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Short communication

DC conduction mechanism in polyvinyl alcohol films doped with potassium thiocyanate

N. Nagaraj, Ch.V. Subba Reddy, A.K. Sharma*,
V.V.R. Narasimha Rao

Department of Physics, S.V. University, Tirupati 517 502, India

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Abstract

The current–voltage characteristics of pure polyvinyl alcohol (PVA) films and those doped with potassium thiocyanate (KSCN) are studied as a function of film temperature and dopant concentration. The conduction mechanisms operative in the films in different temperature and voltage ranges are estimated from the behaviour of log I versus $V^{1/2}$ plots (I = current, V = voltage). For undoped (pure) films, the conduction mechanism appears to be essentially a Schottky type. On doping, there is considerable influence on the type of conduction mechanism, especially at lower temperatures. At higher temperatures, however, there is no significant effect of doping on the conduction mechanism.

Keywords: DC conduction; Current–voltage characteristics; Schottky emission; Poole–Frenkel mechanism; Polymer; Charge transport

1. Introduction

Electrical conduction in polymers has been studied extensively during the past two decades to understand the nature of charge transport in these materials. Various mechanisms, such as Schottky emission [1–4], Poole–Frenkel emission [5,6], space-charge limited conduction [7], and hopping conduction [8,9], have been suggested for the charge transport. More recently, considerable interest has been shown on the effect of doping on the transport properties of polymers [10–14]. Depending on their chemical nature and the way in which they react with the host matrix, the doping substances alter the transport properties to different degrees.

Polyvinyl alcohol (PVA) is a good insulating material with low conductivity and low dielectric loss, and hence is of importance to the microelectronics industry. Its electrical conductivity and charge-storage capability can be markedly influenced by doping with suitable impurities. Although some work [15] has been reported on the conduction phenomena in doped polyvinyl alcohol, no coherent picture is available with respect to charge-transport phenomena. Hence, in the present study, the effect of doping with potassium thiocyanate (KSCN) on electrical conduction in PVA has been undertaken.

2. Experimental

Films (thickness: 150 μm) of pure (undoped) PVA and complexed films of PVA with potassium thiocyanate in the wt.% ratios (90:10), (80:20) and (70:30) were prepared by a solution-cast technique using triple-distilled water as the solvent. The solutions were stirred for 10–12 h and then cast on to polypropylene dishes and evaporated slowly at room temperature. The final products were vacuum dried thoroughly at 10^{-3} Torr. Before taking measurements, the films were annealed by monitoring the resistance while heating from room temperature to 400 K at a constant heating rate, and then cooling down to room temperature. Thickness measurements were made by the capacitance method using an LCR bridge (TF 1313A) assuming the dielectric constant of PVA to be 3.5, and later verified by the gravimetric method.

The current–voltage characteristics were studied in sandwich configuration with an effective area of 0.321×10^{-2} m^2 in the temperature range 300–385 K and the voltage range 0–5 V. Voltages higher than 5 V were not applied as the sandwich structure collapsed under the application of high-biasing voltages. Current measurements were made by means of an electrometer amplifier (EA 815) supplied by ECIL, Hyderabad, India. The temperature was measured using a copper constantan thermocouple in perfect contact with the specimen.

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* Corresponding author.
E-mail address: subbu5reddy@yahoo.com (Ch.V. Subba Reddy).

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3. Results and discussion

The current (I) flowing through the undoped and doped samples as a function of applied voltage (V) was measured whilst maintaining the film at different constant temperatures of 320, 340 or 375 K. At low voltages, the current increased gradually with applied voltage. At higher voltages, the rate of increase was slower.

This behaviour can be explained in terms of the charge-transport mechanism operating in the polymer film in the different voltage ranges. The charge-transport mechanism in these materials can be Schottky's field-assisted thermionic emission equation [16–19], i.e.

$$I = AST^2 \frac{\exp[\phi/K - C(V/\epsilon d)^{1/2}]}{T}$$

where A is the Richardson constant, S the electrode area, ϕ the metal polymer work function, d the thickness of the dielectric, ϵ the permittivity, K the Boltzmann constant, and T is the temperature. If V is expressed in volts and d in cm, the value of the constant C is 4.058. For the Poole–Frenkel effect, the value of C is replaced by $2C$.

