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ORIGINAL PAPER

Molecular motion and detrapping behavior of trapped space charges in polyvinyl pyrrolidone: a thermally stimulated depolarization current study

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Abstract The discharging process of polyvinyl pyrrolidone electret under two different heating rates 3.5 and 2 °C/min has been investigated by the measurement of thermally stimulated depolarization current (TSDC) in the temperature range from 30 to 250 °C. The TSDC spectra of PVP shows three peaks located at 70 ± 10, 150 ± 10, and 230 ± 10 °C, respectively. When explaining the TSDC spectra, this thesis deduced that the first peak, β peak, originates from side group relaxation; the second peak, α peak, corresponds to the relaxation of the frozen dipoles on the molecule chain segments during glass transition; the third peak, ρ peak, is attributed to the detrapping of the trapped space charge under thermal stimulation. The current of the ρ peak is remarkably strong due to the fact that PVP molecules' side groups—the pyrrolidone rings containing lactam structure—are strong polar groups which cause the great increase in the number of bulk traps, trapped space charge, as well as detrapped space charge under thermal stimulation.

Keywords PVP · Thermally stimulated depolarization current (TSDC) · Electret · Dipole relaxation · Glass transition · Space charge · Polar side groups · Trap

Introduction

Polymers acquire persistent polarization due to the alignment of dipoles and migration of space charges over macroscopic distances. Information on charge storage and transport phenomena in polymer electrets is of great interest for several industrial applications. The space charge in polymers is now one of the most serious problems confronting electrical insulation technology [1, 2]. Due to the relative

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simplicity of the experimental setup and the high resolution of the method, thermally stimulated depolarization current (TSDC) has been widely used to study dipole relaxation, charge storage, and charge decay processes in electrets.

Polyvinyl Pyrrolidone (PVP) shows good charge storage capability and high electrical conductivity. The charge-transfer complex, which is the result of the metal doped PVP, is an excellent electrical conductive material which has a very high application value in industry [3–7]. Previous studies on PVP electrets have used the TSDC method, with the help of some supplementary means such as the differential scanning calorimeter (DSC) method, the dynamic mechanical analysis, and the dielectric relaxation spectroscopy, and have achieved a better understanding of PVP's glass transition temperature and the corresponding molecule chain segment motion, as well as the side group movement below glass transition temperature. However, no clear conclusion has been drawn on the trapping and detrapping process of space charge in PVP electrets [8–13].

The purpose of this experiment is to study the molecule movement and space charge in PVP electrets using TDSC. In order to prevent incomplete polarization, the PVP electrets used in this experiment are polarized at 180 °C, which is above PVP's glass transition temperature. A space charge relaxation peak is observed in the spectra at 230 ± 10 °C. In addition, this experiment also examined the impact of the polarity of different polymers on the space charge relaxation peak.

Experimental

Materials

The k30 PVP powder with a molecular weight of 40,000 used in this experiment was produced by Haifeng Fine Chemical Co., Ltd. Anhui.

Characterization

Differential scanning calorimeter analysis was carried out with a Shimadzu DSC-60 equipment. The samples were heated at 10 °C/min from 20 to 300 °C under nitrogen for the scan. According to DSC testing, the glass transition temperature of the sample is 165 °C.

Preparation of polymeric film

Eight grams of PVP powder was dissolved in 50-mL distilled water, and the solution was stirred for 30 min so that the PVP powder was completely dissolved. After standing for 1 h at room temperatures, the opaque pale yellow solution was poured onto a tetrafluoroethylene panel (whose acreage is 0.04 m^2) which was placed on a horizontal plane. After standing for a week, a PVP film with a thickness of 120–160 μm was prepared. Due to the fact that the tetrafluoroethylene panel with a smooth surface was placed horizontally, the thin polymer film prepared had uniform thickness and a smooth surface. Afterward, circular silver electrodes (10 mm in diameter) were coated on both sides of the film sample which was then placed in a desiccator cabinet.

TSDC measurements

The TSDC measurements were carried out on a modified thermal-electric analyzer on the prepared sample in two steps:

The sample was heated from room temperature to the polarization temperature $T_P = 180$ °C, and then polarized for $t_p = 30$ min (which was enough long to attain the equilibrium polarization) by electric fields E_P (four field strength 20, 40, 60, and 80 kV/cm were used in this example). The sample was then cooled, with the polarization field still on, from T_P to room temperature, where orientation polarization P (T_p) was frozen in. The field was cut off and the polymer was made into film electret.

