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Electric Modulus Analysis of Carbon Black/Copolymer Composite Materials

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ABSTRACT

We have investigated the electrical properties of carbon black (CB) loaded in ethylene butylacrylate copolymer composite (EBA) in the frequency range between 10^2 *and* 10^4 *Hz and temperature range between* 153 *and* 353 *K. The frequency dependence of electrical data have been analyzed in two frameworks: the electrical modulus formalism with the Kohlrausch-Williams-Watts stretched exponential function (KWW) and the electrical conductivity by using the Jonscher's power law in the frequency domain. The stretching exponent* β_{KWW} *and n are found to be temperature independent for all CB fractions and decreasing when the CB volume concentrations loaded in copolymer matrix increases. It is found that the activation energy obtained by the modulus method is in good agreement with that obtained by the DC conductivity in the power law which is independent on the CB contents that exist in the copolymer matrix, suggesting that these particles do not interact significantly with the chain segments of the macromolecules in the EBA copolymer.*

Keywords**:** *Electrical Modulus, Polymer Matrix, Nanocomposites, Conducting Particles*

1. Introduction

The analysis of complex plane is a well-known and powerful technique which has long been used for investigating dielectric and electrical properties of materials. In order to analyze and interpret experimental data, it is essential to have a model equivalent circuit that provides a realistic representation of the electrical properties. In recent years, interest has grown in the technological properties of composites made of a mixture of conducting and insulating materials. These systems are characterized by their flexibility to develop new materials with improved properties. The obtained result gives evidence of a relaxation phenomenon. These two processes are related to dipolar orientation effects or space charge migration [1,2]. Along with this, interfacial polarization is also considered as the genesis of dielectric effects. In a series of recent papers, the dispersion of carbon black which is a conducting material into an insulating polymeric matrix yields to a composite material that was studied by several authors [3-9]. For our composite materials, Costa *et al.* [10] used the Cole-Cole model to interpret the complex impedance Z^* spectrum as a function of frequency, at 300 K, for different concentrations of carbon black loaded in a copolymer.

In the present paper, we report the results of the analysis of experimental data of spectrum modulus, using the electrical modulus formalism with a Kohlraush Williams Watt (KWW) distribution of relaxation times and the Jonscher's power law with frequency dependence to extract information about the dielectric relaxation in carbon black particles filled ethylene butylacrylate copolymer composite (EBA) regarding carbon concentrations above the conductivity threshold $\Phi_c \approx 12\%$ [10]. This approach is supported by a wide range of technologically important applications which require highly loaded $\Phi > \Phi_c$ carbon black polymer composites, like light emitting diodes [11] and electromagnetic shielding [12-13]. For these applications, our understanding of the dielectric relaxation mechanisms depends sensitively on the carbon black mesostructure.

2. Theoretical Models

The electrical modulus and the complex impedance formalism for the analysis of the dielectric response of materials have been reported by many authors [14-15]. Impedance analysis provides a simple method to determine various contributions to the total conductivity of materials in terms of four possible interrelated complex formulations: impedance (Z^*), admittance (Y^*), permittivity (ε^*) , and modulus (M^*).

The electrical modulus, M^*, is defined in terms of the reciprocal of the complex relative permittivity, $\varepsilon^*(\omega)$, as:

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M'(\omega) + iM''(\omega) \tag{1}$$

where $M'(\omega)$ and $M''(\omega)$ are the real and imaginary parts of the electrical modulus which can be represented by using the complex dielectric constants with the following relations:

$$M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)} \tag{2}$$

$$M'''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)} \tag{3}$$

The non-exponential conductivity relaxation could be described by using Kohlraush Williams Watt (KWW) function, $\Phi(t)$, which represents the distribution of the relaxation times in charges conducting materials [16]. The modulus can be represented as:

$$M^*_{\beta_{KWW}}(\omega) = M_\infty\left[1 - \int_o^\infty \exp(i\omega t)(-\mathrm{d}\phi/\mathrm{d}t)\,\mathrm{d}t\right] \tag{4}$$

with

$$\phi(t) = \phi_o \exp(-t/\tau_\sigma)^{\beta_{\mathrm{KWW}}} \tag{5}$$

where M_∞ represents the asymptotic value of $M'(\omega)$ when $\omega \to \infty$, τ_σ is the conductivity relaxation time and β_{KWW} is the Kohlrausch exponent with values located in the range $0 < \beta_{\mathrm{KWW}} \leq 1$.

