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Simplex-TSDC spectroscopy: An efficient tool to measure the relaxation time of the isothermal transient depolarization current in organic dielectrics

Halima Benchenane-Mehor [a,b,*], Manil M. Soufi [c], Jean-Marc Saiter [c], Mohamed Benzohra [c]

[a] *Laboratoire CaSiCCE, Département de Génie Electrique, ENSET-Oran, B.P. 1523, El M'Naouer, 31000 Oran, Algerie*
[b] *Laboratoire de Microphysique et de Nanophysique (LaMiN), Département de Physique-Chimie, ENSET-Oran, B.P. 1523 EL M'Naouer, 31000 Oran, Algerie*
[c] *Laboratoire LECAP-AMME, EA 4528, Université de Rouen, Faculté des Sciences, Avenue de l'Université BP 12, 76801 Saint Etienne du Rouvray, France*

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ABSTRACT

The temporal technique analysis by a simplex optimization method of isothermal transient depolarization current measurements (Simplex-TSDC) is presented for the study of the glass transition domain of different polymers. The advantage of the present method compared to the classical TSDC is that it gives direct results comparable to the experiment and allows a good estimate of the relaxation time close to the glass transition temperature in dielectric thin films. The present method also allows a direct determination of two relaxation times corresponding to a fast and a slow dynamics; and then confirms the heterogeneous character of the molecular relaxation dynamics.

1. Introduction

Polymers are now able to provide relevant solutions for the realization of sensors of high specificity and sensitivity [1,2]. They are also requested to accompany the increasing development of microsystems, as they become embedded in silicon microtechnologies. Polymers are widely used in several fields as optical waveguides, diodes and transistors [3–5].

The description of the structural relaxation mechanisms occurring in the vicinity of the glass transition in polymer materials is one of major challenges for the understanding of the amorphous state and its properties. The glass transition domain is often defined as the range temperature where the material changes from the liquid state to the glassy one. The glass transition temperature T_g remains to this day a very difficult parameter to predict.

Even if this transition is associated to important changes in thermodynamic properties (as heat capacity), it is not a true thermodynamic phase transition and must be seen as a kinetic event [6,7]. In fact, T_g depends on many factors, particularly the thermal history of the sample: the cooling rate (q_c) used during the vitrification process [8], the heating rate (q_h) [9,10], the glass age [11] and the glass-forming liquid structural characteristics [12].

Below T_g value, the vitreous state is reached. It is a non-equilibrium thermodynamic system; in fact, the volume occupied by molecules is larger than expected under the equilibrium conditions. Thus, this system will seek to move towards equilibrium state through a structural relaxation which does not affect the chemical characteristics; this phenomenon is known as physical ageing [13]. The study of this molecular relaxation is based on the determination of an important parameter: the characteristic relaxation time.

The study of relaxation phenomena is of great importance in the field of polymer research. For this purpose, several analysis techniques are used among which the thermostimulated depolarization current (TSDC) spectroscopy is one. Developed in 1966 by Bucci et al. [14], the TSDC technique [15–18] is a method to study the molecular movements associated with the relaxation phenomena in polymeric materials [19], solids [20], metal oxides [21], crystals [22], dielectrics [23] and so on. It is a highly sensitive technique for measuring changes in dipole orientation in the material under study [24].

This experimental method was successfully used to analyze both the main and the secondary relaxation processes. At the glass transition temperature T_g, the main relaxation (α-relaxation) process corresponds to the global cooperative movements (simultaneous jumps of several constituent units) of the polymeric chains. The secondary transitions corresponding to the

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* Corresponding author at: Laboratoire CaSiCCE, Département de Physique-Chimie, ENSET-Oran, B.P. 1523, El M'Naouer, 31000 Oran, Algerie.
E-mail address: halima_mehor_2000@yahoo.fr (H. Benchenane-Mehor).

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mobility of side groups (β-relaxation) or to the rotation of end groups (γ-relaxation) occur at relatively lower temperatures [25].

The data of TSDC spectroscopy are typically obtained by the standard experimental protocols leading to well-known spectra, complex spectra and elementary spectra. This technique allows to get the characteristic relaxation time in the glassy state [26,27].

The analysis of the TSDC spectra in polymers requires the introduction of a distribution of relaxation times. The relaxation process, when observed experimentally, is described by the relaxation function, $\varphi(t)$, in the time domain, and the response function, $\varphi^*(w)$, in the frequency domain. These functions are related by Fourier transformation as [28]:

$$\varphi^*(w) = FT\left(\frac{-d}{dt}\varphi(t)\right) \tag{1}$$

$$\varphi(t) = -\int FT^{-1}[\varphi^*(w)]dt \tag{2}$$

where FT and FT^{-1} denote the Fourier transform and its inverse, respectively.

For a simple process with a unique relaxation time, which is often referred to as a Maxwell–Debye relaxation [29,30], we have:

$$\varphi(t) = \varphi_0 exp[-(t/\tau)] \tag{3}$$

where $\varphi(t) = \int_t^\infty I\,dt$; φ_0 is the value of the initially stored charge, τ is the characteristic relaxation time, and I is the depolarization current.

