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Sublinear dispersive conductivity in polymethyl methacrylate at temperatures above the glass transition

M. Mudarra[a,*,1], R. Díaz-Calleja[b], J. Belana[a,1], J.C. Cañadas[a,1], J.A. Diego[a,1], J. Sellarès[a,1], M.J. Sanchis[b]

[a]Department Física i Enginyeria Nuclear, Universitat Politecnica de Catalunya, Campus de la UPC en Terrassa C. Colon, 11 Terrassa 08222 Barcelona, Spain
[b]Department de Termodinàmica Aplicada, UPV Camí de Vera s/n, València 46020, Spain

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Abstract

Dynamic electrical analysis shows that conductivity conditions the electrical properties of a polymer at high temperatures and low frequencies. In this paper we show the possibilities of the electric modulus formalism to study the properties of carrier transport and space charge relaxation processes in polymethyl methacrylate. Asymmetric Argand's plots are observed in the temperature range between 150 and 210 °C. This asymmetry is related to power-law dependencies in the real part of the conductivity, of the form ω^n with $n < 1$, as a result of correlated ion hopping. The complex part of the electric modulus exhibits a peak in the low frequency range that can be associated with these conductive processes. In the case of the relaxation time related to conductive processes, it has been observed that Maxwell time is higher than the characteristic time associated with the crossover frequency which determines the transition from dc to ac regime. This fact is explained by the presence of deep traps. Finally, a maximum in the value of n is observed between 180 and 190 °C which may be related to coupling between charge transport and chain segment motions.

Keywords: Dynamic response; Polymethyl methacrylate; Space charge

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Dielectric electrical analysis (DEA) provides an excellent mean to characterize the electrical properties of a polymeric material. This technique is based on the measurement of the material response to an applied alternating voltage. DEA allows one to study the two fundamental electrical characteristics of a material, capacitance and conductance, as a function of temperature, frequency and time. In the case of a highly insulating polymer, the capacitive nature of the material conditions its electrical properties below the glass transition temperature. Above this temperature, the conductive processes prevail. In the case of poly(methyl methacrylate) (PMMA), this effect was studied by measurements of its conductivity at high temperatures by different methods [1,2]. The conductive processes in DEA measurements result in a sharp increase in the loss factor of the material that can be observed at high temperatures and low frequencies.

Several papers that describe the electrical properties of PMMA can be found in the literature, and recently an increasing interest on its properties has arisen due to the use of this material as host polymer in guest–host polymeric systems for non-linear optics [3,4].

The electrical properties of PMMA at temperatures above the glass transition are conditioned by space charge, as studies by thermally stimulated depolarization currents (TSDC) indicate [5–12]. In the case of most polymers, the relaxation of space charge in TSDC studies is associated with a peak, ρ, that appears at temperatures above the glass transition. The study of this peak results in information about the charge trapping properties of a material. The use of the windowing polarization technique [13–19] allows one to study, at least qualitatively, the trapping level distribution in the material, which has a maximum at approximately 2.35 eV in the case of PMMA [10–12]. This peak was studied by means of the general order kinetic

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[*] Corresponding author. Tel.: +34-937-398-139; fax: +34-937-398-000.
E-mail address: miguel.mudarra@upc.es (M. Mudarra).

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model [10–12,20], that provides information about the relaxation mechanism for space charge. It was concluded that recombination was the most likely relaxation mechanism [10].

A combination of TSDC and a probe technique has been used to determine the potential profile below the glass transition [21]. The potential profile obtained allows one to determine the current–voltage characteristics, which reveal a sub-ohmic character ($J = gV^n$, where $n < 1$ and $g = \text{constant}$). The nature of the electric carriers in this material is not clear still, but D.B. Watson assumes that anionic injection conditions its electric properties at high temperatures [22]. The role of the electrodes has been discussed in previous papers by means of the combination of TSDC and charge profile determination [23]. Dynamic electrical analysis measurements, which were analyzed in terms of Macdonald–Coelho model, have also been used to study the role of electrode [24–26].

