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Depolarization Current Studies in Hydroquinone Doped Poly(Vinyl Alcohol) Thermoelectrets

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Abstract

The effect of hydroquinone doping in poly (vinyl alcohol) thermoelectrets has been studied by the thermally stimulated depolarization [TSD] technique. The activation energy and the relaxation time have been calculated using the initial rise method. The slope of ln J vs 1/T plot for PVA thermoelectrets is constant indicating a single relaxation process. On doping, the slope of the curve indicates two different values of activation energy. The temperature corresponding to the current peak is found to change with the heating rate.

Introduction

A dielectric material carrying semi-permanent electric charges of opposite sign on its sides is known as an 'electret'. When these charges are produced by the simultaneous application of d.c. electric field and thermal radiation, the polarised sample is known as a 'thermoelectret'. The electret phenomenon which was first discovered by EGUCHI (1925) has attracted a great deal of interest because of its practical applications e.g. electret foil microphone (SESSLER and WEST 1962, 1968), ultrasonic transducer (REEDYK 1968) etc.

The electret charging mechanism is interpreted by the two charge theory (GROSS 1964). The sign of the residual charge depends on the nature of the dielectric material and also on polarising conditions. For studying the prospects for practical usage of any material, it is important to elucidate the processes of charge injection and carrier migration in it. The charge carrier migration to the electrodes is affected by the presence of trapping sites in the dielectric. When a polarised sample is heated in the short circuit, the thermally stimulated depolarisation [TSD] current so obtained yields important information in this regard and enables the determination of the dipolar relaxation time and activation energy. The relationship

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between the TSD current and the chemical structure of materials has also been investigated (TAKAMATSU and FUKADA 1970, TURNHOUT 1971).

Poly (vinyl alcohol) [PVA], is one of the most polar polymers. TSD currents have been measured in thermoelectrets prepared from PVA under different polarising conditions (SHARMA et al.). With the addition of impurities, the electrical properties are known to change. Doping may change even the glass-transition temperature (DIMARZIO and GIBBS 1963). JAIN et al. (1978) have shown that the resistance of PVA and its variation with temperature change on doping PVA with inorganic substances such as NaCl, $CuCl_2$ etc. In the present investigations, TSD technique has been used to study the effect of heating rate on the peak temperature and of hydroquinone(para-dihydroxybenzene) doping in PVA film thermoelectrets.

Experimental

Films of PVA and of PVA doped with known concentrations of hydroquinone were prepared in a manner similar to the one used by JAIN et al. (1978). Samples of these films 0.12 mm in thickness and of 2 cm x 2 cm cross-sectional area were fixed in a sample holder having aluminium electrodes and placed in a temperature controlled furnace. For all the samples studied, a static electric field of 7.5 KV/cm was applied between the two electrodes and thermoelectrets were prepared at 373 K for two hours of polarising time. For TSD current studies the electrets were heated at a linear heating rate of 1 K/min. or 4 K/min. from room temperature upto 475 K in the short circuited condition and in the absence of any electric field. The TSD currents so obtained were recorded by means of Keithley electrometer 610C.

Results and Discussions

The TSD spectra for polarised films of PVA and of PVA doped with different concentrations of hydroquinone are plotted in Fig. 1. The spectra consist of a single peak. The activation energy U has been calculated in the temperature range of 300-370K from the slope of the ln J vs 1/T curve shown in Fig. 2, using the relation,

$$\ln J\ (T) = \text{Constant} - U/(kT) \qquad (1)$$

where k is the Boltzmann's constant. The relaxation time τ is calculated from the relation,

$$\tau = \tau_0 \exp[U/(kT)] \qquad (2)$$

where τ_0 is a constant given by,

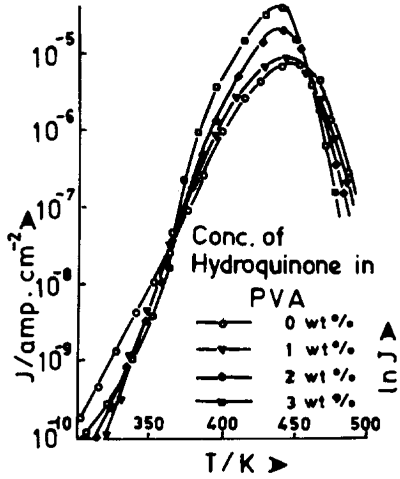

Fig. 1: TSD current spectra with heating rate of 4K/min.

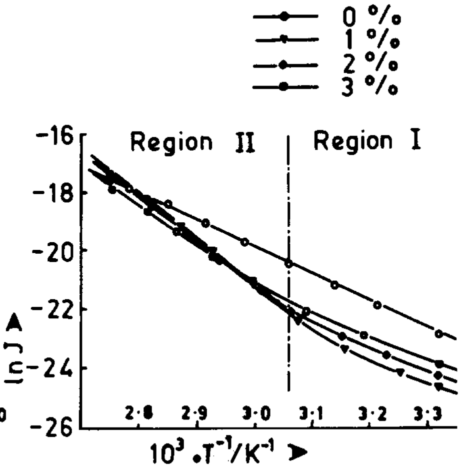

Fig. 2: Determination of activation energy from initial rise of Fig. 1.

$$\tau_0 = \frac{kT_m^2}{BU \exp[U/(kT_m)]} \tag{3}$$

T_m is the temperature corresponding to the current peak and $B = dT/dt$ is the heating rate.

