the composite. According to Gubbels et al. [9] for a lower percolation threshold concentration, it is desirable that

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CB particles be located inside the minor phase of a co-continuous blend or at the interface.

Several factors determine the CB distribution within the polymer blends, such as polarity or surface tension [11], polymer crystallinity [9], viscosity [16, 17], flexibility of polymer chains [16] and processing [9].

In this study, styrene–butadiene–styrene (SBS) block copolymer was used as insulating polymer matrix. SBS matrix should be advantageous due to its thermoplastic–elastomeric nature, i.e. it presents the unique combination of mechanical properties and processability without vulcanisation [8, 9, 17]. Furthermore, it presents a morphology characterised by the two block components segregated into different phases with a typical micro domain structure [8, 9, 17]. When CB is dispersed inside the SBS matrix, the affinity between conductive filler and SBS leads to the formation of a conductive network at a lower concentration of conducting particles [8, 9, 17].

There are some models of electrical transport in composites containing CB in literature among them: Mott's variable range hopping (M-VRH) theory [18–22] Efros-Shklovskii model (ES-VRH) associated with Coulomb effects [23, 24]. Transport phenomena can also be interpreted in terms of the superlocalisation of the electronic states in the presumably fractal CB/polymer percolation network [23–25]. Another model proposed for electrical conductivity is ascribed to tunnelling through a potential barrier of variable height [24].

In the present study, CB/SBS composites were prepared in a mechanical mixer and carried out electrical characterisation. The electrical conductivity of the composites depends on the selective localisation of CB in one phase or at the interface and above all on the double percolation, i.e. percolation of the polymer phases and percolation of the CB particles. The main aim of this study is to use the differential activation energy as a tool to access the precise temperature range associated with different conduction regimes and to calculate the VRH parameters.

Experimental section

Materials and methods

The CB/SBS material was prepared with SBS from Petroflex S.A. (Rio de Janeiro, Brazil) label TR-1061, with PBD content of 70 wt%, average molecular weight 120,000 and density 0.98 g/cm^3 and with CB from Degussa (Frankfurt, Germany) label Printex XE-2 with density of $2.04\text{--}2.11 \text{ g/cm}^3$. The SBS copolymer was first introduced into a Haake internal mixer operating at $160 \text{ }^\circ\text{C}$ and 20 rpm. After 2 min, CB was added, and the rotor speed was increased to 60 rpm for 10 min. The CB/SBS systems

were then compression moulded at various temperatures for 5 min, under 1.0 MPa of pressure. The samples were prepared by compression moulding ($25 \times 25 \times 0.5 \text{ mm}^3$) at $200 \text{ }^\circ\text{C}$ for 5 min [8].

Characterisation

For the Van der Pauw measurements, the samples were cut into $3.0 \times 2.0 \times 0.25 \text{ mm}^3$ squares and the contacts were made of four silver paint drops over the corners of one side of the sample. For the resistivity measurements, a Keithley electrometer model 6517 and a current/voltage source Keithley model 237 were used. Both instruments were used with triaxial cables in guarded-mode measurements. dc electric transport measurements were carried out at temperatures ranging from 8 to 304 K.

Transmission electron microscopy (TEM) was carried out on a sliced sample (obtained with the cryo-ultramicrotome) using a Tecnai G2–20 microscope operating at 200 kV.

Results and discussion

Hopping conductivity

Figure 1 presents ρ as a function of $(k_{\text{B}}T)^{-1}$ in a logarithmic scale for samples CB5 and CB10%. The figure shows at least two distinct behaviours with temperature, which are associated with a metallic-like (i.e. resistivity increases with temperature) and insulating (i.e. resistivity decreases with temperature). Regarding the insulating behaviour, its temperature dependence is quite non-linear indicating that both samples show temperature dependent activation energy and thus meaning that band conduction, or nearest-neighbour hopping (NNH) models, are not sufficient to explain the conduction processes in these composites. In fact as will be shown later on the analysis part, there is an intermediate temperature range where constant activation energy is present. Thus, in order to describe and interpret the data regarding the insulating part, M-VRH formalism was applied.