In a previous paper, it was observed that Argand's plot of electric modulus at temperatures above the glass transition resulted in a depressed arc for the low frequency range [26]. This behavior can be related to a sublinear dispersive conductivity of the form:

$$\sigma(\omega) = \sigma_0 + A\omega^n \tag{1}$$

where σ_0 is the dc conductivity, A is a temperature dependent parameter and n is a fractional exponent which ranges between 0 and 1 and has been interpreted by means of many body interactions among charge carriers. This behavior, termed universal dynamic response, has been observed in highly disordered materials like ionically conducting glasses, polymers, amorphous semiconductors and also in doped crystalline solids [27–32]. Eq. (1) can be derived from the 'universal' dielectric response function for the dielectric loss of materials with free hopping carriers, and this derivation allows one to understand the temperature dependence of parameter A [33].

Power-law dependencies of conductivity, as in the case of Eq. (1), imply a power-law dependence of the form $(\mathrm{j}\omega)^n$ for the complex conductivity [31]. Therefore, this magnitude can be written as:

$$\sigma^*(\omega) = \sigma_0 + A(\mathrm{j}\omega)^n + \mathrm{j}\omega\varepsilon_0\varepsilon_\infty \tag{2}$$

A crossover frequency ω_p can be defined as $\omega_p^n = \sigma_0/A$, so that Eq. (2) can be rewritten as

$$\sigma^*(\omega) = \sigma_0 + \sigma_0\left(\mathrm{j}\frac{\omega}{\omega_p}\right)^n + \mathrm{j}\omega\varepsilon_0\varepsilon_\infty \tag{3}$$

This frequency ω_p is associated with the crossover from the power-law dependence observed at high frequency to a frequency independent dc regime that occurs at low frequencies. The real and imaginary parts of the conductivity are respectively:

$$\sigma'(\omega) = \sigma_0 + \sigma_0\cos\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n \tag{4}$$

$$\sigma''(\omega) = \sigma_0\sin\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n + \omega\varepsilon_0\varepsilon_\infty \tag{5}$$

and, finally, the real and imaginary parts of the electric modulus become:

$$M'(\omega) = \frac{\omega\varepsilon_0\left(\sigma_0\sin\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n + \omega\varepsilon_0\varepsilon_\infty\right)}{\left(\sigma_0 + \sigma_0\cos\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n\right)^2 + \left(\sigma_0\sin\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n + \omega\varepsilon_0\varepsilon_\infty\right)^2} \tag{6}$$

$$M''(\omega) = \frac{\omega\varepsilon_0\left(\sigma_0 + \sigma_0\cos\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n\right)}{\left(\sigma_0 + \sigma_0\cos\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n\right)^2 + \left(\sigma_0\sin\left(n\frac{\pi}{2}\right)\left(\frac{\omega}{\omega_p}\right)^n + \omega\varepsilon_0\varepsilon_\infty\right)^2} \tag{7}$$

Our aim in this paper is to study the conduction processes in PMMA at temperatures above the glass transition by means of DEA measurements at the electrical modulus level. An example of comparison between electrical modulus and permittivity formalism study in the case of a high insulating polymer can be found in Neagu et al. [34]. The electrical modulus $M(t)$ is proportional to the decay of the electric field $E(t)$ under the condition of a time invariant displacement $D(t) = D_0$. An experimental analysis based in time–domain measurements of the electric modulus [35] results in an alternative method to frequency–domain studies, commonly found in the literature.

1. Experimental

Samples of PMMA were cut from commercial sheets of 1.5 mm thickness (Altuglas®, provided by Atoglas). The molar mass is around 3 g/mol with a polydispersity around 2.5, measured by means of size exclusion chromatography calibrated with PMMA standard. The samples were coated with aluminum electrodes of 2 cm diameter on both sides by vaporization in vacuum. DSC measurements indicate that the glass transition temperature, T_g, is approximately 115 °C.

The experimental setup for DEA measurements has been described in a previous paper [36]. The real and imaginary parts of the electrical permittivity were measured at several frequencies in isothermal steps of 10 °C each.

The imaginary part of the electric modulus was calculated from the permittivity and then $M''(\omega)$ was fitted to the imaginary part of the electric modulus given by Eq. (7). In this work we have used simulated annealing to carry out the fitting process. This method has been used successfully in the analysis of thermally stimulated depolarization currents [37,38] and dielectric spectroscopy data [39]. Four independent parameters were used in the fitting process: σ_0, ω_0, n and ε_∞. The maximum likelihood criterion was used to determine the figure of merit. The procedures used for data fitting are based on routines described by others authors [40].

