



Study of thermal currents in CoCl_2 -doped poly (vinyl alcohol) films irradiated with γ -rays

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(Received 28 May 1993; accepted 15 June 1993)

Thermally stimulated depolarisation current (TSDC) and time-dependent conduction current of unirradiated and γ -irradiated pure and CoCl_2 -doped PVA films have been measured. Doses in the range 21–75 Mrad were used. The TSDC of pure and doped PVA before and after irradiation revealed a T_g relaxation peak. The induced changes in the peak current (I_m) of the glass relaxation peak are composition and dose dependent. A marked decrease in TSDC corresponding to the main glass relaxation peak is observed with ageing time. The role of γ -irradiation in perturbing the orientation of the dipoles and/or chain segments was inferred from the disappearance of some sub- T_g relaxation peaks. The thermally activated mobility of charge carriers is confirmed from calculations of drift mobility at different γ doses and temperatures.

INTRODUCTION

The thermally stimulated depolarisation current (TSDC) technique has been developed as a powerful tool to advance our understanding of the molecular relaxation mechanism, trapping parameters and charge storage behaviour of polymers which find very wide industrial applications.^{1–4} The TSDC characteristics can be improved by incorporating a suitable impurity into the polymer.^{5,6} Polyvinyl alcohol (PVA) is a suitable candidate for such studies because it has a single hydroxyl group which makes it easier to understand the storage and discharge mechanism.

High-energy radiation, such as γ -rays, change the physical properties of the materials through which they pass.^{7–10} The changes are strongly dependent on the structure of the absorbing substances. Ionisation occurs, and charged species, both ionic and free radical, are formed.

In the present work, the effect of relatively high doses of γ -rays on the TSDC behaviour and the current–time characteristic of CoCl_2 -doped PVA of various compositions was studied. Relatively high doses of γ -irradiation were used to try to understand the resistance of these samples to radiation damage.

EXPERIMENTAL

The PVA and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in this work were kindly supplied by BDH chemicals. The components, which were nominally free from impurities, were dissolved in distilled water, and PVA– CoCl_2 films prepared with different contents (2.5, 5 and 10 wt%) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Films of appropriate thickness (0.25 mm) were cast on optically flat glass plates from distilled water solutions and were dried in an air oven at 40°C for 48 h. Samples were then irradiated at room temperature with various doses of γ -rays over the range 21–75 Mrad, using a ^{60}Co source.

Thermally stimulated depolarisation current

studies were carried out using the sandwich configuration of samples with an effective area of 1.65 cm^2 . Samples were exposed to a poling process, prior to TSDC measurements. This was done by first heating them to a specific polarisation temperature, $T_p = 100^\circ\text{C}$, and then applying an electric polarising field, $E_p = 2 \text{ kV cm}^{-1}$ for a polarising time of 2 h. After polarisation, the samples were cooled to room temperature with the field on. The field was switched off at room temperature and the samples were shorted for about 1 day to remove frictional and stray charges,¹¹ if any. The depolarisation current was recorded by a Keithly electrometer model 616, by heating the sample at a linear heating rate of $1.5^\circ\text{C min}^{-1}$ from room temperature to about 140°C . All measurements were carried out 24 h after irradiation.

RESULTS AND DISCUSSION

Thermally stimulated depolarisation currents

All peaks found in TSDC spectra have a counterpart in conventional dielectric loss measurements except for space charge, which is likely to appear in TSDC measurements. The TSDC technique is characterised by its high resolving power, allowing a separate investigation of the effects caused by the various types of relaxation of a given polymer.

The TSDC thermograms have been measured for irradiated and unirradiated pure and CoCl_2 -doped PVA films having CoCl_2 concentrations of 2.5, 5 and 10 wt%. Figure 1 shows TSDC thermograms of pure PVA films before and after irradiation with various γ -doses (21, 35, 50 and 75 Mrad). Two current peaks have been observed for the unirradiated PVA sample in fair agreement with those previously reported.¹²⁻¹⁴ The low-temperature peak, which appears near the T_g of PVA, can be attributed to micro-Brownian motions of large chain segments. This micro-Brownian motion is a semi-cooperative action involving torsional oscillation and/or rotation about the backbone bonds in a given chain as well as in neighbouring chains.¹⁵ The high-temperature peak observed at about 122°C may be the result of the diffusion of space charge either at the electrode or due to thermal release of charges at high temperature from the increased chain mobility.^{16,17}

