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# Study of space charge relaxation in PMMA at high temperatures by dynamic electrical analysis

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**Abstract**

Dynamic electrical analysis shows that at high temperatures (above the glass transition temperature), the electrical properties of polymethyl methacrylate are strongly influenced by space charge. In this paper we present an study of space charge in this material and its conductive properties by dynamic electrical analysis, using the electric modulus formalism. The complex part of the electric modulus was fitted to Coelho's model, which considers ohmic conductivity and diffusion as the prevailing mechanisms of charge transport.

The complex part of the electric modulus exhibits a peak in the low frequency range that can be associated with space charge and a good agreement between experimental and calculated data is observed after the fitting process to the Coelho's model. The data obtained indicate that the electrode is partially blocked. The conductivity determined is thermally activated and it increases with the temperature due to an increasing mobility, that is also thermally activated. 

*Keywords*: Electric modulus; Poly(methyl methacrylate); Space charge

## 1. Introduction

Dielectric electrical analysis (DEA), which consists in the measure of a material's response to an applied alternating voltage, provides an excellent means of characterizing the electrical properties of polymeric materials. 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 highly insulating polymers, the capacitive nature of the material dominates their properties below the glass transition temperature and above this temperature the conductive processes prevail. In the case of PMMA, this effect was studied by measurements of its conductivity at high temperatures by different methods [1,2]. The conductive processes in DEA measurements are reflected by a sharp increase in the loss factor of the material, which can be observed at high temperatures and low frequencies.

In the literature can be found several papers that describe the electrical properties of poly(methyl methacrylate) (PMMA), and recently most interest in its properties has arisen due to the use of this material as host polymer in guest–host polymeric systems in non-linear optics [3,4]. Our aim in this paper is to discuss the conduction process in PMMA at temperatures above the glass transition by means of the model of Coelho [5,6]. The electrical behavior at these temperatures is strongly conditioned by space charge, as studies by thermally stimulated depolarization currents (TSDC) indicate [7–14]. The relaxation of space charge in TSDC studies is associated with the peak $\rho$ which appears at temperatures above the glass transition, and the study of this peak mostly reveals the trapping properties of materials. The use of the windowing polarization technique [15–21] allows one to study, at least qualitatively, the trapping level distribution in the material [12–14].

In a recent paper [22] a combination of TSDC and a probe technique has been used to determine the potential distribution below the glass transition. This potential distribution is used to determine the current–voltage characteristics, which reveal a sub-ohmic character ($J = gV^n$, where $n < 1$ and $g =$ constant).

### 1.1. The model of Coelho

The model of Coelho [5] assumes that when an electric field is applied to a sample, free charges move through the sample towards the electrode of opposite sign and finally the accumulation of charges close to the electrodes results in a macrodipole. If the field oscillates, then the macrodipole is

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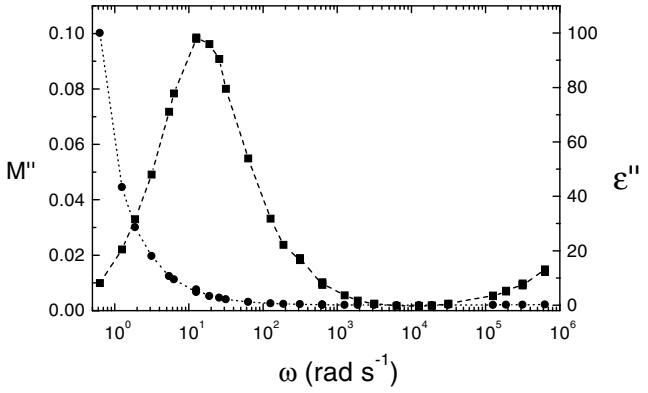


Fig. 1. Imaginary part of the electric modulus (□) and loss factor (●) of PMMA as a function of the frequency at 170°C.

