*Asian Journal of Chemistry* Vol. 6, No. 1 (1994), 138–142

# Electrical Conduction Mechanism in Copper-Poly(Vinyl Alcohol) Composites

M.M. MOSAAD
*Department of Physics, Faculty of Education*
*Kafr-El-Sheikh, Egypt*

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 cannot explain the conduction mechanism on the basis of space-charge limited current. The values of Schottky field lowering constant $\beta_{SR}$ was calculated and compared with $\beta_{exp}$ 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 $\beta_{PF}$ and $\beta_{exp}$ is observed. We conclude that the ln I – $V^{1/2}$ study of these composites samples does not help us in knowing the exact case of the conduction mechanism of these samples.

## 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 a monograph[3] give an adequate account of research activity on such properties, such as synthesis, structure and applications of organic polymers. Furthermore, sustained growth of research in this area is directed toward 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 doped 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 precentage 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 Porluba, Paris, France).

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

The I-V characteristics were studied at different temperatures (30°, 60°, 90°, 120°, 160°C) using a stabilized d.c. power supply, an electrometer (type Keithley 617) and digital voltmeter. Variation of temperature was controled 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 Heathkit). 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 made in U.K.). All measurements were made in air.

## RESULTS AND DISCUSSION

In order to investigate the conduction mechanism operating, the current-voltage temperature characteristics were studied. The variations of log I vs log V at different temperatures for pure and composite samples were also studied. Our electrical measurements were taken during the first cycle, because our reliablity tests indicated that the sample suffers drastic change in its colour after the first cycle. Fig. 1 illustrates this behaviour for the pure sample. Fig 2 illustrates the

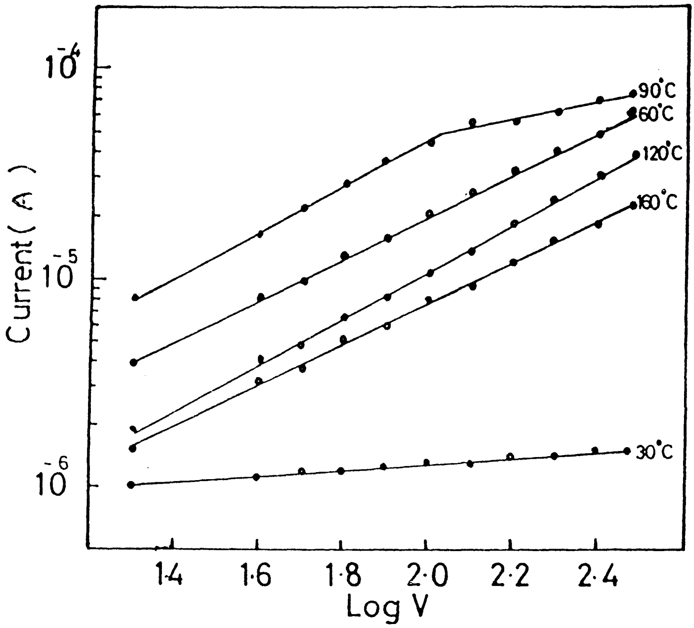

Fig. 1 Current (I) as function of the applied voltage (V) at different temperatures for pure sample

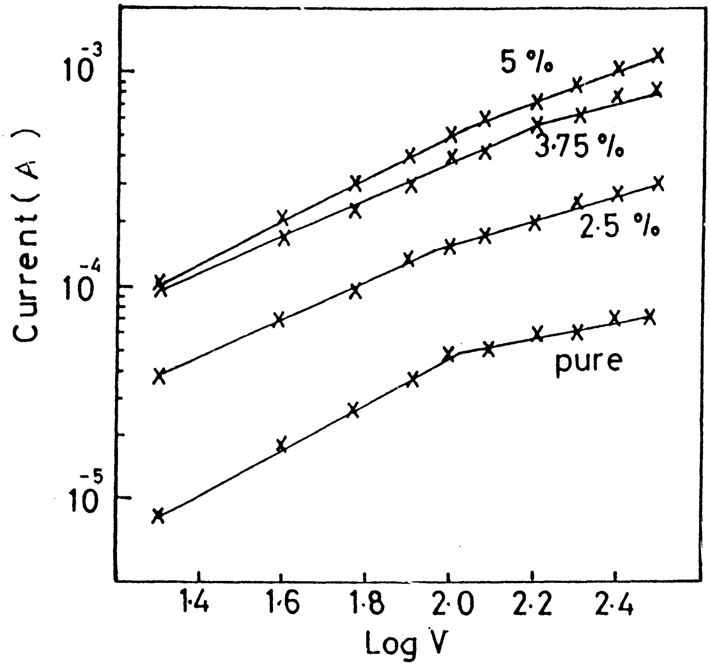

Fig. 2 Current (I) as function of the applied voltage (V) at 90°C for all samples

behaviour for composite samples at 90°C. 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 temperatures and fields, these results are given in Table 1. From the Table we can see that all the samples at 90°C 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°C 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].

TABLE 1
SLOPE VALUES FROM LOG I VS LOG V OF PURE PVA AND CU-PVA COMPOSITE SAMPLES

| Temperature (°C) | Composites | | | |
|---|---|---|---|---|
| | Pure | 2.5% | 3.75% | 5.0% |
| 30 | 0.25 | 0.39 | 0.78 | 0.99 |
| 60 | 1.03 | 1.01 | 0.98 | 1.15 |
| 90 | 1.11<br>(0.45) | 0.89<br>(0.58) | 0.85<br>(0.54) | 1.15<br>(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.

