Effect of the Stabilizer Based on Calcium/Zinc on the α-Relaxation of Poly(vinyl chloride) by the Method of Thermostimulated Depolarization Currents

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Abstract: The thermostimulated depolarization currents (TSDC) technique was used to investigate relaxation in stabilized poly(vinyl chloride) (PVC) over a temperature range that covers the α-relaxation. Analysis of TSDC behavior revealed that these samples are characterized with broad peaks located at the temperature maximum $T_M = 363\,K$ in the vicinity of glass transition. The maximum intensity of the obtained peaks presents a net dependence with regard to the stabilizer contents. The temperature maxima remain unchanged. The parameters characterizing each elementary peak, obtained by the cleaning method and characterized by a single relaxation time, were determined.

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INTRODUCTION

Low thermal stability is an inherent property of poly(vinyl chloride) (PVC). It is known that PVC decomposes at a temperature lower than its processing temperature, and its degradation is accompanied by the loss of HCl with the formation of conjugated double bonds.[1–2]

The poor thermal stability of this polymer requires the use of the stabilizers, the most important ones being metal soaps like Pb, Ca, Ba, Cd, Ca, and Zn carboxylates and some di- and mono-alkyltin compounds. Epoxy compounds are well known as typical nonmetallic stabilizers for PVC.

The aim of this work is to study the influence of the stabilizer Ca/Zn powder on the thermal properties of PVC around the glass transition temperature with the use of the thermostimulated depolarization currents (TSDC) method. This technique is a powerful tool for the detailed investigation of complex processes at the glass transition of amorphous polymers due to its high sensitivity towards dipole orientation as well as its high resolution power.[3–7]

The TSDC method consists of applying DC voltage to a material in order to orient dipoles that are sensitive to electrical field. After cooling down, the sample is short-circuited and the depolarization current is measured at a constant heating rate. The resulting TSD current peaks represent typical relaxation processes similar to those of loss in dielectric measurements. Peak area, maximum temperature, initial rise, and shape of the peak are the main obtainable information of the relaxation process.

In a PVC sample, it is generally accepted that above room temperature, the TSDC spectrum exhibits two main relaxation peaks. The first one is localized around 353–363 K in the range of the glass rubber-transition temperature T_g, and the second one is above 403 K and whose exact nature is subject of controversy in the literature.[8]

We have studied the effect of Ca/Zn stabilizer on the α-relaxation peak that appears around the glass-rubber transition of PVC in the temperature range from 273 K to above T_g for different contents of stabilizer.

The peak cleaning method[9] was applied to study individual modes of relaxation for peaks appearing around the glass-rubber transition temperature. The specific parameters have been obtained using different methods, including the peak integration method.[9]

EXPERIMENTAL SECTION

Samples

The PVC (denominated 3000H) and Ca/Zn powder stabilizer supplied by Cabel (Algiers, Algeria) were mixed at 373 K using various percentages of
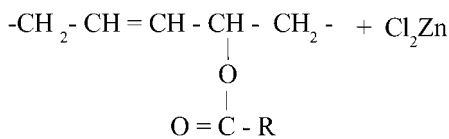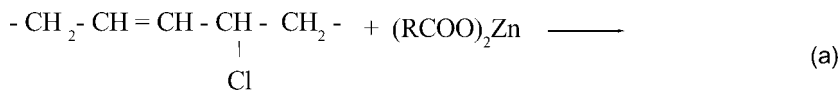
Table I. PVC sample characteristics

Material name	K-value	Polymerization degree	Ohmic resistivity (Ω m)	Apparent density (10^3 Kg/m^3)
PVC 3000H	70.2–72.0	1260–1400	3.5×10^{11}	0.42–0.47

Ca/Zn stabilizer. Table I gives a summary of the characteristics of the PVC sample.

Samples were then prepared in the form of pastilles (12×10^{-3} m diameter and 10^{-3} m thickness) under a pressure of 10^8 kg/m^2.

The first step of the stabilization process is schematized by reaction (a).

$$- CH_2 - CH = CH - CH - CH_2 - \ + (RCOO)_2Zn \longrightarrow \quad (a)$$
$$\mid$$
$$Cl$$

$$-CH_2 - CH = CH - CH - CH_2 - \ + Cl_2Zn$$
$$\mid$$
$$O$$
$$\mid$$
$$O = C - R$$

The zinc chloride is then inhibited by reaction with carboxylate of calcium:

$$(RCOO)_2Ca + Cl_2Zn \longrightarrow (RCOO)_2Zn + Cl_2Ca \qquad (b)$$
$$\text{active again}$$

The obtained carboxylate reacts again according to reaction (a).