If the temperature of the film is maintained constant, then a plot of log I versus $V^{1/2}$ yields the required information with respect to the charge-transport mechanism. The log I versus $V^{1/2}$ plots for undoped and 10, 20 and 30% KSCN-doped films at three different film temperatures are given in Figs. 1–4. The plots show a linear behaviour with appreciable deviation from linearity at lower fields, which can be attributed to accumulation of space charge at the electrodes. The slope of these plots at higher fields yields important information regarding the nature of the conduction process. The current–voltage–temperature dependence obeys the relation

$$I \propto \exp\left(\frac{e\beta F^{1/2}}{KT}\right)$$

where F is the applied field and β a constant characteristic of the conduction mechanism.

The linear behaviour of log I versus $V^{1/2}$ plots in the present study points to an electronic-type conduction mechanism. Here, the charge carriers are released by thermal activation over a potential barrier. The physical nature of such a potential barrier can be interpreted in two ways. It can be the transition of electrons over the barrier between the cathode and the dielectric (Schottky emission). Alternatively, charge carriers can be released from traps into the dielectric (Poole–Frenkel effect). In order to differentiate between these two, the values of β at different temperatures were calculated from the slopes of log I versus $V^{1/2}$ plots.

The theoretical value of β can be calculated separately for either the Schottky or the Poole–Frenkel mechanisms by use of the following respective equations:

$$\beta_{RS} = \left(\frac{e}{4\pi\epsilon\epsilon_0}\right)^{1/2}$$

$$\beta_{PF} = 2\beta_{RS}$$

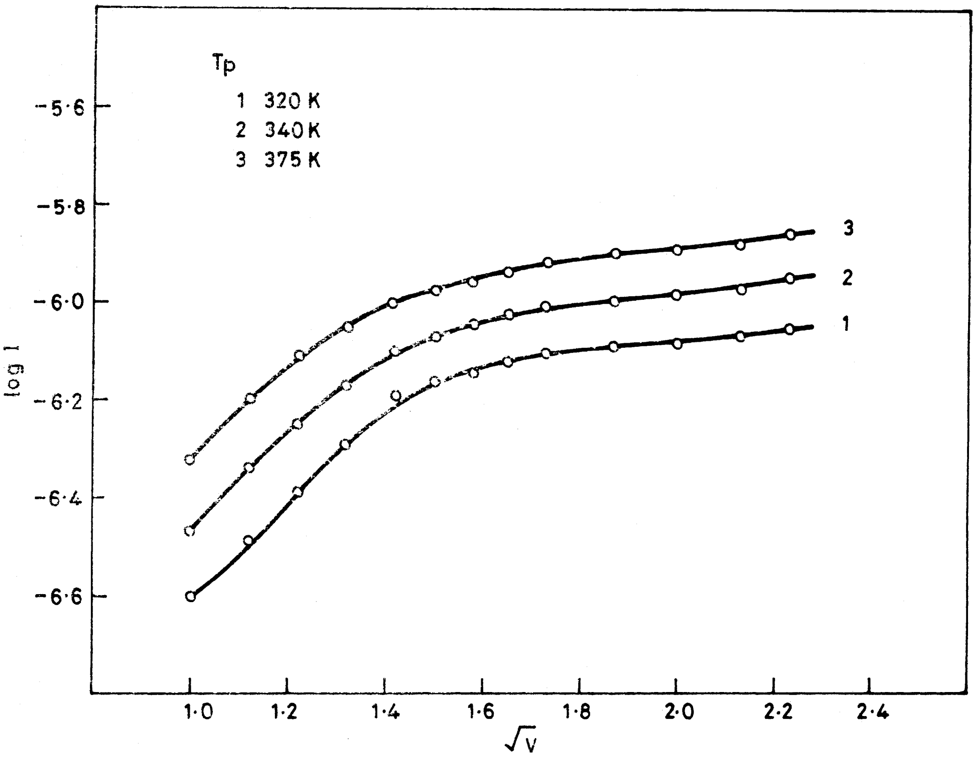

Fig. 1. The log I as function of $V^{1/2}$ for undoped PVA at different film temperatures.

