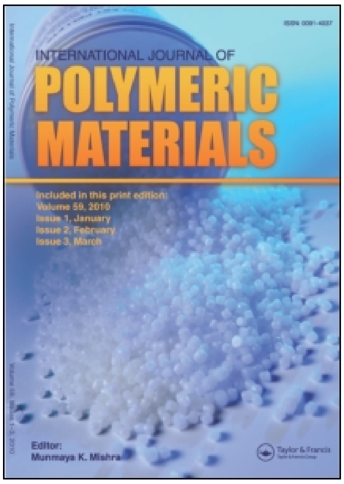

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CORONA CHARGING AND THERMAL SAMPLING OF STRETCHED POLY(VINYL CHLORIDE)

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CORONA CHARGING AND THERMAL SAMPLING OF STRETCHED POLY(VINYL CHLORIDE)

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Corona charging and thermal poling have been used to prepare stretched and unstretched poly(vinyl chloride) (PVC) electrets. Short-circuit thermally stimulated depolarization, as a function of poling parameters, has been recorded. The thermal sampling–thermally stimulated depolarization current relaxation behavior of the stretched PVC was investigated in the frame of relaxation map analysis (RMA). The analysis revealed that stretched PVC is characterized by two compensation temperatures, indicating conformational changes of PVC molecules.

Keywords: PVC, corona charging, transition, T_g

INTRODUCTION

PVC is a typical amorphous polymer whose dynamics have been long and extensively studied by using most of the available experimental techniques. This polymer shows two well-defined relaxation ranges: (i) the α-relaxation that is detectable at $T \cong 357$ K and (ii) the β-relaxation that is active below 182 K, that is far below T_g [1]. The high strength of the dielectric α-relaxation and the very different time scales of both processes justified the common use of PVC as a standard in the investigations of polymer segmental dynamics [2].

Corona discharges have been used from the beginning of the last century in precipitation and ozonizing techniques and later as a source of charged particles, especially electrons for the initiation of chemical reactions. One of the most important uses of corona discharges is their use in

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electrostatic precipitators [3]. Among other applications, point-to-plate corona discharge has been extensively used for charging dielectric surfaces, mainly polymer films, xerography, and static charge elimination. It is known that a metallic grid inserted between the corona point and the dielectric provides a simple way to control the ion flux to the sample surface [4]. Such apparatus is frequently called a corona triode.

On the other hand, the technique of thermally stimulated depolarization current (TSDC) is a dielectric technique in which the dynamics of the system are observed through the trend of previously aligned structural dipoles to orientate at random as the mobility of the system increases during a continuous heating from temperatures far below T_g. The various depolarization processes detected during heating can be correlated to the mechanisms of molecular-motion within the material. This technique has been gaining acceptance on the one hand due to its high resolution power related to its intrinsic low equivalent frequency and, on the other hand, because it offers the possibility of decomposing a complex relaxation mechanism (normally characterized by a distribution of relaxation times) into its elementary contributions, by means of the so-called thermal sampling experiments (TS), allowing the analysis of TSDC spectrum's fine structure. Due to the high resolution of TS technique, it is particularly suitable for analysis of complex and distributed relaxation process and to detect the onset of the segmental motions responsible for the α-relaxation at temperatures well below T_g that is actually in the glassy state [2, 5–8].

The aim of this work is to explore the effect of stretching on the structure and relaxation behavior of Poly(vinyl chloride) (PVC). To do this, PVC samples have been stretched to different draw ratios at $T = 358\,K$ using a homemade cell.

MATERIALS AND EXPERIMENTAL PROCEDURE

Poly(Vinyl Chloride) (PVC) ($M_w = 100{,}000$), used in this work was supplied by BDH Chemicals Ltd., Poole, England. Films of PVC were prepared by dissolving the polymer in tetrahydrofuran (THF). The solution was continuously stirred by means of a magnetic stirrer for about 15 min to ensure homogeneous mixture. To prepare the different samples for electrical measurements, the mixture was then cast onto a glass substrate in an oven at $T = 343\,K$ for a few days. The thickness of the samples ranged from 60 to 100 μm, determined by using a digital micrometer (Mitutoyo No: 293-521-30, Japan). Carbon paste was used as a conducting electrode (Kontact-chemie, Germany).

