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Study of charge relaxations after thermal aging in poly (methyl methacrylate)

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Abstract

Effects of thermal aging on physico-chemical and electrical properties of polymethyl methacrylate (PMMA) are reported in this paper. PMMA samples are submitted to successive heat-cooling cycles ($T_{min} = 20^{\circ}\text{C}$ and $T_{max} = 90^{\circ}\text{C}$) in the ambient air, each cycle lasts 12h. Different techniques are thus employed to investigate structural modifications, dielectric relaxations and conduction processes. These are the Fourier Transform Infrared (FTIR) spectroscopy, thermal step method (TSM), thermally stimulated depolarization currents (TSDC), dielectric spectroscopy (DS) and current-voltage technique. Results are discussed and a relationship between structural modifications and charge relaxations was emphasized. We demonstrated that thermal aging favors oxidation phenomenon. Three distinguishable charge relaxations (β , α and ρ) have been highlighted by TSDC.

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Keywords: PMMA, thermal aging, TSDC, charge relaxation

1. Introduction

PMMA is one of the best polymeric materials broadly used for insulation devices manufacture. Its electrical properties are highly influenced by many environmental parameters such as temperature, mechanical constraints, humidity...

Therefore, investigations on the effects of these constraints have been made by numerous researchers [1-3].

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This paper focuses on the evolution of structural and electrical properties of PMMA submitted to successive heat cooling cycles. The upper temperature of the applied cycle was near to the glass temperature $T_g=110^\circ\text{C}$ [4].

FTIR spectroscopy was investigated to explore effects of heat treatments on PMMA structure. Space charge and relaxations in PMMA were studied by means of TSM, TSDC and DS techniques.

Current voltage measurements have been also carried out to highlight the effect of thermal aging on conduction mechanism in the PMMA.

2. Characterization Methods:

2.1 Infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is used to gather informations about a compound’s structure and to assess its purity. In favorable cases, IR analysis can be quantitative and permits to identify the compound.

In our case, spectra are acquired with an IR BRUKER EQUINOX55 spectrometer in the $400\text{-}4000\text{ cm}^{-1}$ region with a resolution of 4 cm^{-1} .

2.2. Thermal step method (TSM)

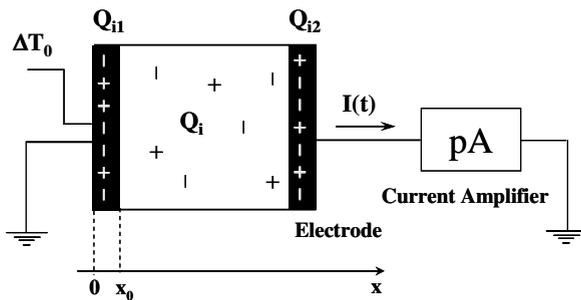
The thermal step method, which has been widely described by A. Toureille [5-6], is based on measurements of the thermomodulation current caused by the application of a so called thermal step on a one face of the sample.

The sample is used in a sandwich configuration (electrode-PMMA sample-electrode) (figure 1). The presence of charges Q_i in the insulator induces image charges on each electrode Q_{i1} and Q_{i2} ($Q_i + Q_{i1} + Q_{i2} = 0$). Then, the propagation of the thermal step (positive or negative), and the resulting expansion (dilatation or contraction) across the sample thickness, modify the equilibrium of these image charges and consequently, a current appears in the external circuit joining the electrodes.

The current is given by:

$$I(t) = -\alpha C \int_{x_0}^{A(t)} E(x) \frac{\partial T(x,t)}{\partial t} dx \quad \text{avec} \quad \alpha = -\frac{1}{C} \frac{\partial C}{\partial T} \tag{1}$$

α is a characteristic constant of the material related to the sample’s expansion and to thermal dependence of the permittivity, C is the sample’s capacity, $E(x)$ is the local electric field in the sample, $T(x,t)$ is the temperature distribution in the sample, x_0 is the equivalent thickness between the temperature source and the beginning of the sample and $A(t)$ is the most advanced position of the thermal step. The current appears when $A(t) > x_0$.



Q_{i1} and Q_{i2} are the image charges
 Q_i : space charge and ΔT_0 : thermal step.