The M-VRH formalism for phonons or small polarons for conductivity of disordered semiconductor materials [20–22, 26] will be described here in summary. Depending on the dimensionality of the system, i.e. $d = n - 1$, the temperature dependent VRH conductivity is given by

$$\rho = \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^{\frac{1}{n}} \right] \quad (1)$$

where ρ_0 is the high temperature limit of resistivity and T_0 the Mott's characteristic temperature associated with the

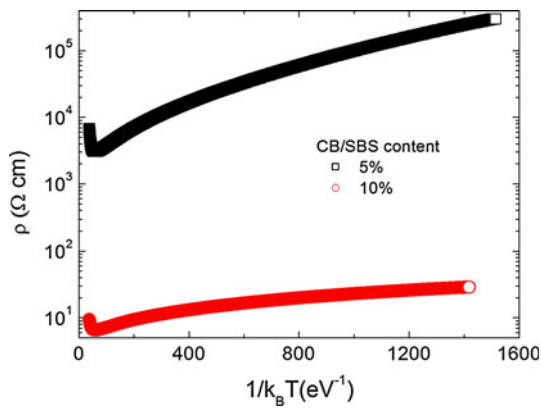


Fig. 1 Arrhenius plots for the resistivity. The abscissa correspond to $(kT)^{-1}$ in units of $(\text{eV})^{-1}$. The symbols corresponding to each sample are indicated

electronic wave function localisation degree. The exponent n assumes 4, 3, and 2 for three, two, and one-dimensional systems, respectively.

By carrying out the derivation of Eq. 1 with $(\partial(\ln\rho)/\partial(kT)^{-1})$ [27], the differential activation energy (DAE) is obtained.

$$\text{DAE} = \frac{k_B T_0^{1/n} T_0^{\frac{n-1}{n}}}{n} \quad (2)$$

In Ref. [27], it was demonstrated that the use of DAE is a very powerful method in order to identify temperature ranges dominated by distinct conduction mechanisms such as band, NNH and also VRH as well as mixed conduction regimes. In the present study, the aim is to demonstrate that the dimensionality of M-VRH can be obtained by direct fittings with the model of Eq. 2. According to our knowledge, it is the first time that DAE is used as a tool in order to clearly identify transport mechanisms in CB composites; however, it was applied to other systems by Zabrodskii et al. [28].

Figure 2 presents the DAE plot (i.e. $\partial(\ln\rho)/\partial(kT)^{-1}$) [27]. It was carried out a polynomial interpolation on $\ln\rho$ versus $(kT)^{-1}$ prior to the differentiation to ensure that the experimental points have constant increments, so that the result are smooth DAE's. Due to the insulating/metallic-like transition identified on Fig. 1 by a resistivity slope sign change, above 140 K DAE has no physical meaning, being negative due to the metallic-like behaviour of the resistivity and will not be presented here. From 8 to 140 K, there is a temperature range with increasing DAE followed by almost constant behaviour. Constant DAE range is associated with NNH whilst the increasing DAE is a candidate for VRH.

In order to verify the applicability of the VRH model to the results, DAE's were fitted for temperatures below 75 K, which were dominated by M-VRH with CT^b for samples CB5 and CB10%, respectively, as indicated by the fittings

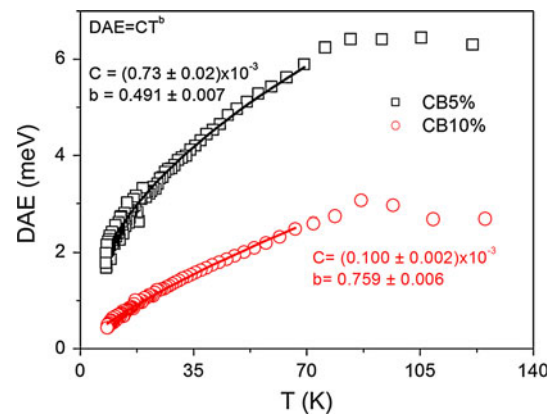


Fig. 2 Differential activation energy calculated from resistivity measurements for samples. For the VRH mechanism, we present the abscissa is $T^{1/2}$ and $T^{3/4}$ for composites containing 5 and 10% of carbon black, respectively, with fittings as in Eq. 2

