The effective complex permittivity stability in filled polymer nanocomposites studied above the glass transition temperature

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Abstract. The temperature effect on the dielectric response of nanocomposite at low frequencies range is reported. The investigated samples are formed by a semi-crystalline ethylene-co-butyl acrylate (EBA) polymer filled with three concentrations of the dispersed conducting carbon black (CB) nanoparticles. The temperature dependence of the complex permittivity has been analyzed above the glass transition temperature of the neat polymer matrix $T_g = -75^\circ\text{C}$. For all CB concentrations, the dielectric spectra follow a same trend in frequency range 100-106Hz. More interestingly, the stability of the effective complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ with the temperature range of 10-70°C is explored. While the imaginary part of the complex permittivity $\varepsilon''$ exhibits a slight decrease with temperature, the real part $\varepsilon'$ shows a significant reduction especially for high loading samples. The observed dielectric response may be related to the breakup of the three-dimensional structure network formed by the aggregation of CB particles causing change at the interface EBA-CB. This interface is estimated by the volume fraction of constrained polymer chain according to loss tangent data of dynamic mechanical analysis.

1 Introduction

The addition of nanoparticles to a polymer matrix has received much attention over several decades\cite{1}. Nanoparticles offer improved mechanical, electrical and thermal properties of polymer systems \cite{2}. Due to their interesting dielectric properties, nanocomposite materials with polymeric matrix have a great potential for advanced application such as electromagnetic shielding materials, dielectric resonator antennas, capacitors, electro-active materials to cite a few\cite{3,4,5}. Challenge now is focused on increasing the polymer permittivity without compromising the other characteristics especially ease and quality of polymer processing. For example high permittivity values are needed for reducing the applied electric field to actuate electro-active materials for artificial muscle applications \cite{6} or for increasing the energy density of capacitors \cite{7}. Carbon Black (CB) nanoparticles filled elastomers are among the most commonly nanocomposite widely studied because lightweight, large area, low cost, high flexibility \cite{8}, and temperature requirements exist. In addition, the use of nanoscale high dielectric constant fillers make possible to manufacturing polymer thin films at thickness of the order of microns. This study aims at the understanding the temperature dependence of the effective complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ of ethylene-co-butyl acrylate copolymer (EBA) filled with spherical nanoparticles of CB. Three composite samples containing with fraction volume of CB varying from 6.8 to 19.9% have been examined. The direct current electrical conductivity $\sigma_{DC}$ versus temperature of this series of composites have been already reported by us elsewhere \cite{9}. From that study, it is found that $\sigma_{DC}$ shows a decreasing tendency as the temperature rises indicating a partial breakdown of the CB network in the host matrix.

In addition, the CB network restricts the motions of the polymer chains above the glass transition temperature of the polymer and consequently increase the thermal stability as is probed by thermogravimetric analysis tests. Here, attempt has made to investigate the stability of the
electrical properties under dynamic external filed as function of temperature in terms of the effective complex permittivity. Three selected composite samples EBA/CB were studied. The frequency of the applied field was taken between 100 and $10^7$ Hz for various temperatures in the range 10–70°C.

2 Experimental

2.1 Materials

The samples of EBA copolymer filled with acetylene carbon black used in this investigation were obtained from Borealis AB (Sweden)[9]. The butylacrylate monomer (EBA) contains butylester side groups, providing a certain polarity and a relatively low crystallinity (about 20% in volume). The glass temperature transition of the neat polymer matrix is $T_g = -75°C$ [10]. A three samples with nominal carbon black volume fraction has been studied.

2.2 Differential thermal analyzes (ATD)

The differential thermal analyzes (ATD) are carried out between temperatures of 20 to 180 °C. 20 mg of sample are placed in a platinum crucible. The acquisition takes place under ambient conditions and the heating rate is programmed at a rate of 10 °C/min.

2.3 Raman measurements

Raman spectra were collected at room temperature using Invia Reflex device (Renishaw). The laser line 514 nm was used. The scattered light was collected in backscattering configuration with a holographic grating (2400 lines/mm) to diffract the light on a CCD detector. The frequency range studied was 900-2000cm$^{-1}$.