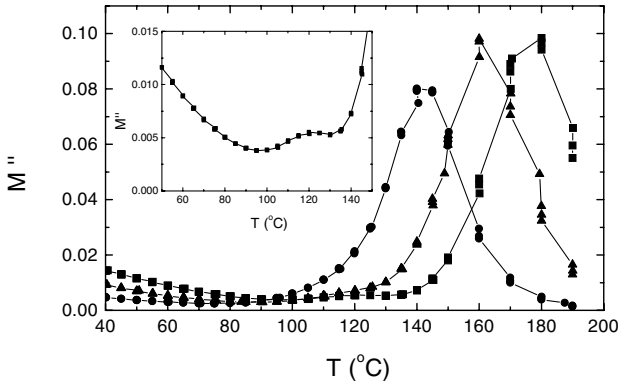


Fig. 2. Imaginary part of the electric modulus of PMMA versus the temperature for several frequencies: ●, 0.1 Hz; ▲, 1 Hz; ■, 5 Hz. In the inset it can be seen an enlargement corresponding to the temperature range at which the glass transition is observed.

forced to oscillate with the frequency of the field, and a relaxation process appears, similar to dipolar relaxation.

This model considers two processes for space charge relaxation, ohmic conduction and diffusion. The complex permittivity in this model is given by:

$$\epsilon^* = \epsilon_m \left[ \frac{(1 + i\omega\tau)\left(1 + \gamma \dfrac{\tanh(X_D)}{X_D}\right)}{i\omega\tau + [(1 + i\omega\tau)\gamma + 1]\dfrac{\tanh(X_D)}{X_D}} \right] \quad (1)$$

where

$$X_D = \frac{d}{L_D}\sqrt{1 + i\omega\tau} \quad (2)$$

In these equations $\omega$ is the frequency of the applied field, $\tau = \epsilon/\sigma$ the Maxwell relaxation time, $\sigma = n_0 e\mu$ the conductivity, and

$$L_D = \sqrt{\frac{\epsilon kT}{n_0 e^2}} \quad (3)$$

is the characteristic Debye length. The parameter $\gamma$ is the transparency factor that indicates the character of the electrodes.

In the case of blocking electrodes $\gamma = 0$, otherwise the electrode is partially blocked. The ratio $\delta = d/L_D$, where $d$ is half the thickness of the sample, is used to determine the conductive properties of the medium [5]: the case $\delta \ll 1$ corresponds to an extrinsic conducting material, with a low concentration of carriers of relatively high mobility. The opposite limit, $\delta \gg 1$ is associated with intrinsic conductors, with high carrier concentration of relatively low mobility.

### *1.2. The electric modulus*

The electric modulus is the reciprocal of the permittivity, $M^* = (\epsilon^*)^{-1}$, and it was introduced by McCrum et al. [23] and Macedo et al. [24] to study interfacial polarization phenomena. 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, so that the electric modulus represents the real dielectric relaxation process [25–27], as it can be expressed as:

$$M^*(\omega) = M_\infty \left[ 1 - \int_0^\infty \left( -\frac{d\Phi}{dt} \right) \exp(-i\omega t)\, dt \right] \quad (4)$$

that can be converted to [28]:

$$\frac{M^*(\omega)}{M_\infty} = 1 + \dot{\Phi}^*(\omega) = i\omega\Phi^*(\omega) \quad (5)$$

where $\Phi(t)$ is the dielectric response function and $\Phi^*(\omega)$ its Fourier's transform. In a recent publication, Wagner and Richter have introduced a method that allows one to evaluate $M(t)$ from voltage measurements in themostimulated depolarizations [25].

The interest of the electric modulus formalism arises from

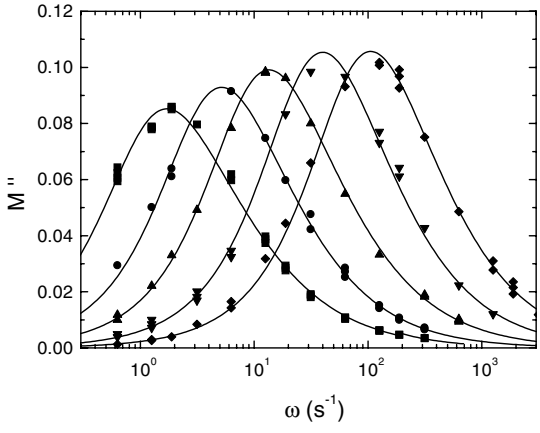


Fig. 3. Imaginary part of the electric modulus of PMMA versus the frequency at several temperatures: ■, 150; ●, 160; ▲, 170; ▼, 180; ◆, 190°C. The symbols are measured values and the continuous curves are the calculated values using the values of Table 1 resulting from the fitting process to the model of Coelho.