In many systems, however, the dynamical behavior shows pronounced deviations from the ideal exponential pattern. The relaxation function in the time domain are often described in terms of the Kohlrausch–Williams–Watts (KWW) or stretched exponential function [31,32] given by:

$$\varphi(t) = \varphi_0 exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right] \tag{4}$$

where β_{KWW} is a stretching parameter, whose magnitude can vary from 0 to 1 (the value $\beta_{KWW}=1$ corresponds to the Debye model).

The original Kohlrausch–Williams–Watts function (see Eq. 4), whose failure is widely reported [33], has recently been modified [34] to eliminate some unphysical aspects and in order to account for nonexponentiality, Viciosa et al. [34] proposed a modified Kohlrausch decay function where the Debye relaxation time needs to be multiplied by a factor which contains always the β_{KWW} parameter.

On the other hand, previous works which investigated the relation between the relaxation mechanisms and the physical ageing phenomenon have revealed the existence of two large peaks of relaxation showing clearly the presence of at least two different kinetic mechanisms [35]. The presence of two ageing kinetic mechanisms: one fast and another slow is also confirmed by the random walk model proposed by Arkhipov [36,37] and was used in other works [38] to describe the glass former liquid behavior in a temperature domain close to T_g value.

In the present work, the simplex method fitting in the temporal analysis [39] of the isothermal transient depolarization current measurement using TSDC transient experimental protocol [40] is applied for the study of different polymers. The present method will be designated by the term "simplex-TSDC" spectroscopy in the whole paper. Our aim is to show that using it, not only the relaxation time is rigorously calculated but the two kinetic mechanisms are determined in a natural way. We claim also that this method is well suited for all organic dielectrics.

2. Experimental

The measurements were performed first on an amorphous Polyethylene Terephthalate (PET) provided as a film (Eastman Kodapak E.K. 7352) with a thickness of 0.625 mm. Amorphous Polyethylene Terephthalate glycol (PETg) samples were obtained from Eastman Chemical Company (KODAR PETG 6763). Poly L-Lactique Acide (PLLA) samples were obtained from Cargill Dow Company in amorphous forms. Bisphenol A Polycarbonate (PC) samples were supplied by General Electrics. The polymer grade used is LEXAN 141. Before moulding, PC pellets were dried at 110 °C for 5 to 10 h. PC samples were moulded at 250 °C to obtain 1 mm thick sheets.

The Differential Scanning Calorimetry (DSC) measurements were performed on a Thermal Analysis Instruments heat flow calorimeter DSC Q100. The DSC apparatus was calibrated in temperature and energy using the melting of an Indium sample. All experiments were carried out under a nitrogen atmosphere. For each sample, the DSC experiments were performed with a cooling rate q_c equal to the heating rate $q_h = 10\ \mathrm{K\ min}^{-1}$. This DSC measurement was used to determine the glass transition temperature T_g. The glass transition is characterized by an obviously endothermic event on the curve, and the value of the glass transition temperature T_g was determined using the mid-point of this endothermic step. We found $T_g = 76$ °C for PET and PETg, $T_g = 59$ °C for PLLA and $T_g = 143$ °C for PC.

The TSDC spectroscopy experiment [41] was performed at the Laboratory of Characterization of the Amorphous Polymers at the University of Rouen. The depolarization current was measured with a pico-electrometer system "Keithley System Electrometer 6514", whose maximum sensitivity is around 10^{-15} A. Variations of this current are instantaneously registered by a computer coupled to the pico-electrometer.

3. Presentation of the TSDC protocols

3.1. Standard TSDC spectroscopy

Classically, relaxation processes are described in terms of an exponential function which is often referred to as Maxwell–Debye relaxation (Eq. 3) [29,30]. The current density measured during the TSDC experiment can be written as a function of temperature:

$$J(T) = \frac{I(T)}{A} = -\frac{d\varphi(T)}{dt} = -q\frac{d\varphi(T)}{dT} \tag{5}$$

Where $I(T)$ is the depolarization current at temperature T, A is the surface area of the sample and $q = dT/dt$ is the constant heating rate. The depolarization at a given temperature is:

$$\varphi_d(T) = -\frac{1}{A\,q}\int_{T_0}^{T} I(T')\,dT' \tag{6}$$

T_0 is the temperature at which the depolarization current peak starts to appear, and the remaining polarization at temperature T is given by:

$$\varphi(T) = \frac{1}{A\,q}\int_{T}^{T_\infty} I(T')\,dT' \tag{7}$$

where T_∞ is the infinite temperature, i.e.; T_∞ is the temperature at which the considered transition considered is achieved (in this case the temperature where the current above the peak reaches practically nil value). The exponential function (Eq. 3) fulfills the relaxation time equation:

$$\tau_{Debye}(T) = -\frac{\varphi(T)}{d\varphi(T)/dt} = -\frac{1}{q}\,\frac{\varphi(T)}{d\varphi(T)/dT} \tag{8}$$