Upon irradiation, the space charge relaxation peak disappeared while the T_g relaxation peak exhibited an increase in peak current (I_m) as the γ -dose increased. The increase of I_m is mainly due to carriers generated by γ -rays which escape recombination. The inset in Fig. 1 shows a linear dependence of peak current on irradiation dose over the whole range of exposure dose. Furthermore, a close examination of Fig. 1 shows that the temperature peak position (T_m) of the T_g relaxation peak is shifted towards lower temperatures with increasing dose of γ -irradiation. This is probably due to the generation of low-molecular-weight species and free chain ends on irradiation.¹⁸ In addition, the change in the shape of the T_g relaxation peak and the increase in its width on irradiation may result from a change in the distribution function of the associated relaxation times. This suggests that the width of the relaxation time spectrum has increased, and that the average relaxation time has been shifted to larger values due to structural changes.

Figure 2 shows TSDC thermograms of 2.5 wt% CoCl_2 -doped PVA films before and after γ -irradiation. The addition of 2.5 wt% CoCl_2 to PVA changes the picture drastically. A new, less intense peak appears around 50°C for the unirradiated sample and the samples irradiated with 21 and 35 Mrad doses, and the intensity of the T_g -relaxation current peak increases by about one order of magnitude for both unirradiated and irradiated samples. The space charge relaxation peak is absent in the spectra of all 2.5 wt% CoCl_2 -doped PVA samples. The small peak observed at the low-temperature end of the glass transition relaxation is probably related to the so-called sub- T_g intermediate relaxation.^{14,19-22} This corresponds to a temperature region too far from $T_g \approx 20^\circ\text{C}$ to have a non-equilibrium glassy structure, but sufficiently high to allow considerable orientation of chain segments within the time scale of the experiment. The exposure to higher γ -doses, of 50 and 75 Mrads, leads to the formation of one broad peak. The inset in Fig. 2 shows a linear dependence of peak current on irradiation dose, which is similar to that found in the inset of Fig. 1. The only difference is that the slope of the linear relationship is somewhat lower in PVA than in 2.5 wt% CoCl_2 -doped PVA, which implies a higher sensitivity to radiation in the case of the doped polymer.

