ELSEVIER

Thermochimica Acta 395 (2003) 183–189

thermochimica acta

www.elsevier.com/locate/tca

Comments on the compensation effect observed in thermally stimulated depolarization current analysis

E.R. Neagu[a,*], R. Neagu[b]

[a]Departamento de Ciências dos Materiais, CENIMAT, Faculdade de Ciencias e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b]Applied Statistics Laboratory, General Electric Research Institute, Information and Decision Technologies,
Bldg. K1, 4C41A, 1 Research Circle, Niskayuna, NY 12309, USA

Received 14 November 2001; received in revised form 6 March 2002; accepted 6 March 2002

Abstract

Compensation has been reported for the relaxation parameters (the activation energy W and the pre-exponential factor τ_0) determined by using the thermal sampling (TS) technique. For the peaks obtained by the thermally stimulated depolarization current (TSDC) measurement, there is a relationship between W, τ_0 and the temperature of maximum intensity of the peak T_m that can be employed to deduce a general relationship between W, T_m, the compensation temperature T_c and the compensation time τ_c. This relationship can be used for a basic analysis of the compensation effect. By numerical simulations, and using parameters similar to those reported for concrete measurements, we show that it is possible to observe a compensation point only if the activation energy is a monotonically increasing power function of temperature of power coefficient between 1 and 2, more precisely, if W increases with temperature stronger than linearly but weaker than quadratically. The actual values of the compensation parameters are determined by the relationship between the activation energy and the temperature. The experimental uncertainties affecting the compensation temperature and the compensation time are significant, and consequently, it is not possible to have a precisely defined compensation point.

Keywords: Thermally stimulated depolarization current; Compensation effect

1. Introduction

Many thermally stimulated processes obey the so-called compensation law. In terms of the Arrhenius equation the compensation law or isokinetic relationship or the Meyer–Neldel law [1] consists of a linear relationship between the logarithm of the pre-exponential factor τ_0 and the activation energy W. In terms of the Eyring equation of the rate theory, the compensation law involves a linear relationship between the activation entropy ΔS and the activation enthalpy ΔH [2]. The compensation law has been observed in a wide range of circumstances, from chemical kinetics [3], conductivity in oxides [1] and amorphous semiconductors [4] to conductivity in ionic conductors [5] and flow processes in glassy polymers [6]. Compensation has been controversial for more than 30 years. Exner [7] discussed the danger of attempting to correlate W and log τ_0 because they are not independent of each other. Although significant effort was devoted to dismissing the validity of compensation [7–9], it is still prevalent in the relaxation literature [10,11]. Ngai [12] showed that the Meyer–Neldel rule and

---

[*] Corresponding author.
E-mail address: neagu@dcm.fct.unl.pt (E.R. Neagu).

PII: S0040-6031(02)00137-5

anti-Meyer–Neldel rule (log τ_0 decreases while W also decreases) could originate from the cooperative dynamics of ionic motions.

Compensation has been reported in some thermally stimulated depolarization current (TSDC) experiments [2,13–15]. The measurement of TSDC, especially in its modification known as thermal sampling (TS) [2] (or windowing polarization) has been expansively utilized to study the dielectric properties of various materials, crystalline and amorphous insulators, and organic substances. The specific parameters of the material can be determined through integration of the experimental current or by fitting the experimental current with an analytical expression, the latter particularly useful in the temperature range where the current reaches its maximum. In a TS experiment, the polarization field is applied in a narrow temperature range in order to allow the isolation of different contributions involved in a relaxation process [2]. It is considered that at the compensation temperature T_c all relaxations occur with a single relaxation time τ_c [2] and that T_c can be correlated with the glass–rubber transition temperature of the amorphous phase. On the other hand, it was suggested that it is not generally valid to assume that the states derived by analyzing the results of TS experiments correspond to states actually present in the system [16] and that the compensation temperature cannot be correlated with any physical observable quantity [15].

The aim of this paper is to analyze the compensation effect observed in the case of TSDC measurements. In this respect, a general relationship between the peak and compensation parameters is deduced. The maximum uncertainty of the compensation temperature and compensation time resulting from the experimental errors is estimated.

