Electrical properties of carbon black/ copolymer composites above and below the melting temperature

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Received: 04 Dec 2010; Revised 17 Jan 2011; Accepted: 17 Jan 2011
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Abstract

The electrical properties of a composite, consisting in a matrix of ethylene butylacrylate (EAB) reinforced with carbon black particles (CB) are studied in the temperature range from 27 to 127 °C. The DC conductivity measurements show an insulator/conductor transition at a volume concentration of about $\Phi^* \approx 11\%$. The electrical resistivity is constant with temperature, at concentrations below the conduction threshold Φ^*. For concentrations above Φ^*, the resistivity presents a significant increase for temperatures above the melting point, $T_m \approx 91$ °C, which corresponds to the phenomenon known as positive temperature coefficient in resistivity (PTCR effect). Besides, the AC conductivity of these composites was analysed in the frequency range from 40 Hz to 0.1 MHz. The frequency dependence of the AC conductivity is characterized by a low frequency region of constant conductivity followed by a gradual transition at higher frequencies to a frequency dependent conductivity. This behavior can be approximated by the empirical power law of Jonscher. We found that the activation energy is insensitive to the presence of the carbon particles, it means that the carbon particles do not interact or only weakly with the chain segments of the macromolecules in the copolymer.

Keywords : Composite; Percolation threshold; Melting temperature; PTCR effect.

1. Introduction

The dispersion of carbon black, which is a conducting material, into an insulating polymeric matrix yields to a composite material, which was studied by several authors [1-9]. Some of these electrically conductive composites show a sharp increase in electrical resistivity at elevated temperature close to the polymer melting point. This is specially pronounced in some specific semicrystalline polymers with carbon fillers. This phenomenon is known as positive temperature coefficient in resistivity (PTCR effect). Because of the sharp increase in the electrical resistivity, PTCR materials have a wide range of industrial applications.
Nevertheless, the application of PTCR materials is limited by the decrease of the electrical resistivity at temperatures beyond the melting point, which is so-called as negative temperature coefficient in resistivity (NTCR effect), although, many efforts are made in the composites prepared by using carbon black as conductive fillers. Concerning the mechanism of NTCR effect, Narkis et al. [10-11] and Tang et al. [12] reported that the decrease of resistivity is attributed to the reagglomeration of CB. Differential scanning calorimetric (DSC) has been used to estimate the melting temperature and the values of activation energy can be obtained from AC conductivity measurements at ($\omega \rightarrow 0$).

2. Experimental details

All the samples of an EBA copolymer filled with acetylene carbon black used in this investigation are obtained from Borealis AB (Sweden). The butylacrylate monomer contains butylester side groups, providing a certain polarity and a relatively low crystalline (about 20 % in volume). The average size of the carbon black particles is about 30 nm and the mean size of the primary aggregates is of the order of 150 nm. A series of eight samples with nominal carbon concentrations was studied. The samples were prepared as discs of thickness about 1 mm, with aluminium electrodes of 10 mm diameter on the opposite sites of the sample. The electrical contacts were formed by silver paint. The dielectric measurements are carried in the frequency range from 10 Hz to 100 kHz, using a SR850 DSP Lock-In Amplifier, in the typical lock-in configuration.

3. Results and discussion:

3.1. Influence of the carbon black volume fraction on DC conductivity at room temperature

In Fig. 1 the variation of the DC conductivity as a function of carbon black fraction can be divided into three regions [13]. At low concentration of CB, a small increase in conductivity of composite can be attributed to the transportation of the small number of charged particles through the system without having any continuous conductive path. At average concentrations, the conductivity increases sharply due to a continuous conductive path developed in the polymer matrix (the threshold is estimated $\Phi^* \approx 11$ %), and finally, at higher concentrations, the further addition of filler has a marginal effect on the conductivity.

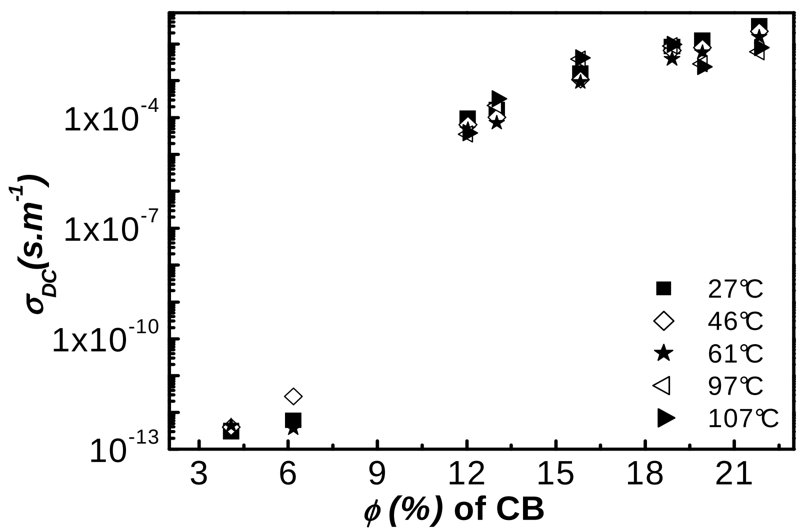


Fig 1: *DC conductivity as a function of the carbon black concentration for 5 temperatures.*