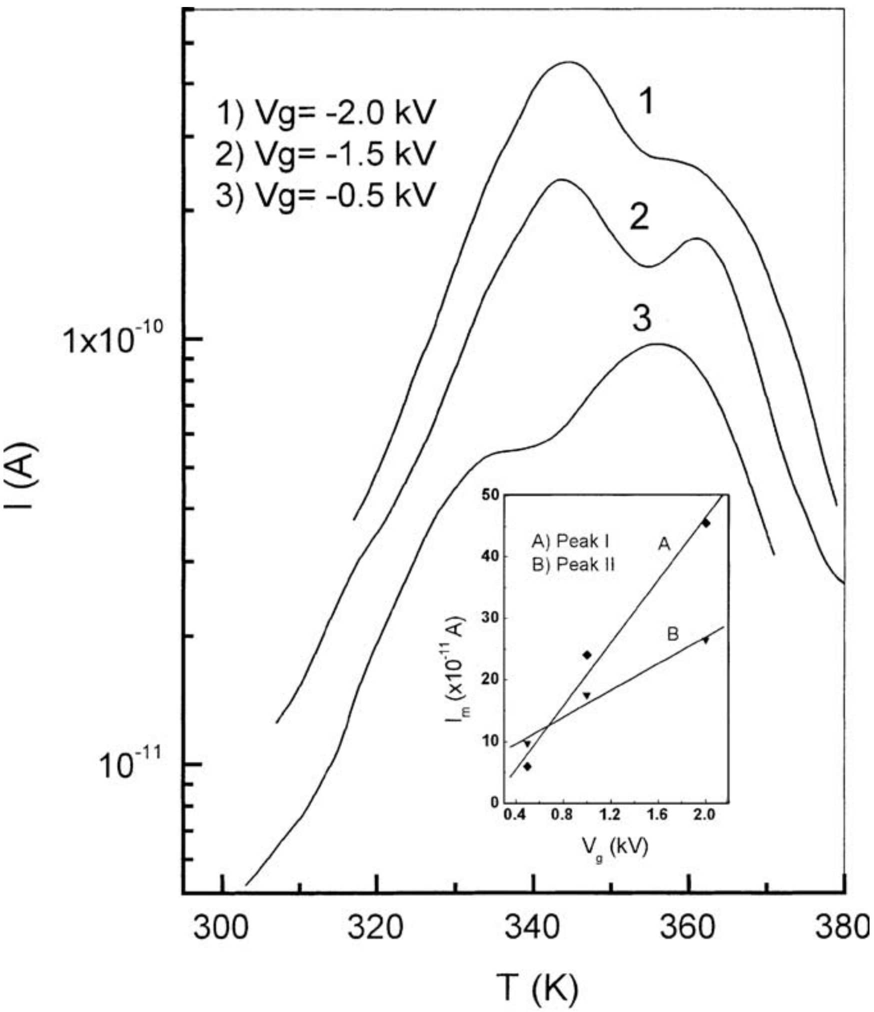
Corona charging is used to polarize the dipoles inside the material. It is based on a corona discharge in air. Ions produced in the discharge are deposited on the sample surface and generate an electric field between the exposed surface and the grounded rear electrode. Depending on the viscosity of the material, the dipoles orient themselves more or less in the direction of the electric field. All samples were poled with a corona triode method in atmospheric air inside a homemade cylindrical Faraday cage. The corona voltage (V_C) was kept at -8 kV and the grid voltage (V_g) was variable. The grid was kept about 4 mm from the film. The corona charging process has been done at different conditions such as the grid voltage (V_g) and sample temperature (T_c).

Thermal poling was carried out using a static electric field E_p at a temperature T_p, for a given time interval t_p. The sample was then cooled down in the presence of the field to a temperature $T_o << T_p$ and, after an isothermal period, with the field off, the sample is then reheated at a constant heating rate $b = 3$K/min to a final temperature $T_f >> T_p$. Thus, the electric current is measured and recorded as a function of the temperature. The result of a global TSDC experiment is a global spectrum that contains all dielectrically active relaxations excited by the field between T_o and T_p.

In the thermal sampling (TS) experiment, the electric field is applied at T_p for t_p and the sample is cooled down in the presence of the applied field to a temperature T_d, where $T_p - T_d = T_w$ (polarization window) is typically $\cong 5$ K. With the field off, after an isothermal period, the sample was short-circuited and cooled down to $T_o << T_p$. At that temperature the remaining polarization corresponds to the dipolar orientation in the temperature region between T_d and T_p. The thermal release of the polarization is recorded during heating at a constant heating rate $b = 3$K/min, up to a final temperature $T_f >> T_p$. Thus the elementary peaks of the global TSDC spectrum can be obtained at different poling temperatures.

RESULTS AND DISCUSSION

Figure 1a depicts the typical TSDC spectra of unstretched PVC films negatively corona poled as a function of the charging voltages at $T_c = 358$ K and $t_c = 30$ min. It can be seen that two peaks characterize each resultant spectrum. The first peak is located at $T_{m1} = 343$ K, whereas the second one is positioned at $T_{m2} = 359$ K. Similar behavior for annealed PVC samples has been reported elsewhere [9]. As is well known, the charging process consists of the deposition of real charges either on the surface or into the bulk material at room temperature or at elevated temperature. Hence, the first peak may be due to the contribution of the surface traps whereas the second current peak is connected to the bulk traps [10]. In other words, the TSDC peak for



(a)

FIGURE 1 (a) TSDC spectra from a negatively corona-charged unstretched PVC film, $V_c = -8\,KV$, $T_c = 358\,K$, and $t_c = 30\,min$. Heating rate $b = 3\,K/min$, carbon paste was used as a conducting electrode. (b) Plots of $\log I$ vs. $1/T$ for the evaluation of activation energy.

PVC samples polarized by corona-poling can be related to the relaxation of the oriented dipole moments and the molecular motion of the polymer matrix. Hence, the first current peak may be due to the contribution of sub-T_g whereas the second current peak is ascribed