After the previous preparation, the sample was short-circuited for 30 min to remove fast-relaxing surface charges and to stabilize the sample temperature. And the TSDC spectra of PVP was obtained by linearly increasing the temperature with a constant rate β (two heating rates 3.5 and 2 °C/min were used in this example) to the final temperature T_{end} at 250 °C.

In the first step, the dipoles on the polymer's chain segment were oriented by the electric field, and the orientation was frozen during the cooling process. Space charges were captured in the traps. In the linear heating process of the second step, the oriented dipoles depolarized, and the trapped space charges detrapped. As a result, the depolarization process and detrapping process generated the TSDC spectra in the external circuit [14, 15].

Results and discussion

TSDC results

The TSDC spectra of PVP electret are shown in Fig. 1.

It can be observed from Fig. 1 that the curve is not smooth around 160 °C, indicating a relaxation process around this temperature. In order to separate this relaxation peak which overlapped with another peak at 232 °C, the spectra was theoretically fitted based on the fact that TSC is a thermally stimulated process whose general kinetic equation was [16]

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = \left(\frac{n}{n_0}\right)^b s n_0 \exp(-E/kT) \tag{1}$$

where I is the current intensity, n is the density of the carrier in the trap, s is the frequency factor, n_0 is the initial concentration of the carrier in the trap, k is Boltzmann's constant, T is the absolute temperature, E is the activation energy or the depth of the trapping sites, and b is the kinetic order (usually equals 1 or 2 but

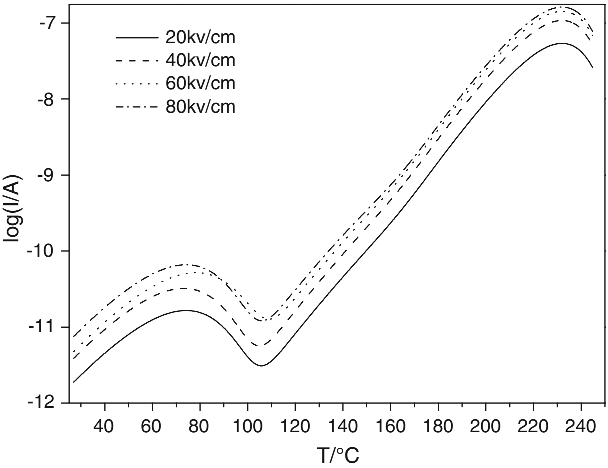

Fig. 1 TSDC spectra of PVP electret. $T_\mathrm{P} = 180$ °C, $t_\mathrm{p} = 30$ min, $E_\mathrm{P} = 20$–80 kv/cm, $\beta = 3.5$ °C/min, with the longitudinal coordinates being log (I)

with exceptions). In the case of a constant heating rate β, $T = T_0 + \beta t$. And the solution of the Eq. 1 is

$$I(T) = n_0 s \exp(-E/kT) \exp\left[(-s/\beta)\int_{T_0}^{T} \mathrm{e}^{-\frac{E}{kT'}}\mathrm{d}T'\right] \quad (b = 1) \tag{2}$$

$$I(T) = n_0 s \exp(-E/kT)\left[1 + (b-1)(s/\beta)\int_{T_0}^{T} \mathrm{e}^{-\frac{E}{kT'}}\mathrm{d}T'\right]^{b/(1-b)} \quad (b \neq 1) \tag{3}$$

According to the multi-point fitting program based on three-point method developed in the laboratory, the characteristic parameters, including the activation energy of the dipole relaxation process and the trap depth of the detrapping process can be obtained by theoretically fitting the data within ±20 °C range of the peaks in the TSDC spectra based on Eqs. 2 and 3 [17]. In order to judge the accuracy of the multi-point theoretical fitting, Fig. 3 compares the measured spectra with the fitted curve based on the TSDC spectra of PVP electret in Fig. 1 (the strength of polarization field was 40 kV/cm). In Fig. 2, the solid line represents the measured values, and the dashed line represents the theoretically fitted results. The overlapping peaks were separated after the fitting procedure, and it shows good agreement between the theoretical spectra and the measured results.