2. Theoretical considerations

The parameters of the Eyring and Arrhenius equations are mathematically convertible into each other. Thus, there is no difference between the Eyring and Arrhenius model for the analysis of the compensation effect [13]. In what follows the Arrhenius dependence of relaxation time on temperature is assumed:

$$\tau(T) = \tau_0 \exp\left(\frac{W}{kT}\right) \tag{1}$$

where τ_0 represents the relaxation time at infinite temperature, W the activation energy of dipole (dis)-orientation and k the Boltzmann constant. The current density measured during the TSDC experiment can be written as a function of temperature [17]:

$$j(T) = \frac{P_0}{\tau(T)} \exp\left(-\frac{1}{b}\int_{T_0}^{T} \frac{\mathrm{d}T'}{\tau(T')}\right) \tag{2}$$

where P_0 is the equilibrium polarization produced during the polarization of the sample, $b = \mathrm{d}T/\mathrm{d}t$ the heating rate and T_0 the initial temperature. The maximum current occurs when [17]

$$\frac{\mathrm{d}\tau(T)}{\mathrm{d}T} = -\frac{1}{b} \tag{3}$$

From Eqs. (1) and (3) we have

$$\tau_0 \frac{W}{kT_m^2} \exp\left(\frac{W}{kT_m}\right) = \frac{1}{b} \tag{4}$$

where T_m is the temperature of maximum intensity of the TS peak. From Eq. (4) it results that the analysis of the TSDC data does not allow an independent determination of W and τ_0 and consequently it is possible to observe a so-called compensation effect. Further we will analyze this possibility.

Compensation is defined either in terms of the linear dependence of W on the logarithm of the pre-exponential factor τ_0, or, equivalently, the linear dependence of the activated state enthalpy and entropy. It is considered that

$$\tau_0 = \tau_c \exp\left(-\frac{W}{kT_c}\right) \tag{5}$$

where $\tau_c = \tau(T_c)$ is the compensation time and T_c the compensation temperature. At the temperature T_c, all elementary processes would have the same relaxation time τ_c [2]. Eliminating τ_0 between Eqs. (1) and (4) yields

$$\tau(T) = \frac{kT_m^2}{bW} \exp\left(-\frac{W}{kT_m}\right) \exp\left(\frac{W}{kT}\right) \tag{6}$$

From this relation, and using the Bucci method [18] (representation of log $\tau(T)$, determined by integration of the experimental current, versus $1/T$), we can determine W for the elementary peaks obtained by TS technique. Subsequently, τ_0 is determined from Eq. (4). Following this method there is no need for extrapolation (as it would be in the case when Eq. (1) is employed) and the errors affecting the two parameters (W and τ_0) decrease. Eq. (6) represents a line of slope W/k in the plane defined by $1/T$ and $\log \tau(T)$. For $T = T_c$ the line passes through the compensation point (defined by T_c and τ_c). Consequently, for every elementary peak obtained by the TS technique, it is expected to obtain a line in the above-mentioned plane defined by the two parameters of the peak (W and T_m). The problem is (i) under which condition the lines corresponding to the elementary peaks form a pencil of lines having the point ($1/T_c$, $\log \tau_c$) as its vertex, and (ii) if this point exists, can it be correlated with any physically observable quantity?

The pre-exponential factor τ_0 has no obvious simple physical meaning and it is useful to eliminate it from Eq. (1) using Eq. (4). It follows for the TSDC density that

$$j(T) = P_0 \frac{bW}{kT_m^2} \exp\left(\frac{W}{kT_m}\right) \exp\left[-\frac{W}{kT} - \frac{W}{kT_m^2} \times \exp\left(\frac{W}{kT_m}\right) \int_{T_0}^{T} \exp\left(-\frac{W}{kT'}\right) \mathrm{d}T'\right] \tag{7}$$

P_0 can be determined by integration of the experimental current and consequently, Eq. (7) depends only on one adjustable parameter, namely W. W can be determined by fitting the experimental data to Eq. (2) [19–22] or better to Eq. (7), which represents an improved form of Eq. (2).

3. Experimental results and simulations

For $T = T_c$ Eq. (6) becomes

$$\tau_c = \frac{kT_m^2}{bW} \exp\left(-\frac{W}{kT_m}\right) \exp\left(\frac{W}{kT_c}\right) \tag{8}$$

In Eq. (8) W and T_m are variable parameters and it is known from experimental data [2,13–17,19,20] that W increases monotonically as T_m increases and approaches the glass–rubber transition temperature T_g. We will further consider that the heating rate b is the same for all the scans used in the TS technique. To check the existence of a compensation point, it is necessary to verify that for any elementary peak characterized by the two parameters T_m and W (with $T_m < T_g$ and in the vicinity of T_g, where it is known that the data obtained using the TS technique shows a significant increase in W as T_m increases [2,13–17,19,20]), the function

$$\frac{b\tau_c}{k} = \frac{T_m^2}{W} \left[\exp\left(-\frac{W}{kT_m}\right)\right]^{(1-T_m/T_c)} \tag{9}$$

is constant. The above relation represents a modified form of Eq. (8). By considering a number of successive elementary peaks, it is immediate that T_m is a monotonously increasing quantity and that $T_m < T_c$. W can have any value but the relation (9) will be satisfied only if there is a relationship between T_m and W for all elementary peaks of a complex TSDC spectrum.