2. Results

In Fig. 1 we have plotted the peak that is associated with the conductive process in PMMA for several temperatures above its glass transition. It can be noted that the peak shifts to higher frequencies with the temperature. To study the charge transport process at these temperatures we have assumed a sublinear frequency dispersive ac conductivity. Electric modulus versus frequency data have been fitted to Eq. (7). The fitting method is described in Section 1 and the values of the parameters obtained are shown in Table 1. A good agreement between experimental and calculated data (symbols and continuous line respectively) has been obtained, as it can be seen in Fig. 1. The values of the unrelaxed permittivity (ε_∞) obtained by curve fitting decrease smoothly with the temperature from approximately 4.5 at 150 °C to 4.0 at 220 °C. In a corrected modulus formalism proposed by Macdonald [41] in order to solve some problems that arise in the scaling properties of the electric modulus formalism [42], this parameter is expected to arise from the contribution of both the underlying bulk material (nonionic dipolar and electronic polarization) and from mobile charge carriers effects. We have assumed that in the case of PMMA charge carrier inertial effects may decrease with the temperature due the increase of their mobility [26]. For this reason, we attribute the decrease observed in ε_∞ to the decrease of the contribution of dipolar-like motion of charge carriers that are located in potential wells without long-range hopping.

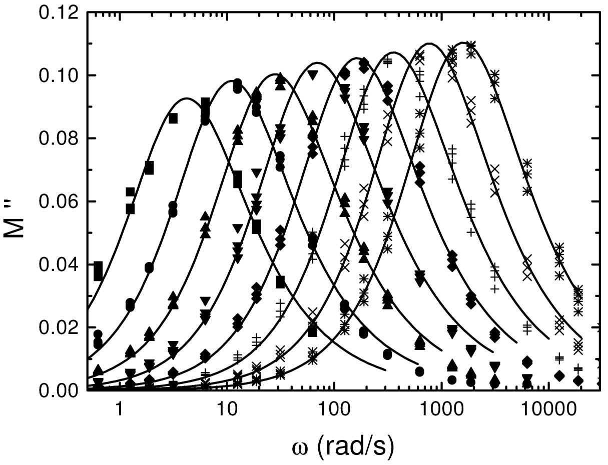

Fig. 1. Imaginary part of the electric modulus of PMMA as a function of the frequency. Temperatures: (■) 150 °C; (●) 160 °C; (▲) 170 °C; (▼) 180 °C; (◆) 190 °C; (+) 200 °C; (×) 210 °C; (∗) 220 °C.

Table 1

Parameters obtained by means of fitting the data of Fig. 1 to Eq. (7)

T (°C)	n	ω_p (s^{-1})	ε_∞	σ_0 (Ω^{-1} cm^{-1})
150	0.208	4.55	4.52	7.64×10^{-11}
160	0.204	14.7	4.20	1.91×10^{-10}
170	0.223	24.9	4.20	4.60×10^{-10}
180	0.238	56.2	4.04	1.08×10^{-9}
190	0.226	129	4.03	2.54×10^{-9}
200	0.221	264	4.00	5.49×10^{-9}
210	0.203	593	3.94	1.19×10^{-8}
220	0.202	1201	3.94	2.45×10^{-8}

The dc conductivity of this material (σ_0) increases with the temperature as it can be seen in Table 1. An Arrhenius plot shows that the conductivity is thermally activated (Fig. 2). This increase has been attributed to an increase of carrier mobility as the carriers concentration does not vary in the temperature range considered [43].

Concerning the relaxation time, it has been proposed that the crossover frequency can be associated with a characteristic time τ_p by means of $\tau_p = 1/\omega_p$, and experimental evidence has been given [31] to support the idea that this characteristic time is actually the same time than an average relaxation time $\langle\tau\rangle$, which can be defined in terms of the area under the Kohlrausch–Williams–Watts (KWW) function $\Phi(t)$:

$$\langle\tau\rangle = \int_0^\infty \Phi(t)\mathrm{d}t = \frac{\Gamma(1/\beta)\tau^*}{\beta} \tag{8}$$

where τ^* is the relaxation time of KWW function

$$\Phi(t) = \exp[-(t/\tau^*)^\beta] \tag{9}$$

and $\Gamma(\ )$ is Euler gamma function.