Figure 2 shows three distinct current peaks. Comparing Fig. 2 with the measured results of DSC testing, it can be found that the new peak at 156 °C is close to PVP's glass transition temperature of 165 °C in the DSC testing. According to the paper by Khare et al. [9–13], it is deduced that this dipole relaxation peak is the α peak corresponding to the glass transition of PVP, the dipole relaxation peak at 72 °C, which is not shown in the DSC results, is the β peak originating from side-group

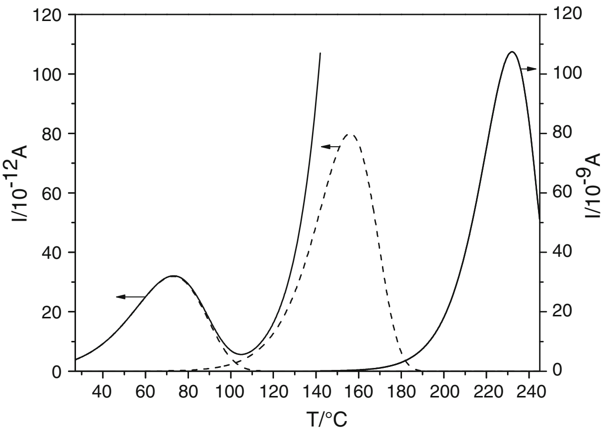

Fig. 2 The multi-point fitting process for the TSDC spectra of PVP electret. $T_P = 180$ °C, $t_p = 30$ min, $E_P = 40$ kv/cm, $\beta = 3.5$ °C/min. *solid line* the original TSDC curve, *dashed line* the fitted curve

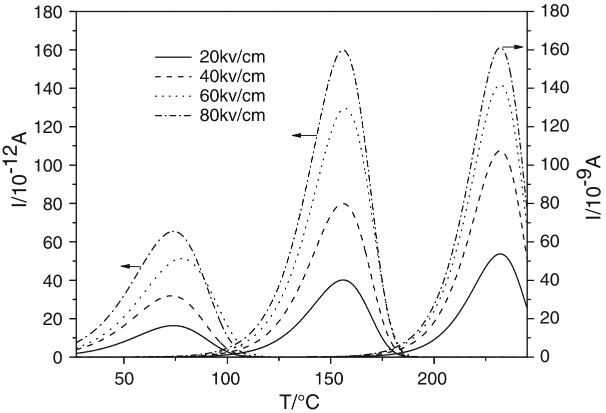

Fig. 3 The fitted TSDC current curves of PVP electret. $T_P = 180$ °C, $t_p = 30$ min, $E_P = 20$–80 kv/cm, and $\beta = 3.5$ °C/min

relaxation [8, 10], and the peak at 232 °C is the ρ peak attributed to the space charge detrapping.

Figure 3 shows the multi-point fitting results of the TSC spectra of PVP electret. The relationship between the peaks and the different field strength was calculated and shown in Fig. 4.

The Bucci–Fieschi theory, which was put forward in 1964 to describe the dipole relaxation process, has been successfully used to explain the temperature dependence of TSDC [18].

$$I(T) = \frac{P_0}{\tau_0}\exp\left[-\frac{E_a}{kT} - \frac{1}{\beta\tau_0}\int_{T_0}^{T}\exp\left(-\frac{E_a}{kT}\right)\mathrm{d}T\right] \tag{4}$$

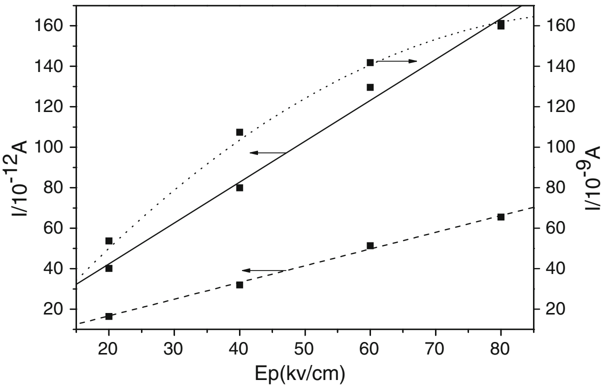

Fig. 4 Polarization field dependence of the peak current. *dashed line* β peak, *solid line* α peak, *dotted line* ρ peak

where P_0 is initial polarization intensity $P_0 = N\mu^2 E_p\alpha/kT_p$, τ_0 is relaxation time constant, E_a is apparent activation energy, k is Boltzmann constant, and T is absolute temperature. Following the theory, polarization field has not an effect on the temperature but a linearly effect on the current value of the dipole depolarization peak.

