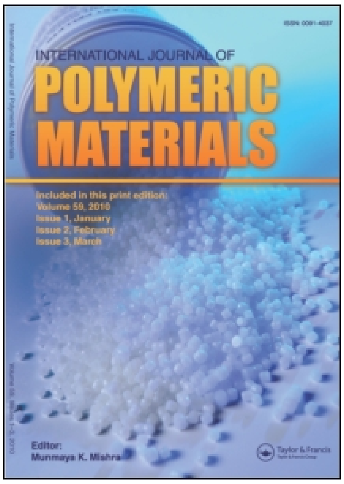

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A. E. Kotp[a]; M. T. Ahmed[a]
[a] Polymer Research Laboratory, Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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Dielectric and Electric Modulus of Poly(3-hydroxybutyrate) Semi-crystalline Polymer

A. E. Kotp and M. T. Ahmed
Polymer Research Laboratory, Physics Department, Faculty of Science,
Mansoura University, Mansoura, Egypt

We present results of dielectric investigation of poly(3-hydroxybutyrate) (PHB) semi-crystalline polymer. The data obtained are treated in the view of electric modulus formalisms in order to correlate the effects of the conductivity on the net dielectric relaxation phenomena. The results reveal that the conductive relaxation processes contribution in the low frequency region is much larger than in the high frequency region. At high temperatures (above the glass transition temperature), the electrical properties are strongly influenced by the space charge. Finally the plot of the complex electric modulus for a given temperature in Argand's plane shows that the conductive processes are reflected by an arc at low frequency which agrees with the model of Coelho.

Keywords: conductive processes, dielectric relaxation, electric modulus, PHB

INTRODUCTION

As a bacterially synthesized semi-rystalline polymer, poly(3-hydroxybutyrate), PHB, has attracted much research interest for its biodegradability and biocompatibility [1]. Dielectric spectroscopy (DS) is an important experimental technique to study the conformation and relaxation properties in polymers. Depending on the monomer structure, polymers can develop an amorphous or crystalline phase or both (i.e., semi-crystalline). These phases are different in response to the perturbation fields. In this general context, the understanding of the

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Address correspondence to M. T. Ahmed, King Saud University, Faculty of Science, Al-Kharj, P.O. Box 83, Al-Kharj, Saudi Arabia. E-mail: moustf_1@yahoo.com

molecular dynamics that govern these responses is of great importance. Dielectric spectroscopy (DS) allows one to study the two fundamental electrical characteristics of materials, capacitance and conductance, as a function of temperature, frequency and time. In the case of highly insulating polymers, below the glass transition temperature (T_g) the capacitive nature of the materials dominates their properties. But above this temperature the conductive nature prevails. Using dielectric spectroscopy (DS) the relaxed dielectric constant (ε') can be obtained, which is especially important to determine dipolar correlations as well as the dielectric strength of relaxation processes.

However, the measurements of the dielectric constant may in certain cases involve some difficulties due to the conductivity contribution to the dielectric loss (ε''), which, at low frequencies, may be much larger than the dipolar one. For this purpose, the electric modulus formalism is used to separate dipolar and conductive contribution to the glass-rubber relaxation. From the physical point of view, the electrical modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant. The electric modulus represents the real dielectric relaxation process.

In the present paper we report the dielectric relaxation studies in PHB semi-crystalline polymer regarding the temperature and frequency dependence of dielectric constant (ε') and dielectric loss (ε''). The scope is to analyze the dielectric properties in the view of the electric modulus formalism in order to correlate the effect of the conductivity on the net dielectric relaxation phenomena.

EXPERIMENTAL

Poly(3-hydroxybutyrate), PHB, was supplied by Aldrich Chemical Company, Milwaukee, USA. The sample was prepared for the dielectric measurement as a thin film between two circular copper disks (diameter = 2 cm) as electrodes. The studied materials were first melted at the melting temperature on one of the electrodes, then the spacers were added to the sample, and the other electrode was added. The whole system (i.e., the sample and the two electrodes) was then quenched to room temperature. The sample thickness was 2×10^{-2} mm and the electrode thickness was 2 mm each. Spacers were added to the samples in order to measure at the samples' melting temperatures. The spacers were thin rods made from silica, which has a very high melting temperature.