The glass transition temperature of 363 K was determined by differential scanning calorimetry (DSC). The DSC measurements were performed in a Q-10 TA apparatus. The temperature was calibrated with indium. The sample (m $= 10^{-5}$ kg) was sealed in aluminium foil, and the recording of the DSC spectra was carried out at heating rate of 0.17 K/s.

In order to measure the TSDC spectrum, the sample placed between the plates of the condenser is put in a measurement cell maintained at constant pressure of 5.3 kPa under inert He gas. Then, it is polarized by an electrical field $E_p = 3 \times 10^5$ V/m at the polarization temperature $T_p = 368$ K, for an interval of time $t_p = 180$ s, usually much longer than the polarization relaxation time, in order to reach saturation. The temperature is then decreased to $T_0 = 273$ K with the polarizing field still on. The field is then suppressed, the sample quenched to liquid nitrogen temperature, and the electrodes short-circuited for 900 s in order to minimize the parasitic charge. Then, the condenser is connected to the input of an electrometer, the sample is heated at a constant rate (0.12 K/s); the relaxation time decreases, and a depolarization current is detected by an

electrometer (Keithley 610C) and recorded by using an X-Y recorder. All measurements were repeated to verify the reproducibility of the results.

Analysis of the Peaks

The current density released during a thermally stimulated measurement can be expressed by different equations that can be arranged in a general form[5]:

$$J(T) = A \exp\left\{\frac{-\Delta H}{(kT)} - B/b \int_{T_0}^{T} \exp\left[\frac{-\Delta H}{(kT')}\right] dT'\right\} \qquad (1)$$

where ΔH is the activation enthalpy of the process, T and T' are the temperature, k is the Boltzmann constant, and b is the heating rate. The expressions for A and B depend on the exact processes involved in the release of the current. If the current is determined by dipole disorientation, the two constants are given by:

$$A = P_0/\tau_0; \quad B = 1/\tau_0$$

where τ_0 is the pre-exponential factor, which is a characteristic time constant for the process, and P_0 is the initial polarization. Its expression is:

$$P_0 = \left(\frac{N\mu^2 E_p}{3kT}\right) \qquad (2)$$

where N is the concentration of dipoles, E_P is the local electric field, and μ is the dipole moment, which is dependent on temperature.

For the determination of the characteristic parameters of the process, i.e., the activation enthalpy and the pre-exponential factor, the integration peak method is mostly used.[9] This method is based on the fact that for an elementary single motional process, we can write:

$$\frac{dP(T)}{dt} = -\frac{P(T)}{\tau(T)} \qquad (3)$$

where $P(T)$ is the polarization at temperature T and $\tau(T)$ is temperature-dependent relaxation time, characteristic of the elementary mode, with:

$$\tau(T) = \frac{P(T)}{J(T)} \qquad (4)$$

where $P(T)$ is the area under the elementary studied peak.

$$P(T) = \int_{T}^{\infty} J(T') dT' \qquad (5)$$

The plot of $\ln(\tau)$ as a function of $(1/T)$ is a straight line whose slope gives the value of ΔH, and the value of τ_0 is obtained by extrapolation at infinite temperature.

Compensation is defined in terms of the linear dependence of ΔH on the logarithm of the pre-exponential factor τ_0, or, equivalently, the linear dependence of the activated state enthalpy and entropy.[10] It is considered that:

$$\tau_0 = \tau_c \exp\left(-\frac{\Delta H}{kT_c}\right) \tag{6}$$

where $\tau_c = \tau(T_c)$ is the compensation time and T_c is the compensation temperature. At the temperature T_c, all elementary processes would have the same relaxation time τ_c.