Let us consider two elementary peaks characterized by T_{m1}, W_1 and T_{m2}, W_2, where $T_{m2} > T_{m1}$. From Eq. (8), the expression for T_c becomes

$$T_c = \frac{W_2 - W_1}{k} \frac{1}{\log((T_{m1}^2/W_1)(W_2/T_{m2}^2)) + (1/k)(W_2/T_{m2} - W_1/T_{m1})} \tag{10}$$

In general, assuming that W increases linearly (for example, $W = W_0 + aT_m$) or proportionally ($W_0 = 0$) with temperature, we get $W_2 > W_1$. Under these conditions and from Eq. (10), it results that T_c is negative which means that there is no compensation point. This observation can explain why for the local β relaxation a compensation point was not observed. The experimental results obtained using the TS technique for the β relaxation in polymethyl methacrylate [15], poly(vinyl acetate) [23,24], poly(n-hexyl isocyanate) [25] and a series of side-chain liquid crystalline polysiloxananes [26–29] and polyacrylates [30] show that W increases linearly with T_m and consequently no compensation point can be observed, as demonstrated above.

If W is proportional to T_m^n it can be shown that for $n > 2$ the right-side term of Eq. (9) is a decreasing function (T_m^2/W and the exponential term are decreasing as T_m increases) and consequently there is no compensation point.

The only possibility to have the right-side term of Eq. (9) constant is to have $1 < n \leq 2$, meaning that W is, for example, a quadratic function of T_m ($n = 2$). Eq. (8) cannot be solved to obtain $W_{T_c,\tau_c} = f(T_m)$. More information about the dependence of W on T_m and the possibility to observe a compensation point, can be obtained through numerical simulation. Eq. (8) can be solved to obtain the formula for the compensation temperature:

$$T_c = \frac{1}{1/T_m + (k/W)\log(bW\tau_c/kT_m^2)} \qquad (11)$$

We will use Eqs. (8) and (11) in our simulations. T_c and τ_c are considered as parameters and T_m as variable, meaning that we will consider all elementary peaks than can contribute to a global spectrum. Fig. 1 presents $W = f(T_m)$ for $\tau_c = 0.006$ s and for three values of T_c, namely 248, 258 and 268 K. It can be seen that for T_m increasing from 200 to 240 K, W must increase quite a lot, from 0.6 to 2 eV, in order for the compensation to be satisfied. Fig. 2 presents $W = f(T_m)$ for $T_c = 258$ K and for three values of τ_c, namely 0.003, 0.006 and 0.009 s. We observe the same significant increase in W with T_m. The values for the compensation parameters (258 K and 0.006 s) are taken from Ref. [2]. We emphasize that an increase in W with T_m in the region of the glass–rubber transition temperature of the amorphous phase of a polymer is expected [2,13–15,17,19–22] but not to the extent seen here.

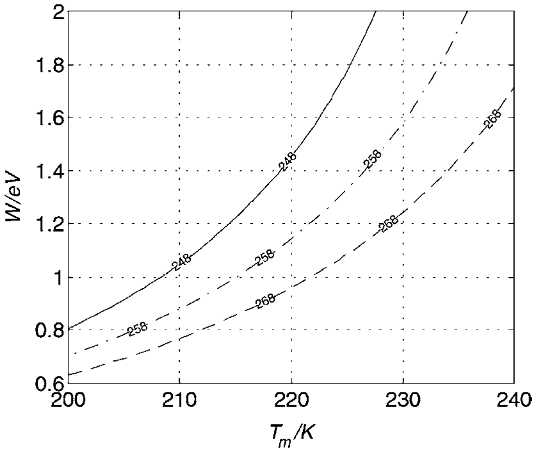

Fig. 1. The simulated variation of the activation energy W with the temperature of the maximum intensity of the current peak for a compensation time $\tau_c = 0.006$ s and for three values of the compensation temperature T_c: 248, 258 and 268 K.