The dielectric system used is commercially available and supplied by NOVOCONTROL GmbH, Germany. The measurements lie in the range (10^{-3}–10^{7} Hz), which is called "broad band dielectric spectroscopy." The device is supported by a liquid nitrogen cryostat. The system used in measuring dielectric data is an Alpha dielectric material analyzer. It is controlled by a computer program. The measuring and controlling software is called "WinDETA." The controlling and measuring software were provided by NOVOCONTROL, GmbH, Germany.

The capacitance and conductance of the sample condenser were measured, using commercially available device supplied by NOVOCONTROL, GmbH, Germany, in the frequency range 10^{-3}–10^{7} Hz and the temperature range 113–650 K. The impedance measurements in this frequency range can be performed step by step. From the measurements of the complex impedance, the analyzer evaluates the capacitance and conductance values. The computer program records the capacitance and conductance data at different frequencies from the analyzer and calculates the dielectric permittivity ε' and dielectric absorption ε'' simultaneously.

The experimental error in the determination of the real part ε'' is mainly determined by the geometry of the sample thickness and diameter including the influence of the spacers. The absolute error occurrence for the real part ε' is estimated to about 1%.

Theoretical Background

The complex permittivity or permittivity plane plots are used to represent the response of dielectric systems [2]. The complex electric modulus [3–6] is the reciprocal of the permittivity and is given by the general formula $M^* = (\varepsilon^*)^{-1}$, which is related to the complex dielectric constant, ε^*, by the relation [7]:

$$M^* = \frac{1}{\varepsilon_0} = M' + M'' \tag{1}$$

For materials in which both conductivity relaxation and polarization relaxation (i.e., relaxation of permanent dipoles) occur, as in ionic conductors, the complex permittivity is given by:

$$\varepsilon^* = \varepsilon' + i\left(\varepsilon'' + \frac{\sigma_0}{w\varepsilon_0}\right) \tag{2}$$

where σ_0 is the frequency independent dc conductivity and ε_0 is the permittivity of free space. In this case, the imaginary component of the electric modulus (which is the quantity usually plotted) becomes

$$M'' = \frac{\varepsilon''}{\left(\varepsilon'^2 + \left(\varepsilon'' + \frac{\sigma_0}{w\varepsilon_0}\right)^2\right)} + \frac{\sigma_0}{w\varepsilon_0\left(\varepsilon'^2 + \left(\varepsilon''^2 + \frac{\sigma_0}{w\varepsilon_0}\right)^2\right)} \tag{3}$$

Equation (3) is a function of frequency and exhibits a maximum peak. The use of the electric modulus formalism arises from the fact that in the case of the conductive processes that are observed at low frequencies, the real part M′ exhibits a sharp monotonic increase, whereas the imaginary part of the electric modulus M″ shows a peak. This function is suitable to study the space charge relaxation phenomena, as they are reflected by the changes of this peak.

RESULTS AND DISCUSSION

Dielectric measurements were performed as a function of frequency at 15 different temperatures; the real (ε') and imaginary (ε'') parts of the complex dielectric constant relating to the PHB material are plotted in Figures 1 and 2. Generally, the dielectric loss spectra (ε'') curves in Figure 2 show relaxation processes which display fairly discrete

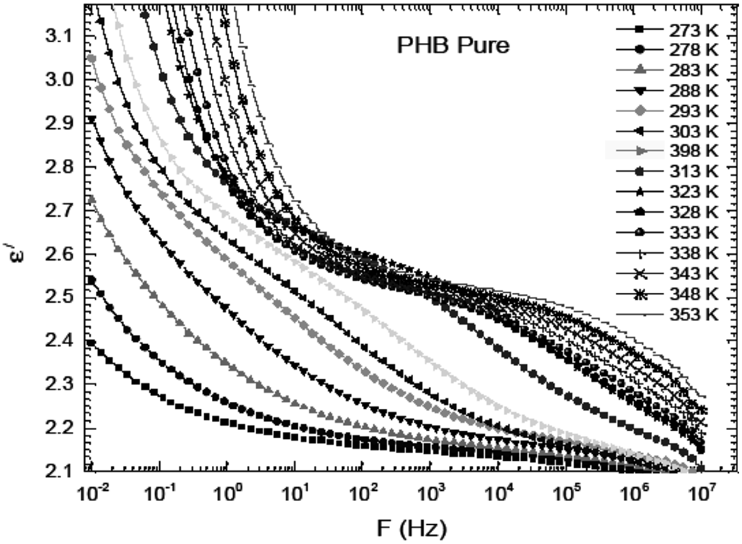

FIGURE 1 The dielectric constant (ε') for pure PHB measured at the temperature range 273–353 K and frequency range 10^{-2}–10^7 Hz.