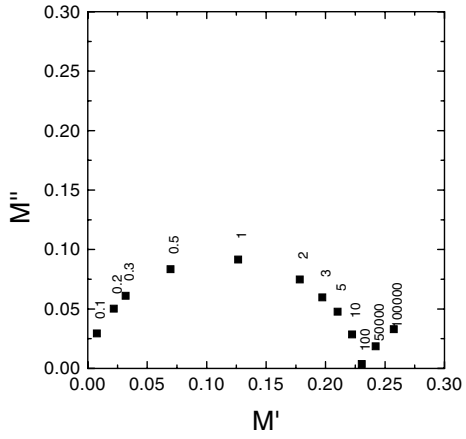


Fig. 4. Argand diagram of the electric modulus of PMMA at 160°C. The labels in the plot are the frequencies in Hz. It must be noted the arc at low frequencies associated to the conductive processes.

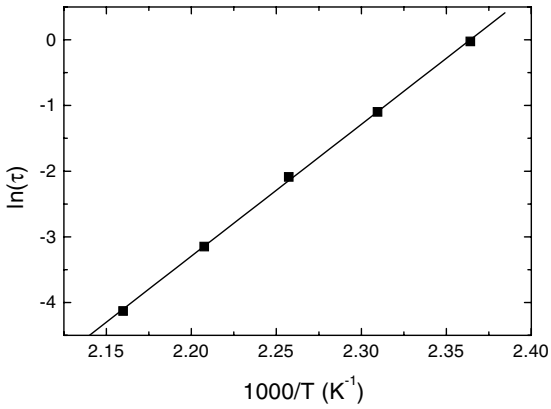


Fig. 5. Arrhenius plot of the relaxation time $\tau$ of space charge in PMMA at temperatures above the glass transition.

the fact that in the case of the conductive processes that are observed at low frequencies, the loss factor exhibits a sharp monotonic increase whereas the imaginary part of the electric modulus shows a peak [24], so that this function is suitable to study the space charge relaxation phenomena, as they are reflected by the changes of this peak [6,24,27].

## 2. Experimental

Samples of PMMA were cut from commercial sheets of 1.5 mm thickness (Altuglas®). 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 set up for DEA measurements has been described in a previous paper [29]. The real and imaginary parts of the electrical permittivity were measured at several frequencies in isothermal steps of 5°C each.

The imaginary part of the electric modulus was calculated from the permittivity and, finally, $M''(\omega)$ was fitted to the imaginary part of the electric modulus given by the model of Coelho using software developed by us which is based on routines described by others authors [30]. Four independent parameters were used in the fitting process: $\delta$, $\gamma$, $\tau$, and $\epsilon$. The maximum likelihood criteria were used to determine the figure of merit [30].

## 3. Results

At low frequencies and at temperatures above the glass transition temperature, the conductive processes in PMMA result in a sharp increase of the imaginary part of the permittivity. These processes are reflected by a peak in the electric modulus and that for $T = 170$°C has its maximum at approximately 20 Hz (Fig. 1)

In Fig. 2 we have plotted the imaginary part of the electric modulus as a function of temperature at low frequencies. It can be noted that the peak originated by conductive processes has its maximum at approximately 140°C for 0.1 Hz and that this temperature shifts to higher temperatures with the frequency. The peak corresponding to the glass transition of the material, that in this material takes place at approximately 115°C, is shown in the inset of the curve corresponding to 0.1 Hz included in Fig. 2.