Fig 1. Principe of the thermal step method.

2. 3. Thermally Stimulated Depolarization Currents (TSDC)

The basic principle of the technique involves the application of high electric field at a specified temperature followed by cooling, leading to the polarization of the sample being “frozen” into the material. The charged sample is short-circuited through an electrometer (keithley 610) in a Memmert oven, which is programmable to rise linearly with time. The depolarization current of the sample occurs by thermal activation. TSDC provides information on relaxation processes that occur in polymers. In contrast to the experimental simplicity of the TSDC technique, the analysis experimental data is not easy, as the polarization may be due to several microscopic processes (associated with dipolar or trapped charge mechanisms), whose relaxation will contribute to the depolarization current.

The current due to a dipole reorientation is given by the following expression [7-8]:

$$J(T) = A \exp \left[-\frac{E_a}{kT} - \frac{1}{v\tau_0} \int_0^T \exp \left(-\frac{E_a}{kT'} \right) dT' \right] \quad (2)$$

E_a is the activation energy, k is the Boltzmann constant, v is the rate of heating, τ_0 is the relaxation time at T_0 . The

pre-exponential factor A is related to the dipole moment p and to dipoles volume density N : $A = \frac{Np}{\tau_0}$

In the temperature range considered in this study (25-140°C), the proposed relaxation mechanisms are the depolarization of permanent dipoles and the release of charges from traps. The present study, TSDC measurements were carried out at a heating rate of 2°C min^{-1}

2.4. Dielectric Spectroscopy:

Dielectric spectroscopy (DS) consists in analysis of both capacitive and resistive properties of materials. It is based on frequency-dependent impedance measurement, as response to a small periodic excitation signal. The measurements are performed with a Solartron 12962 impedance analyser in the frequency range from 1 Hz to 1 MHz.

2.5 Current-voltage measurements:

Measurements are performed using “DEL” DC high Voltage generator and a Keithley 6514 electrometer. The investigated samples were coated with circular graphite electrodes, of 5 cm diameter on both sides (Fig 2).

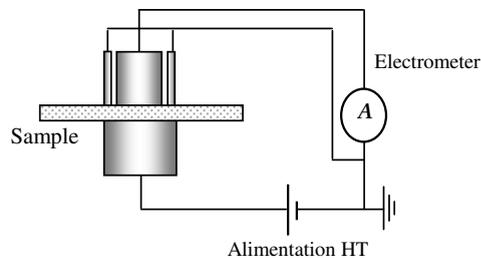


Fig. 2. Principle of current-voltage method.

3. Experimental

3. 1. Preparation of samples

PMMA samples were slabs (100×100×2) mm³, provided from commercial source (MADREPERLA, Italy). The glass transition temperature (T_g) of a virgin PMMA, performed with a differential scanning calorimeter (Perkin Elmer Pyris 1), was found equal to 110°C [4].

In order to study the influence of thermal aging on PMMA properties, different samples were submitted to successive cycles of heat-cooling ($\Delta T=70^\circ\text{C}$) in an oven (Mettler ULE500). Duration of each cycle was 12 hours (Fig 3). Samples were then labelled as listed in table 1.

Before TSM and TSDC measurements, each sample was coated with circular graphite electrodes, of 5 cm diameter on both sides, then an electric field of 7.5 kV/mm was applied during 2 hours at the temperature of 90°C. TSDC measurements were recorded, in the temperature range of 25 to 140°C, with a thermal rate of 2°C/min.

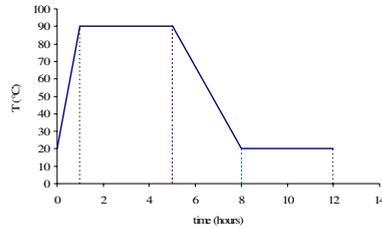


Fig. 3. An applied heat-cooling cycle with $\Delta T = 70^\circ\text{C}$.

Table 1: Samples label according to the number of applied cycles.

Samples	Number of cycles
E_0	0
E_4	4
E_8	8
E_{14}	14
E_{20}	20
E_{24}	24
E_{48}	48
E_{72}	72
E_{96}	96

3. 2 Infrared results

Fig. 4 shows the IR spectrum of the virgin PMMA sample. The assignments of the principal absorption bands are based on spectroscopic data [9-12]. Some of these assignments are indicated on this figure.