The addition of the higher concentrations of 5

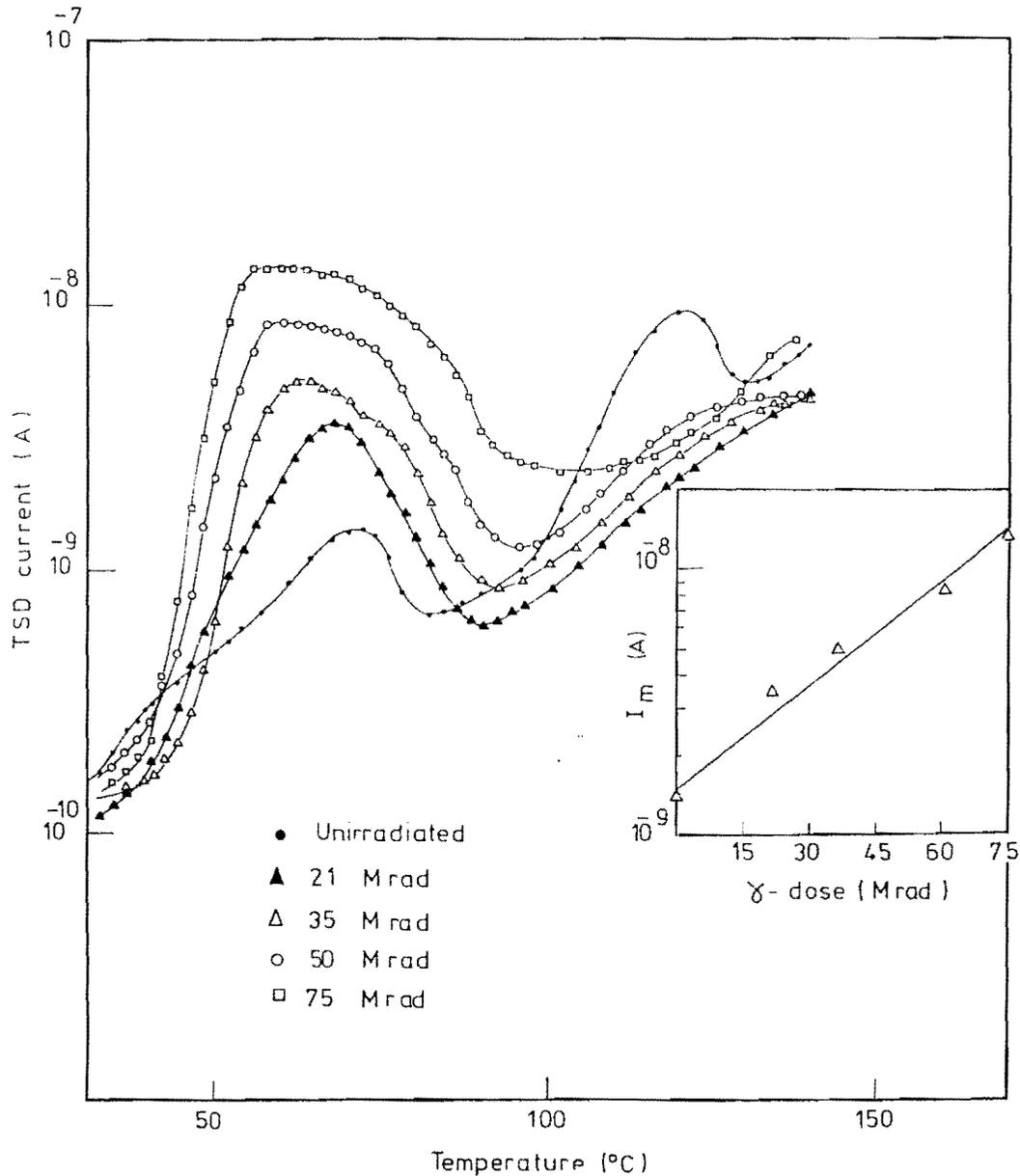


Fig. 1. Effect of γ -radiation on TSD current for pure PVA samples.

and 10 wt% CoCl_2 leaves the general behaviour of unirradiated samples nearly unchanged. The strength of the T_g relaxation peak appears to be more pronounced and is shifted towards higher temperatures (see Figs 3 and 4). On irradiation, the sub- T_g relaxation peak disappears over the dose range studied for the 10 wt% CoCl_2 -doped sample, and is only present at 21 Mrad dose for 5 wt% CoCl_2 -doped sample. The TSDC thermogram of the 10 wt% CoCl_2 -doped sample irradiated with 75 Mrad reveals a shoulder on the higher temperature side of T_g relaxation peak at about 90°C. The insets in Figs 3 and 4 show a linear dependence of peak current with γ -dose

up to 75 Mrad. The dependence of the I_m of the T_g relaxation peak on the irradiation dose, namely on the total amount of radiation energy absorbed by the sample, may provide information about the process of trap filling and thermal release. The observed linearity between I_{\max} and dose suggests the possibility of using these doped materials as γ -ray dosimeters. From the pronounced effect of γ -irradiation on T_m and I_m in each sample, we might conclude that the thermally stimulated current is not related to intrinsic properties of the material but is indicative of the existence of trapped carriers in the material. These carriers might have been