Furthermore, the total conductivity at a given temperature over a wide range of frequency can be written as [17]:

$$\sigma_{tot}(\omega,T) = \sigma_{DC}(T) + \sigma_{AC}(\omega,T) \tag{6}$$

where $\sigma_{DC}(T)$ is the DC conductivity and:

$$\sigma_{AC}(\omega,T) \propto \omega^{n(T)} \tag{7}$$

This relation represents the electrical conductivity model of Jonscher's power law and $n(T)$ represents the power exponent depending on the temperature $0 \leq n(T) \leq 1$.

3. Experimental

For the experiments, we used CB particles obtained from Columbian Chemicals Co. The average size of the primary CB particles is about 30 nm [7] and the average size of the primary aggregate is approximately 150 nm [18]. The density of the CB particles is 1.89 g·cm^{-3} and the specific surface area (NSA) is 639 m^2·g^{-1}. 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 crystallinity (around 20% in volume). The density of the EBA copolymer is 0.923 g·cm^{-3}. Nominal CB volume fractions, Φ, between 0% and 22% were incorporated in the polymer matrix. Six samples were fabricated by mechanical mixture and have been studied.

For the electrical measurements, the samples were prepared as discs of 1 mm thick, with aluminium electrodes of 10 mm diameter on the opposite sites of the sample. Crosschecking experiments were made by different sizes of electrodes. The electrical contacts were formed by silver paint. The dielectric measurements were carried out between 153 to 353 K for frequencies ranging between 10^2 and 10^4 Hz by using a SR850 DSP Lock-In Amplifier in the typical lock-in configuration.

4. Results and Discussion

4.1. Room Temperature Dielectric Modulus Properties

Figure 1 shows the variation of real $M'(\omega)$ and imaginary $M''(\omega)$ parts of the electric modulus as a function of frequency at room temperature for different volume concentrations of CB. $M'(\omega)$ shows a dispersion tending to M_∞ at higher frequencies, while the asymmetric $M''(\omega)$ is immediately suggestive of stretched exponential relaxation behavior.

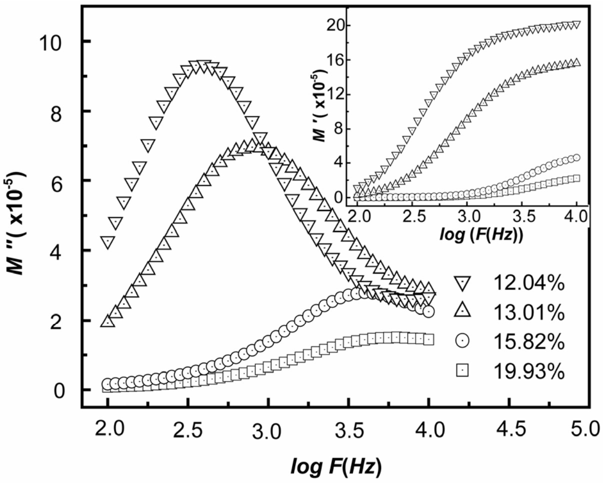

Figure 1. Real and imaginary parts of the complex modulus at room temperature for various concentrations of carbon black.

The parameter β_{KWW} for the studied samples was estimated as a function of volume concentrations of CB by using the modulus formalism *i.e.*, the $M''(\omega)$ spectrum. The corresponding full width at half height (FWHH) is wider than the breadth of the Debye Peak (1.14 decades) and results in a value of β_{KWW} =1.14 per FWHH. The parameter β_{KWW} is calculated by using the relation $\beta_{\mathrm{KWW}} = 1.14/\mathrm{FWHM}$. The total conductivity $\sigma_{tot}(\omega,T)$ at a given temperature over a wide range of frequency can be written as [17] (Equation (6)).

Figure 2 shows the variation of AC conductivity as a function of frequency for different volume concentrations of CB at room temperature. At low frequencies, the conductivity does not almost depend on the frequency and is dominated by a percolative behavior [10]. At high frequencies, the AC conductivity increases with increasing of frequency, by using the Jonscher's power law (Equation (7)) the values of exponent n are calculated. **Figure 3** shows the variation of exponents β_{KWW} and n as a function of $\Phi(\%)$ of CB at room temperature.