The absorptions around 2928 and 2949 cm^{-1} characterize the $\nu(\text{C-H})$ stretching vibrations of (CH_2) and (CH_3) respectively. The stretching vibration of C=O bonds associated with the ester groups appears around 1722 cm^{-1} . The two doublet bands at (1270, 1239 cm^{-1}) and (1190, 1142 cm^{-1}) are due to the $\nu(\text{C-O})$ stretching vibrations of ester groups.

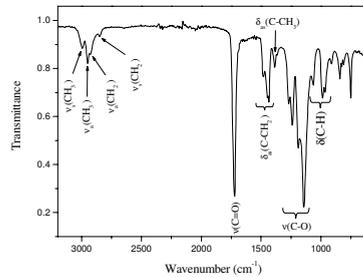
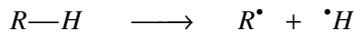


Fig. 4. Infrared spectrum of a virgin PMMA sample

Infrared measurements were also used to highlight structural changes in PMMA under thermal aging effect (Fig.5).

The most significant changes in the spectra of thermal aged samples occur at the [2600-3200] cm^{-1} region. We note an increase of the $\nu_s(\text{CH}_3)$ band intensity to the detriment of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$. This evolution, appearing up to 72, is due to chain scission phenomenon under thermal aging. For sample submitted to 96 cycles, the increase of CH_2 band intensities ($\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$) at 2927 and 2850 cm^{-1} respectively accompanied with a decrease of $\nu_s(\text{CH}_3)$ band intensity, suggests that crosslinking reaction occurs in material. These structural changes are probably due to oxidation of the PMMA under the effect of heat. In fact, the thermal aging of samples was realized in ambient air, where oxidation reactions can take place in the specimens. Thus, under heating the oxidation phenomena can be described by the following reaction [13]:



Oxidation affects partially the secondary chains, which can lead to the formation of dipoles and/or trapped charges. This will be confirmed later by electric measurements

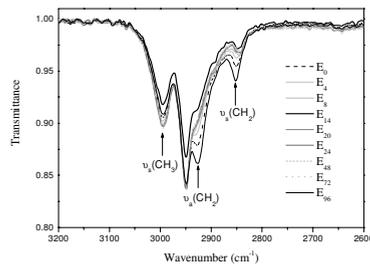


Fig. 5. Infrared spectra of virgin and thermally aged samples.

3.3. TSM and TSDC results

The thermal step current profiles are represented on Fig 6. We call the ‘anode’, the face of the sample where the positive polarization voltage was applied. Anodic current is the thermodilatation current when the thermal step is applied on the anodic face. The cathodic current is the current registered when thermal step is applied on the cathodic face.

The currents measured on un-aged and thermally aged samples after poling, present the same profile, characteristic of majority polarisation phenomenon.

The remarkable decrease of the current magnitude in heated samples can be due to a decrease of the polarisation, and/or charges injection phenomenon from electrodes. In fact, the successive application of heat cycles up to 90°C

(Which is close to glass transition temperature) allows the rearrangement of chains as well as the decrease of free volume. Dipoles are then frozen in depth traps and they can not be easily oriented under the applied electric field during pooling process. Moreover, as it has been shown by IR spectroscopy, oxidation can take place under heating, which leads to the formation of charge traps and favours the injection of charges from electrodes.

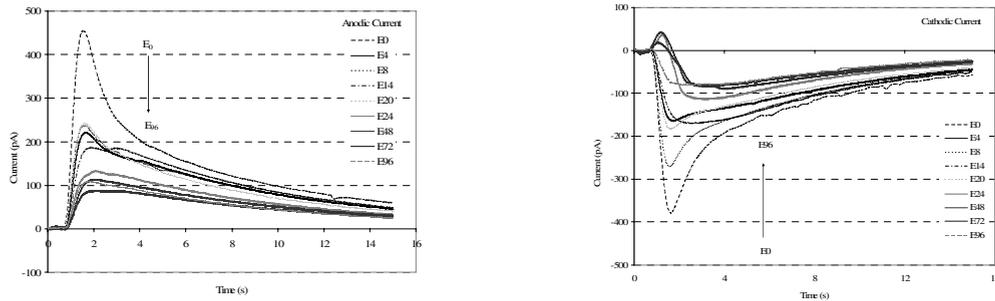


Fig 6. : Thermal Step currents in un-aged and thermally aged PMMA samples after 2h of pooling under 7.5kV/mm at 90°C.