regions of activity in frequency: the existence of broad relaxation peaks in the high frequency region ($\sim 10^2$–10^7 Hz), which are shifted towards lower frequencies as the temperature increases. The glass transition (α-process) caused by dipole orientation and observed in the frequency range (10^2–10^4 Hz) and relatively high temperature ($Tg + 25K$) reflects relatively slow long-range motion. Higher temperature (>300 K) relaxation processes are present as a result of charge accumulation in different interspaces. These processes are attributed to Maxwell-Wagner-Sillars (MWS) interfacial polarization [8]. Higher frequency (10^4–10^7 Hz) transitions might involve side group motions or conformational changes in side groups. These transitions are usually observed in the glassy state and correspond to low temperature transitions. Further, these transitions may occur because of the polymer confinement in the crystalline structure. Frequency dependence of loss permittivity below 10^3 Hz is a characteristic of ionic conduction.

Previous studies showed that an analysis of the electric modulus is useful to describe the conductivity relaxation behavior in polymers. In Figure 3, at low frequencies and at temperatures above the glass transition, a sharp monotonic increase in the real part (M′) of the electric modulus is observes which is attributed to the conductive processes in

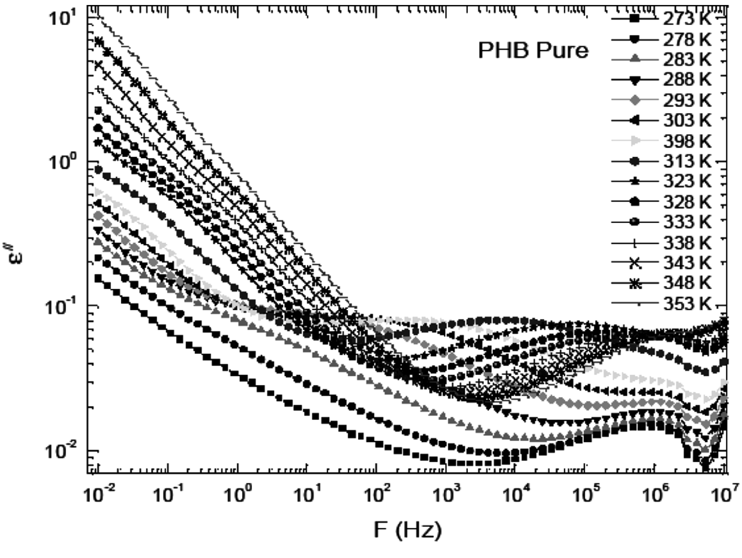

FIGURE 2 The dielectric loss (ε'') of pure PHB measured at the temperature range 273–353 K and frequency range 10^{-2}–10^7 Hz.

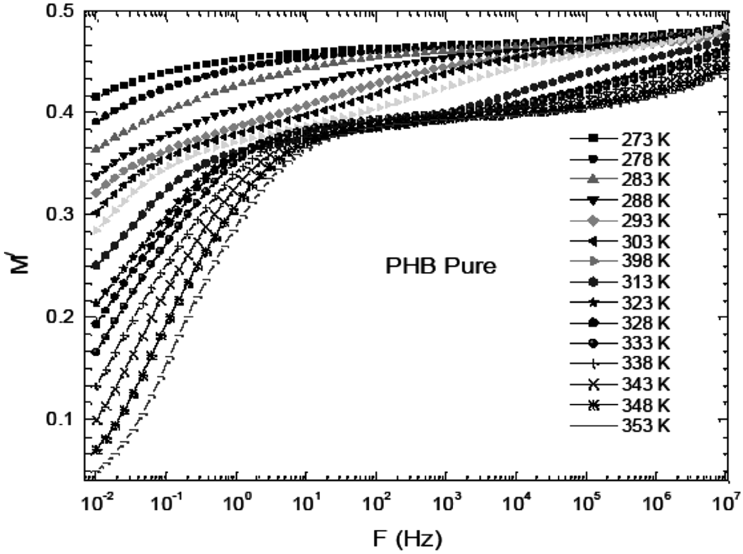

FIGURE 3 The real part of the electric modulus (M′) for pure PHB measured at the temperature range 273–353 K and frequency range 10^{-2}–10^{7} Hz.