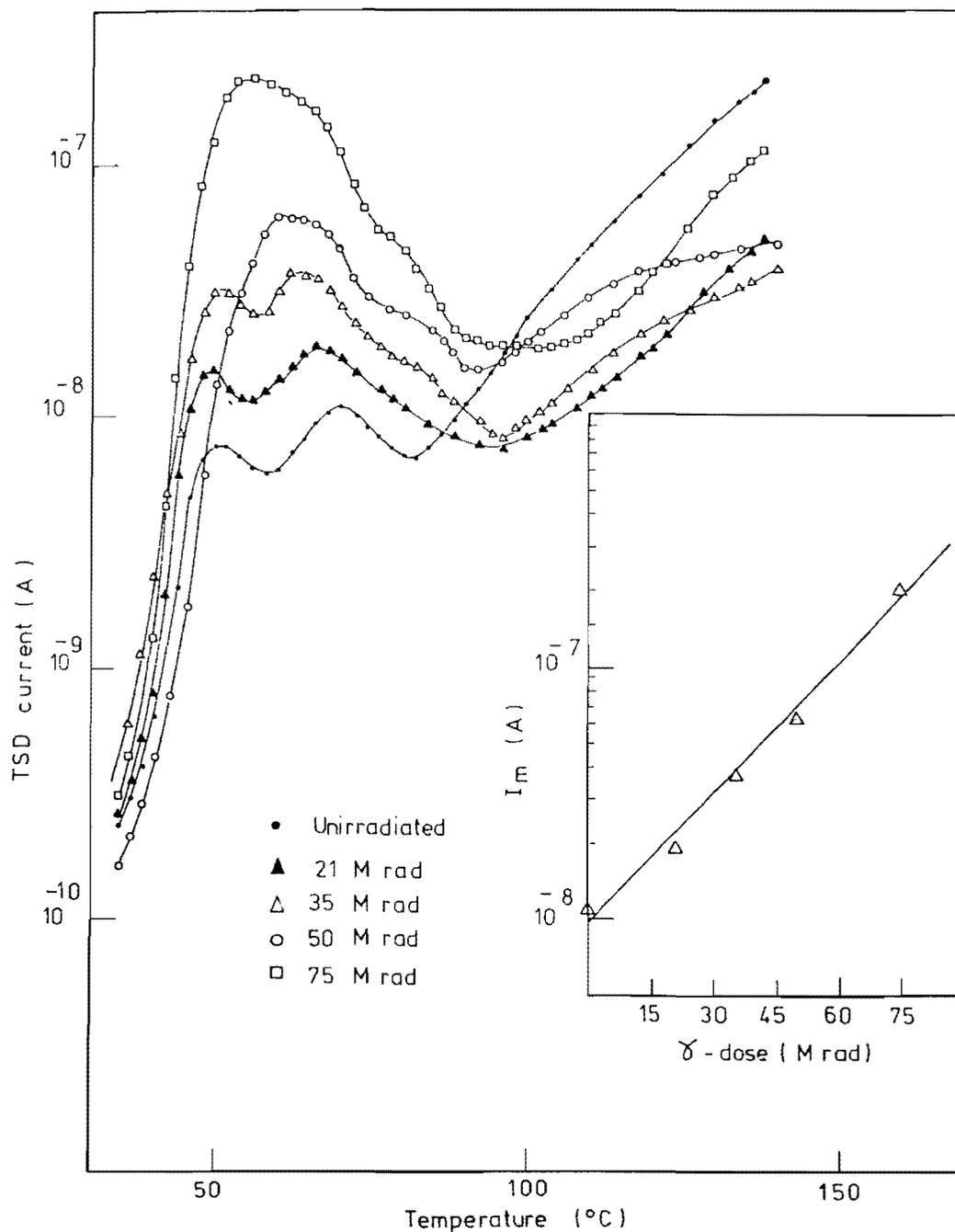


Fig. 2. Effect of γ -radiation on TSD current for 2.5 wt% CoCl_2 doped-PVA samples.

generated by the irradiation process through thermal activation.

The effect of storage on the TSDC of irradiated 5 wt% CoCl_2 -doped PVA samples stored in the dark at room temperature of 25°C has been studied. After 3 weeks, about 15% reduction in the relative I_m intensity at the T_g relaxation peak is observed. On the other hand, the shape and position of the peak are not significantly affected. The reduction in TSDC may be due to random recombinations of free

radicals formed by radiation, together with continued thermal degradation of the polymer.