RESULTS

As a first step, a routine investigation of PVC and PVC stabilized by Ca/Zn stabilizer powder (5×10^{-3} kg of stabilizer were added to 10^{-1} kg of PVC) materials by DSC was performed. Figure 1 shows the DSC curve obtained for 10^{-5} kg of PVC powder. Figure 2 shows the DSC measurements of the stabilized PVC.
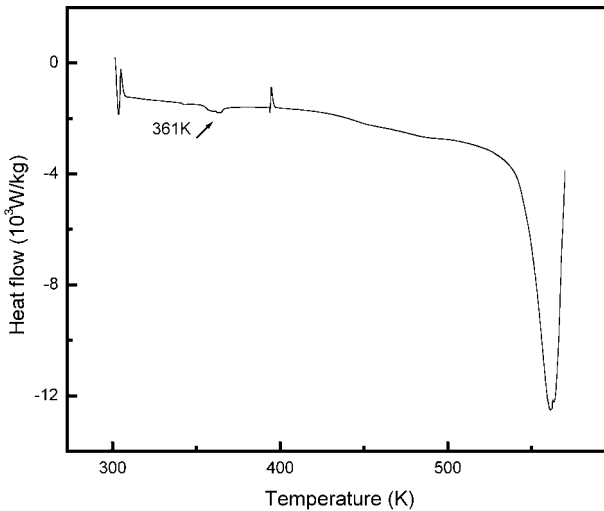

Figure 1. DSC spectrum of amorphous poly(vinyl chloride); scanning rate 0.17 K/s, PVC mass used 10^{-5} kg.
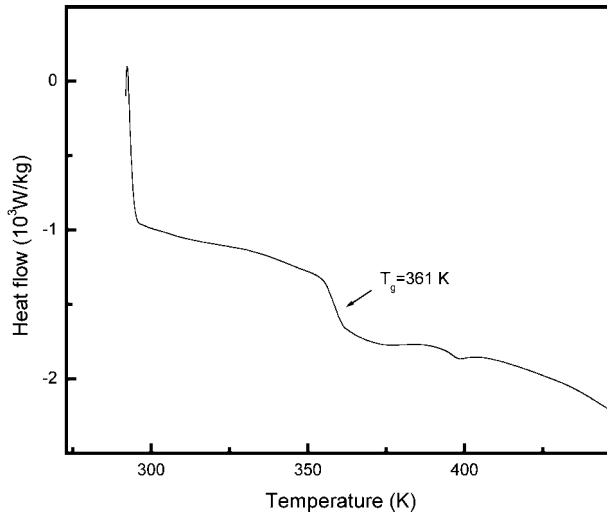
Figure 2.   DSC spectrum of stabilized poly(vinyl chloride) (5×10^{-3} kg of stabilizer were added to 10^{-1} kg of PVC); scanning rate 0.17 K/s, stabilized PVC mass used 10^{-5} kg.

The two figures show a broad and a weak glass-rubber transition around 361 K (the thermogram shows the glass transition as a step in the specific heat capacity).

