DIELECTRIC PROPERTIES OF CARBON BLACK COPOLYMER

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Abstract
The dielectric properties of carbon black (CB) loaded in ethylene butylacrylate copolymer composite (EBA) were investigated in the frequency range between 10 and 10^5 Hz and temperature range between 250 and 400 K.
The frequency dependence of the dielectric response has been analyzed using the modulus formalism and the electrical conductivity using the Jonscher's power law. It is found that the activation energy obtained by the modulus method is in good agreement with that obtained by the DC conductivity, which is independent of the CB contents inside the copolymer matrix, suggesting that these particles do not interact significantly with the chain segments of the macromolecules in the EBA copolymer.

1 Introduction
Conducting polymers are a quite important class of materials with several industrial applications. The primary uses of conducting polymer composites include interference shielding and electrostatic dissipation of charges [1-3]. In the last years, the electrical properties and electromagnetic performance of carbon black-polymer composites have been extensively studied [4-7]. The electrical performance of these composite materials is closely related to the conductivity of the constituent components, and also the size, shape and concentration of the conducting particles. Polymer epoxy matrix composites are principally electrical insulators, due to the low concentration of free charge carriers. Also, their electrical response is essentially associated with relaxation occurrences that are affected by an alternating field.

At lower temperatures, polar side groups enhance the electrical performance of the composites. The interfacial polarization results from the heterogeneity of the system.

When the carbon black filler content is low, the mean distance between charge particles or clusters is large and conductance is limited by the presence of the dielectric polymer matrix. At a critical volume fraction of the filler, the percolating threshold, a physical path is formed in a way that the current can flow, percolating the whole system [8].

These conducting composites show a sharp increase in the electrical resistivity at high temperature, close to the polymer melting point. 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 [9,10].
This paper presents a study of the effect of carbon black particles on the electrical properties of ethylene butylacrylate copolymer.

2 Materials and testing methods

The samples of EBA copolymer filled with acetylene carbon black, used in this work 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 size of the primary aggregates about 150 nm. Eight nominal carbon concentrations were 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 10^5 Hz, using an Agilent 4294A Precision Impedance Analyzer. The general approach is to apply an electrical stimulus and observe the response of the material. It is then assumed that the properties of the electrode-material system are time invariant, which is an important purpose to the measurement method. The amplitude of the applied voltage was 1 V. From a practical point of view, dielectric spectroscopy can provide the complex permittivity, $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$, or derived quantities related to it, such as the dielectric modulus, $M^* = \frac{1}{\varepsilon^*}$, from the measurement of the R-C impedance of the sample.

3 Results

Figures 1 and 2 show the AC conductivity as a function of frequency, for different temperatures, for a sample with 22% of carbon black particles. All the concentrations show the same behavior.

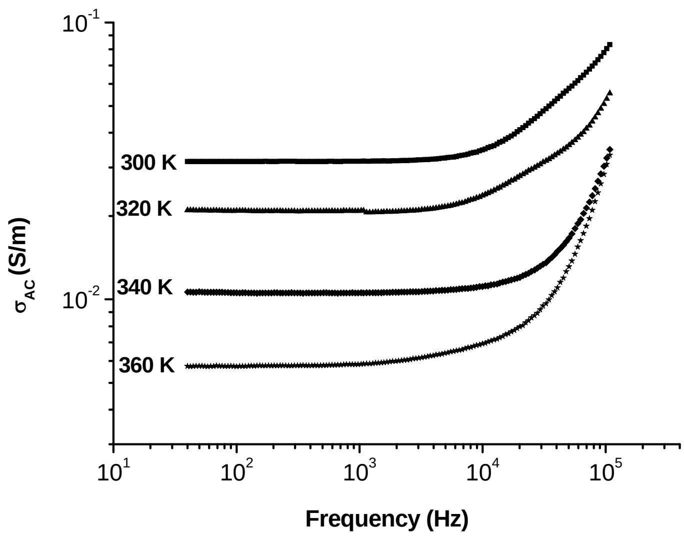

Figure 1. AC conductivity as a function of frequency, for different temperatures, for a sample with 22% of carbon black particles (T < 365 K).