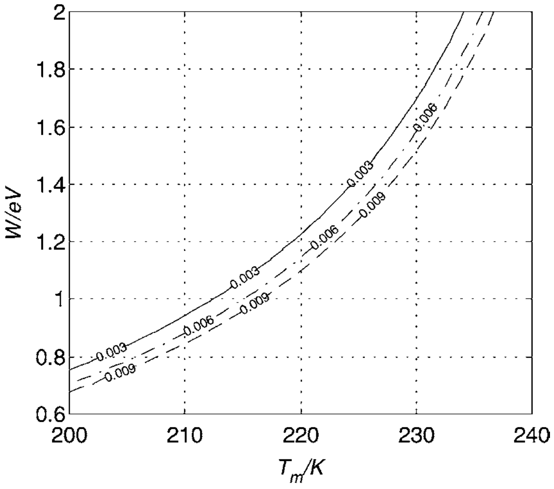

Fig. 2. The simulated variation of the activation energy W with the temperature of the maximum intensity of the current peak for a compensation temperature $T_c = 258$ K and for three values of the compensation time τ_c: 0.003, 0.006 and 0.009 s.

The data shown in Fig. 1 can be presented using the equivalent parameters ΔH and ΔS [2] for the same range of variation for W and T_m. This graph is presented in Fig. 3. From Fig. 3 it can be seen that in order to have a compensation point it is necessary to have a linear relationship between ΔH and ΔS.

A global TSDC spectrum can be analyzed by decomposing it into elemental currents using the partial heating (or peak cleaning) technique [17]. In every successive partial heating, a current is obtained that increases faster with the temperature from run to run. The activation energy can be determined using the initial rise method [31]:

$$W = \log\left(\frac{j_2}{j_1}\right)kT_1\left(1+\frac{T_1}{\Delta T}\right) \qquad (12)$$

where j_1 is the current density at the initial temperature T_1 and j_2 the current density at the final temperature $T_1 + \Delta T$. For example, we have used the partial heating technique to analyze the TSDC spectrum of biaxially stretched polyethylene terephthalate (PET) [20] in a temperature interval from 20 to 140 °C, meaning a temperature interval that includes the glass–rubber transition region. The global current

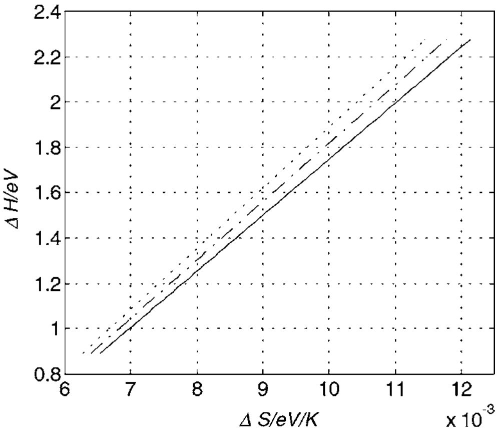

Fig. 3. The relation between the activation enthalpy ΔH and the activation entropy ΔS for the data presented in Fig. 1. The symbols are as follows: solid line (—) for 248 K, dash-dotted line (– · – · –) for 258 K and dotted line (· · ·) for 268 K, respectively.

was decomposed into four elemental currents (only four shoulders were revealed by the experimental data). The activation energy, determined by fitting the experimental data with Eq. (12), increased from 0.21 to 1.37 eV. It was not possible to have a well-defined relationship between W and T. The activation energy determined from dielectric relaxation measurements on the same material, in the same temperature range and the frequency range from 10^{-2} to 10^{6} Hz, was 1 eV [32]. The value reported for W in the temperature range from 150 to 200 °C was $W = 1.5$ eV [33,34].

In order to proceed further, simulations considering data similar with those obtained for the α relaxation in PET will be presented. It is assumed that the relaxation time at T_{m} is approximately 100 s [13–15,19,22]. We will assume that W varies from 0.2 to 1.4 eV when temperature varies from 320 to 420 K, in agreement with the data presented above. Fig. 4 presents the dependence of W upon T_{m} for $\tau_{\mathrm{c}} = 100$ s and for three possible values of the compensation temperature, namely 400, 410 and 420 K. Fig. 5 presents the same dependence for three possible values of the compensation time 50, 100 and 200 s, assuming $T_{\mathrm{c}} = 410$ K.