shown in Fig. 2. The exponents values $b = \frac{n-1}{n}$ of (0.491 ± 0.007) and (0.759 ± 0.007) for samples CB5 and CB10%, respectively, obtained from these fittings are in agreement with expected from Eq. 2 for 1D and 3D M-VRH, respectively. The constant values $C = \frac{k_B T_0^{1/n}}{n}$ were obtained as $C = (0.73 \pm 0.02) \times 10^{-3} \text{ eV K}^{(-1/2)}$ and $C = (0.100 \pm 0.002) \times 10^{-3} \text{ eV K}^{(-3/4)}$ for samples CB5 and CB10%, respectively, confirm that the assumption of the 1D and 3D M-VRH if one uses the $T_0^{1/n}$ obtained from fittings with Eq. 1 that will be presented latter on. From the data associated with NNH for the temperature range between 75 K and about 140 K (i.e. identified by a DAE plateau), the NNH activation energy ε_3 was obtained as (6.4 ± 0.1) and (2.8 ± 0.1) meV for samples CB5 and CB10%, respectively.

The experimental exponent b about 0.5 obtained for sample CB5% could also be interpreted as ES-VRH; however, it should hold only for very low temperatures, and a transition to b about 0.75 should be observed for increasing temperatures and before the NNH temperature region as expected from hopping theory [26]. For this reason, and from the obtained values for the C fitting constant, we conclude that one (1D) and a three-dimensional (3D) systems were obtained for samples CB5 and CB10%, respectively and consequently $n = 2$ and $n = 4$ in Eq. 1 and 2, and all other equations will be presented for these conditions.

The temperature dependence of the resistivity of lightly doped semiconductors in the NNH hopping conduction regime is

$$\rho = \rho_3 e^{\frac{\varepsilon_3}{k_B T}} \quad (3)$$

This implies that the NNH hopping [26] conduction is governed by the temperature dependence with constant

activation energy ϵ_3 . As a consequence, this means that at the temperature range governed by the NNH mechanism the average hopping length is of order of the mean separation between impurities, and it does not vary with temperature.

From the temperature range below 75 K, it can be inferred that 1D or quasi 1D [26] M-VRH conduction is observed in the composite containing 5 vol% of CB due to unique VRH fitting with $T^{1/2}$ for temperature up to 75 K obtained from DAE (see Fig. 2). The 1D [29] characteristic Mott temperature T_0 can be expressed in terms of

$$T_{01D} = \frac{2}{k_B a \eta(E_F)} \tag{4}$$

where k_B the Boltzmann constant, a the wave function localisation radius and $\eta(E_F)$ the density of states at the Fermi level. T_0 can be obtained from the experimental data through fittings with Eq. 1 usually in a linearised form. From T_0 , $\eta(E_F)$ was calculated and it was used to determine the mean hopping distance R , the mean density of hopping carriers N and the mean energy necessary for a hop E [29],

$$R_{1D} = \left\{ \frac{a}{[\pi k_B T \eta(E_F)]} \right\}^{\frac{1}{2}} \tag{5}$$

$$N_{1D} = \frac{1}{\pi R_{1D}} \tag{6}$$

$$E_{1D} = \frac{N_{1D}}{\eta(E_F)} \tag{7}$$

A three-dimensional M-VRH is observed in the composite containing 10 vol% of CB due to unique M-VRH fitting with $T^{3/4}$ for temperature up to 75 K obtained from DAE (see Fig. 2). The 3D characteristic Mott temperature T_0 can be expressed in terms of

$$T_{03D} = \frac{\lambda}{k_B \eta(E_F) a^3} \tag{8}$$

where λ is a dimensionless percolation constant (~ 18.1) [30–33].