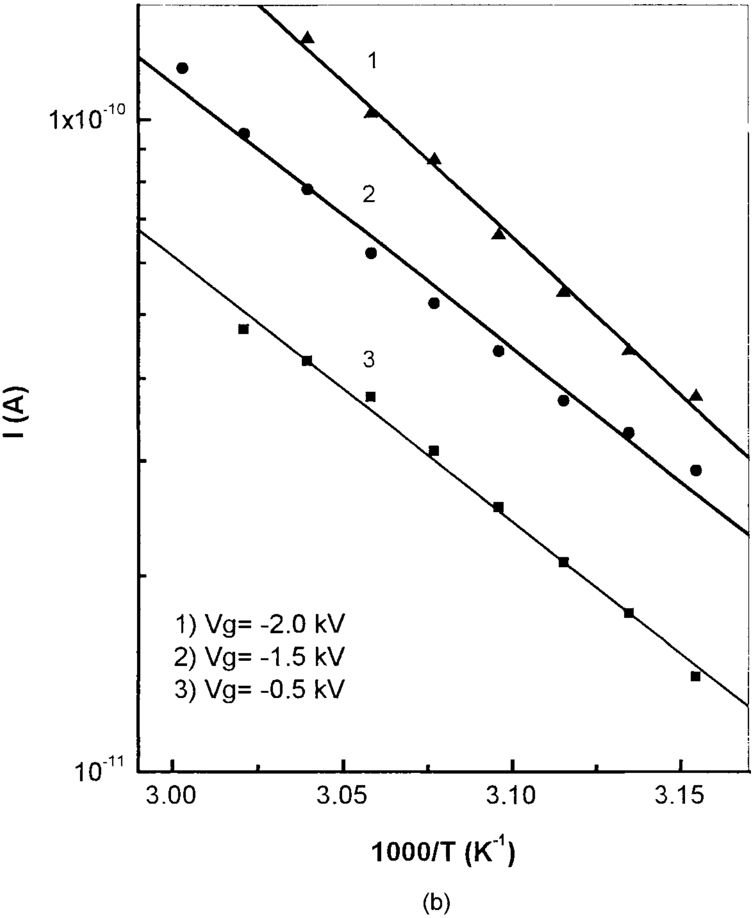


FIGURE 1 (Continued).

to the release of the segmental molecular motion, which is related to the glass transition temperature. The appearance of the high temperature peak around glass transition temperature, indicates that traps are closely linked or form a part of the native polymer structure. In order to investigate the origin of these peaks, the maximum current (I_m) is examined as a function of grid voltage (V_g). A linear increase in maximum current (I_m) of each peak with grid voltage (V_g), as shown in the inset, was obtained, suggesting the dipolar nature of the stored polarization. The activation energies values associated to the first peak were estimated using the initial rise method by a linear fitting of ln I versus 1/T data for the initial increase of the peaks, as shown in Figure 1b [11]. The activation energy values were 0.35, 0.35, 0.41 eV, respectively.

Figure 2 displays the TSDC spectra of unstretched PVC films corona poled at various poling temperatures. It was observed that the position of the first peak shifted to higher temperature with increasing poling temperature T_p. On the other hand, the T_m of the α-relaxation was hardly affected by the change of the T_p and was nearly constant. The shift of this peak position was from 355 to 359 K. This behavior is commonly observed in dipolar TSDC spectra, in which the peak shifts when $T_p < T_g$ and does not shift for $T_p > T_g$ [12–13]. In addition, Figure 3 shows the TSDC spectra of stretched PVC films corona poled at different stretching ratios. It can be seen that, as the stretching ratio increases, the current intensity decreases. This decrease could be explained by the decrease in the segmental mobility of the polymer chain with stretching. This decrease reduces the possibility of dipolar orientation by the application of an electric field, and the material is then polarized to a lower degree under the same polarization conditions.

TSDC technique is a useful tool for probing the depolarization profile, due to the reorientation of aligned dipole moments. When the dipole moment and segmental dipole moment randomize at a favorable temperature, the specific discharge current peak can be obtained in the TSDC spectra. The TSDC spectra polarized at $T = 358\,K$ and recorded from 300 to 373 K for unstretched and stretched PVC samples are presented in Figure 4. In this temperature range two relaxation modes are observed at 339 K and 359 K. The contribution of TSDC spectra may come from dipole disorientation due to the motion of smaller chain segments. On the other hand, at temperatures near and above the T_g, a contribution to the dipolar relaxation due to the main-chain motion can also occur. Therefore, the low temperature zone (at $T \cong 339\,K$) could be attributed to the sub-T_g relaxation, whereas the high temperature mode (at $T \cong 359\,K$) is the α- relaxation, which is the dielectric manifestation of the glass rubber transition occurring in the amorphous zones of the material. Sub-T_g-relaxation could be considered as a process arising from the localized molecular motions or local conformational changes [14]. Moreover, no shift in the α-peak position was observed, indicating that the main contribution to the TSDC peak was from the relaxation of the dipole (C-C1) rather than from induced dipoles [15]. It was found that the global TSDC peak around T_g reflects a cooperative motion of various dipoles with different relaxation times. The cooperative motion of the main polymer chain segments initiates this relaxation, when they regain sufficient mobility at T_g. This TSDC behavior is in good agree-