Samples were then depolarized by TSDC measurements. The corresponding TSDC spectra of the investigated samples (E_0, E_4, \dots, E_{96}) are given on Fig 7. Each of them presents, in low temperatures range (from 40 to 80°C), a broad peak which is attributed to the β relaxations. The intense peak (α) associated with the glass transition temperature appears at 111°C for the un-heated sample. In previous works [6, 14, 15] this peak was observed in the temperature range from 100 to 120°C. The peak which appears at high temperature (around 130°C) is associated to the release of trapped charges, injected from electrodes during pooling process. We notice a decrease of relaxation peaks amplitude when the number of the applied heat-cooling cycles increases, indicating a decrease of relaxation phenomena after thermal treatment. TSDC spectra show also that α and ρ relaxations are more sensitive to the thermal ageing effect [16].

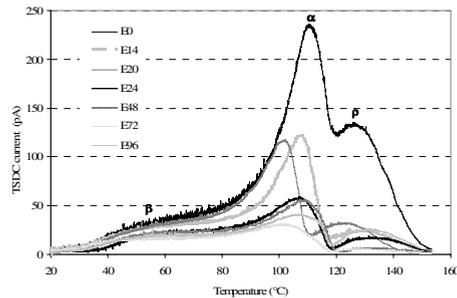


Fig 7. TSDC spectra of un-aged and thermally aged PMMA samples

In order to determine the activation energies of the different relaxation processes, we have isolated each current peak (α and ρ) using the cleaning method. Experimental process of this technique is given by the following:

- electrical pooling of samples (7.5 kV / mm to $T_c=90^\circ\text{C}$ during 2 hours).
- insulation of the first peak (β) by linear heat up to a temperature slightly upper than the temperature which corresponds to the maximum of this peak. Then sample is cooled down.
- insulation of the second peak (α) by linear heat up to a temperature slightly upper than the maximum of this peak.
- insulation of the ρ peak.

We represent on Fig 8 the isolated peaks α and ρ for sample E_0 (as an example).

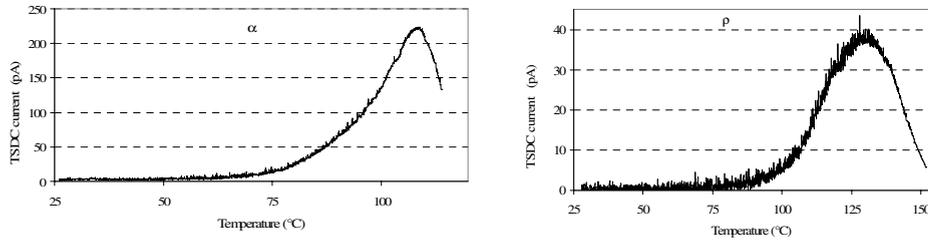


Fig 8: TSDC bands separated by cleaning method

Activation energies of the different relaxation processes have been determined by the initial slope method [17]. In

the low temperatures, factor $\exp\left(-\frac{E_a}{kT}\right)$ predominates in the expression of the thermally stimulated depolarisation current (Eq 2). Consequently, the expression for the thermally stimulated depolarisation current at the beginning of the rise of the curve can be written as:

$$J(T) = A \exp\left(-\frac{E_a}{kT}\right) \quad (3)$$

Where T is the temperature in Kelvin, k the Boltzmann constant, A the pre-exponential factor and E_a the activation energy.

A plot of $-\ln(J)$ versus $1/T$ is a straight line with a slope of E_a/k , from which we can deduce the activation energy. Figure 9 shows the variation of $-\ln(J)$ versus $1000/T$ of α and ρ peaks for the un-heated sample (E_0). The corresponding activation energies are given in table 2. Our results are in agreement with those reported in [5-6, 18-19].