$$R_{3D} = \left\{ \frac{9a}{[8\pi k_B T \eta(E_F)]} \right\}^{\frac{1}{4}} \tag{9}$$

$$N_{3D} = \frac{3}{4\pi R_{3D}^3} \tag{10}$$

$$E_{3D} = \frac{N_{3D}}{\eta(E_F)} \tag{11}$$

Figure 3 presents ρ versus $T^{-1/2}$ plotted in a logarithmic scale for CB5% sample. Good accuracy fittings were obtained at low temperatures using plots with $T^{-1/2}$. The fitting is indicated by straight line, and the value of T_0 obtained from Fig. 2 is listed in Table 1.

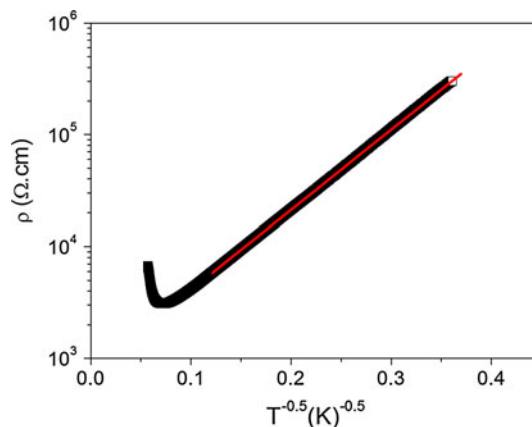


Fig. 3 Resistivity measurements for composite containing 5% of carbon black with the abscissa axis as $T^{-1/2}$. Fittings for the VRH regime are indicated by *straight line*

Figure 4 presents ρ versus $T^{-1/4}$ plotted in a logarithmic scale for CB10% sample. Sample CB10% has slightly lower resistivity than sample CB5%.

Table 1 presents the different parameters obtained by fitting the experimental results to M-VRH theory. The T_0 values depend on CB concentration. Table 1 shows that the mean energy associated with one hop decreases by increasing the CB concentration.

Investigating the temperature and doping level dependence of the dc resistivity is an important tool and gives insight in the transport process. On the insulating side of the insulator/metallic-like transition (IMT), the dc resistivity is determined by Eq. 1. Investigating the dependence of n and T_0 on doping level provides the opportunity to distinguish between the hopping models and extract parameters determining the conductive properties such as density of states and localisation length [34].

In general, most composites designed as conductive materials, such as ours, can be viewed as 3D granular metallic systems and the inhomogeneous disorder of the insulating matrix material leads to the formation of well conducting 3D regions separated by poorly conducting interchain connections. For CB5%, the charge carriers are supposed to be strongly localised on single chain or 1D bundle of chains as expected. M-VRH is possible along chains, whilst in the direction perpendicular to the chains, the conduction occurs with vanishingly small interaction overlap and only NNH is allowed. The quasi-1D model predicts $n = 2$ has been applied not only for anisotropic effective conductivity perpendicular to the chains but also it has been successfully applied to randomly oriented polymer systems [34].

To include a transition from quasi 1D hopping to 3D hopping as a function of doping level, the model mentioned above need to be extended. In the quasi 1D model, such a

Table 1 Parameters obtained by fitting dc resistivity data of the samples and $a = 12\text{\AA}$

Sample	T_0 (K)	$\eta(E_F)$ (eV.m) ⁻¹	R (Å) at $T = 50$ K	N (m ⁻¹)	E (meV) $T = 50$ K
CB5%	271.3	7.1×10^{10}	11	2.9×10^8	4.1
CB10%	590.7	2.1×10^{29}	8.3	4.2×10^{26}	2.0