From Figs. 4 and 5 it can be concluded that the compensation point can be observed only if there is a significant increase of W with T_{m} (the temperature of maximum intensity of the TS peak).

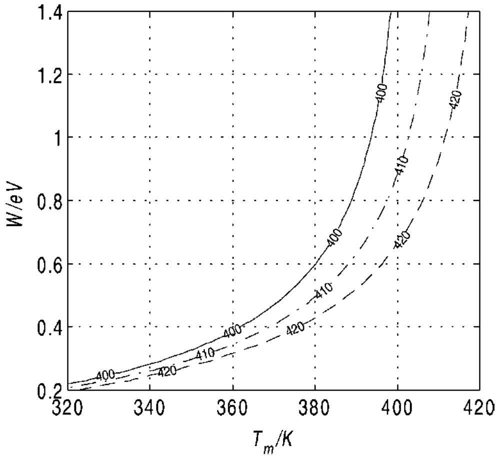

Fig. 4. The simulated variation of the activation energy W with the temperature of the maximum intensity of the current peak for three possible values of the compensation temperature: 400, 410 and 420 K and for $\tau_{\mathrm{c}} = 100$ s. The variation intervals for W and T correspond to those determined experimentally for PET.

We will further analyze the problem from another point of view: how accurately can the compensation point be estimated? An estimate may be obtained assuming that the right-side term in Eq. (9) is constant. The percentage error for determining T_{m} is around 0.5%. The most important error is that affecting the activation energy and it has two components. One is

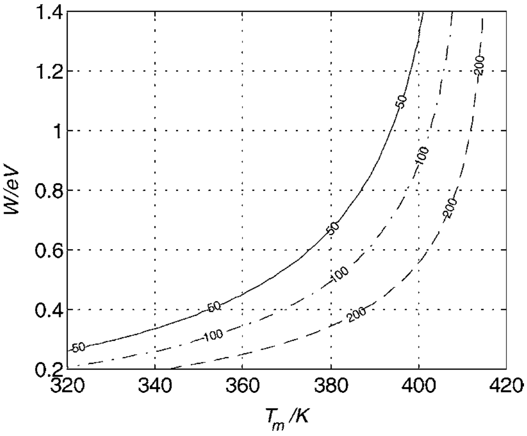

Fig. 5. The simulated variation of the activation energy W with the temperature of the maximum intensity of the current peak for three possible values of the compensation time: 50, 100 and 200 s and considering $T_{\mathrm{c}} = 410$ K. The variation intervals for W and T correspond to those determined experimentally for PET.

determined by the measurement procedure and amounts to approximately 5% when W is determined by fitting the experimental data with the analytical expression of the current and 10% when it is determined by the integration of the experimental current (the Bucci method [18]). There is a second component [22] that has to be considered and which is due to the presence of a thermal energy kT. The error for W determined by the thermal energy is about $2kT_m$ for an elementary peak having the temperature of maximum intensity of the peak T_m. For numerical evaluation, we will assume that $b = 7/60$ K/s, $T_c = 258$ K and $\tau_c = 6 \times 10^{-3}$ s [2]. From relation (8) we find that for $W = 1.5$ eV the temperature of maximum intensity of the peak is $T_m = 239.6$ K. Accepting that the error for W is 0.08 eV, the maximum error for T_c is determined as about 22 K. A similar behavior can be observed in Figs. 1 and 4. This means that, in the limits of the experimental errors, we do not expect to find an accurately defined compensation temperature.

As concerns the compensation time from Fig. 2, it can be observed that, in the limits of the experimental error of W, the percentage error of τ_c could be even higher than 100%.

4. Conclusions

We took advantage of the fact that the parameters of a peak (the activation energy W, the pre-exponential factor τ_0 and the temperature of maximum intensity of the peak T_m) cannot be determined independently using the TSDC technique, and a relationship between W, T_m, the compensation time τ_c and the compensation temperature T_c was deduced. Using this relation we demonstrated that a compensation effect may be observed only for a material for which the activation energy is a monotonically increasing power function of temperature, with power coefficients between 1 and 2.

For the local β relaxation it was demonstrated that it is not possible to observe a compensation point as long as the activation energy increases linearly with T_m. This fact is in agreement with the majority of the experimental results reported in the literature showing that the pre-exponential factor is roughly universal for the β relaxation. In the case of the non-local main relaxation α, a significant increase of W with the temperature of maximum intensity of the peak is observed only when the TS technique is used. This large increase in W is accompanied by a drastic decrease in τ_0. An increase of W is not observed when complementary methods like dielectric relaxation, direct conductivity current or dynamic mechanical measurements are carried out. Consequently, a set of energies is deduced by the TS technique and one can expect that the energy corresponding to the strongest thermally sampled peak has some relation with the energy related to other methods. The uncertainties affecting the compensation parameters are significant and consequently it is not possible to have a well-defined compensation point.