We observe that both β_{KWW} and n decrease by increasing carbon concentrations. We conclude that the dielectric response results from the prevalence of polarization by the deformation of the electronic cloud wherein the movements of the electrons are uncorrelated [8]. Furthermore, the values of exponent n are found to be low for all samples and the compositional dependence of n can be linked to the combined effect of distribution of relaxation path, mechanism on the structure, like the nature of disorder and the degree of interaction. Similarly, the lower value of n could be attributed to a higher rate of successful jumps and in turn culminate in high DC conductivity [19].

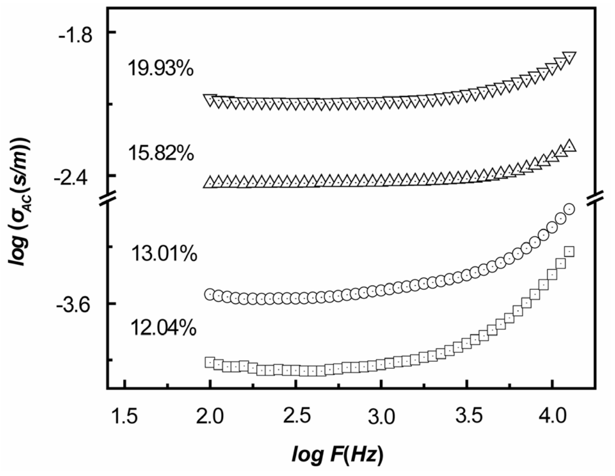

Figure 2. AC conductivity as a function of volume concentrations of CB loaded in EBA composite, at room temperature.

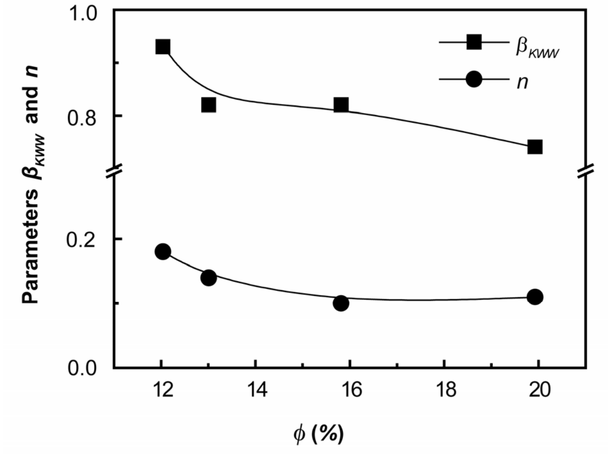

Figure 3. Electrical parameters, β_{KWW} (obtained from fitting by KWW function) and n (from the conductivity power law), as a function of volume concentrations of CB, at room temperature.

4.2. Temperature Dependence of Dielectric Modulus

The variation of real $M'(\omega)$ and imaginary $M''(\omega)$ parts of the electrical modulus as a function of frequency and temperature are shown in **Figures 4** and **5** respectively at 13.01% of CB fractions. $M'(\omega)$ shows a dispersion tending to M_∞ at higher frequencies for several temperatures, while the asymmetric $M''(\omega)$ is suggestive of the stretched exponential relaxation behavior. By using the relation $\beta_{\mathrm{KWW}} = 1.14/\mathrm{FWHM}$, the values of β_{KWW} are calculated.

In the aforementioned Jonsher's power law, **Figure 6** shows the variations of AC conductivity as a function of frequency at 13.01% of CB concentrations for different temperature and is used to calculate the values of exponents n. **Figure 7** shows the variations of the exponents β_{KWW} and n as a function of temperature for different volume concentrations of CB. From this figure, it appears that both β_{KWW} and n remain almost constant with increasing temperature. This behavior which can be explained by the fact that dielectric response does not significantly change, and we are in the presence of uncorrelated behavior of the free charge, that is, these materials retain a rigid structure [20] and ($0.73 \le \beta_{\mathrm{KWW}} \le 0.93$; $0.05 \le n \le 0.27$). In the present case, we can infer that the exponent β_{KWW} obeys the Ngai's relation [21] $\beta_{\mathrm{KWW}} = 1 - n$.