This average relaxation time $\langle\tau\rangle$ is related to the DC

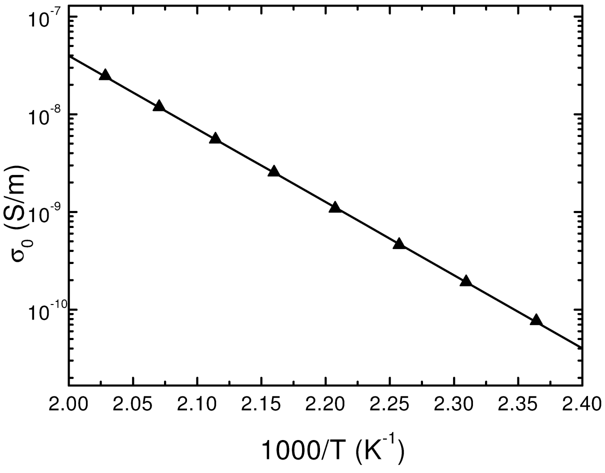

Fig. 2. Arrhenius plot of PMMA dc conductivity σ_0.

conductivity according to the expression

$$\langle\tau\rangle = \frac{\varepsilon_0\varepsilon_\infty}{\sigma_0} \tag{10}$$

We have calculated the values of $\langle\tau\rangle$ and τ_p. An attempt to compare both magnitudes in an Arrhenius plot can be seen in Fig. 3. Both magnitudes represent a thermally activated relaxation time of the form

$$\tau = \tau_0\exp(E/kT) \tag{11}$$

but do not represent the same property, as their activation energies and pre-exponential factors are different, as it can be seen in Table 2. The agreement between these values was used by León et al. to support the hypothesis of a common origin for both dc and ac regimes [31].

We think that the differences that we have obtained between the kinetic parameters of both characteristic times do not presuppose evidence against such common origin. In the case of macromolecular materials, the microscopic processes that lead to ionic conduction may not be reduced to mere hops over a barrier between adjacent sites. Amorphous polymers, such as PMMA, are disordered materials and deep traps, which play a relevant role in microscopic charge relaxation processes, may be present in them. The mechanism that leads to dc conduction regime consists of long range displacements of ions. At higher frequencies, short range ion hopping is viewed as a correlated motion in which an ion performs several reiterated forward–backward hops before completing any successful forward displacement. Reiterative hopping is the origin of the dispersive regime and it occurs until the crossover frequency. For lower frequencies successful hops can be completed [29].

If one assumes that the only process that contributes to ionic conduction is hopping, the crossover frequency can be associated with the frequency below which ions can follow the variations of the applied field, so that their characteristic relaxation time is shorter than the inverse of the applied field frequency. At such frequencies, dc conductivity determines the relaxation process, therefore Maxwell time determines the crossover frequency. If deep traps are present, deeply trapped ions have a longer relaxation time, so that their contribution should be evident at frequencies below the crossover frequency and their effect should represent a slowing down of space charge relaxation process. On the other hand, ions located in deep traps can not follow the field oscillations at higher frequencies and they do not contribute to the relaxation process at such frequencies. As a consequence, the presence of deep traps can be associated with a slowing down of the relaxation process that results in an apparent Maxwell time longer than the relaxation time that corresponds to the crossover frequency. The higher value of $\langle\tau\rangle$ and its higher activation energy observed can thus be explained by the presence of such traps.

Table 2
Pre-exponential factors and activation energies of conductivity (σ) and relaxation times ($\langle\tau\rangle$ and τ_p), obtained from the corresponding Arrhenius plots

Magnitude	Pre-exponential factor	Activation energy (eV)
σ	$3.72\times10^{7}\ \Omega^{-1}\ \mathrm{m}^{-1}$	1.48
$\langle\tau\rangle$	4.45×10^{-19} s	1.52
τ_p	4.26×10^{-18} s	1.40