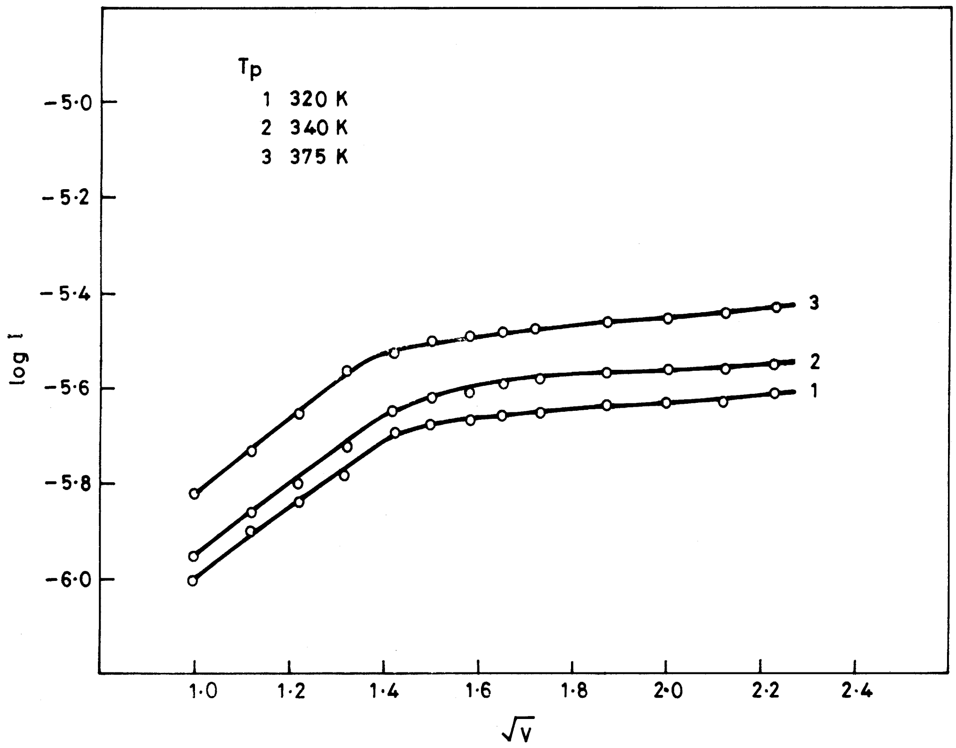

Fig. 2. The log I as function of $V^{1/2}$ for complexed (PVA + KSCN) (90:10) film at different temperatures.

where, for PVA, the dielectric constant $\epsilon = 3.5$ F/m, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m and $e = 1.602 \times 10^{-19}$ C.

The experimental as well as the theoretical values of β for both the Schottky and Poole–Frenkel mechanisms are shown in Table 1. For undoped films, the experimental value of β_{exp} is closer to the theoretical value of β_{RS}. This suggests that the charge conduction is through the Schottky mechanism, where the charges are injected from the electrodes into

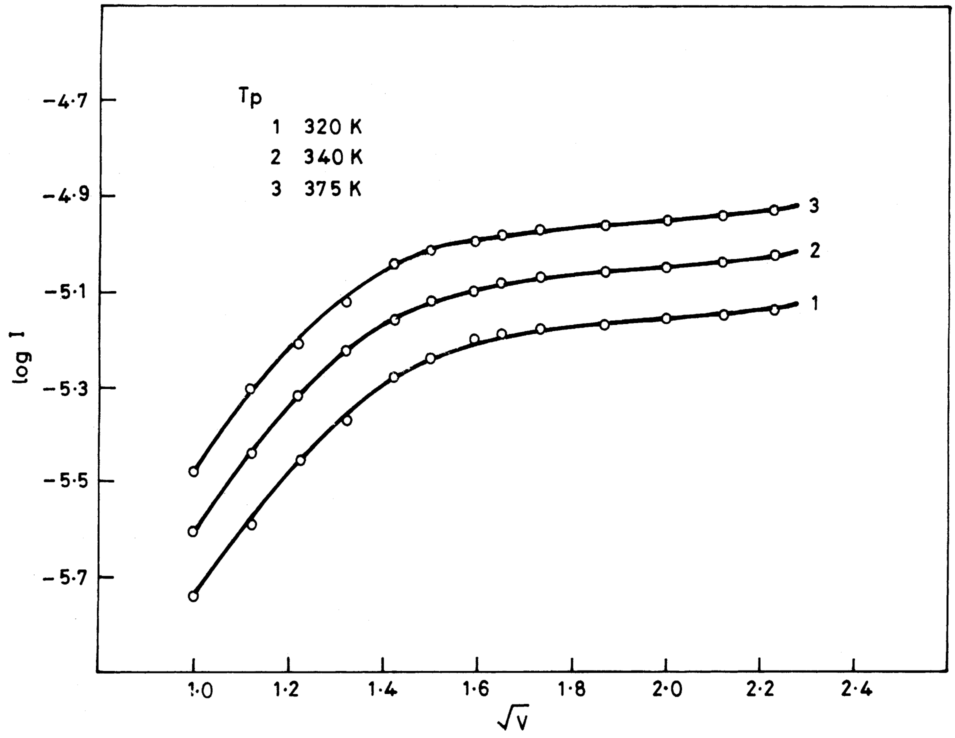

Fig. 3. The log I as function of $V^{1/2}$ for complexed (PVA + KSCN) (80:20) film at different temperatures.