The results summarised in Figs 1–4 confirm that there is considerable variation in the number of extrinsic charge carriers as a result of subsequent trapping of impurities and γ -radiolysis. It is known that many halogen-containing polymers with the halogen bonded to the main chain and/or side-chains readily undergo γ -radiolysis.^{23,24} Due to the ability of Co^{2+} to coordinate with hydroxyl groups, the

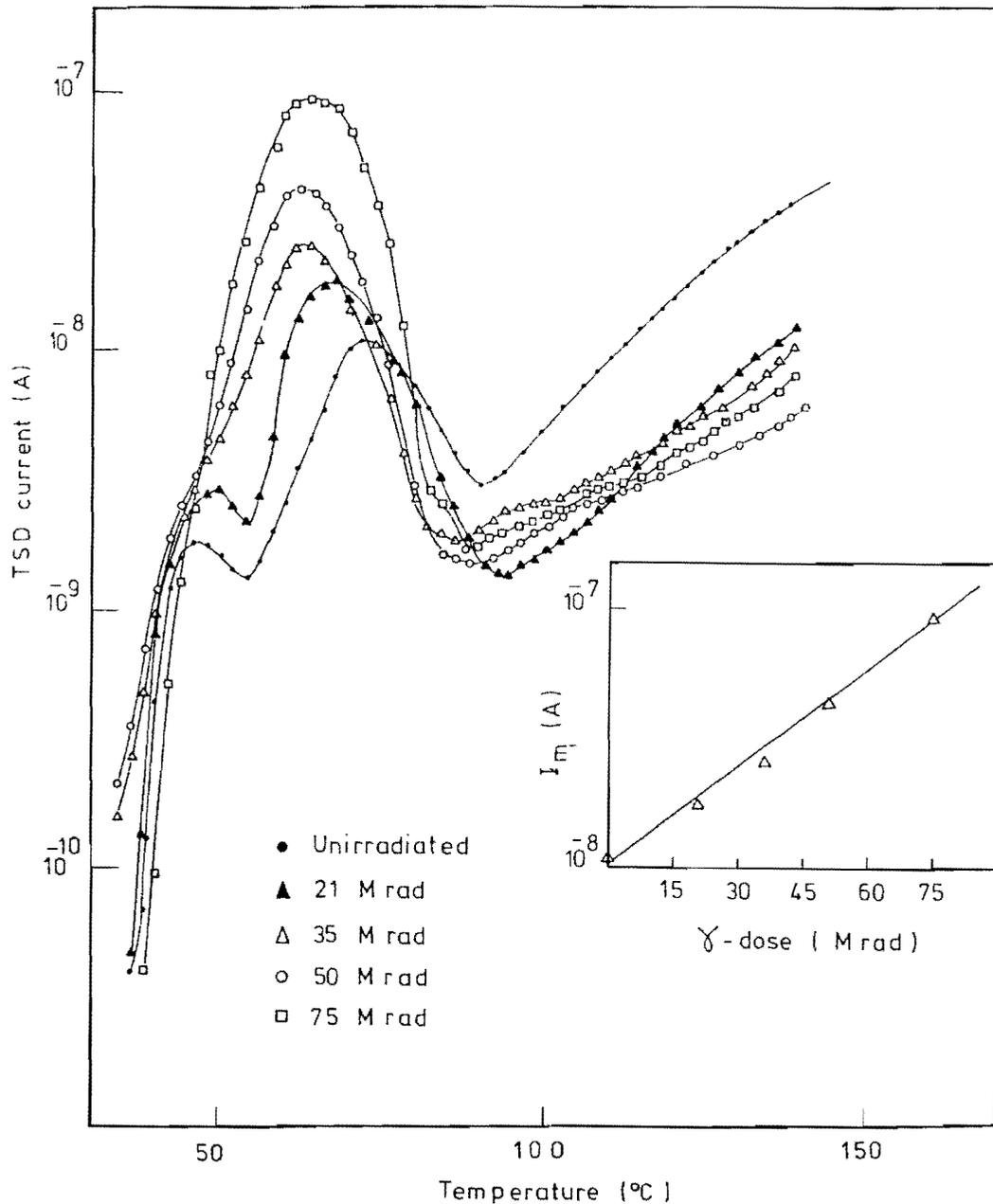


Fig. 3. Effect of γ -radiation on TSD current for 5 wt% CoCl_2 doped-PVA samples.

interaction between Co and OH results in a stronger poling effect. The dispersed Co^{2+} increases the mobility by aiding charge transfer between the polymer molecules. The relaxation process has been attributed to the statistical thermal motion of the polymer polar groups. This relaxation can be described in terms of dipolar polarisation associated with the micro-Brownian motion in the glassy state.