It is also observed for the concentrations 18.91 and 21.84% a decrease in conductivity with rise in temperature. The mechanism responsible for change in conductivity at this stage is predominantly tunneling, where in the carbon particles are not in physical contact and the electrons tunnel through the insulating copolymer gap between them. As the temperature in increased, the gap between particles also widens and tunneling becomes less probable [14].

3.2 . Influence of the temperature on the DC conductivity

The DC conductivity, obtained for $\omega \rightarrow 0$, as a function of temperature is shown in Fig. 2. Comparing these curves with that ones obtained by DSC measurements, plotted in Fig. 3, we can observe the changing of comportment at the melting temperature, that is $T_m \approx 91$ *°C*. This effect may be related to the decrease of crystallinity of this composite material compared with the results of studies of polyethylene-acetylene black composites obtained by Luo et al. [15].

DC conductivity increases exponentially with temperature indicating that is a thermally activated process. This can be expressed mathematically by [16]:

$$\sigma_{DC} \propto \frac{1}{T}\exp\left(-\frac{E_a}{k_b T}\right) \quad (1)$$

where E_a is the activation energy, k_b is the Boltzmann's constant (k_b =1.381.10^{-23} J/K) and T is the absolute temperature. Fig. 4 shows the linear relationship between ln ($\sigma_{DC}.T$) and the inverse of T. for $T > T_m$, The values of the activation energies are calculated via a linear regression using Eq. (1), are reported in Table 1. The obtained values, between 0,117±0,006 and 0,549±0,017 eV means that, when carbon black is present inside the EAB polymer matrix, the carbon particles does not interact or only weakly with the chain segments of the macromolecules in the copolymer [17].

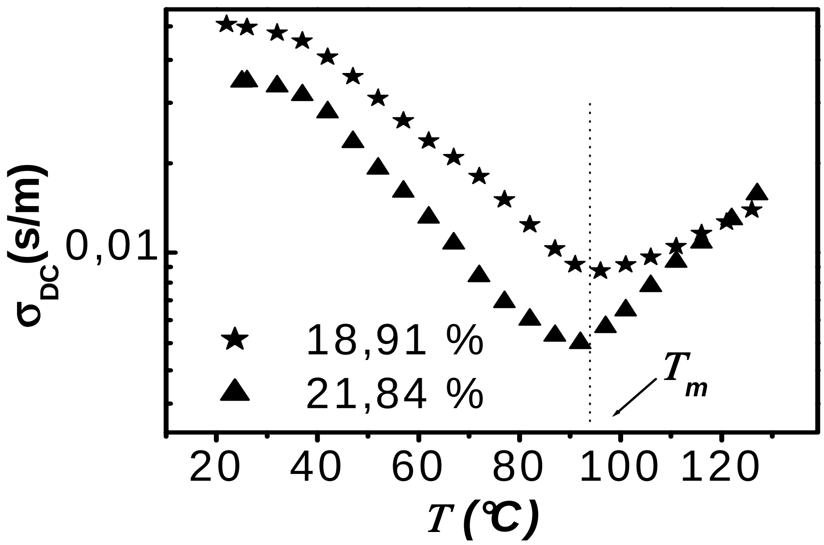


Fig. 2: *DC conductivity as a function of temperature for different volume fractions of CB.*

