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CURRENT VOLTAGE CHARACTERISTICS IN COPPER-POLY (VINYL-ALCOHOL) COMPOSITES

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Electrical conduction of pure poly (vinyl-alcohol) (PVA) and copper poly (vinyl- alcohol) composites (Cu-PVA) is studied as function of voltage and temperature. From log I - log V relations, it is found that we can not explain the conduction mechanism on the basis of space-charge limited current. The values of Schottky field lowering constant β_{SR} was calculated and compared with β_{exp} which was calculated from the slope of $\ln I$-$V^{1/2}$. It is found that at low temperature for pure sample the conduction may be due to a combination of electronic and ionic parts. But for other samples a quite large difference between $\beta_{P.F}$ and β_{exp} is observed. We conclude that, the $\ln I$ - $V^{1/2}$ study of these composites samples dose not help us in knowing the exact case of the conduction mechanism of these samples.

Key words: Polymer, Poly (vinyl-alcohol), Electrical-conductivity.

Introduction

The possibility of replacing metals of semiconducting inorganic materials with recently discovered conducting polymers has generated intensive interest in such materials. Two recent reviews [1,2] and monograph [3] give an adequate account of research activity on such properties, such as synthesis, structure and applications of organic polymer. Furthermore, sustained growth of research in this area is directed towards tailoring new materials of high electrical conductivity, thermal stability and low glass transition temperature. An investigation has so far been reported on the electrical conductivity of pure and dopped poly (vinyl-alcohol), thin film [4]. It was suggested that the conduction beyond the glass transition temperature is ionic in nature. In our recent study on the variation of dielectric constant [5], and conductivity [6] of Cu-PVA composites with the percentage of Cu in PVA, we found that the dependence of the measured dielectric constant and conductivity on the weight percentage in the composites were reproducible, and the percolative model gives suitable description for the system studied.

Experimental

Cu-PVA composites were made in different compositions including 2.5, 3.75 and 5.00% by weight of copper and then milling the compound together. Then the samples were compressed into discs of 1.0 mm thickness and 12 mm diameter at 0.4 GN/m^2 at room temperature. The PVA used has molecular weight 1700 (from Osaka Hayashi Chemical Industries Ltd., Japan) and the copper has 98.5% very fine powder, atomic weight 63.54 (from proluba Paris, France).

The size of the copper grains in our samples was much smaller than the resolution of our optical microscope at magnification of 1000.

The I-V characteristics were studied at different temperature (30°, 60°, 90°, 120° and 160°) using a stabilized D.C. power supply, an electrometer (type Keithley 617), and digital voltmeter. Variation of temperature was controlled by connecting the furnace to contact thermometer and relay. Measurement of the sample temperature was confirmed using thermocouple which was made to touch the upper surface of the sample. The capacitance measurements were performed on R-L-C bridge (type Healthkit). A sample holder with brass electrodes was specially designed to suit the present electrical measurement. Good conduction was attained by painting the sample on both surfaces with air drying silver paste (type RC, U.K.). All measurement were made in air.

Results and Discussion

In order to investigate the conduction mechanism operating, the current-voltage temperature characteristics were studied the variation of log I vs log V at different temperature for pure and composites samples were studied. Our electrical measurements were taken during the first cycle, because our reliability tests indicate that the sample suffer drastic change in its colour after the first cycle. Figure 1 illustrate this behaviour for the pure sample. Figure 2

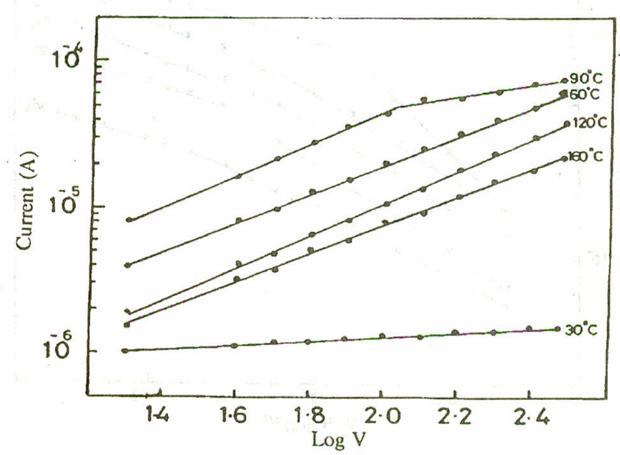

Fig. 1. Current (I) as function of the applied voltage (V) at different temperatures for pure sample.

illustrate the behaviour for composites samples at 90°. Similar plots were carried out for other samples, but they are not presented here. The slopes of these plots for different samples were calculated at different temperature and fields, these results are given in Table 1. From the Table we can see that all the samples at 90° have sublinear behaviour. This may be due to the presence of the samples in the transformation region from glassy state to rubbery state. Also from Table 1 we can see that all samples above 120° have linear behaviour, but we can not explain this result on the basis of space - charge limited current, as the slope of this type of mechanism is around two [7].

If Poole - Frenkel (PF) or Schottky - Richardson (SR) is assumed the current - voltage relationship for (SR) emission is given by

$$I = A\, s\, T^2 \exp(-\phi_s/KT + \beta_{SR} V^{1/2}) \quad (1)$$

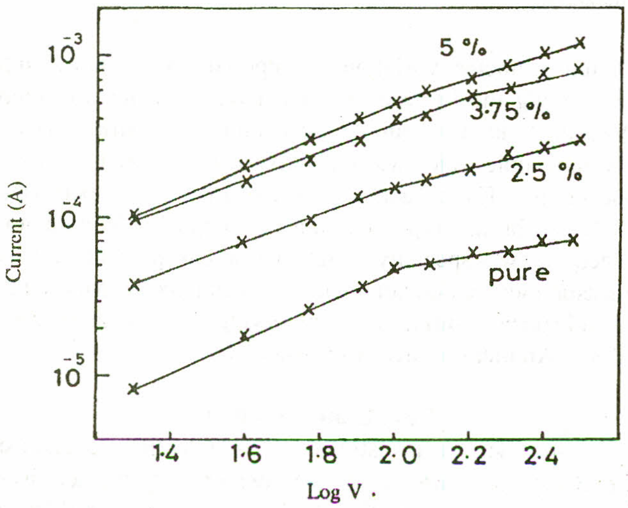

Fig. 2. Current (I) as function of the applied voltage (V) at 90° for all samples.