The temperature dependence of the parameter n is shown in Fig. 4. This parameter characterizes the power-law conduction regime, which is associated with the slowing down of the relaxation process in the frequency domain as a result of cooperative effects, in the same way as the KWW function does in the time domain. An important connection between these two approaches stems from the coupling model of Ngai and Kannert [44,45]. This model predicts a power-law conductivity associated with the KWW relaxation function (Eq. (9)) given by

$$\sigma_{\mathrm{KWW}} = B\exp(-E_{\mathrm{a}}/kT)\omega^{1-\beta} \tag{12}$$

Therefore, if any other contribution is sufficiently smaller than that of σ_{KWW}, then the conductivity of the material may

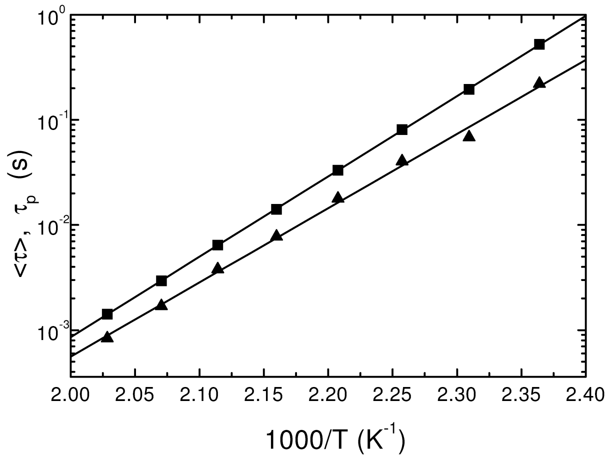

Fig. 3. Arrhenius plot of relaxation time: (■) Maxwell relaxation time $\langle\tau\rangle$; (▲) $\tau_p = 1/\omega_p$.

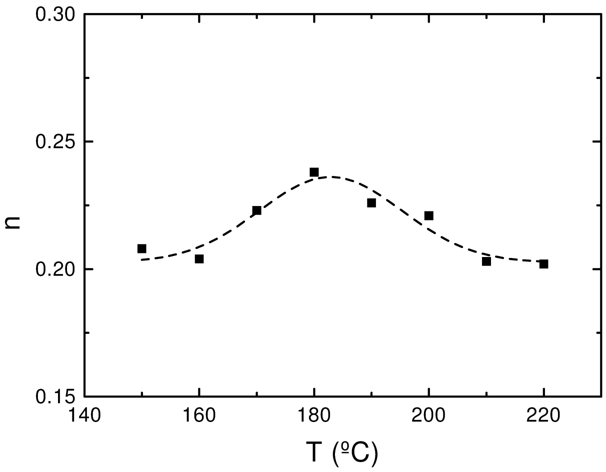

Fig. 4. Powerlaw exponent n as a function of the temperature.

be described by $\sigma(\omega)_{\mathrm{KWW}}$ [45]. The sublinear dispersive ac conductivity observed in polyetherimide can be associated with a KWW relaxation mechanism with $\beta = 1 - n$ where n is the power-law exponent determined from $\sigma(\omega)$.

The stretched exponential parameter β may represent a correlation index of ionic motion, as the stretched exponential relaxation time has been associated with as slowing of the relaxation process that results from correlated ion hopping. For this reason, one would expect β to be close to zero for strongly correlated systems and close to 1 for random Debye-like hops. As we can see in Fig. 4, the power-law exponent increases with temperature initially, reaches a maximum for approximately 185 °C, and for higher temperatures decreases and it seems to tend to a plateau. We think that coupling between charge transport and polymer chain-segments motions can explain this peak in the power-law exponent with the temperature. The relevance of chain-segments motions on space charge relaxation processes in polymers has been stated in previous works [10,11]. In these papers a compensation rule that relates the attempt to escape frequency of the carriers and the trapping depth was observed. This correlation was confirmed to be independent from experimental conditions.

3. Conclusions

Conductive processes in polymethyl methacrylate have been studied and it has been found that they condition the behavior of this material at high temperatures and low frequencies. Data analysis at the electric modulus level has resulted suitable to analyze DEA data in order to characterize these processes.

The dispersive conductivity observed in PMMA has resulted to be explained by means of a sublinear frequency dispersive ac conductivity that results from correlated ion hopping. The power-law exponent reaches a maximum value for approximately 185 °C that we suggest that can be related to a coupling between charge transport and polymer chain-segments motions.

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