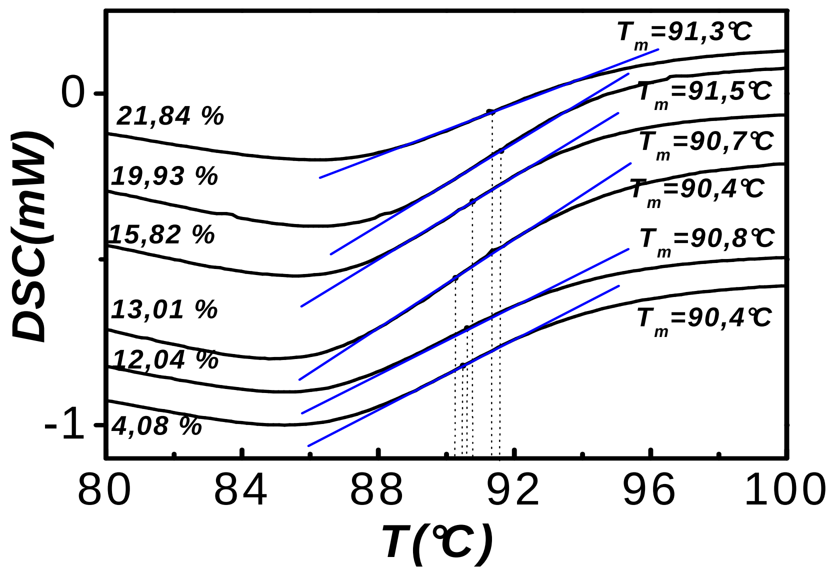


Fig. 3: *DSC curves of EBA polymer/CB composites.*

Table 1: The values of the activation energy for different volume concentrations of CB.

ø(%) of CB	E_a **(ev)**	**Rco**	T_m **(°C)**
12,04	0,221±0,014	0,988	90,8±2,2
13,01	0,549±0,017	0,997	90,4±2,7
15,82	0,117±0,006	0,992	90,7±2,4
18,91	0,207±0,010	0,994	-
21,84	0,396±0,008	0,999	91,3±2,8

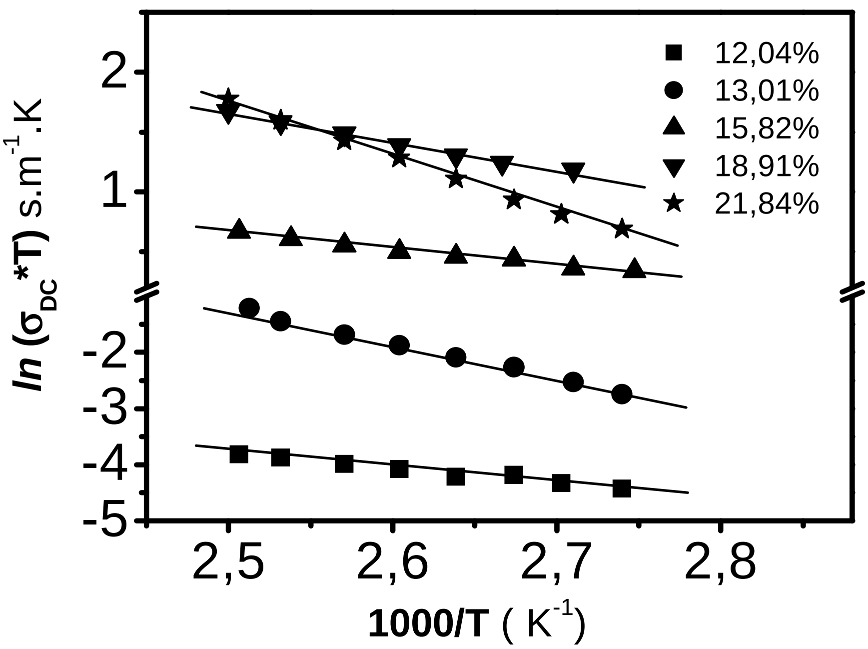


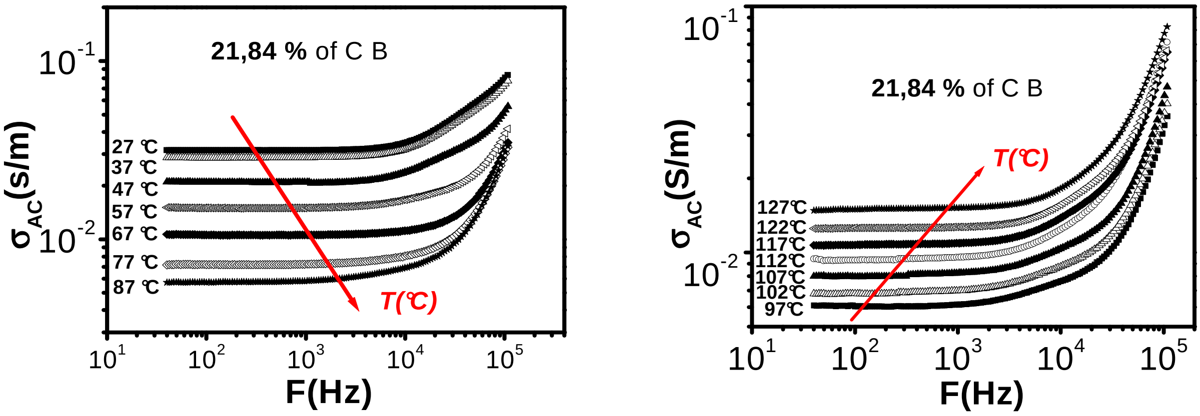
***Fig. 4**: Arrhenius plot of the DC conductivity versus 1/T for different concentrations of CB particles*