Current-time characteristics

The time variation of conduction current at different temperatures and fixed applied field was

studied to throw more light on the drift mobility and the concentration of charge carriers operating in the used material. Figures 5 and 6 show the current (I)-time (t) curves for pure and 5 wt% CoCl_2 -doped PVA samples irradiated with 35 Mrad at 2 kV cm^{-1} field strength and temperatures 120 and 160°C . Similar plots were obtained for the other unirradiated and irradiated pure and 5 wt% CoCl_2 -doped PVA samples.

The application of direct and reverse polarities was carried out in succession. The duration of the direct polarity phase is extended until the conduction current reaches its steady state value. On reversing the polarity, the time t_{max} required

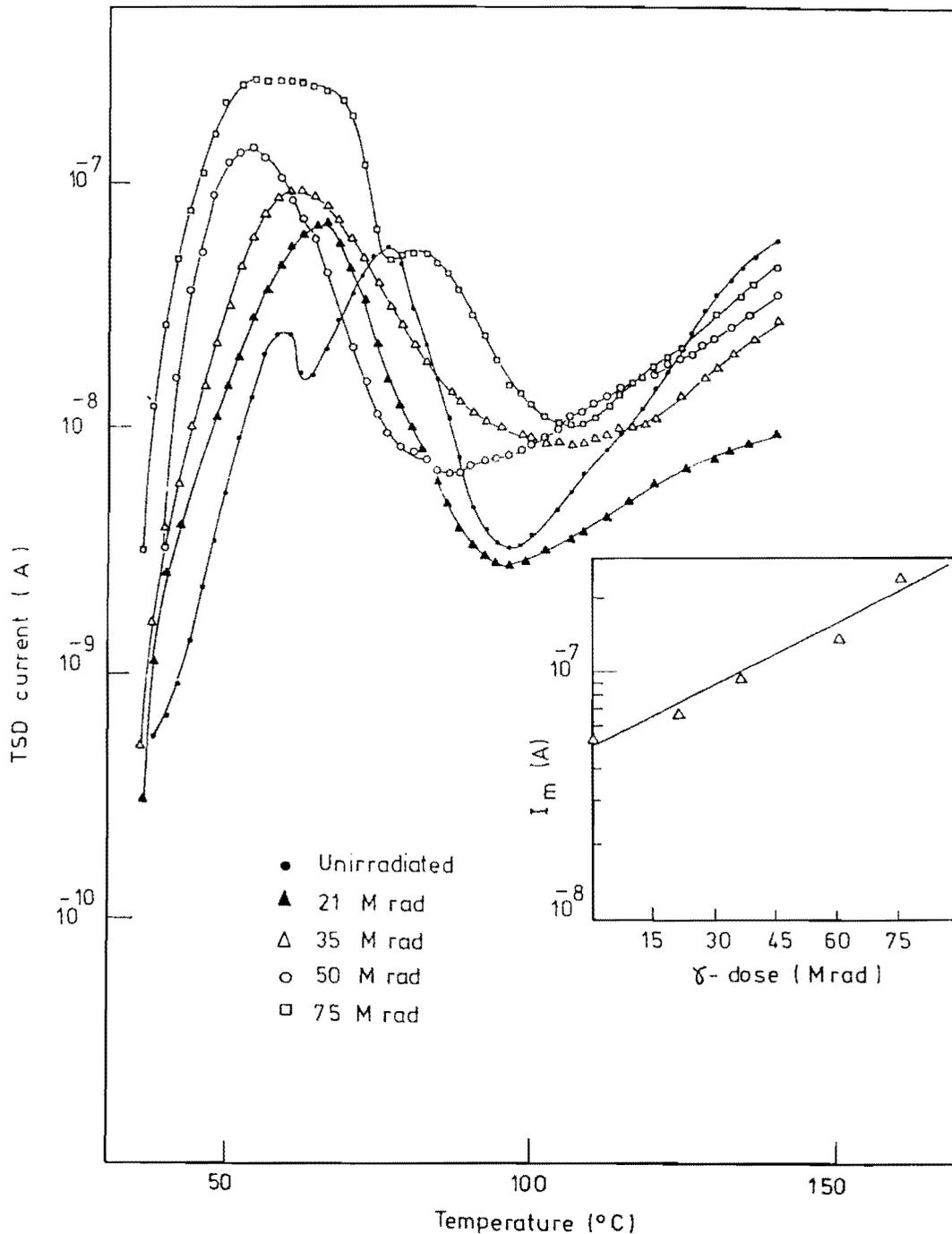


Fig. 4. Effect of γ -radiation on TSD current for 10 wt% CoCl_2 doped-PVA samples.

for the current to attain its maximum value decreases greatly with increase of temperature.