(a) Effect of Heating Rate

The value of T_m for undoped as well as doped PVA thermoelectrets is found to increase when the heating rate is increased from 1K/min. to 4K/min. In our earlier studies (SHARMA et al.), it was observed that for PVA thermoelectrets T_m does not depend on the polarising conditions such as polarising field, temperature and time. The results are quite in agreement with the observations of TURNHOUT (1971) that T_m is independent of the polarising conditions but increases or decreases with heating rate. The results are summarised in Table 1.

(b) Effect of Hydroquinone Doping

As seen from Table 1, there is apparently no relation in the value of T_m and the dopant concentrations studied. However, it is observed from Fig. 1 that the magnitude of TSD current is influenced by the hydroquinone concentration. Initially, at low temperatures the current is small because the free carriers

TABLE 1

Effect of Heating Rate on Peak Temperature T_m

Conc. of Hydroquinone in PVA in wt. - %	T_m/K corresponding to heating rate of	
	1K/min.	4K/min
0	425	445
1	425	443
2	423	441
3	424	441

are trapped. With increase in temperature, the trapped carriers are released by thermal excitation and also owing to considerable increase in the mobility of the carriers, the current increases. The magnitude of peak current J_m increases with dopant concentration.

The addition of hydroquinone to PVA is also seen to affect the activation energy. For undoped PVA thermoelectrets its value is 0.77 ev. The thermoelectrets prepared from doped PVA films show two values of activation energy in the temperature range studied. In region I, corresponding to temperatures slightly above room temperature, its value U_1 is less than that of undoped PVA thermoelectrets. However, with increase in temperature, in region II, the value of activation energy, U_2, increases. The change in the activation energy takes place at a temperature T_u which increases slightly with the dopant concentration. A similar change is also observed in Hall coefficient or resistivity studies in semiconductors, as a function of temperature (KATON 1968) and is attributed to 'freezing out' of free carriers onto impurity centres in the lower temperature range. The results are summarised in Table 2.

Activation energy in the higher temperature range is greater than that in the lower temperature range has also been reported in the conductivity studies of certain polymers (SAITO et al. 1968, SASABE and SAITO 1968). The increase is observed at a temperature which coincides approximately with the glass-transition temperature T_g, of the given polymer and is attributed to the increase in free volume and hence the mobility of carriers, with increase in temperature. In the present investigations the observed values of T_u for doped PVA thermoelectrets are found to be below T_g of undoped PVA. To understand the observed results a distinction may be made here in the two processes, namely the electrical conduction under an applied electric field and the TSD current on account of the increase in temperature of the previously polarised

TABLE 2

TSD Studies in Hydroquinone doped PVA thermoelectrets

Dopant Conc. in wt.-%	J_m in A/cm^2	Region I		T_u in K	Region II	
		U_1 in ev.	$\tau.10^{-2}$ at T_m in sec.		U_2 in ev.	$\tau.10^{-2}$ at T_m in sec.
0	$7.6x10^{-6}$	0.77	3.30	--	0.77	3.30
1	$8.0x10^{-6}$	0.69	3.68	322	1.42	1.78
2	$2.1x10^{-5}$	0.69	3.65	326	1.28	1.97
3	$3.5x10^{-5}$	0.63	3.99	328	1.12	2.24

sample. The electrical conduction in a polymer results from the migration of charge carriers (electrons and ions). The carrier mobility will increase significantly near T_g resulting in an increase in the current. On the other hand, the TSD current in a polar polymer such as PVA results from the dipole orientation and displacement of space-charges. With increase in temperature, the current increases due to decay of polarisation. The addition of impurities is known to influence the charge retaining capacity, relaxation time, resistivity and other parameters (JAIN et al. 1975). The impurity incorporation, in the present study, is responsible for the observed increase in the activation energy of doped PVA thermoelectrets at a temperature below T_g of undoped PVA.

The temperature dependence of the dipole reorientation differs from that of the motion of space-charges. The current maximum for dipole reorientation occurs at a lower temperature than that of the space-charge motion. The first process requires only a rotational motion of the molecular groups, whereas the latter process involves a motion of the molecular groups (ions) over macroscopic distances. The position of the single current peak in the TSD spectra and also the value of the activation energy indicate that ions may be the major current carriers. In general, for ionic conduction the magnitude of the activation energy is large in comparison to that for electronic conduction (JONSCHER 1967, SAITO et al. 1968). At lower temperatures the current is small as the ions are trapped. On heating the thermoelectrets, the trapped ions are released due to thermal excitation which results in an increase in the observed current and correspondingly the activation energy.

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