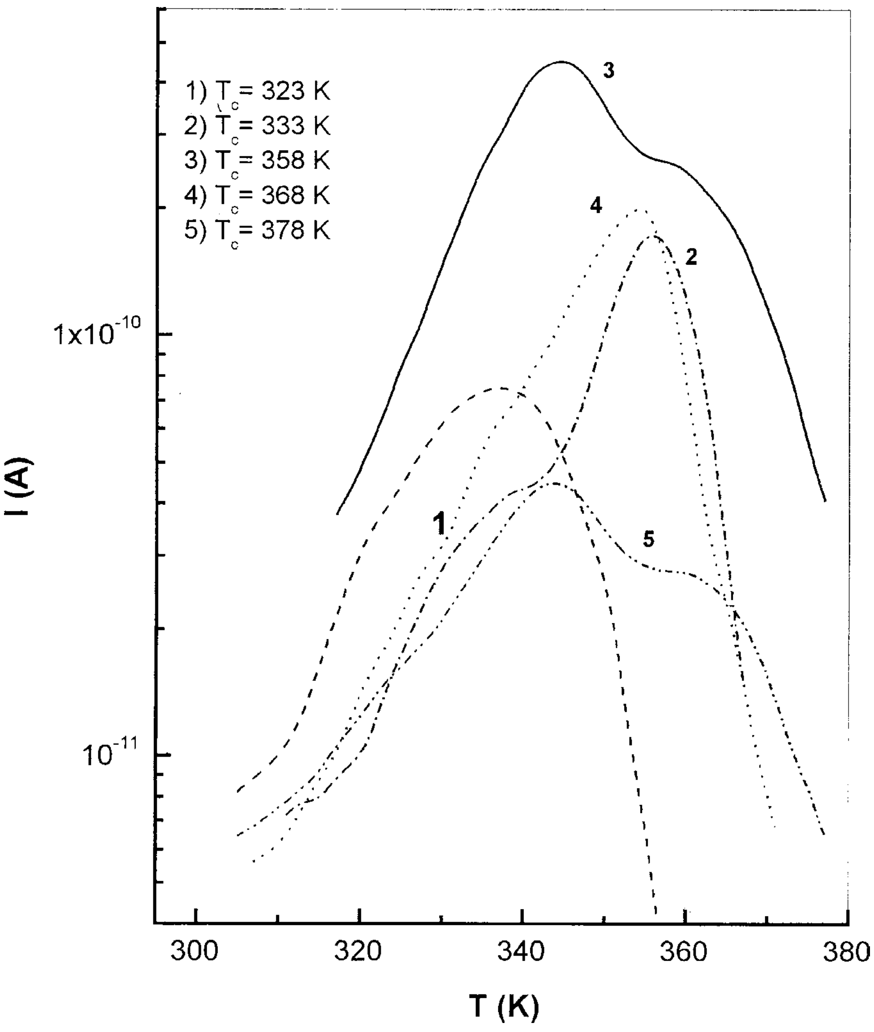


FIGURE 2 TSDC spectra from a negatively corona-charged unstretched PVC film, $V_c = -8\,KV$, $t_c = 30\,min$, and $V_g = -2\,KV$. Heating rate $b = 3\,K/min$, carbon paste was used as a conducting electrode.

ment with the corona poled samples as shown in Figure 1. Moreover, it was observed that, as the stretching ratio increases, a significant decrease in the maximum current and a shift in the α-peak position have occurred. This behavior is explained by the decrease in the mobility of the molecular chain segments, which is also related to

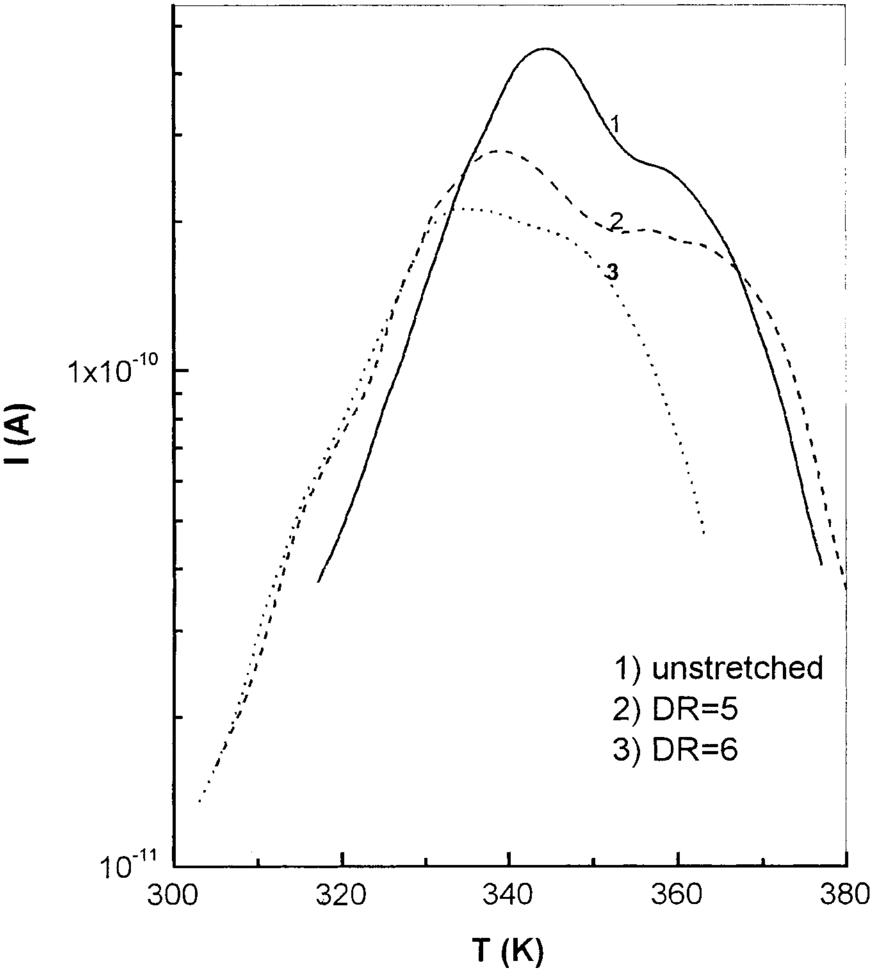


FIGURE 3 TSDC spectra from a negatively corona-charged unstretched PVC film, $V_c = -8\,KV$, $T_c = 358\,K$, $t_c = 30\,min$, and $V_g = -2\,kV$. Heating rate $b = 3\,K/min$, carbon paste was used as a conducting electrode.

the reduction of free volume in the sample. This behavior is associated with the decrease of the total amorphous fraction, that is an increase in the crystallinity degree has occured [16].