The observed relaxation phenomenon can be analysed using the equations.^{25,26}

$$J = nq\mu E \quad (1)$$

and

$$\tau \cong t_{\max} = d^2/\mu V \quad (2)$$

where J is the current density at a particular voltage V on a sample of thickness d ; E is the

electric field intensity; q is the electronic charge; μ is the drift mobility and τ ($\cong t_{\max}$) is the relaxation time.

The calculated values of charge carrier concentrations n and mobility μ using eqn (1) are listed in Table 1 for pure and 5 wt% CoCl_2 -doped PVA samples before and after γ -irradiation. It can be seen from Table 1 that the values of μ and n are affected by the subsequent trapping of CoCl_2 impurities in the PVA matrix, the thermal

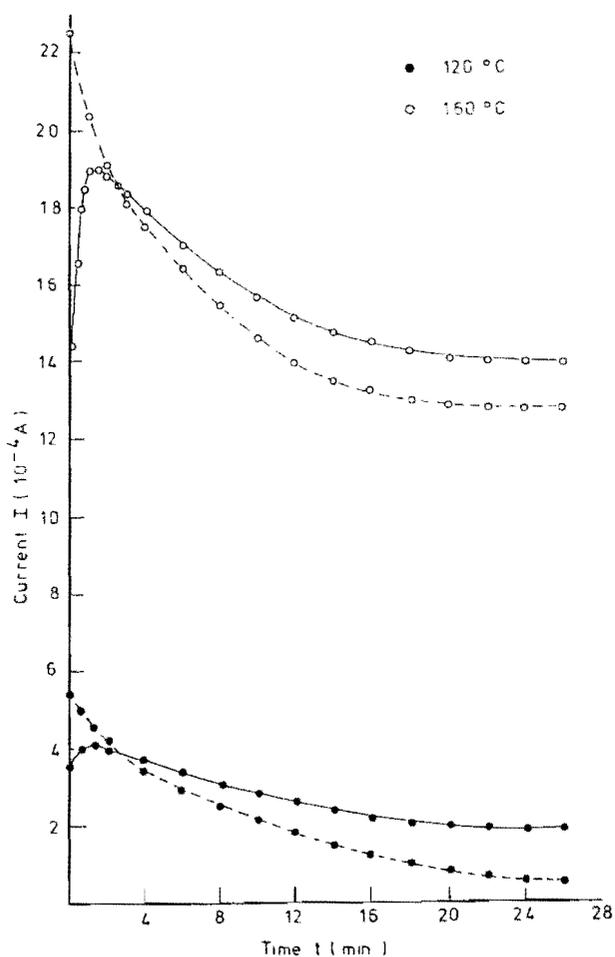


Fig. 5. Current relaxation curves for pure PVA sample (0.25 mm thick) irradiated with 35 Mrad γ -rays at field 50 V and temperatures 120°C and 160°C. Dotted lines refer to the first application of voltage and solid lines to the reversed polarity.

motion of molecular segments and γ -irradiation doses. Impurities act as localised centers in the bulk and then hinder the charge carrier mobility, giving rise to hopping transport. As both the γ -irradiation dose and the temperature increase, a reduction in the internal viscosity of the