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

$$I = AST^2 \exp(-\phi_S/KT + \beta_{SR}V^{1/2}) \qquad (1)$$

where $\beta_{SR}$ is Schottky field lowering constant and is given by

$$\beta_{SR} = (1/KT)(e^3/4\pi\varepsilon\varepsilon_0 d)^{1/2} \qquad (2)$$

A is constant, S is the surface area of the sample, T is the temperature, K is Boltzman constant, $\varepsilon_0$ is the permittivity of the free space, $\varepsilon$ is the dielectric constant, d is the thickness of the sample, V is the applied voltage, and $\phi_S$ is the potential barrier. Equation (1) predicts a linear relation between ln I and ln V, with slope $\beta_{SR}$ at constant temperature. The Poole-Frenkel relation also predicts linear relation between ln I and ln V, similar to equation (1) with $\beta_{SR}$ replaced by $\beta_{PF}$ and $\phi_S$ replaced by $\phi_{PF}$ Theoretically $\beta_{PF} = 2\beta_{SR}$.

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

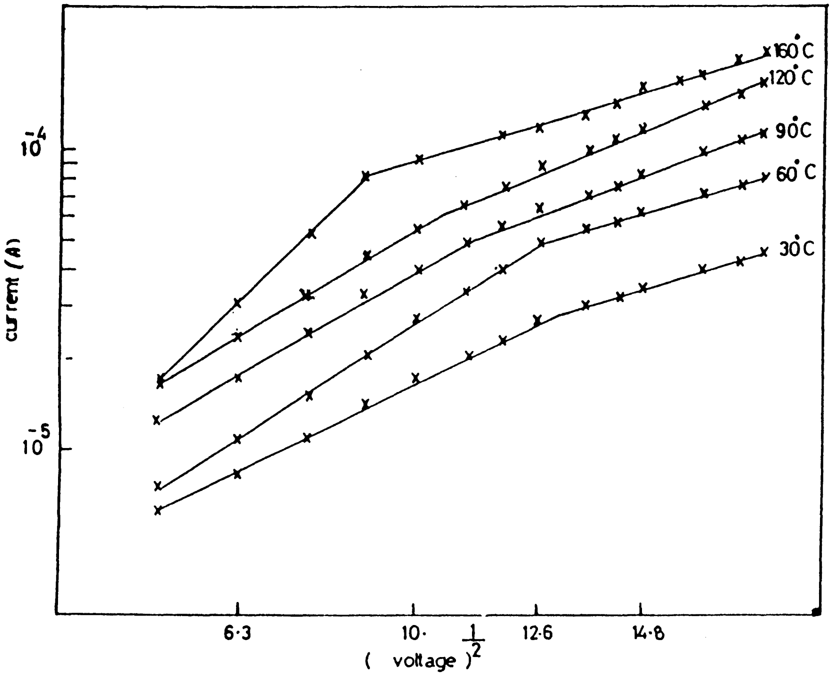

**Fig. 3** Dependence of current on the square root of the voltage for the sample Cu-PVA 2.5% at different temperatures

The values of $\beta$ calculated ($\beta_{exp}$) from the slope of log $I - V^{1/2}$ plots along with the theoretical calculated values of $\beta_{SR}$ and $\beta_{PF}$ 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 $\beta_{PF}$; thus the mechanism of conduction might be a combination of electronic and ionic mechanisms. But for other samples a quite large difference between $\beta_{SR}$ or $\beta_{PF}$ and $\beta_{exp}$ is observed. For these samples we suggest that 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 slope d log $I/d\sqrt{V}$ relative to the value $\beta_{SR}$.

TABLE 2

VALUE CALCULATED FROM LOG I VS $V^{1/2}$ PLOT OF PURE PVA AND CU-PVA COMPOSITE SAMPLES

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

In fact the I-V study not tell us the exact cause of mechanism of conduction in these samples in this temperatures range. We suggest that, for such mixture samples, to know the conduction mechanism it is beter to study the frequency dependence of a.c. conductivity.

Our recent study[6] of d.c. electrical conductivity in Cu-PVA composites shows 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 mechanisms. The first mechanism predominates at lower temperature, where the conductivity is decreased by thermal expansion of hopping paths between copper particles or aggregates. The other one, becoming effective at higher temperature, is due to the thermally activated conduction mechanism obeying the Arrhenius relation.

## REFERENCES

1. R.H. Baughman, *Chem. Rev.,* **82**, 209 (1981).
2. D. Bloor and B. Movagher, *IEE Proc.* **130**, 225 (1983).
3. R.B. Seymour, Conducting Polymer, Plenum, New York (1981).
4. V.K. Jain, C.L. Gupta and R.P. Jain, *Indian. J. Pure and Appl. Phys.*, **16**, 625 (1978).
5. M.M. Mosaad, *J. Materials Sci. Lett.* **9**, 32 (1990).
6. ________, *Czech. J. Phys.*, **40**, 589 (1990).
7. M.A. Lampert and P. Mork, Current Injection in Solid Academic, New York (1970).
8. S.M. Sze, Physics of Semiconductor Devices John Wiley & Sons, New York (1981).

(*Received*: 10 February 1993; *Accepted*: 15 May 1993) AJC–613