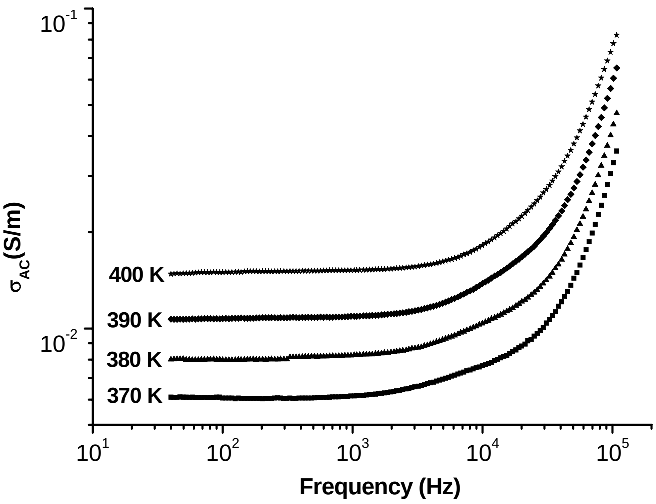

Figure 2. AC conductivity as a function of frequency, for different temperatures, for a sample with 22% of carbon black particles (T > 365 K).

As we can observe the behavior is different, as for T < 365 K, the conductivity decreases with the temperature, and for T > 365 K, it is the inverse. The DC conductivity can be calculated with these graphics, making $\omega \to 0$. Then, it is possible to plot the graphics of DC resistivity, as a function of temperature. For concentrations higher than the percolation threshold, that is x > 12% [11], we could observe the PTCR effect, for temperatures below the melting point, $T_m \approx 365$ K. That is, for T < 365 K, the resistivity increases, but the inverse is observed for T > 365 K. Figure 3 shows this behavior, for two different concentrations of carbon black particles above the percolation critical concentration.

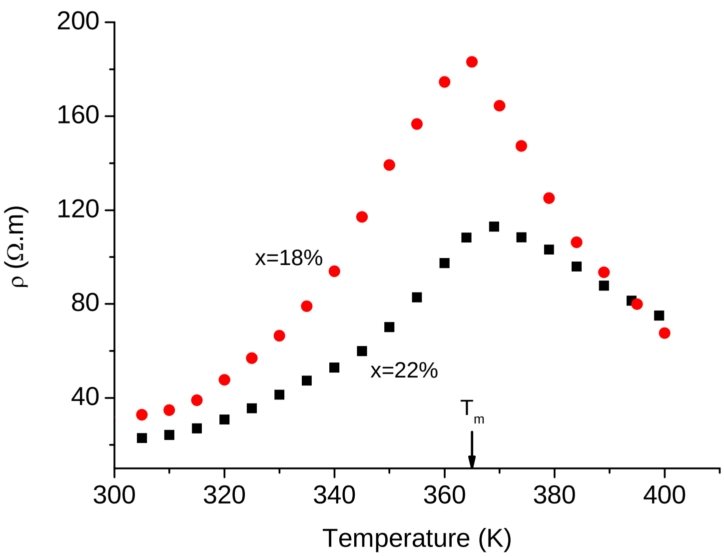

Figure 3. DC resistivity versus temperature, for two concentrations of carbon black particles.

At low frequencies the conductivity does not depend on the frequency, but at intermediate frequencies, it depends progressively of it. This phenomenon could be attributed to the resistive conduction through the bulk composite including tunneling between particles and polymer. The Jonscher power law can be used to fit this result,

$$\sigma_{AC}(\omega) = A\omega^{S(T)} \tag{1}$$

Where *s(T)* is the exponent depending of the temperature. Figure 4 show this parameter for two different concentrations of filler content, as a function of temperature. For $T < T_m$, the *s* parameter increases, but the reverse is observed for $T > T_m$. This is in accordance with the resistivity measurements.