α-Relaxation Mode

The complex spectra shown in Figures 3(a) and 4(a) were obtained by polarizing the pure PVC and the stabilized PVC to $T_p = 368$ K during 180 s (long enough to reach equilibrium polarization) by a static field $E_p = 3 \times 10^5$ V/m. The spectra reveal peaks located at the position $T_M = 363$ K related to α-relaxation. To study in detail this relaxation mode, the obtained peaks have been experimentally resolved into a set of elementary spectra with the peak cleaning method and a thermal window of 5 K, as shown in Figures 3(b) and 4(b). The envelope of the elementary peaks obtained with the cleaning method reproduces qualitatively the shape of the main peak. The transformation of all elementary peaks obtained with the thermal windowing method into their Arrhenius representations (Figures 5 and 6) allows the correlation between single relaxation modes and thermokinetic (free energy, free entropy, and enthalpy) and/or physical variables (Tables II and III).
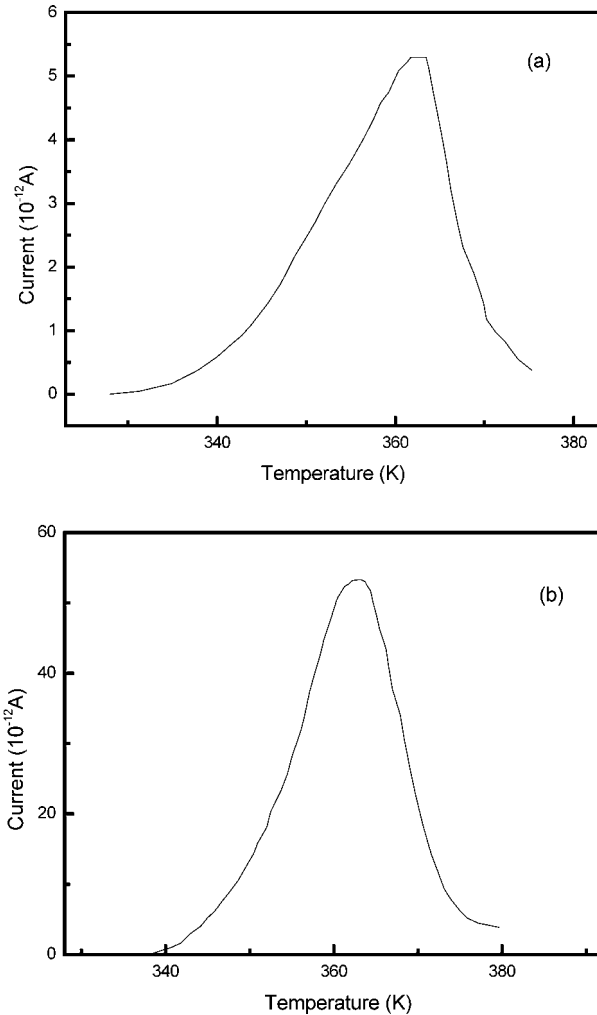
Figure 3. TSDC spectra: (a) TSDC peak of pure PVC sample polarized at $T_p = 368$ K, with electrical field $E_p = 3 \times 10^5$ V/m; (b) TSDC peak of stabilized PVC sample (5×10^{-3} kg of stabilizer were added to 10^{-1} kg of PVC) polarized at $T_p = 368$ K, with electrical field $E_p = 3 \times 10^5$ V/m.

Influence of Polarization Conditions on α Peak

Figure 7 shows the behavior of the α peak in the case of stabilized PVC (5×10^{-3} kg of stabilizer were added to 10^{-1} kg of PVC), as a function of the polarization time t_p at $T_p = 368$ K and at a constant polarizing voltage $V_p = 300$ V. The inset graph displays a dependence of α peak
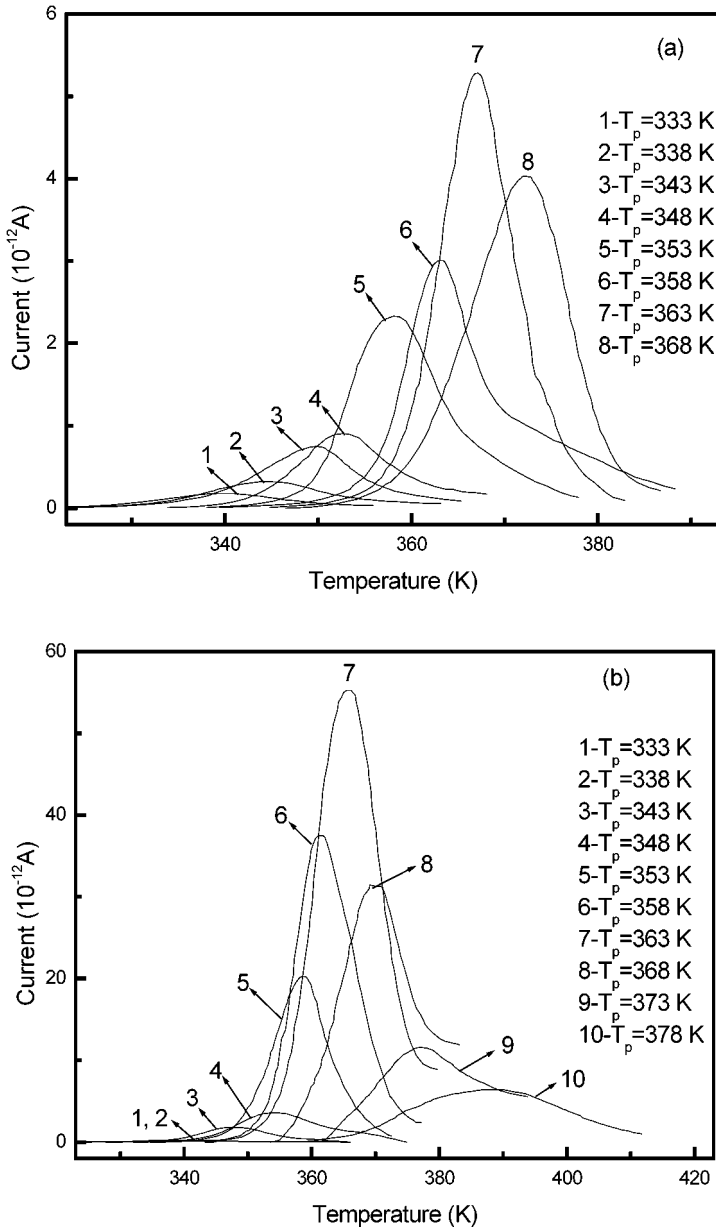
Figure 4. Elementary TSDC spectra: (a) pure PVC; (b) stabilized PVC $(5 \times 10^{-3}\,\mathrm{kg}$ of Ca/Zn stabilizer were added to $10^{-1}\,\mathrm{kg}$ of PVC).
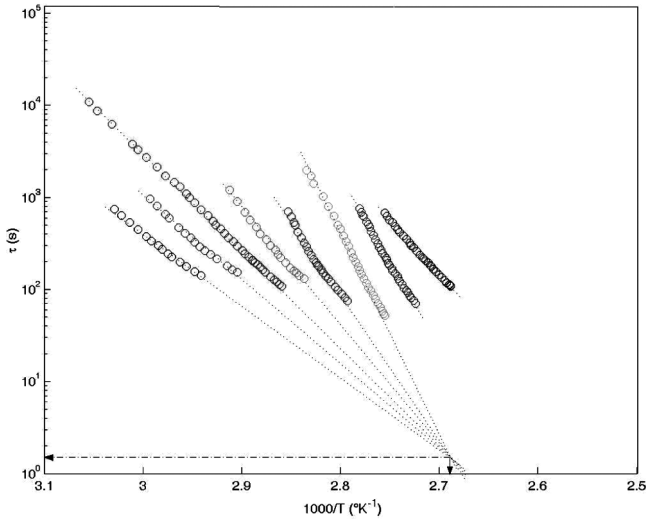
Figure 5. Arrhenius plot of the relaxation times obtained from TSDC measurement for α peak of pure PVC. The graph shows a positive compensation around ($T_c = 369$ K, $\tau_c = 1.5$ s).