As shown in Figure 5, the maximum of the α-relaxation is located at $T = 359\,K$. To isolate the α-peak from any sub-T_g relaxation overlap, the low temperature tail of the peak is partially cleaned and the resulting peak is shown in the figure. This cleaning is necessary

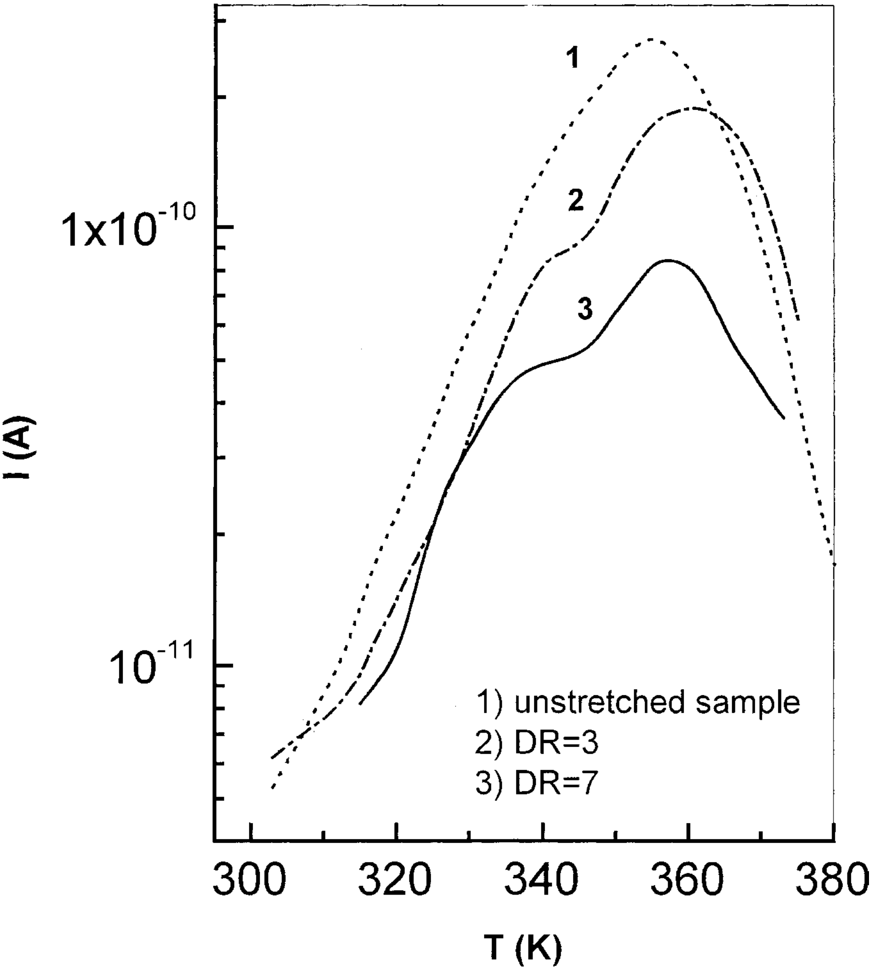


FIGURE 4 Global TSDC spectra of unstretched and stretched PVC film at $T_p = 358\,K$, $t_p = 30\,min$, and $E_p = 3 \times 10^6$ V/m. Heating rate $b = 3\,K/min$, carbon paste was used as a conducting electrode.

for the analytical decomposition of the TSDC peak into elementary curves as the temperature dependences of the sub-T_g and T_g-relaxation times are different.

An interesting feature of the TSDC technique is the possibility to isolate experimentally overlapping relaxation peaks. The asymmetry of the TSDC spectra may be attributed to the distribution function of relaxation times because of the various processes involved. Methods