The results obtained in the temperature range studied indicate that the peak arising from the contribution of conductive processes shifts to higher frequencies with temperature (Fig. 3). The plot of the electric modulus for a given temperature in Argand's plane (Fig. 4) shows that conductive processes are reflected by an arc for low frequencies. It must be pointed out that in the corresponding

Table 1
Parameters obtained by means of fitting the data of Fig. 4 to the model of Coelho. From these parameters we have calculated the conductivity, $\sigma$, the carrier concentration $n_0$ and the carrier mobility $\mu$

| $T$ (°C) | $\epsilon_m$ | $\delta$ | $\tau$ (s) | $\gamma$ | $\sigma$ ($\Omega^{-1}$ m$^{-1}$) | $n_0$ (m$^{-3}$) | $\mu$ m$^2$ s$^{-1}$ V$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 150 | 1.01 | 19.25 | 0.975 | 68.22 | $9.18\times10^{-12}$ | $7.55\times10^{14}$ | $7.59\times10^{-8}$ |
| 160 | 1.17 | 15.23 | 0.337 | 17.62 | $3.12\times10^{-11}$ | $5.62\times10^{14}$ | $3.46\times10^{-7}$ |
| 170 | 1.03 | 11.71 | 0.124 | 32.29 | $7.39\times10^{-11}$ | $2.99\times10^{14}$ | $1.54\times10^{-6}$ |
| 180 | 1.15 | 6.60 | 0.043 | 13.35 | $2.37\times10^{-11}$ | $1.08\times10^{14}$ | $1.38\times10^{-5}$ |
| 190 | 1.17 | 6.56 | 0.016 | 12.94 | $6.43\times10^{-10}$ | $1.11\times10^{14}$ | $3.62\times10^{-5}$ |

Table 2
Preexponetial factors and activation energies of relaxation times ($\tau$), conductivity ($\sigma$) and mobility ($\mu$) obtained from the corresponding Arrhenius plots

| Magnitude | Preexponential factor | Activation energy (eV) |
|---|---|---|
| $\tau$ | $7.9\times10^{-20}$ s | 1.98 |
| $\sigma$ | $3.6\times10^{8}\ \Omega^{-1}\,m^{-1}$ | 1.98 |
| $\mu$ | $4.2\times10^{12}\ m^2\,s^{-1}\,V^{-1}$ | 2.20 |

plot of the permittivity, the contribution of the conductivity is evidenced by a sharply increasing tail (not shown). These results agree with the model of Coelho [5,6], which predicts an arc for the contribution of space charge relaxation, that in the case of blocked electrodes approximates to a semicircle.

We have fitted the peaks shown in Fig. 3 to the imaginary part of the electric modulus given by Coelho's model. The parameters that result from the curve fitting can be seen in Table 1. The curves calculated using these values have been superimposed (continuous line) to the experimental values (symbols) as an indication of the accuracy of the fitting processes.

The values of the transparency factor ($\gamma$) obtained, indicate that the electrodes are partially blocked, as it can be expected from the shape of the arc shown in Fig. 4, which differs from a semicircle. This result agrees with the conclusion of Adamec [1] on the possible contribution of charge accumulation close to the electrodes to the conductive properties of PMMA at temperatures above the glass transition. On the other hand, the values obtained for the double of the ratio of the sample thickness and Debye's length do not correspond to any of the limit cases considered by Coelho is his original work. Nevertheless, as the values obtained are significantly greater than unity, specially for $T < 170$°C, we think that we must consider the case of an intrinsic conduction process, with a relatively high concentration of carriers with low mobility.

The relaxation time of space charge in this material, $\tau = \epsilon_0\epsilon/\sigma$, decreases with temperature due the increasing conductivity of the material (Table 1). Both, the relaxation time and the conductivity are thermally activated, as the linear behavior observed in the respective Arrhenius plots indicates (Figs. 5 and 6). The activation energies and preexponetial factors of these magnitudes are shown in Table 2. The values that we have found for the conductivity and its activation energy are in accord with the values obtained by other authors (reviewed in Ref. [1]).