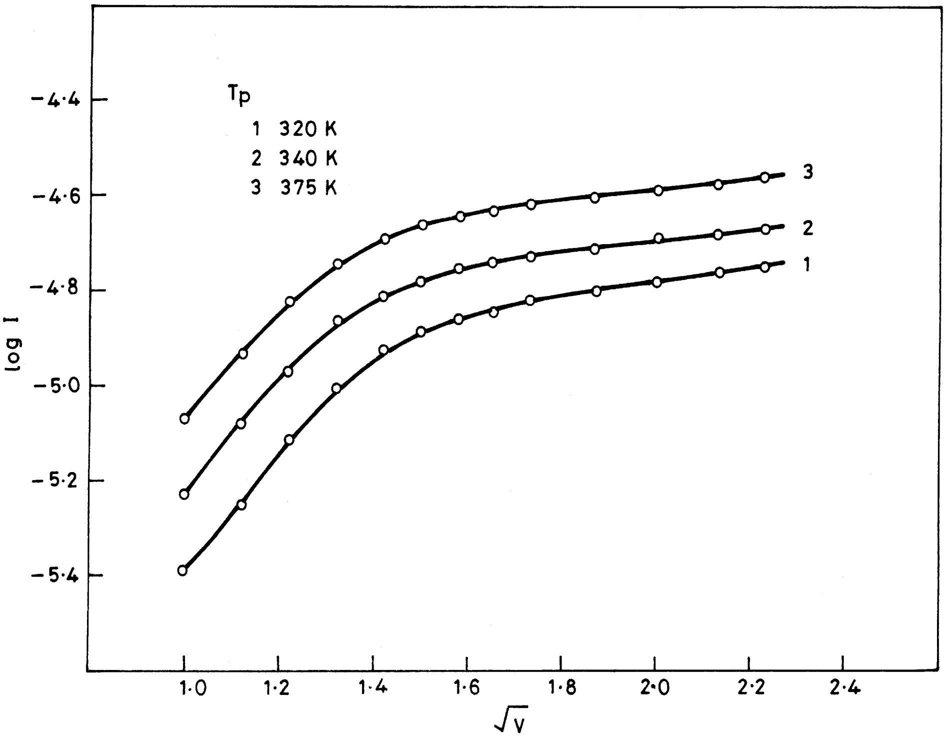

Fig. 4. The log I as function of $V^{1/2}$ for complexed (PVA + KSCN) (70:30) film at different temperatures.

Table 1
Theoretical and experimental values of β for undoped and KSCN-doped PVA films at different temperatures

Sample	Temperature (K)	Experimental β_{exp} ($\times 10^{-5}$ eV)	Theoretical β	
			β_{RS} ($\times 10^{-5}$ eV)	β_{PF} ($\times 10^{-5}$ eV)
Undoped PVA	320	2.25		
	340	2.28		
	375	2.95		
10% doped PVA	320	2.08		
	340	2.91		
	375	2.48		
			2.09	4.05
20% doped PVA	320	2.74		
	340	2.35		
	375	2.64		
30% doped PVA	320	2.69		
	340	2.53		
	375	2.85		

the polymer over a potential barrier, the magnitude of which is field-dependent.

For doped films, the experimental values of β_{exp} indicate that at low temperature, the Schottky mechanism alone is not sufficient to explain the conduction. At high temperatures, however, the conduction mechanism is essentially Schottky type.

4. Conclusions

Current–voltage characteristics for KSCN-doped PVA films show a linear behaviour with an appreciable deviation from linearity at lower voltages, which may be due to accumulation of space charge at the electrodes. The slopes of the linear regions of these plots give information regarding the nature of the conduction mechanism operating in these films. Evaluation of the value of β_{exp} from these slopes suggests that Schottky emission is the dominant charge-transport mechanism in the films.

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