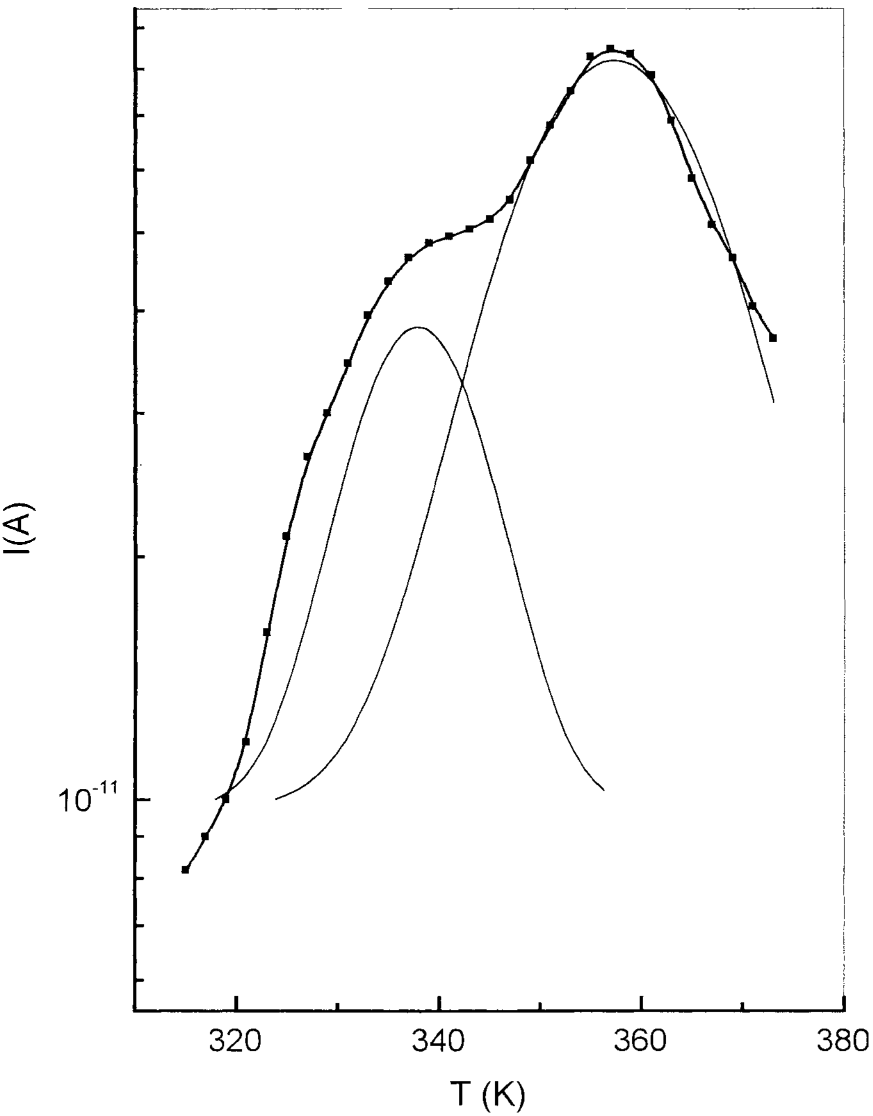


FIGURE 5 Peak cleaning curve of TSDC spectrum.

like thermal sampling (TS) have been extensively used to obtain single relaxation processes, that is quasi-nondistributed peaks, so that the interpretation of the resulting spectra is easier than the depolarization discharge, which is obtained from a conventionally polarized electret [6–8]. Figure 6 shows elementary TSDC spectra of the stretched

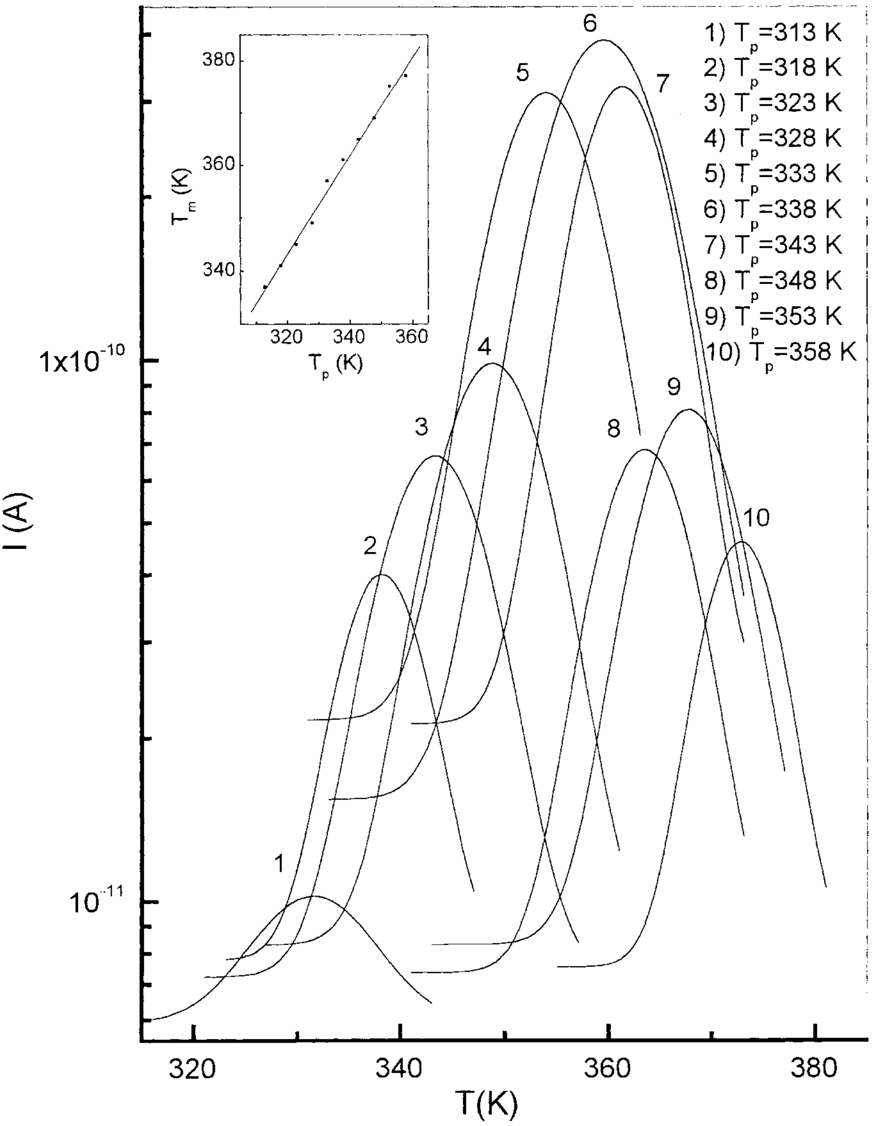


FIGURE 6 Typical TS spectra of stretched PVC with drawing ratio = 7.