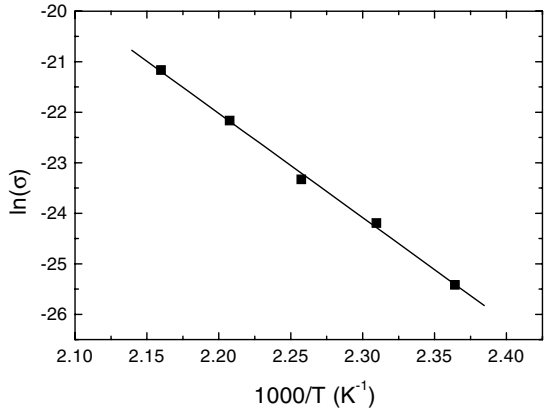


Fig. 6. Arrhenius plot of PMMA conductivity $\sigma$ at temperatures above the glass transition.

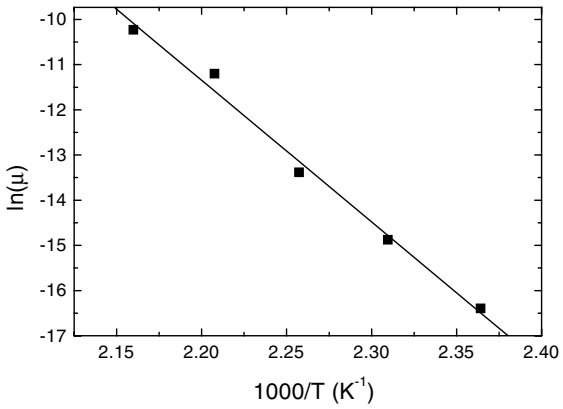


Fig. 7. Arrhenius plot of PMMA carrier mobility $\mu$ at temperatures above the glass transition.

In the temperature range studied, the conductivity increases by two orders of magnitude. There are two explanations for this sharp increase: the increase of the carrier concentration or the increase of the carrier mobility with temperature. The calculation of these magnitudes (Table 1) allows us to say that the carrier concentration does not vary significantly over the temperature range considered, although it seems to decrease slightly. Therefore, the rise in the conductivity must be attributed to the increasing mobility of the carriers, as this magnitude increases more than two orders of magnitude (Fig. 7).

## 4. Conclusions

At high temperatures the electric behavior of PMMA is strongly influenced by its conductive properties. The model of Coelho is adequate to explain the conductive properties of this material at temperatures above the glass transition.

We have observed a decrease of the relaxation time observed for space charge that can be related to a thermally activated conductivity. The dependence on the temperature of the conductivity can be associated with a rise of the mobility with temperature, as the variation of the carrier concentration does not vary significantly in the temperature range studied.

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## References


[1] Adamec V. Electric polarization and conduction in polymethyl methacrylate and polyvinyl chloride in unidirectional electric field. Kolloid-Z u Z Polymere 1971;249:1085–95.

[2] Adamec V, Mateová E. Electrical conductivity of PMMA at linearly increasing temperatures. Polymer 1974;16:166–8.

[3] Bauer S, Ren W, Bauer-Gogonea S, Gerhard-Multhaupt R, Liang J, Zyss J, Alheim M, Stähelin M, Zysset B. In: Lewiner J, Morisseau D, Alquié C, editors. Proceedings of the Eighth International Symposium on Electrets (ISE8), Piscataway, NJ: Service Center, 1994. p. 800–5.

[4] Zhang H, Xia Z, Zhou S, Ding H, Cao Y, Lin H, Zhu J. In: Xia Z, Zhang H, editors. Proceedings of the 9th International Symposium on Electrets (ISE9), Piscataway, NJ: IEEE Service Center, 1996. p. 462–7.

[5] Coelho R. Sur la relaxation d'une charge d'espace. Revue Phys Appl 1983;183:137–46.

[6] Mudarra M, Belana J, Díaz-Calleja R, Cañadas JC, Diego JA, Sellarès J, Sanchis MJ. Electric charge in solid insulators. In: Damamme G, editor. Proceedings of CSC3, Paris: Société Française du Vide, 1998. p. 604–7.

[7] Solunov CA, Ponevsky CS. Thermostimulated depolarization currents in thermorheologically simple materials. J Polym Sci: Polym Phys Ed 1977;15:969–79.