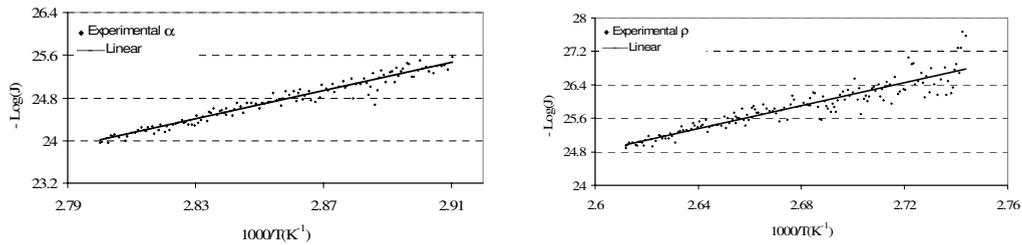


Fig 9 : Variations of $-\text{Log}(J) = f(1000/T)$ for the un-heated sample E_0 .

For α relaxation process, the obtained activation energies do not show a variation with the number of the applied heat-cooling cycles. Contrary a remarkable increase of the activation energy associated with trapped charges (ρ) after applying 24 heat-cooling cycles is observed. This can be explained by the surface oxidation after heat treatment which leads to the formation of deep trap charges in the vicinity of samples surfaces. Indeed heat treatment was realized in ambient air and consequently oxidation affects the surface properties rather than the bulk ones.

Table 2 : Activation energies (eV)

Relaxation Process		
Samples	α	ρ
E ₀	1.41 ± 0.02	1.90 ± 0.03
E ₁₄	1.08 ± 0.01	1.89 ± 0.08
E ₂₀	1.04 ± 0.01	1.51 ± 0.06
E ₂₄	0.98 ± 0.02	1.32 ± 0.02
E ₄₈	1.01 ± 0.01	2.79 ± 0.02
E ₇₂	0.99 ± 0.01	2.00 ± 0.02
E ₉₆	1.01 ± 0.02	2.26 ± 0.09

3.4 Impedance Spectroscopy

The representation of the imaginary part (ϵ'') versus the real part (ϵ') of the permittivity for the un-heated sample (Fig 10) shows the presence of two semi-circles indicating the presence of two phenomena, dipolar and interfacial relaxations.

Evolution of the complex dielectric permittivity can then be described by the Cole-Cole law according to the following equation [20]:

$$\epsilon(\omega) = \epsilon_{\infty} \frac{\epsilon_s - \epsilon_{\infty}}{1 + (j\omega\tau)^{1-\alpha}} \quad (4)$$

where $\omega = 2\pi f$, is the radial frequency, τ is a mean relaxation time and $\Delta\epsilon = \epsilon_s - \epsilon_{\infty}$ is the dielectric strength. The exponent α is discussed as the parameter of the relaxation time distribution.

Figure 11 shows the variation of ϵ'' versus ϵ' for the thermally aged PMMA samples. This figure shows that the relaxations of charges are sensitive to the number of applied the temperature cycles, as it was observed on TSDC spectra.

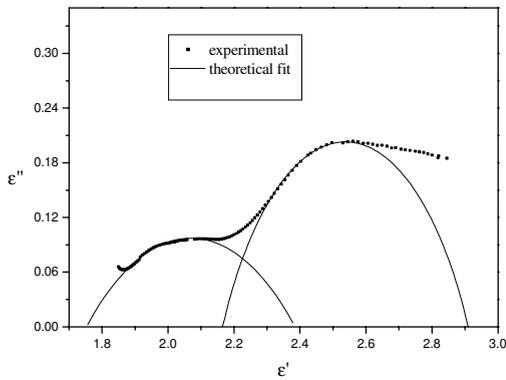


Fig 10. Cole-Cole plots of the dielectric permittivity of the un-heated sample. The two semi circles represent the best fitting of the experimental data.

