Journal of Non-Crystalline Solids 356 (2010) 270–274

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Dielectric properties of the ethylene butylacrylate/carbon black nanocomposites

L.C. Costa [a,*], M.E. Achour [b], M.P.F. Graça [a], M. El Hasnaoui [b], A. Outzourhit [c], A. Oueriagli [c]

[a] I3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal
[b] Laboratoire LASTID, Département de Physique, Faculté des Sciences, Université Ibn Tofail, B.P. 133, 14000 Kénitra, Morocco
[c] Laboratoire de Physique des Solides et des Couches Minces, Faculté des Sciences, Sémlalia, Marrakech, Morocco

ARTICLE INFO

Article history:
Received 24 March 2009
Received in revised form 22 September 2009
Available online 16 December 2009

Keywords:
Dielectric properties, relaxation, electric modulus
Carbon
Polymers and organics

ABSTRACT

In this paper we report the d.c. electrical conductivity measurements between 80 and 350 K, and the dielectric properties at low frequencies (10 Hz < f < 100 kHz) at constant temperature T = 300 K, of the ethylene butylacrylate/carbon black nanocomposites, with different concentrations of the dispersed conducting particles. The concentration of the conductive inclusions has been proved to be a crucial parameter, governing the electrical behavior of these nanocomposites. Above the critical percolation concentration, that is 12% of conducting particles, the Cole–Cole model of dielectric relaxation can be used to interpret the obtained data. The calculated relaxation parameters of the model show that, with the increasing concentration of carbon black nanoparticles, the system becomes more heterogeneous, which is confirmed by the broader distribution of the relaxation times.

1. Introduction

The dielectric spectroscopy has proven to be a very useful tool for studying the structure and the dynamics of polymeric systems [1–3]. This knowledge is very important for the development of new materials for industrial applications, with specific electrical properties. In particular, the conducting polymers have been proposed for use as conducting wires, electromagnetic shielding materials [4,5], light emitting diodes [6], sensors [7], etc.

The electrical properties of an insulating polymer can be altered by adding different conducting particles [8–10], and can be controlled by properly choosing the components, their shape and their relative concentrations. Generally, the conductivity of a polymer, rather than being a linear function of the concentration of the added particles, is almost insensitive for lower concentrations, and rises abruptly as the percolation threshold is reached [11–13]. This occurs at a critical concentration where the particles contact with each other and, as a consequence, a continuous electrical path of the doped particles is built throughout the polymer matrix. That is, when the filler content is low, the mean distance between conducting particles is large and the conductivity is restricted by the presence of the insulating matrix, but by increasing the conductive phase content, the conducting particles get closer and at that critical concentration the electrical properties are dominated by them.

Nanocomposites containing carbon as additives find different applications due to their unusual mechanical and electrical properties. It is known that, among different substances used in composites, carbon black is unique in its ability to significantly enhance the properties while lowering cost.

2. Experimental

All the samples of an EBA copolymer filled with acetylene carbon black used in this investigation were obtained from Borealis AB (Sweden). The butylacrylate monomer (EBA) contains butylester side groups, providing a certain polarity and a relatively low crystallinity (about 20% in volume). The average size of the carbon black particles is about 30 nm [14]. A series of eight samples with nominal carbon black volume fraction ranging between 6.2% and 21.5% in volume has been studied.

For the electrical measurements, the samples were prepared as disks of thickness about 1 mm, with aluminum electrodes of 10 mm diameter on the opposite sites of the sample. Crosschecking experiments were made, using different size electrodes. The electrical contacts were formed by silver paint.

The d.c. electrical conductivity was measured as a function of the temperature (from 80 to 350 K). During the measurements the samples, inside a cryostat, were maintained in helium gas, to improve the heat transfer and eliminate the moisture. The current was measured with a Keithley electrometer, model 617, and the temperature controlled and measured with an Oxford temperature

* Corresponding author. Tel.: +351 234370944.
E-mail address: kady@ua.pt (L.C. Costa).

0022-3093/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2009.11.008

controller. The stabilization of temperature was better than 0.1 K over the period of measurement of the current.

The dielectric measurements were carried out at 300 K, in the frequency range from 10 to 100 kHz, using a SR850 DSP Lock-In Amplifier, in the typical lock-in configuration. We measured the in-phase (V_f) and the out-of-phase (V_q) components of the sample signal, and then we calculated the real and imaginary parts of the impedance.

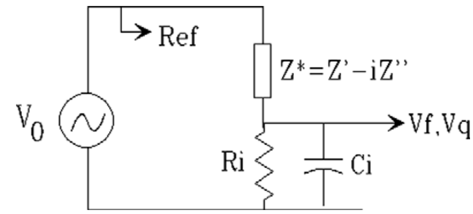

Fig. 2. Schematic representation of the lock-in technique.