2.4 Dielectric measurements

For the dielectric measurements, the samples were prepared as square and the electrical contacts were formed by sputtering gold-palladium of 100 nm thickness on the opposite sites of the sample. The measurements were carried out, in the frequency (F) range from 100 to $10^7$ Hz and temperature from 10 to 70°C using an Agilent 4294A Precision Impedance Analyzer. The permittivity may be a complex number quantity, in order to represent both stored energy and losses within the material. Under dynamic external fields, the permittivity $\varepsilon$ and conductivity $\sigma$ are related via equation:

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon' - i\left(\varepsilon''_d + \frac{\sigma}{2\pi F\varepsilon_0}\right)$$

The two terms forming the imaginary component represent polarization ($\varepsilon''_d$) and conduction ($\frac{\sigma}{2\pi F\varepsilon_0}$) losses that it is not possible, in practice to be measured separately. $\varepsilon_0 = 8.854 \times 10^{-12} F\ m^{-1}$ is the permittivity of vacuum.

3 Results and Discussion

The differential thermal analysis (DTA) for elastomer matrix filled with different CB volume fraction reported in Figure 1. The DTA curves show a small endothermic peak between 75°C and 98°C. Melting peak indicates the melting of crystals part on the composite. The peaks have become broader and lower with increasing the filler volume fraction indicating the effect of CB on the thermal stability of the matrix. This result agree with the data obtained from the thermogravimetric analysis (TGA) [9].

![Fig. 1. DTA curves of ethylene-co-butyl acrylate polymer filled with three volume fractions of carbon black: (a) 6.8%, (b) 15.8% and (c) 19.9% versus of temperature.](image)
We turn now to the main focus of our study and examine the temperature dependence of the effective complex permittivity. The obtained spectra exhibit high values of both parts of the complex permittivity in the range of frequency considered here indicating a best dispersion of CB into the EBA matrix. In this frequency range, the spectra variation is generally attributed to the interfacial polarization [12] that occurs in heterophase materials. Figure 3 represents the variation of real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the complex permittivity $\varepsilon$ versus the temperature for three CB volume fractions at two frequencies (a) of 10kHz and (b) 1MHz representative of capacitor or actuator applications. Three remarks can be addressed. Firstly, both $\varepsilon'$ and $\varepsilon''$ increase with increasing CB volume fractions. This trend is obvious since the density of CB/EBA interfaces increases by adding more CB amount. In fact, the attractive interactions between fillers and polymer result in a so-called constrained layer[13]. The volume fraction of constrained polymer chain $\nu_c$ can be estimated according to the dynamic mechanical analysis (DMA)[13]. The $\nu_c$ values that are 0.342, 0.375 and 0.422 are found to increases with the three CB concentrations 6.8, 15.8 and 19.9%. Secondly, we observe a slight decrease of the imaginary part $\varepsilon''$ with temperature for all composites samples as can be seen in Figures 3. This behavior agree with the result reported in the Ref 9 concerning the dc electrical conductivity versus temperature and is attributed to the thermal expansion coefficient (TEC) of the matrix which is larger than that of the CB [14,15]. Thermal expansion resulting from temperature increase causes greater separation between the CB particles and hence leading to a decrease of losses. However, the real part $\varepsilon'$ behaves differently with temperature. When the temperature exceeds 40°C a significant decrease is clearly observed especially for high loading samples. We suggest that TEC has more effect on the $\varepsilon'$ than that on $\varepsilon''$ and consequently reduces the energy stored in the composite material.

4 Conclusion
This paper probes the dielectric properties of nanocomposites formed by incorporating highly conductive carbon black particles in an insulating ethylene butylacrylate matrix. The effective complex permittivity stability in function of temperature is studied in a radio frequency range and above the glass transition temperature ($T_g$) of the polymer matrix. At the first time, both real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the complex permittivity are found to increase with the CB amount. The volume fraction of constrained polymer chain $V_c$ calculated from the DMA tests is used to explain the effect of the CB on dielectric response of the matrix. Secondly, the effect of the temperature on the complex permittivity exhibits a difference behavior between the real and imaginary parts of the permittivity. A small decrease is only observed for the imaginary part $\varepsilon''$ and it is attributed to the difference of the thermal expansion coefficient (TEC) of the matrix and CB particles. However, the real part $\varepsilon'$ of the complex permittivity is found to be more sensitive to temperature especially for high loading composite samples. More investigations are needed for a best understanding of the permittivity stability in particularly at wide temperature and high frequency ranges.

**Acknowledgments**

The authors and especially F. Elhaouzi thank CNRST-Morocco for the Excellence Scholarship.

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