3.3. Influence of the temperature on the AC conductivity

Fig. 5 shows the dependence of AC conductivity as a function of the frequency at different temperatures. In the vicinity of 91 °C, the PTCR effect in the AC conductivity of the composite can be observed. In Fig. 5(a) AC conductivity decreases with increasing temperature and in Fig. 5(b) AC conductivity increase with increasing temperature. At low frequencies we observe that the conductivity does not depend on the frequency and is dominated by a percolative behavior [18], but at intermediate frequencies, it depends progressively of the frequency. This phenomenon could be attributed to the resistive conduction through the bulk composite including tunneling between particles and polymer. The values of the exponent $s(T)$ of the Jonsher power law can be then calculated:

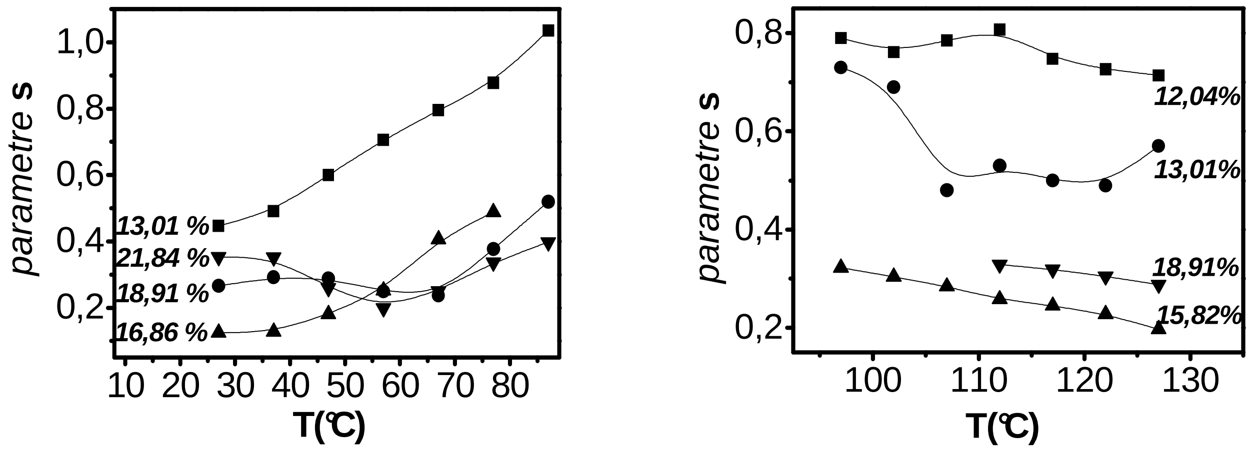
$$\sigma_{AC}(\omega) = A\omega^{S(T)} \tag{2}$$

In Fig. 6 we can observe that the parameter s increases with the increasing temperature for $T < T_m$, and increases for $T > T_m$. When the temperature is close to T_m, the values of s are close to 1, traducing a completely correlated system [18]. At high frequencies, the AC conductivity is proportional to the frequency, characteristic of the intrinsic hopping conductivity [9].



(a) **(b)**

Fig. 5: *Log-Log plot of the AC conductivity as a function of frequency at various temperatures (a): for* $T < T_m \approx 91$ *°C and (b): for* $T > T_m \approx 91$ *°C.*



(a) **(b)**

Fig. 6: *Variation of parameter* ***s*** *as a function of temperature (a): for* $T<T_m$ *and (b): for* $T>T_m$

4. Conclusion

Polymer composites of ethylene butylacrylate (EAB) reinforced with carbon black particles CB were studied using the dielectric spectroscopy, in the frequency range 0.1 Hz to 100 kHz and temperature range from 27 to 127 °C. The PTCR effect is observed at temperatures slightly above 91°C, which makes this material potentially interesting for industrial applications. The mechanism responsible for the change in resistivity is predominantly tunnelling, wherein the conductive filler particles are not in physical contact. It is found that the activation energy is insensitive or weakly to the presence of carbon in the range of the concentration considered.

Acknowledgments

The authors are grateful to Professor F. Carmona (Paul Pascal Research Centre–CNRS, University of Bordeaux I, France) for supplying the composite materials. This work is partially supported by Morocco-Portugal cooperation program (No. Physique/04/08/09).

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