References

[1] W. Meyer, H. Neldel, Zh. Tekh. Fiz. 12 (1937) 58.
[2] G. Teyssedre, P. Demont, C. Lacabanne, J. Appl. Phys. 79 (1996) 9258.
[3] F.H. Constable, Proc. Roy. Soc. Lond. A 108 (1925) 355.
[4] D. Wagner, P. Irsigler, D.J. Dunstan, J. Non-Cryst. Sol. 59–60 (1983) 413.
[5] D.P. Almond, A.R. West, Solid State Ionics 18–19 (1986) 1105.
[6] R.N. Haward, The Physics of Glassy Polymers, Wiley, New York, 1973.
[7] O. Exner, Nature 201 (1964) 488.
[8] P.D. Garn, J. Therm. Anal. 10 (1976) 99.
[9] B.E. Read, Polymer 30 (1989) 1439.
[10] A.S. Nowick, W.K. Lee, H. Jain, Solid State Ionics 28–30 (1988) 89.
[11] T. Pfeiffer, Solid State Ionics 105 (1998) 227.
[12] K.L. Ngai, Solid State Ionics 105 (1998) 231.
[13] B.B. Sauer, P. Avakian, Polymer 33 (1992) 5128.
[14] J.J. Moura Ramos, J.F. Mano, B.B. Sauer, Polymer 38 (1997) 1081.
[15] B.B. Sauer, J.J. Moura Ramos, Polymer 39 (1997) 4065.
[16] V. Halpern, J. Phys. D 30 (1997) 458.
[17] J. van Turnhout, in: G.M. Sessler (Ed.), Electrets, Topics in Applied Physics, Vol. 33, Springer, Berlin, 1980 (Chapter 3).
[18] C. Bucci, R. Fieschi, G. Guidi, Phys. Rev. 148 (1966) 816.
[19] R. Neagu, E.R. Neagu, A. Kyritsis, P. Pissis, J. Phys. D 33 (2000) 1921.
[20] E.R. Neagu, J.N. Marat-Mendes, D.K. Das-Gupta, R. Neagu, R. Igreja, J. Appl. Phys. 82 (1997) 2488.
[21] E.R. Neagu, J.N. Marat-Mendes, D.K. Das-Gupta, R. Neagu, J. Appl. Phys. 85 (1999) 2330.
[22] R.M. Neagu, E.R. Neagu, I.M. Kalogeras, A. Vassilikou-Dova, Mater. Res. Innov. 4 (2001) 115.
[23] A.B. Dias, J.J. Moura Ramos, G. Williams, Polymer 35 (1994) 1253.

[24] A.B. Dias, N.T. Correia, J.J. Moura Ramos, A.C. Fernandes, Polym. Int. 33 (1994) 293.

[25] J.F. Mano, N.T. Correia, J.J. Moura Ramos, J. Chem. Soc., Faraday Trans. 91 (1995) 2003.

[26] J.F. Mano, N.T. Correia, J.J. Moura Ramos, S. Andrew, G. Williams, Liq. Cryst. 20 (1996) 201.

[27] J.F. Mano, N.T. Correia, J.J. Moura Ramos, A.C. Fernandes, J. Polym. Sci., Polym. Phys. Ed. 33 (1995) 269.

[28] J.F. Mano, J.J. Moura Ramos, J. Therm. Anal. 44 (1995) 1037.

[29] J.F. Mano, J.J. Moura Ramos, D. Lacey, G. Nestor, J. Polym. Sci., Polym. Phys. Ed. 34 (1996) 2067.

[30] J.F. Mano, J.J. Moura Ramos, A.C. Fernandes, G. Williams, Polymer 35 (1994) 5170.

[31] G.F.K. Garlick, A.F. Gibson, Proc. Phys. Soc. Lond. 60 (1948) 574.

[32] E.R. Neagu, P. Pissis, L. Apekis, J.L. Gomez Ribelles, J. Phys. D 30 (1997) 1551.

[33] K. Miyairi, J. Phys. D 19 (1986) 1973.

[34] V. Adamec, J.H. Calderwood, J. Phys. D 24 (1991) 969.