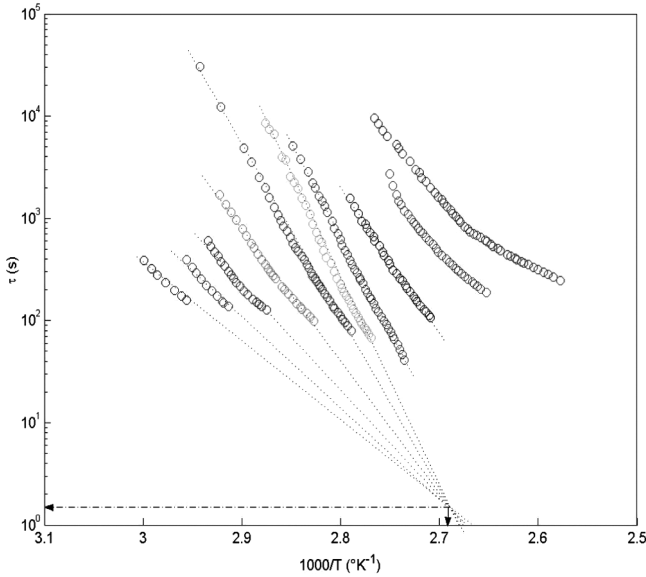**Figure 6.** Arrhenius plot of the relaxation times obtained from TSDC measurement for α peak of stabilized PVC (5×10^{-3} kg of Ca/Zn stabilizer were added to 10^{-1} kg of PVC). The graph shows a positive compensation around ($T_c = 369$ K, $\tau_c = 1.5$ s).

Table II. Specific parameters for α-relaxation in PVC involved in the release of the current, determined by the use of the peak integration method

T_P (K)	T_M (K)	ΔH (10^{-19} J)	τ_0 (s)
333	340	2.691	1.591×10^{-23}
338	344.5	3.009	4.341×10^{-26}
343	350	3.262	4.663×10^{-28}
348	352.5	4.227	2.022×10^{-36}
353	358	5.539	1.375×10^{-47}
358	363	6.390	2.195×10^{-54}
363	367	5.769	2.630×10^{-48}
368	371	4.054	4.946×10^{-33}

maximal intensity on t_p. Concerning the temperature position of the peak maxima, it does not seem to be affected by the polarization time t_p.