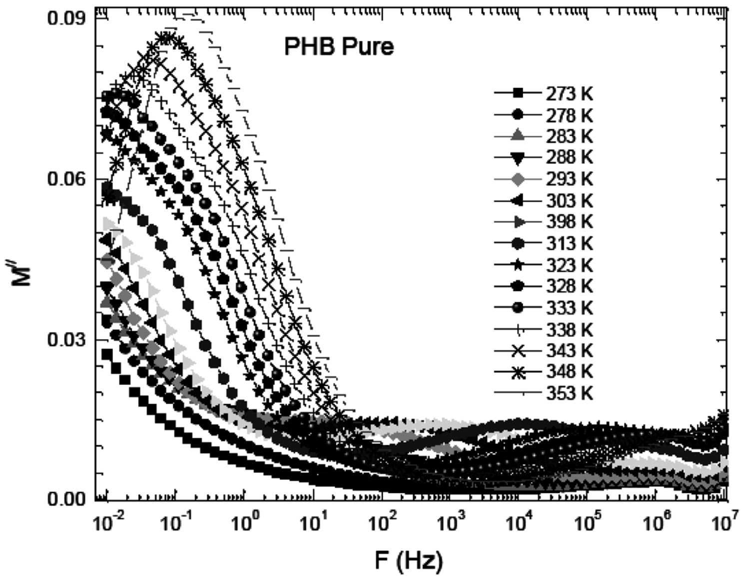

FIGURE 4 The imaginary part of the electric modulus (M″) for pure PHB measured at the temperature range 273–353 K and frequency range 10^{-2}–10^{7} Hz.

PHB. In Figure 4, we have plotted the imaginary part M″ of the electric modulus as a function of frequency which shows a peak at low frequency region (10^{-2}–10^{2} Hz). The results obtained in the temperature range studied (273–353 K) indicate that this peak is shifted to higher frequencies with temperature increase. This peak arises from the contribution of conductive processes (see Figure 4, M″ vs. frequency).

In the literature about ionic solids, conductivity based on ionic movement is classified into two different processes [9,10]. Dc conductivity is a result of a continuous hopping process over extended distances. Ac conductivity does not demand a percolation path through the sample and is thought to result from reversible ion movement over limited space. Both processes are thermally activated following the Arrhenius law.

The plot of the complex electric modulus for a given temperature in Argand's plane in Figure 5 shows that the conductive processes are reflected by an arc at low frequency which agrees with the model of Coelho [11] which predicts an arc for the contribution of space charge relaxation, that in the case of blocked electrodes approximates a semicircle.

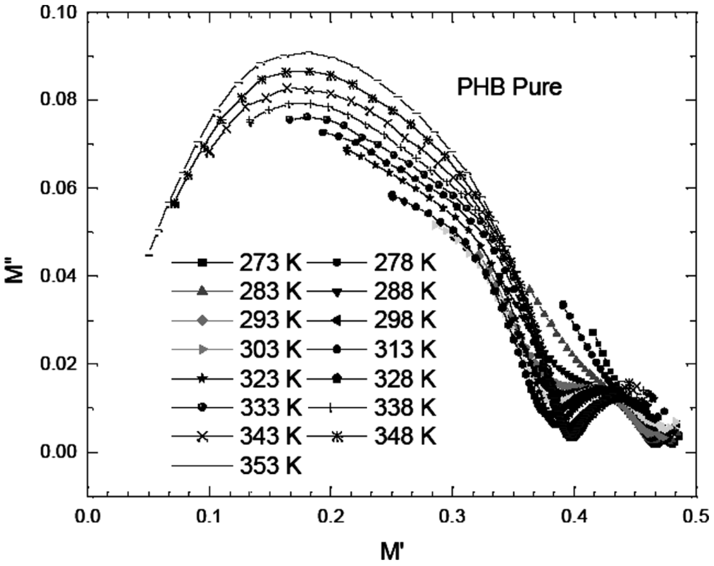

FIGURE 5 The plot of the complex electric modulus for a given temperature in Argand's plane for pure PHB measured at the temperature range 273–353 K and frequency range 10^{-2}–10^{7} Hz.

CONCLUSION

Electric modulus analysis of the dielectric data obtained for the PHB polymer reveals that at high temperatures (i.e., above the glass transition temperature), the electrical properties are strongly influenced by space charge. The plot of the complex electric modulus for a given temperature in Argand's plane shows that the conductive processes are reflected by an arc at low frequency which agrees with the model of Coelho which predicts an arc for the contribution of space charge relaxation, that in the case of blocked electrodes approximates a semicircle.

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