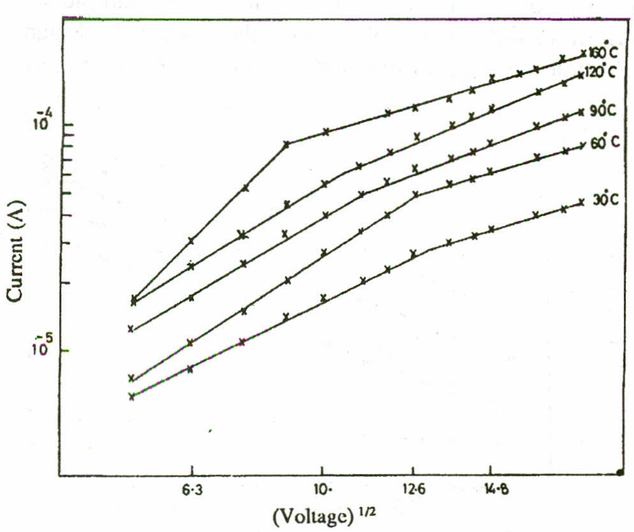

Fig. 3. Dependence of current on the square root of the voltage for the sample Cu-PVA 2.5% at different temperatures.

where β_{SR} is Schottky - field lowering constant and is given by

$$\beta_{SR} = (1/KT)\,(e^3/4\pi\epsilon\epsilon_0 d)^{1/2} \quad (2)$$

A is constant, S is the surface area of the sample, T is the temperature, K is Boltzman constant, ϵ_0 is the permitivity of the free space, ϵ is the dielectric constant, d is the thickness of the sample, V is the applied voltage, and ϕ_s is the potential barrier. Equation (1) predicts a linear relation between 1n I and 1n V with slope β_{SR} at constant temperature. The Poole-Frenkel relation also predicts linear relation between 1n I and 1n V, similar to equation (1) with β_{SR} replaced by $\beta_{P.F}$ and ϕ_S replaced by $\phi_{P.F}$ theoretically $\beta_{P.F} = 2\beta_{SR}$

Figure 3 indicates the dependence of current on the square root of voltage of sample Cu-PVA 2.5% at different temperature. Similar plots were carried out for other samples, but they are not presented here.

The values of β calculated (β_{exp}) from the slope of log I -$V^{1/2}$ plots alongwith the theoretical calculated values of β_{SR} and $\beta_{P.F}$ is given in Table 2. From the Table we can see that the slope value for pure sample at high field and at low temperature is about two times $\beta_{P.F}$, thus the mechanism of conduction might be a combination of electronic and ionic mechanisms. But for other samples a quite large difference between β_{SR} or $\beta_{P.F}$ and β_{exp} is observed. For these samples we suggest that

Table 1. Slope Values from Log I vs Log V of Pure PVA and Cu-PVA Composites Samples.

Temperature (°C)	Pure	Composites 2.5%	3.75%	5.0%
30	0.25	0.89	0.78	0.99
60	1.03	1.01	0.98	1.15
90	1.11	0.89	0.85	1.15
	(0.45)	(0.58)	(0.54)	(0.73)
120	1.18	1.01	1.01	0.95
160	0.97	0.92	0.92	1.26

Figures in parentheses are the slope values at high fields.

Table 2. Values Calculated from Log I vs $V^{1/2}$ Plot of Pure PVA and Cu-PVA Composites Samples.

Sample	TC	β_{SR}	$\beta_{P.F}$	β (experimental) Low field	High field
Pure	30	3.42×10^{-3}	6.84×10^{-3}	0.033	0.013
	160	8.74×10^{-4}	1.74×10^{-3}	0.175	0.109
2.5%	30	2.65×10^{-3}	5.30×10^{-3}	0.183	0.108
	160	1.10×10^{-3}	2.20×10^{-3}	0.350	0.112
3.75%	30	2.37×10^{-3}	4.74×10^{-3}	0.159	0.063
	160	1.20×10^{-3}	2.40×10^{-3}	0.193	0.117
5.0%	30	1.76×10^{-3}	3.52×10^{-3}	0.153	0.123
	160	1.30×10^{-3}	1.60×10^{-3}	0.222	0.160

the addition of Schottky - Richardson current with ionic (or ohmic) current which is proportional to voltage may lead under certain condition to the increase of the sloped 1g I/d$\sqrt{v}$ relative to the value β_{SR}. In fact the I - V study not tell us the exact cause of mechanism of conduction in these samples in this temperature range. We suggest that, for such mixture samples, to know the conduction mechanism it is better to study the frequency dependence of A.C. conductivity.

Our recent study [6] of D.C. electrical conductivity in Cu- PVA composites show that at $T>T_g$ (where T_g is the glass transition) there is a minimum in the reciprocal temperature conductivity. This can be assumed as a result of the competition between two conduction mechanism. The first mechanism predominates at lower temperature, where the conductivity is decreased by thermal expansion of hopping paths between copper particles of aggregates. The other one becoming effective at higher temperature, this due to the thermally activated conduction mechanism obeying Arrhenius relation.

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