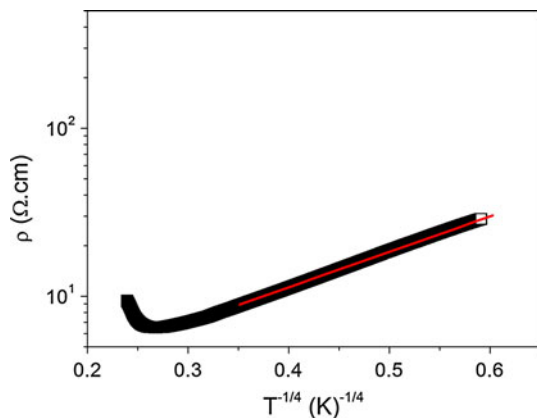


Fig. 4 Resistivity measurements for composite containing 10% of carbon black with the abscissa axis as $T^{-1/4}$. Fittings for the VRH regime are indicated by *straight line*

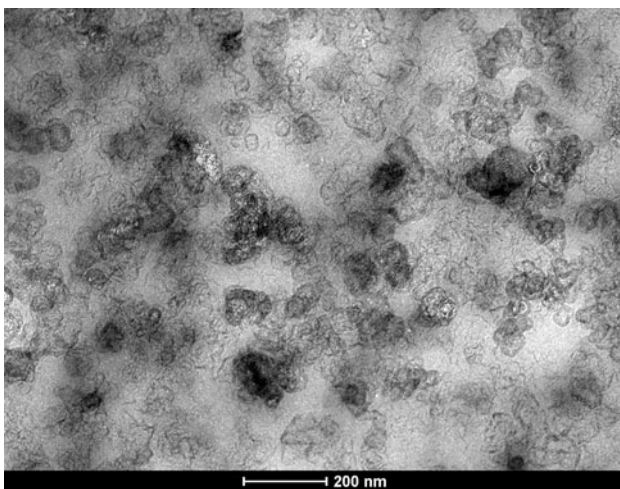


Fig. 5 TEM image of composite containing 5% of carbon black

transition is expected when the transverse overlap is sufficiently increased. A transition from 1D to 3D hopping is induced by an increase of the interchain connectivity in the system, this increase is due to additional CB particles that cannot be placed along the chains since they have already been filled and start to be placed between the 3D oriented bundles of chains, i.e. increasing the interchain connectivity. This transition with the concentration of conductive particles has already been reported to be strongly influenced by microstructure and morphology [34, 35].

In Ref. [35], this scenario was proposed for polyaniline and polypyrrole conductive particle systems. The strong disorder and the formation of inhomogeneous “metallic islands” mask the exponent $n = 4$ behaviour expected and observed for homogeneously doped samples. In doped polyaniline samples, the temperature dependence was interpreted in terms of VRH in one dimension [35]. The resistivity dependence over a wide range of temperature for samples with inhomogeneous disorder has a different origin from resistivity dependence in the ES-VRH conduction limit, usually associated with the homogeneous phase. Phase segregation of the doped and undoped regions results in the formation of granular metals [35].

In order to verify 1D hopping model for the 5% carbon content sample, TEM image is presented (see Fig. 5). We obtained a TEM picture in a 200-nm scale for the 5% carbon content sample that shows the carbon nanoparticles (i.e. as black particles) entangled with the SBS fibers (not oriented in light gray). As seen carbon nanoparticles occur only associated with fibers and do not contact with other particles. This is compatible with our results of 1D M-VRH hopping model since the percolating network is associated with the SBS fibers preferably instead of between fibers.

Conclusions

In summary, CB/SBS composites were prepared by in a mechanical mixer. Electrical conduction in composites is due to the conducting carbon black. The carbon black distribution and conductive mechanisms were investigated. From an analysis of the differential activation energy, we have shown that the results are consistent with Mott’s variable range hopping being one-dimensional for composite containing 5% of carbon black and three-dimensional for the composite containing 10% of carbon black. The analyses removes any doubt that Efros and Shklovskii variable range hopping or barrier models are absent in the samples. The changes in the dimensionality of the hopping model from one-dimensional to three-dimensional are consistent with literature reports [34, 35] and TEM image obtained for sample with 5% carbon black content, that by increasing the conductive particle content induces structural transition from 1D bundles of chains to a 3D conduction associated with an increase of the interchain connectivity. In the present study, this role is played by the carbon black.

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