PVC film with draw ratio ≅7, as a representative curve of stretched PVC samples, isolated by TS experiments with ΔT and steps of 5 K. All of these elementary spectra can be considered as single Debye peaks, that is characterized by a single value of activation energy and relaxation time. It can be concluded that the enlargement of the TS peaks with increasing T_p can be understood by formally analyzing the change in the width of simple Debye peaks with increasing activation energy. In addition, a linear relationship between maximum temperature (T_m) of each TS peak and the polarizing temperature (T_p), as shown in the inset, with a slope close to unity, has been obtained, which is in good agreement with theoretical prediction for a flat continuous distribution [17–18]. Because the depolarization of the sample is thermostimulated, time and temperature are related by a linear relationship, so the relaxation time $\tau(T)$ is temperature dependent and can be represented as follows:

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

where τ_0, E_a, and k are defined as a pre-exponential factor, activation energy, and Boltzmann's constant. Hence, all the molecular parameters characterizing TS peaks have been calculated and listed in Table 1. The relatively high activation energies may be explained by the existence of strong cohesive forces of polar origin in the amorphous region. These cohesive forces lead to a high degree of cooperativity of the molecular motions of the chain around the glass transition tem-

TABLE 1 Peak Parameters of Isolated TS Peaks of Stretched PVC Samples

Sample	T_p (K)	T_m (K)	E_a (eV)	τ_0^{-1} (sec^{-1})
DR = 3	318	343	1.01	1.83×10^{14}
	323	345	1.06	9.44×10^{14}
	328	353	1.07	6.04×10^{14}
	333	355	1.33	3.01×10^{18}
	338	359	1.34	2.15×10^{18}
	343	361	1.13	1.84×10^{15}
	348	367	1.57	1.56×10^{21}
	353	369	1.19	6.10×10^{15}
	358	373	1.49	1.13×10^{18}
DR = 7	318	341	0.81	2.16×10^{11}
	323	345	0.89	2.64×10^{12}
	328	349	1.04	2.65×10^{14}
	333	357	1.05	1.71×10^{14}
	338	361	1.19	1.22×10^{16}
	345	365	1.31	3.88×10^{17}
	348	369	1.12	6.15×10^{14}
	353	375	1.10	1.46×10^{14}
	358	377	1.24	1.21×10^{16}

perature of the polymer, and then the value of the apparent activation energy is increased [7]. Moreover, the increase of E_a of stretched PVC could be explained on the basis of decreasing the mobility of polymer chain segments. With the decreased mobility higher activation energy is necessary to activate the depolarization process.

According to the theory of TS, the (τ^{-1}_o) factor obtained from TS experiments should be a decreasing function of the T_p where a distribution in natural frequencies is concerned. As listed in Table 1, both activation energy (E_a) and natural frequency (τ^{-1}_o) are increasing functions of the T_p in the same temperature range. Thus, in this case, the distribution of relaxation times is interpreted as a distribution in activation energies because the sloping portions of the plot are representing the distribution.

Assuming the Arrhenius-like temperature dependence of relaxation times, the distribution of relaxation times can be treated either as a distribution in natural frequency or as a distribution in activation energies [19–20]. Thus the temperature dependence of the relaxation times can be used to draw the relaxation map analysis (RMA) of the respective elementary spectra in the vicinity of the glass transition temperature as shown in Figure 7. It can be seen that the linearity of $\ln\tau$ vs. $1/T$ was observed even in the higher-temperature region near T_g because elementary spectra were always obtained in the very narrow temperature range. It was observed that most Arrhenius plots converge to a single point, the compensation point, with coordinates ($\log\tau_c, 1/T_c$), where τ_c, T_c are defined as the compensation time and compensation temperature. Therefore, the compensation law is expressed as follow:

$$\tau_0 = \tau_c \exp\left(-\frac{E_a}{kT_c}\right) \tag{2}$$

Then Eq. 1 becomes

$$\tau(T) = \tau_c \exp\left\{\left(\frac{E_a}{k}\right)\left[\frac{1}{T} - \frac{1}{T_c}\right]\right\} \tag{3}$$

Therefore, the relaxation map analysis (RMA) provides an in-depth analysis of polymer structure. Such behavior is well known in kinetic measurements and is called the isokinetic analysis [21], in electrical conductivity measurements [22], as well as in relaxation phenomena [23]. In the case of solid polymers this effect is observed only if data for different materials are compared, and by means of thermal sampling this effect can be observed in one polymer. Thus making it