[8] Van Turnhout J. Thermally stimulated discharge of polymer electrets. Tesis, Centraal Laboratorium TNO, Delft, 1975.

[9] Vanderschueren J. L'effect thermoélectret et des phénomènes de relaxation dans les polymères à l'état solide. Tesis, Université Liège, 1974.

[10] Belana J, Mudarra M, Calaf J, Cañadas JC, Menéndez E. TSC study of the polar and free charge peaks of amorphous polymers. IEEE Trans Electr Insul 1993;28(2):287–93.

[11] Kryszewski M, Zielinski M, Sapieha S. Analysis of relaxation processes in methacrylate polymers by thermally stimulated discharge. Polymer 1975;17:212–6.

[12] Mudarra M, Belana J. Study of poly(methyl methacrylate) space charge relaxation by TSDC. Polymer 1997;38:5815–21.

[13] Mudarra M, Belana J, Cañadas JC, Diego JA. Polarization time effect on PMMA space charge relaxation by TSDC. J Polym Sci B: Polym Phys 1998;36:1971–80.

[14] Mudarra M, Belana J, Cañadas JC, Diego JA. Windowing polarization: considerations to study the space charge relaxation in poly(methyl methacrylate) by thermally stimulated depolarization currents. Polymer 1999;40:2659–65.

[15] Hino T. Measurement of dipolar relaxation times and dielectric constants using thermally stimulated currents. J Appl Phys 1973;46:1956–60.

[16] Zielinski M, Kryszewski M. Thermal sampling technique for the thermally stimulated depolarization currents. Phys Status Solidi A 1977;42:305–14.

[17] Duaconu I, Dumitrescu SV. Dielectric relaxation in atactic polystyrene determined by thermally stimulated depolarization currents. Eur Polym J 1978;14:971–5.

[18] Lacabanne C, Goyaud P, Boyer RF. Thermal stimulated current study of the $T_g$ and $T_{ll}$ transitions in anionic polystyrenes. J Polym Sci B: Polym Phys 1908;18:277–84.

[19] Shrivastava SK, Ranade JD, Shrivastava ASP. Thermally stimulated currents in polystyrene films. Thin Solid Films 1980;67:201–6.

[20] Gourari A, Bendaoud M, Lacabanne C, Boyer RF. Influence of the tacticity on $T_\beta$, $T_g$ and $T_{ll}$ in polymethacrylate by the method of thermally stimulated current. J Polym Sci B: Polym Phys 1985;23:889–916.

[21] Belana J, Colomer P, Pujal M, Montserrat S. Análisis de la polarización de equilibrio en el politereftalato amorfo por estimulación térmica. Anales de Física, serie B 1985;81:136–46 (in spanish).

[22] Mazur K. More data about dielectric and electret properties of poly(methyl methacrylate), . J Phys D: Appl Phys 1997;30:1383–9.

[23] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids. London: Wiley, 1967.

[24] Macedo PB, Moynihan CT, Bose R. The role of ionic diffusion in polarization in vitreous ionic conductors. Phys Chem Glasses 1972;13:171–9.

[25] Wagner H, Richert R. Thermally stimulated modulus relaxation in polymers: method and interpretation. Polymer 1997;38:5801–6.

[26] León C, Lucía ML, Santamaría J. Correlated ion hopping in single-crystal yttria-stabilized zirconia. Phys Rev B 1997;55:882–7.

[27] Richert R, Wagner H. The dielectric modulus: relaxation versus retardation. Solid State Ionics 1998;105:167–73.

[28] León C, Lucía ML, Santamaría J. Analytical distributions of relaxation times for the description of electrical conductivity relaxation in ionic conductors. Phil Mag B 1997;75(5):629–38.

[29] Díaz-Calleja R, Friederichs S, Jaïmes C, Sanchis MJ, Belana J, Cañadas JC, Diego JA, Mudarra M. Comparative study of mechanical and electrical relaxations in poly(etherimide) Part 2. Polym Int 1998;46:20–8.

[30] Press WH, Flannery BP, Teukolsky SA, Vetterling WT. Numerical recipes. Cambridge: Cambridge University Press, 1986.