It is generally accepted that TSDC spectra arise from dipole reorientation as well as from the migration of impurities and ionic conductors in the polymer (space charge). One way to differentiate between them is to examine the relationship between the current intensity and the electrical field. Figure 8 represents the behavior of the α peak as a function of the polarizing electrical field E_p. A linear dependence of the α peak value on E_p may be observed in the inset graph. On the other hand, no influence with regard to the maximum temperatures has been observed. The temperature position of the peak maxima remains constant ($\approx$363 K)

Effect of Percentage of Stabilizer on α Peak Behavior

Stabilized PVC samples were investigated for different weight ratios. The complex spectra obtained for each sample are reported in Figure 9.

Table III. Specific parameters for α-relaxation in stabilized PVC (weight ratio: 5×10^{-3} kg of stabilizer for 10^{-1} kg of PVC) involved in the release of the current, determined by the use of the peak integration method

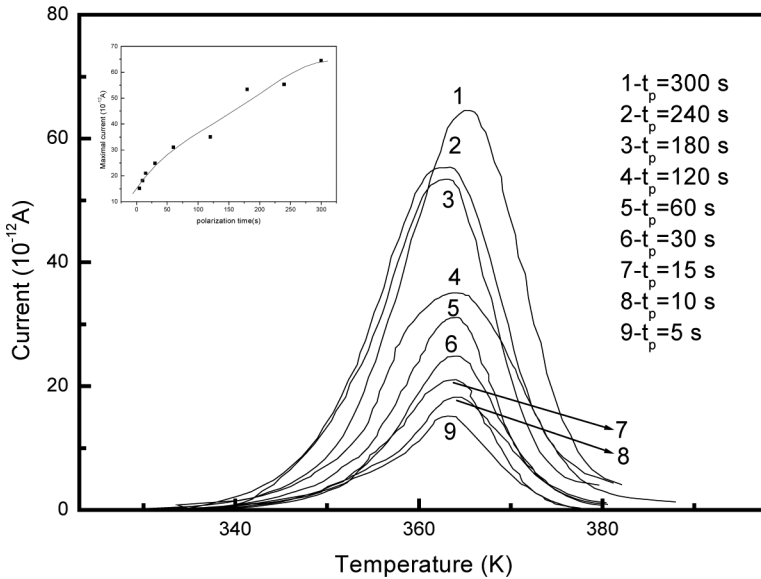| T_P (K)	T_M (K)	ΔH (10^{-19} J)	τ_0 (s)
333	340	2.846	5.138×10^{-25}
338	343	3.438	3.817×10^{-30}
343	348.5	3.780	6.909×10^{-33}
348	354	4.332	2.473×10^{-37}
353	358.5	5.324	2.416×10^{-54}
358	361	6.361	7.712×10^{-48}
363	366	5.670	2.007×10^{-36}
368	369	4.424	2.007×10^{-36}

Figure 7. TSDC spectra of stabilized PVC corresponding to different times of polarization t_p; polarization temperature $T_p = 368 \, K$, electrical field $E_p = 3 \times 10^5 \, V/m$, heating rate 0.17 K/s. The dependence of the α peak value on the polarization time is shown in the inset.

It is important to note that the same conditions of polarization have been maintained for each recording, i.e., the same electrical field $E_p = 3 \times 10^5 \, V/m$, polarization time $t_p = 180 \, s$, and polarization temperature $T_p = 368 \, K$.

The maximum intensity of the obtained peaks represents a net dependence with regard to the stabilizer percentage. Concerning the temperature position of the peak maxima, it does not seem to be affected by the stabilizer percentage and remains constant ($\approx 363 \, K$) (see Figure 10).