Figures 8 and **9** show the relationship between temperatures and peak frequency $\omega_{\max}$ as well as DC conductivity respectively. The straight lines through the data indicate that the system is in the thermally activated conduction mechanisms or the so-called Arrhenius behavior. This enables us to measure the activation energy for charges hopping rates, which are inversely propor-

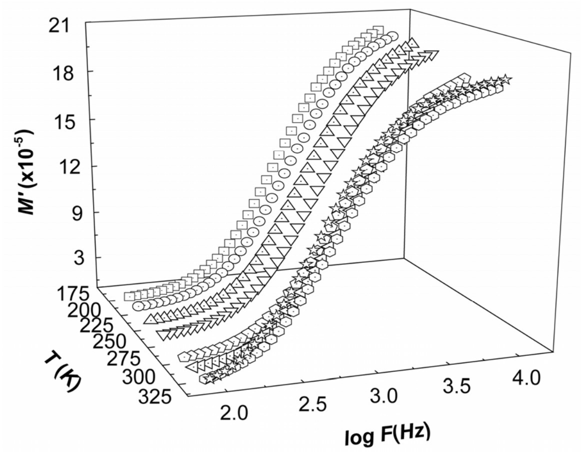

Figure 4. The variation of real part of the complex electric modulus, $M'(\omega)$, as a function of frequency and temperature, for 13.04%.

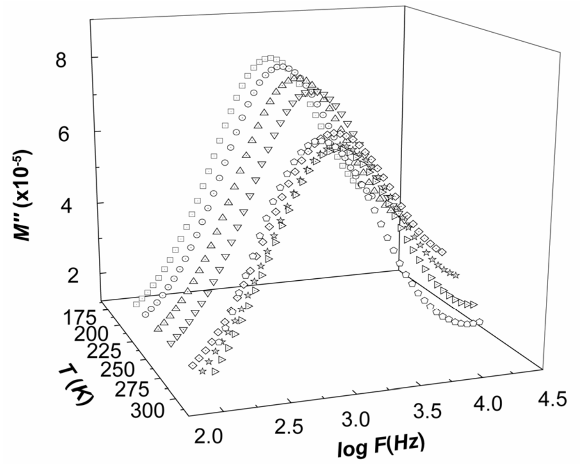

Figure 5. The variation of imaginary part of the complex electric modulus, $M''(\omega)$, as a function of frequency and temperature, for 13.04%.

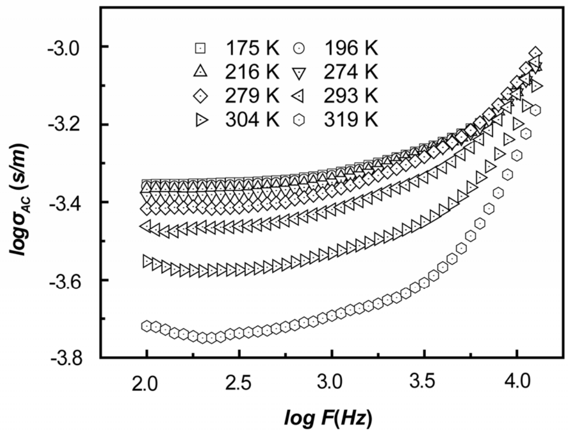

Figure 6. AC conductivity as a function of frequency for different temperature at 13.01% of CB loaded in EBA composite.

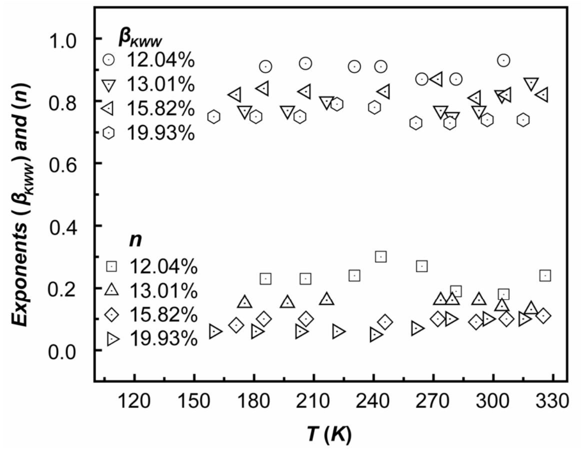

Figure 7. The temperature independence of the stretched exponent β_{KWW} obtained from fitting by KWW function and the exponent n from the conductivity power law.