It can be observed from Fig. 3 that the temperatures of β and α peaks change little as the polarization field increases, while the impact of the field strength on peak value is shown in Fig. 4. The current of β and α peaks demonstrates a linear increase with the increase of the polarization field, indicating that more dipole orientation took place under higher polarization field strength. This result is consistent with the Bucci–Fieschi theory, confirming that the dipole relaxation peak at 72 °C corresponds to β peak, and the peak at 156 °C is α peak. Both peaks can be attributed to the depolarization of oriented dipoles being thermally stimulated. In the TSDC process when the sample was polarized by external electric fields, the activated dipoles on the polymer's chain segment and side groups were oriented by the electric field, and the orientation was frozen when the sample was cooled to room temperature. When the polymer electret was linearly heated, the frozen dipoles depolarized, therefore, a current relaxation peak was generated in the external circuit.

The ρ peak, which located at about 232 °C, had not been observed in the past. According to the peak temperature, it is inferred to be a space charge peak. It can be seen from Fig. 4 that the increasing speed of ρ peak becomes slow as the polarization field increases, which is correlating with the space charge detrapping mechanism. This evidence confirms that ρ peak is a space charge peak which can be attributed to detrapping of space charge during the thermal stimulation process [14]. In fact, when the sample was polarized, not only did the dipoles of chain segment orient, but the charge carriers also moved under the action of electric field and then were trapped in the trap. The trapped carriers detrapped from the localized energy state and then produced the space charge peak in TSDC spectra. Simmons [19] proposed an equation describing the space charge detrapping process and investigated related mechanisms.

Khare and others used polarization temperatures below 100 °C, which was lower than the PVP k30 sample's glass transition temperature of 165 °C. Therefore, the sample might not be completely polarized, so the space charge depression peak did not emerge in the TSDC spectra [20]. The polarization temperature used in this experiment is 180 °C, which exceeds the sample's glass transition temperature of 165 °C. As the sample was completely polarized, a space charge peak was observed at 232 °C.

The temperature of ρ peak is higher than the first two peaks due to the fact that the detrapped space charge, which caused the ρ peak, had to move across many times the distance between atoms. It was discussed earlier that α peak and β peak are dipole relaxation peaks, and the depolarization of dipoles only requires local rotation. The trapped space charge, however, is unevenly distributed among the electret, and when the sample was heated, the detrapped charge was counteracted near the electrodes, or counteracted by the heterocharge in the sample. During the period after detrapping and before counteraction, the space charge may move under the impact of its local electric field, or it may diffuse along the concentration gradient of charge distribution. As a result, the detrapped space charge had to move across many times the distance between atoms [15].

The current of ρ peak, compared with those of the first two dipole relaxation peaks, is three orders of magnitude larger, which is relatively rare. The following table is a comparison between the current of ρ peak and those of several common polymers.

It can be found from Table 1 that the current of ρ peak and the initial concentration of carrier significantly vary among the five types of polymers. Judging from their molecule structure, PVP molecules' side groups, i.e., the pyrrolidone rings, contain lactam structure which is a strong polar group with a dipole moment of $4D$; the dipole moment of the whole chain in PET molecules is about $2.51D$; PMMA's side groups are long and pliable ester groups with a dipole moment of about $1.8D$; the side groups of polystyrene are benzene, a highly symmetrical molecule on a same plane, on which there is a conjugated π bond and whose dipole moment is $0.5D$; the side groups of polypropylene are methyl whose dipole moment is $0D$. From the analysis, it can be seen that a polymer's current of ρ peak and initial concentration of carrier are proportional to the polarity of its side groups.

In polymers, surface states, chain folding, molecular disorders, crystalline-amorphous boundaries, and chain ends may act as trapping sites. In addition, if the polymer contains polar groups, each dipole of these polar groups can act as an

Table 1 The comparison of the current of ρ peak and initial concentration of carrier between five types of polymers ($E_P = 40$ kv/cm)

Polymer type	Current of ρ peak (A)	Initial concentration of carrier n_0 (C)
PVP	1.1×10^{-7}	1.8×10^{-5}
PET	1.2×10^{-10}	2.1×10^{-8}
PMMA	5.4×10^{-11}	6.8×10^{-9}
APS	1.0×10^{-12}	1.84×10^{-10}
PP	5.0×10^{-13}	6.1×10^{-11}

electron or hole trap [21]. Therefore, in polymers containing polar groups, the bulk traps will be greatly increased, so will the space charge captured in these traps. The strong polar lactam groups in PVP' side groups capture a great deal of additional space charge, and the trapped space charge will detrap under thermal stimulation and participate in the total conduction. Accordingly, the number of detrapped space charge in PVP electret under thermal stimulation is much stronger than those of polymers whose side groups have relatively low polarity. As a result, the current of ρ peak observed in this experiment is remarkably strong.