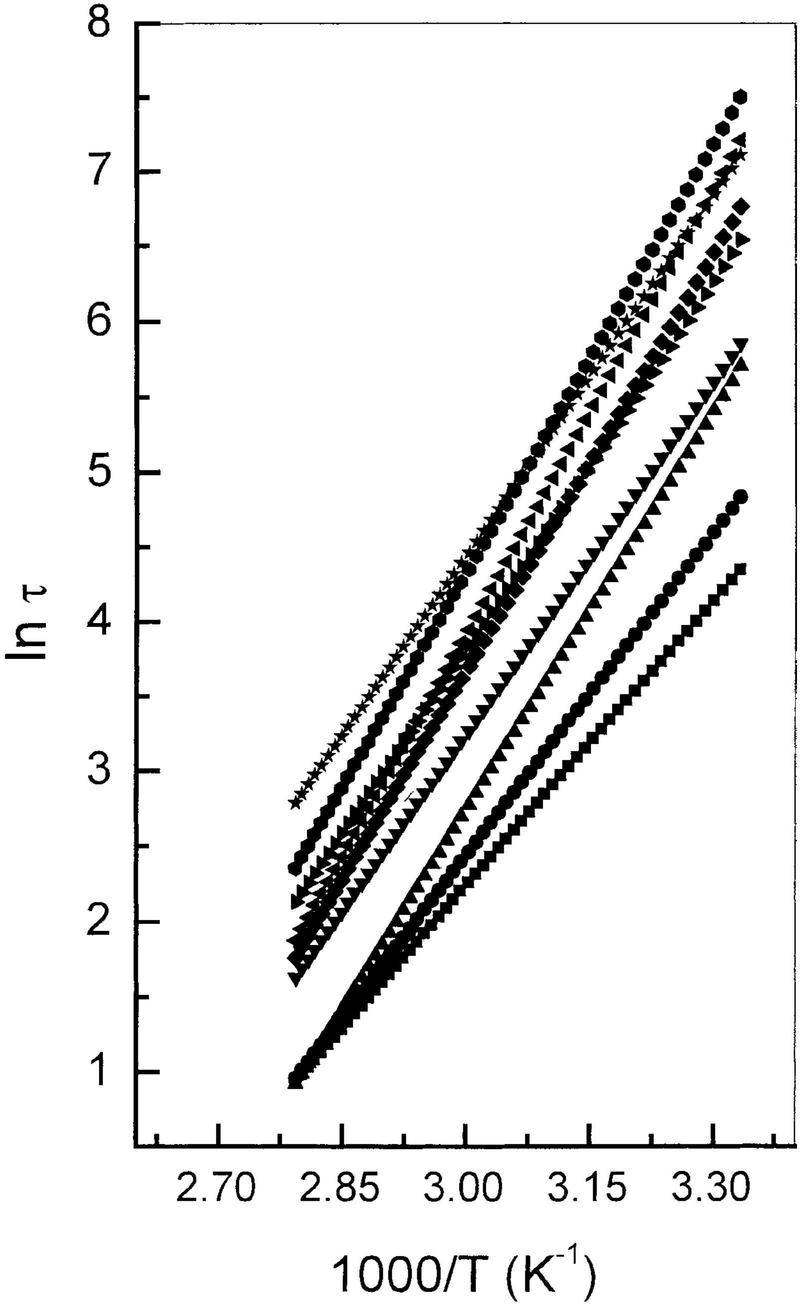


FIGURE 7 Relaxation map analysis of stretched PVC film with drawing ratio = 7.

possible to eliminate the inevitable source of errors due to differences in compositions, structure and preparation of different samples.

The compensation phenomenon is a well-known behavior observed in TSDC experiments, namely during the glass transition relaxation of amorphous materials [24–25]. One of the most usual assumptions for the compensation law in polymers is based on the possibility of a process where chain segments of increasing length contribute at increasing temperature until a maximum size is reached at the compensation temperature [26]. On examining Figure 7, it can be concluded that two compensation points are obtained, indicating that both the sub-T_g and the α-relaxation follow the same compensation law. A set of compensation parameters such as T_c and τ_c for sub-T_g and α-relaxation processes of the stretched PVC sample (DR = 7, as a representative data) are estimated, that is $T_{c1} = 348.06$ K, $\tau_{c1} = 1.438$ sec, and $T_{c2} = 368.32$ K, $\tau_{c2} = 0.992$ sec. The values of the unstretched PVC has been published previously [7].

The coordinates of the compensation point (T_c, τ_c) are very important because they transcribe the coupling characteristics between the different modes of relaxation observed as individual activated processes in the set of converging Arrhenius lines. Hence, it was found that the interactive coupling between various relaxation modes across the T_g, such as the compensation phenomenon observed in RMA, is well related to the change of fundamental material analysis as shown in Figure 7. Two compensation points with different coordinates are obtained characterizing stretched PVC samples compared to the unstretched PVC, which is characterized by a single compensation point around its glass transition temperature. The compensation temperature (T_c) can be used to estimate the coefficient of thermal expansion of the material according to the following empirical formula $\beta = 1/4T_c$ [7, 27]. The values of β and $\Delta\beta$ are estimated, where $\Delta\beta$ is defined as the difference of the coefficient of thermal expansion below and above glass transition temperature, $\Delta\beta = 1/9T_c$ [28]. The values of β and $\Delta\beta$ are 6.48×10^{-4} and 3.012×10^{-4} K^{-1}, respectively.

CONCLUSION

Global TSDC spectra of stretched and unstretched PVC samples negatively corona charged are characterized by two peaks located at 343 K and 359 K, respectively. The combined use of TSDC and TS in this study results in complementary information on the electret behavior. This combined study allows an explanation of the mechanism of the polarization in this material. In the case of stretched PVC, these methods allow assignment of a dipole orientation mechanism for both sub-T_g and α-relaxation. It was observed that, in global TSDC spectra as the stretching ratio increased, a significant decrease in the maximum current and a shift in the α-peak position have occurred. This behavior is explained by the decrease in the mobility of the molecular chain segments, which is also related to the reduction of free volume in the sample. Moreover, the relaxation map analysis (RMA) revealed that stretched PVC is characterized by two compensation temperatures.

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