DISCUSSION

The α-relaxation mode observed at $T_M = 363 \, K$ is attributed to glass transition, which is detected in amorphous polymers. It is associated with the micro-Brownian motions of the main-chain segments. Disordered movements animate the amorphous segments.[11] The elementary peak exploitation of the α relaxation allows plotting $\ln(\tau) = f(1000/T)$ diagrams according to the Arrhenius equation. The values ($6.390 \times 10^{-19} \, J$) and ($6.361 \times 10^{-19} \, J$) of the activation enthalpy, in the vicinity of the glass transition of PVC and stabilized PVC (in the weight ratio: $5 \times 10^{-3} \, kg$
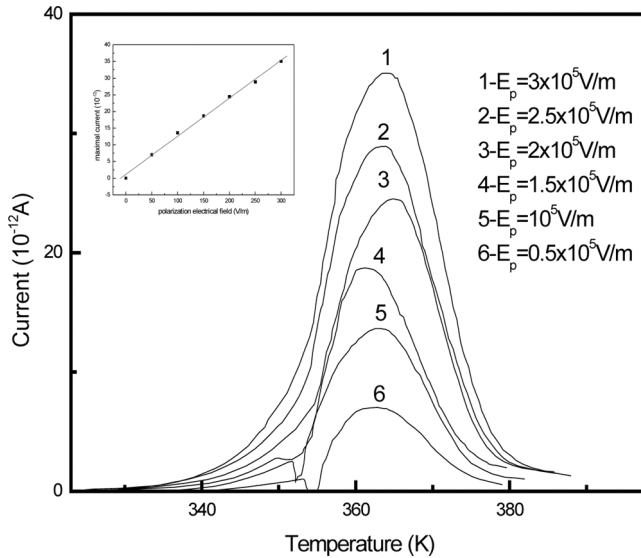
Figure 8. TSDC spectra of stabilized PVC corresponding to different electrical fields of polarization E_p ($5 \times 10^4 - 3 \times 10^5$ V/m with an increment of 50 V/m); heating rate 0.17 K/s, polarization temperature $T_p = 368$ K. The dependence of the α peak value on the polarization electrical field is shown in the inset.
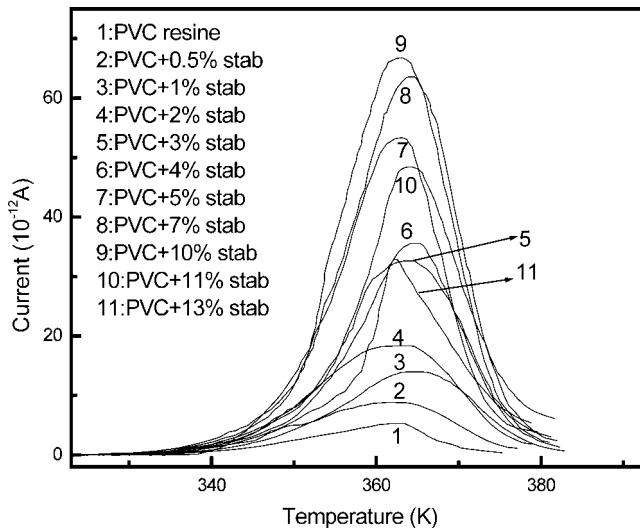

Figure 9. TSDC spectra of stabilized PVC in different ratios; polarization temperature $T_p = 368$ K, polarization time $t_p = 180$ s, electrical field $E_p = 3 \times 10^5$ V/m.
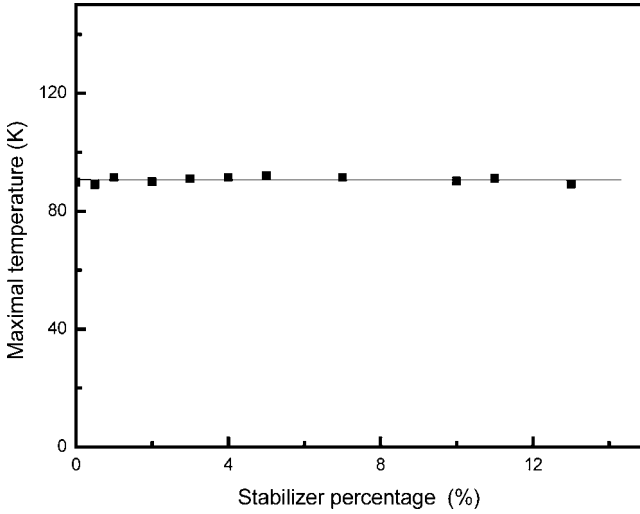
Figure 10. Stabilizer concentration dependence of the maximum temperature of the TSDC peaks.

of stabilizer for 10^{-1} kg of PVC), characterize a main relaxation mode. For the two samples, ΔH remains unchanged.