Activation energy

Khare and others, in the study of PVP molecular movement, calculated the activation energy of two dipole relaxation peaks [10, 11]: the β peak, which locates at a relatively low temperature, has a relatively low activation energy because side-group relaxation does not required much energy; and the α peak has a higher activation energy because it corresponds to the segment chain relaxation during glass transition, which requires more energy. Besides, the activation energy of both peaks does not change with the polarization field. In order to investigate the activation energy and trap depth of each relaxation process, this experiment used two different heating rates while maintaining the same polarization conditions. The TSC spectra of PVP electret at two different heating rates are as follows in Fig. 5.

As can be seen from Fig. 5, with the increase of heating rate, the peaks move to higher temperatures and become stronger. For the dipole relaxation peaks, the frozen polymer chain segments and side groups cannot relax timely at higher heating rates, resulting in the relaxation peaks' movement toward higher temperatures. However, the energy barrier of each peak does not change with the heating rates, because thermally stimulated current process is a dynamic equilibrium

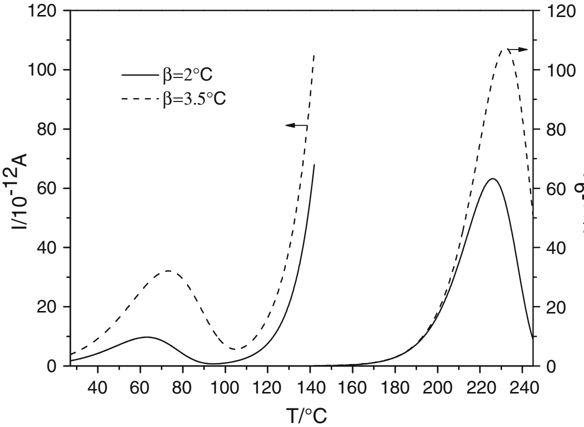

Fig. 5 TSDC spectra of PVP electret. $T_P = 180$ °C, $t_p = 30$ min, $E_P = 40$kv/cm, and $\beta = 3.5$ and 2 °C/min

Table 2 Theoretically fitting results of the energy barrier of each peak by changing heating rate

Peak	β_1 (°C/min)	T_{m1} (°C)	β_2 (°C/min)	T_{m2} (°C)	E (eV)
β	3.5	72	2	63	0.58
α	3.5	156	2	149	1.10
ρ	3.5	232	2	225	1.70

process in which the value of heating rates does not affect the activation energy of molecular motion.

The activation energy of the β peak and α peak, as well as the trap depth of the ρ peak, was calculated using multi-point fitting software.

Compared with the activation energy of the β peak and α peak in the paper of Khare et al. [10, 11], the activation energy values listed in Table 2 are almost twice as large. This may be caused by the fact that in the experiment carried out by Khare et al., the polarizing temperature was below 100 °C. Since the glass transition temperature of PVP is about 156 °C, and the secondary transition temperature is about 72 °C, the sample in their experiment was incompletely polarized; the chain segments with high energy barrier were not polarized, leading to the result that the activation energy was relatively small. In the experiment, the polarizing temperature is 180 °C, the polarizing time is 30 min (due to the fact that the experimental result of a longer polarizing time is the same as that of 30 min, it is concluded that 30 min is long enough). As a result, PVP was completely polarized.

Conclusion

The TSDC spectra of PVP shows three peaks located at 70 ± 10, 150 ± 10, and 230 ± 10 °C, respectively. When explaining the TSDC spectra, this thesis deduced that the first peak, β peak, originates from side-group relaxation; the second peak, α peak, corresponds to the relaxation of the frozen dipoles on the molecule chain segments during glass transition; the third peak, ρ peak, is attributed to the detrapping of the trapped space charge under thermal stimulation, and the number of traps relates to the polar side groups. In polymers, surface states, chain folding, molecular disorders, crystalline-amorphous boundaries, chain ends, and polar groups may act as trapping sites. The strong polar side groups in PVP molecules result in the great increase in the number of bulk traps, trapped space charge, as well as detrapped space charge under thermal stimulation. Therefore, the current of PVP's ρ peak is much stronger than those of polymers whose side groups have relatively low polarity.

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