3. Results

Fig. 1 shows the d.c. electrical conductivity, at constant temperature, as a function of the carbon black concentration. The percolation threshold is visible, at a critical volume concentration x_c where the conductivity begins to increase abruptly. The electrical conductivities are negligible up to the critical concentration and are several orders of magnitude larger at higher concentrations, indicating the existence of a percolating path via connecting carbon black particles. At this stage, the conductivity of the composite is controlled by these conducting particles. To calculate the complex impedance, $Z^*(\omega) = Z'(\omega) - iZ''(\omega)$, with the lock-in technique, we used the expression [15],

$$Z^* = \frac{R_i(V_fV_0 - V_f^2 - V_q^2) - \omega C_i^2 R_i^2 V_q V_0}{(1+\omega^2 C_i^2 R_i^2)(V_f^2 + V_q^2)} - i\frac{V_q V_0 R_i + \omega C_i^2 R_i^2 (V_f V_0 - V_f^2 - V_q^2)}{(1+\omega^2 C_i^2 R_i^2)(V_f^2 + V_q^2)}. \quad (1)$$

This equation was obtained when the sample impedance is in series with a known resistance (1 kΩ which is in parallel with the lock-in input impedance). In Fig. 2 we show the measurement technique. Here, R_i represents the equivalent resistance of the lock-in input resistance (10 MΩ) in parallel with the known resistance, C_i the lock-in input capacitance (25 pF), V_0 the input signal, and V_f and V_q the in-phase and the out-of-phase components of the measured signal. The reference signal is available at the same frequency as the signal to be measured and is digitally synthesized. All the components of the input signal are multiplied by the reference signal. As sine waves of differing frequencies are orthogonal, the average of the product of two sine waves is zero unless the frequencies are the same. The product of this multiplication yields a DC output signal proportional to the component of the signal whose frequency is exactly locked to the reference frequency. Using reference signals, one in-phase and one out of phase with respect to the reference input, which are generated internally, we can simultaneously measure both the in-phase and quadrature components of the input signal [16,17].

In Figs. 3 and 4 we present the real and imaginary parts of the complex impedance, $Z^*(\omega) = Z'(\omega) - iZ''(\omega)$, respectively, of composites for different carbon black concentrations, at constant temperature. A relaxation process is observed for all the samples with carbon black concentration higher than the critical percolation concentration, about 12%. Nevertheless, the relaxation is not present for lower concentration of the doping conducting particles.Estimating relative errors on both real and imaginary part of the complex permittivity are $\frac{\Delta\varepsilon'}{\varepsilon'} = \frac{\Delta\varepsilon''}{\varepsilon'} \leqslant 5\%$.

4. Discussion

The variation of conductivity with conducting filler can be divided into three regions (Fig. 1) [18]. In region I, the small increase in conductivity of the composite can be attributed to the transport of the small number of charged particles through the system without having any continuous conductive path. In region II the conductivity increases sharply due to a continuous conductive path developed in the polymer matrix. In region III, further addition of filler has a marginal effect on the conductivity.

The d.c. conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process, which can be observed in Fig. 5.Mathematically, it can be expressed by the well-known Arrhenius relation as,

$$\sigma_{dc} \propto \exp\left[-\frac{E_a}{KT}\right], \quad (2)$$

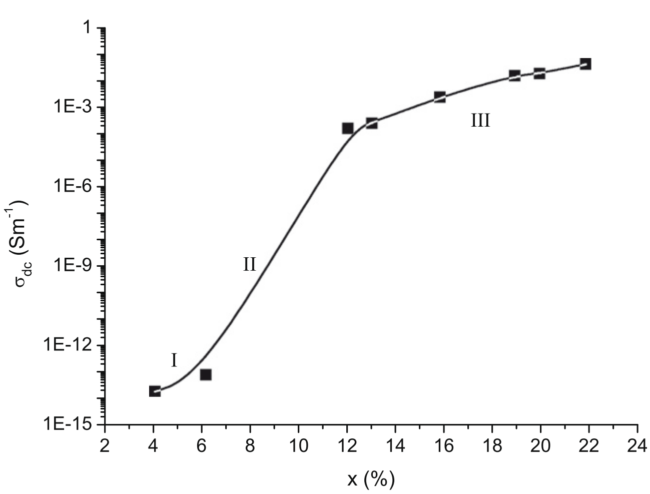

Fig. 1. σ_{dc}, at constant temperature T = 300 K, as a function of the carbon black concentration.

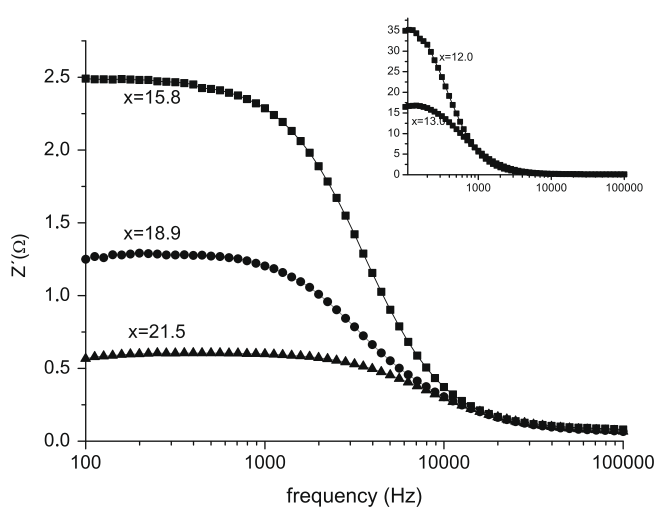

Fig. 3. Real part of the complex impedance, for different carbon black concentration composites, at constant temperature T = 300 K.