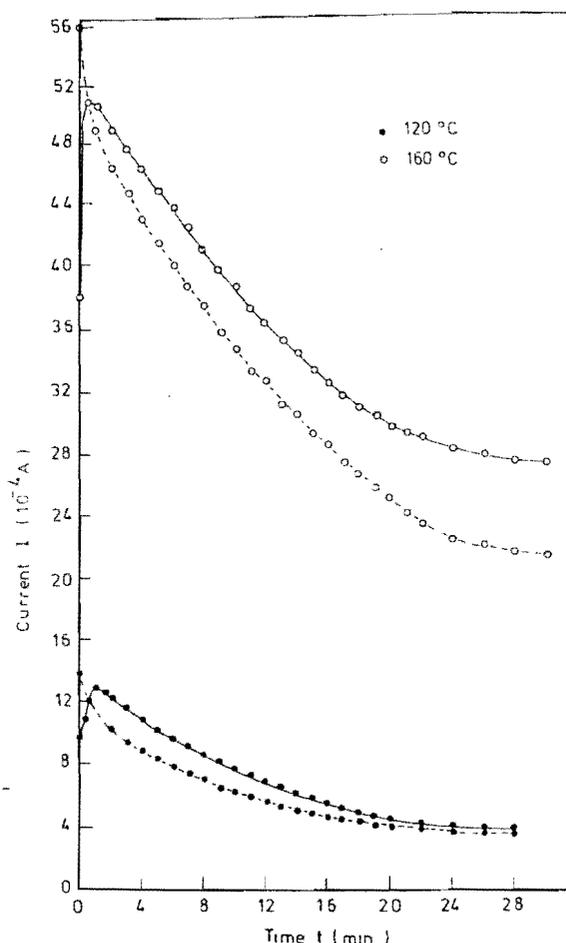


Fig. 6. Current relaxation curves for 5 wt% CoCl_2 doped-PVA sample (0.25 mm thick) irradiated with 35 Mrad γ -rays at field 50 V and temperatures 120°C and 160°C. Dotted lines refer to the first application of voltage and solid lines to the reversed polarity.

material allows the dipoles to rotate freely, hence the structural polarisation takes place.

The increase of drift mobility with both temperature and γ -dose indicates that the conduction is apparently due to thermally activated mobility. Furthermore, the small values

Table 1. Value of μ ($\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$) and n (cm^{-3}) for pure and 5 wt% CoCl_2 -doped PVA samples (2.5 mm thick) at different γ -doses and temperatures

γ -Doses (Mrad)	PVA				5 wt% CoCl_2 -PVA			
	120°C		160°C		120°C		160°C	
	μ	n	μ	n	μ	n	μ	n
Unirradiated	6.94×10^{-8}	2.48×10^{18}	1.38×10^{-7}	6.2×10^{18}	9.26×10^{-8}	3.12×10^{18}	1.04×10^{-7}	7.14×10^{18}
21	1.09×10^{-7}	3.80×10^{18}	1.58×10^{-7}	1.1×10^{19}	1.39×10^{-7}	8.62×10^{18}	1.66×10^{-7}	1.15×10^{19}
35	1.73×10^{-7}	4.49×10^{18}	1.98×10^{-7}	1.8×10^{19}	2.08×10^{-7}	1.18×10^{19}	4.17×10^{-7}	2.41×10^{19}
50	2.78×10^{-7}	8.60×10^{18}	3.47×10^{-7}	7.5×10^{19}	4.17×10^{-7}	4.47×10^{19}	5.21×10^{-7}	7.05×10^{19}
75	3.21×10^{-7}	3.45×10^{19}	4.63×10^{-7}	9.83×10^{19}	6.94×10^{-7}	8.27×10^{19}	8.27×10^{-7}	1.14×10^{20}

of drift mobility reflect the probable occurrence of a hopping mechanism.

CONCLUSION

γ -Irradiation can produce different valency states of the transition metal ions in the matrix of the chelated compounds. At the same time irradiation can affect the electronic state of the ligand molecules in the polymer matrix. These factors inevitably affect the thermal currents of the chelated compounds. The results obtained in the present work allow one to argue that the current increase is due to carriers generated by γ -rays which succeed in escaping recombination and trapping. The TSDC and $I-t$ properties of PVA are sensitive to the level of oxidation which is induced either thermally or by radiation and the presence of low molecular weight additives. The I_m of the T_g relaxation peak for the samples investigated is shown to be dose dependent while their resistance to γ -ray induced degradation is remarkably sensitive to dopant concentration. Such dependence may be interpreted in terms of the relative number of tie molecules in the investigated samples.

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