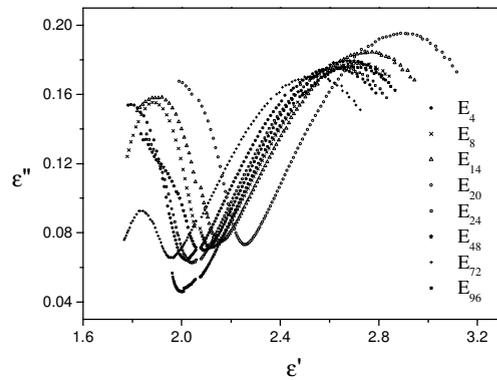


Fig 11. The dielectric permittivity ϵ'' versus ϵ' of thermally aged PMMA samples.

In order to follow the evolution of dielectric parameters (ϵ_s , ϵ_{∞} and α), we have applied the Cole-Cole model (equation 4). The parameters evaluated by fitting data were gathered in Table 3.

TSDC results have shown that heating leads to an increase of the α_2 value as well as the dielectric strength $\Delta\epsilon_2$. This is related to trapped charges formation. Conversely, the same treatments cause a decrease of both α_1 and $\Delta\epsilon_1$ values, confirming the reduction of the relaxed dipoles number as a consequence of dipoles mobility diminution.

Table 3. Dielectric parameters: derived from Cole–Cole plots

Samples	Dipolar relaxations				Interfacial relaxations			
	ϵ_{s1}	$\epsilon_{\infty1}$	α_1	$\Delta\epsilon_1$	ϵ_{s2}	$\epsilon_{\infty2}$	α_2	$\Delta\epsilon_2$
E ₀	2.385	1.752	0.620	0.633	2.910	2.165	0.365	0.745
E ₄	2.006	1.577	0.207	0.429	3.275	1.952	0.672	1.323
E ₈	2.090	1.685	0.167	0.405	3.454	2.005	0.694	1.449
E ₁₄	2.151	1.639	0.291	0.512	3.490	2.038	0.685	1.452
E ₂₀	2.279	1.690	0.345	0.589	3.661	2.160	0.680	1.501
E ₂₄	2.012	1.706	0.111	0.306	3.270	2.009	0.656	1.261
E ₄₈	2.153	1.483	0.529	0.670	3.350	2.008	0.668	1.342
E ₇₂	1.993	1.685	0.315	0.308	3.200	1.900	0.672	1.300
E ₉₆	–	–	–	–	3.415	2.000	0.689	1.415

3. 5 Current-voltage measurements

Current voltage measurements have been carried out on the investigated samples. The obtained characteristic of the virgin sample was represented on Fig. 12. This curve includes three parts [21-22]:

- from 1 to 11kV (region I): a linear part indicates that the current is controlled by space charge limited (model with traps), there are a filling of traps.
- at 11kV (region II): all traps were filled, the current presents a drastic increase at VTFL voltage (≈ 11 kV).
- Beyond 12kV (region III) the current has a linear behavior characteristic of trap-filled limited conduction.

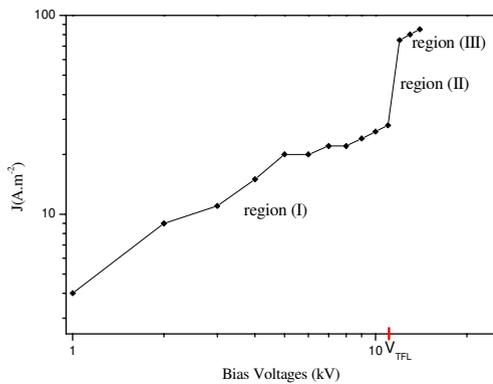


Fig. 12. Current-voltage characteristic of the virgin sample

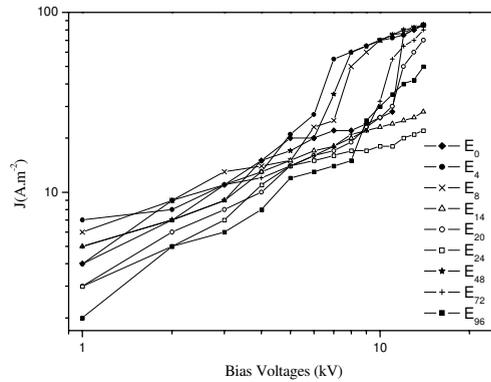


Fig. 13. Current-voltage characteristics of aged samples.