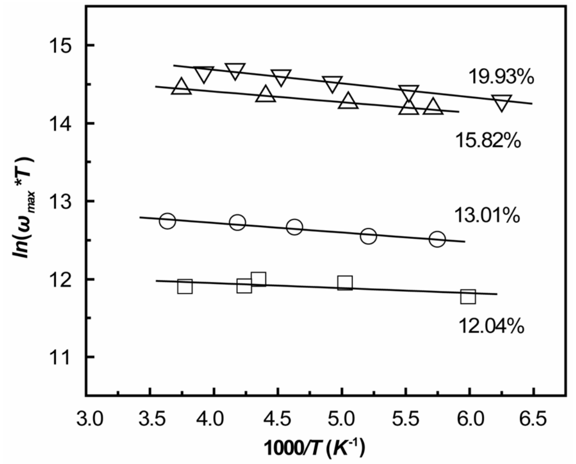

Figure 8. $\ln(\omega_{\max}\cdot T)$ versus $1000/T$ for the EBA/CB composites for different concentrations of CB with the best linear fittings.

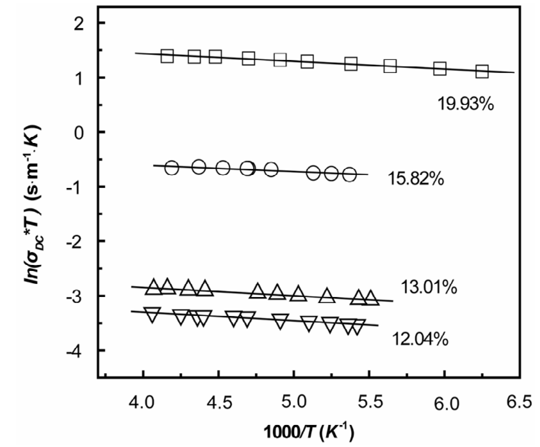

Figure 9. $\ln(\sigma_{DC}\cdot T)$ versus $1000/T$ for the EBA/CB composites for different concentrations of CB with the best linear fittings.

tional to the characteristic relaxation time $\omega_{\max}\tau = 1$ where $\omega_{\max} = 2\pi f_{\max}$, $f_{\max}$ is the peak frequency corresponding to maximum value of $M''(\omega)$. The activation energy for conduction, which was computed by using Arrhenius relation $\omega_{\max}\cdot T_\infty\ (-E_{am}/k_b T)$,was found to be in the range 10.5 - 14.9 meV when carbon is present inside the EBA polymer (see **Table 1**). We suggest that the absence of difference in the activation energy for the different investigated samples is an indication of the dynamically heterogeneous nature of CB aggregates within the polymer matrix. It is interesting to compare this results of the activation energy with those for the DC conductivity obtained by using the relation $\sigma_{DC}\cdot T_\infty\ (-E_a/k_b T)$ from **Figure 9**, which were found to be in the range 10.3 - 13.1 meV (see **Table 1**). We observe that the activation energies calculated by the two methods are almost the same and are insensitive to carbon black volume fraction, indicating that both methods are acceptable in manipulating the conduction mechanism. This result means that, when carbon is present inside the EBA polymer matrix, the conducting particles do not interact or interact weakly with the chain segments of the macromolecules in the copolymer. Furthermore, it helps to understand that there is a poor bond between the polymer matrix and the carbon black particles.

5. Conclusions

The complex electric modulus model and power law have been used to investigate the electrical conductivity in the charge conducting materials. The temperature dependencies of the observed modulus $M''(\omega)$ peak frequency $\omega_{\max}$ and DC conductivity follow the Arrhenius law. The activation energies of electrical conduction are nearly the same for both methods and their values do not change with the increase of CB fraction. The stretching exponent β_{KWW} representing the degree of interaction is found to be temperature-independent confirms that exponent n obtained by Jonscher's power law. This result can be explained by the fact the dielectric response does not significantly change with temperature.

Table 1. Values of the activation energy for different volume concentrations of CB obtained from the electric modulus and DC conductivity.

Φ (%)	***Electrical modulus***		***DC conductivity***	
	E_{am} **(mev)**	***Rco***	E_{ac} **(mev)**	***Rco***
12.04	11.9 ± 2.5	0.90	13.1 ± 0.7	0.98
13.01	10.5 ± 1.4	0.97	12.9 ± 0.6	0.99
15.82	11.7 ± 0.7	0.99	10.3 ± 1.4	0.94
19.93	14.9 ± 1.4	0.99	12.2 ± 0.4	0.99

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