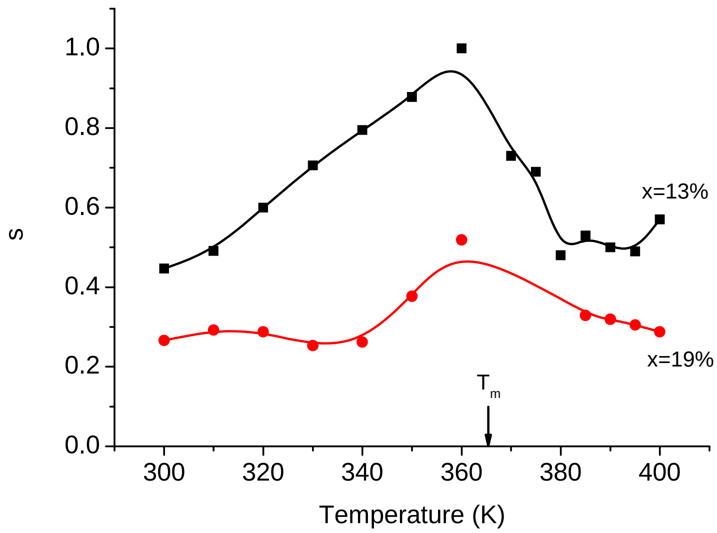

Figure 4. s parameter versus temperature, for two concentrations of carbon black particles.

The dielectric spectroscopy measurements permits to calculate the modulus [12],

$$M^*(\omega) = \frac{C_0}{C - i\omega^{-1}R^{-1}} \tag{2}$$

where $C_0 = \varepsilon_0 A / d$, being *A* the surface area and *d* the distance between electrodes.

Figure 5 shows the real and imaginary parts of the dielectric modulus, *M*(ω)*, for two different temperatures in a sample with x = 13%, where a relaxation process is visible. The maximum in M'' and the corresponding inflexion in M' is a consequence of the Kramers-Kronig relations, and indicative of the relaxation phenomenon.

The obtained *M*(ω)* as a function of temperature allows to calculate the activation energy, that was of the order of 0.06 eV, independent of the quantity of conducting particles in the matrix. These very low values, means that, when carbon black is present inside the copolymer matrix, the carbon does not interact or only weakly with the chain segments of the macromolecules [13].

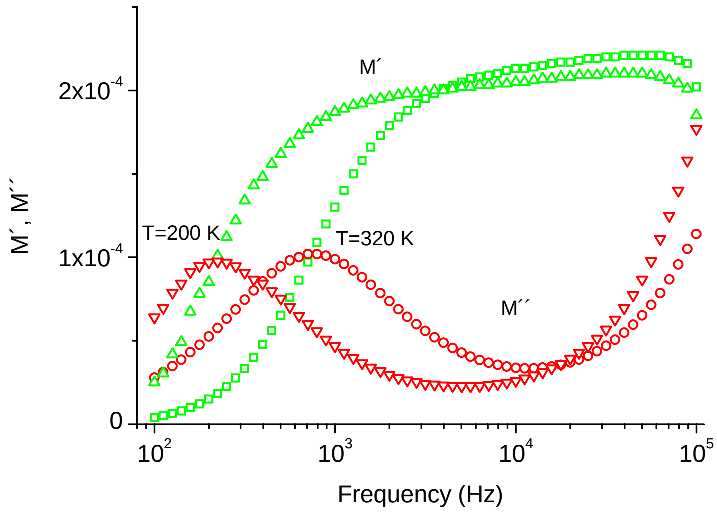

Figure 5. Real and imaginary parts of the complex modulus, as a function of frequency.

4 Conclusion

Positive temperature coefficient in resistivity (PTCR) is observed in these copolymer loaded carbon nanoparticles, for temperatures below the melting point and concentrations higher than the percolation critical concentration. For higher temperatures, negative temperature coefficient in resistivity is observed (NTCR).

Jonscher power law fits correctly the conductivity data.

The relaxation process, observed using the modulus formalism show that the activation energy is very low, about 0.06 eV, and independent of the carbon black concentration, meaning that the carbon does not interact or only weakly with the chain segments of the macromolecules.

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