In Figure 13 we represent I(V) characteristics of thermally aged PMMA samples. We notice that all curves have the same behavior which can be well explained using standard space charge limited conduction, with variable V_{TFL} voltage. This voltage is weaker in samples aged by 4, 8, and 14 cycles.

4. Conclusion

In this study structural and dielectric properties of PMMA have been investigated under thermal aging. IR spectroscopy results have shown that heat causes oxidation phenomenon. The latter favours charge injection from electrodes during poling stage, and stabilize them in depth levels.

TSDC and DS results have shown the existence of dipolar and interfacial relaxations in PMMA: dipolar and interfacial relaxations. Activation energies of the different relaxation processes have been determined by the cleaning method using the initial slope method. Dielectric spectroscopy and current-voltage characteristics of the PMMA polymer have been investigated. The evolution of dielectric permittivity is well described by the Cole-Cole model. The I(V) characteristics behaviour can be well explained using standard space charge limited conduction.

References

- [1] A. C. Gjaerde, IEEE Transaction on Dielectrics and Electrical Insulation 4 (1997) 674.
- [2] L. A. Dissado, G. Mazzanti and G. C. Montanari, IEEE Transaction on Dielectrics and Electrical Insulation 4 (1997) 496.
- [3] Le. Gressus C and G. Blaise. IEEE Transactions on electrical insulation. 27 (1992) 472.
- [4] F. Namouchi, H. Smaoui, H. Guermazi, C. Zerrouki, N. Fourati, S. Agnel, A. Toureille, J.J. Bonnet, European Polymer J. 43 (2007) 4821
- [5] A. Toureille Journal of Electrostatics.32 (1994) 277.
- [6] A. Toureille supplément à la Revue "le vide: Science, technique et applications"- N° 275 (1995) 334-344
- [7] V. Turnhout Elsevier, Amsterdam (1975).
- [8] Vanderschueren J Electrets edited by Perlman (1973).
- [9] H.W. Choi, H.J. Woo, W. Hong, J.K. Kim, S.K. Lee, C.H. Eum, Appl. Surf. Sci. 169 (2001) 433.
- [10] X. Colom, T. Garcia, J.J. Sunol, J. Saurina, F. Carrasco, J. Non-Cryst. Solids 287 (2001) 308.
- [11] B.J. Holland, J.N. Hay, Polymer 42 (2001) 4825.
- [12] JianMing Yu, XiaoMing Tao, HwaYaw Tam, M. Suleyman Demokan, Appl. Surf. Sci. 252 (2005) 1283.
- [13] S. Kumagai, N. Yoshimura, IEEE Trans. D & EI. 7 (2000).
- [14] H. Guermazi, S. Guermazi, S. Agnel, Y. Mlik, A. Toureille Polymers in the Third Millenium, (P3M), Montpellier, France (2001) 2.
- [15] P. Ropa Thèse, Université Montpellier II (1997).
- [16] V.M Gun'ko, V.I Zarko, E.V Goncharuk, L.S Andriyko, V.V Turov, Y.M Nychiporuk, R Lebeda, J Skubiszewska-Zieba, A.L Gabchak, V.D Osovskii, Y.G Ptushinskii, G.R Yurchenko, O.A Mishchuk, P.P Gorbik, P Pissis and J.P Blitz. Advances in Colloid and Interface Science 131 (2007) 1.
- [17] Garlick and Gibson, Proc. Roy. Ser A 184 (1945) 365.
- [18] N. Vella, A Joumha, A Toureille, ISE 8, 8th Internationl Symposium on Electret, Paris, France, 7-9 Septembre (1994).
- [19] M. Mudarra and J. Belana, Polymer 38 (1997) 5815.
- [20] K.S.Cole, R.H.Cole, J. Chem. Phys. 9 (1941) 341.
- [21] A. Rouis, C.Dridi, R.Ben Chaabane, J.Davenas, S.Aeiayach, H.Ben Ouada, I.Dumazet-Bonnamour, H. Halouani, Mater. Sci. Eng. C 26 (2005) 240.
- [22] A. Rihani, N. Boutabba, L. Hassine, S. Romdhane and H. Bouchriha, Synthetic metals 45 (2004) 129.