The existence of a compensation phenomenon is observed. Indeed, from the Arrhenius diagram (Figures 5 and 6), it was observed that the six first
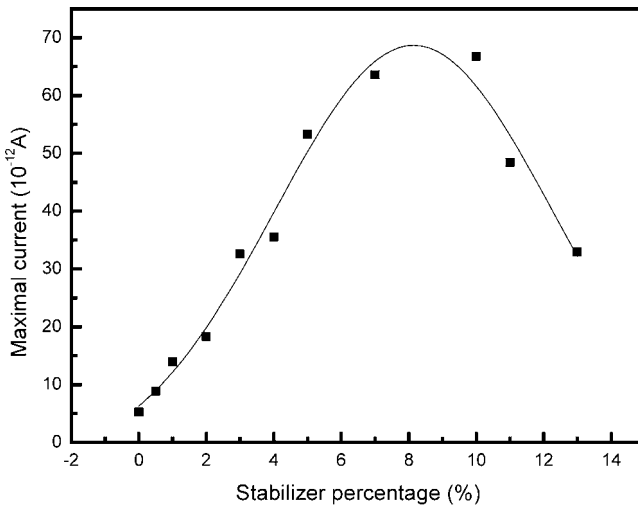
Figure 11. Stabilizer concentration dependence of the maximum current intensity of the TSDC peaks.

lines converge towards the same point. Its coordinates give the parameters ($T_c = 369\,\mathrm{K}$, $\tau_c = 1.5\,\mathrm{s}$) representing respectively the temperature and the time of compensation. We notice that the same phenomenon was observed within amorphous poly(ethylene terephtalate) (PET) at $T_c = 360\,\mathrm{K}$[7] and amorphous poly(vinyl chloride) (PVC) at $T_c = 359\,\mathrm{K}$.[6] Moreover, the linear evolution of $\ln(\tau_0)$ versus ΔH confirms the existence of such a phenomenon characterizing the mobile amorphous phase. This phenomenon is associated with the existence of an order in the amorphous phase of the materials[7] and reveals the existence of a cooperative motion into the material. The stabilizer has no effect on the activation enthalpy in the vicinity of glass transition of the two samples and on the compensation phenomenon.

The polarization electric field influence is manifested by an increase in the peak current amplitude, confirming the dipolar relaxation process. This increase is explained by the fact that the electrical field E_P affects more dipoles as its intensity increases. A similar behavior was observed with the PET[7] and amorphous PVC.[6]

Figure 11 shows that the current evolution as a function of the stabilizer percentage exhibits a maximum at 8% of the stabilizer. This behavior can be explained by the fact that for stabilizer percentages below 8%, the number of dipoles that contribute to the α-relaxation mode increases. However, for stabilizer percentages above 8%, the quantity of the stabilizer added to the material is important. This fact induces a diminution of the free volume in the sample and, consequently, a decrease in TSD current peaks.

CONCLUSION

We have reported on the effect of the stabilizer based on Ca/Zn powder on the thermal physics properties around the glass transition temperature of PVC by the use of the thermostimulated depolarization currents (TSDC) method.

According to the results of the present study, it can be concluded that:

- Measurements of TSDC spectra carried out with the stabilized PVC of different weight ratios have revealed broad peaks around glass-rubber transitions of the materials.
- The maximum intensity of the obtained peaks represents a net dependence with regard to the percentage of stabilizer.
- No influence with regard to peak maximum temperature has been observed. It is situated at $T = 363\,\mathrm{K}$, which corresponds to the glass transition temperature of the sample.
- The enthalpy determination from Arrhenius plots is around ($6.390 \times 10^{-19}\,\mathrm{J}$) and ($6.361 \times 10^{-19}\,\mathrm{J}$) in the case of pure PVC and

stabilized PVC (5×10^{-3} kg of stabilizer were added to 10^{-1} kg of PVC), respectively. Activation enthalpy is the same for the two samples. The stabilizer has no effect on the activation enthalpy of the material.
- A compensation phenomenon has been observed at $T = 369$ K. It reveals the existence of a cooperative motion into the materials at this temperature.

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