

# Effect of Temperature on the Electrical Conductivity of Poly(vinyl Chloride)–Copper Composites

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## Synopsis

Effect of temperature on the electrical conductivity of PVC-copper composites has been studied. The temperature coefficient of dc resistivity of composites with fillers containing negligible oxide content in the range of 77–303 K is positive, indicating metallic-type conduction. The temperature coefficient of dc resistivity of composites with fillers containing intermediate level of oxide at higher temperatures is negative, indicating a semiconducting behavior. Plots of log conductivity versus log frequency for composites in the insulating region show the hopping-type conduction.

## INTRODUCTION

In previous communications<sup>1–4</sup> we have reported that the electrical resistivity of metal–polymer composites decreases suddenly by several orders of magnitude at a critical volume concentration which depends upon the size, shape, and oxide content of the metal particles. The electrical resistivity of the composites increases with increase in the oxide content of the metal particles, and the critical volume concentration shifts to lower values with increase in the  $r_p/r_m$  ratio, where  $r_p$  and  $r_m$  are the radii of the polymer and metal particles, respectively. Similar observations have been made by others.<sup>5–8</sup> The conductive polymer composites may find practical applications such as electrical shielding, electrical heating, and discharging static electricity.

In this paper we report our results on the investigations of the effect of temperature on the electrical resistivity of poly(vinyl chloride)–copper composites. For composites in the insulating region (where metal concentration is smaller than critical volume concentration), we have studied the ac conductivity at different frequencies, while for other composites we have studied the dc conductivity at different temperatures. Nicodemo and co-workers<sup>13</sup> have recently studied the effect of temperature and filler content on electrical resistivity of styrene–acrylonitrile polymer filled with iron or aluminium powders.

## EXPERIMENTAL

### Materials

Commercially available PVC powder sieved out into three fractions of average particle sizes 181, 128, and 90  $\mu\text{m}$  was used. The polymer particles were rounded and regular, as revealed by the Cambridge Stereoscope S<sub>4</sub>-10 model scanning electron microscope.<sup>2</sup>

Copper powder was partially oxidized by keeping the sample in an air oven

at 200–250°C for 2 hr. The oxide content value was determined through the weight loss by complete reduction in a hydrogen atmosphere at 600°C for 1 hr.

The study of the effect of oxide content was carried out by using (a) pure copper oxide, (b) the same oxide particles reduced to negligible oxide content, (c) the same particles reoxidized to an oxide content value of 47% by weight. The three types had similar regular shape (equiaxed) and size.

### Preparation of the Composites

Three series of samples depending on the oxide level of copper powders were prepared. Details of the preparation technique were described earlier.<sup>2-4</sup> Only composites with negligible oxide content of copper powder at 10 and 15 vol % were prepared with two fixed annular stainless steel rings at a distance of 1 cm from the ends with a gap of 1.0 cm between the rings. The length and thickness of the rings were 0.5 and 0.05 cm, respectively, while the diameter was the same as that of the composite. Composites with fillers containing negligible oxide content only were used for cryogenic measurements.

### Measurement of DC resistivity

Composites of resistivity less than  $10^3$  ohms were measured using a four-point probe. The ends of the sample were silver painted to minimize effects due to space charge and contact resistance. The ends of the samples were used as current electrodes, and two sharply pointed brass contacts to the embedded stainless steel rings were used as potential terminals. Samples of resistance higher than  $10^3$  ohms were studied using the two end electrodes.

At low temperatures (77–303 K) the electrical resistance was measured in a specially designed cryostat. The rate of heating or cooling was 1°C/min. Composites with fillers containing negligible oxide content were used for studies at low temperatures.

Current was drawn from a dc source and measured with a picoammeter (model EA 813B, Electronic Corp. of India Ltd.) or a digital multimeter (model DM 752, Electronic Corp. of India Ltd.) depending on the magnitude of the current. The voltage was measured with digital multimeter/dc voltmeter (Philips, model PP 9004) depending on the magnitude. The sample temperature was measured with a copper–constantan thermocouple connected with a dc microvoltmeter.

### Measurement of AC conductivity

Measurements were carried out at room temperature on a capacitance bridge (type 726-C) using a null detector (type GR 1212-A), an oscillator (type GR 1612-RC), and an inversion condenser (GR 722 MD) in the frequency range of  $10^2$  to  $10^5$  Hz. The least capacitance is 0.02 pF. Accuracy in dielectric constant ( $K$ ) and  $\tan \delta$  values are, respectively, 3 and 0.05 or 5%, whichever is more.

The conductivity ( $\delta$ ) was calculated using the following equation:

$$\sigma = \frac{fK \tan \delta}{1.8} \times 10^{-12} \text{ mho/cm}$$

where  $f$  represents the frequency.

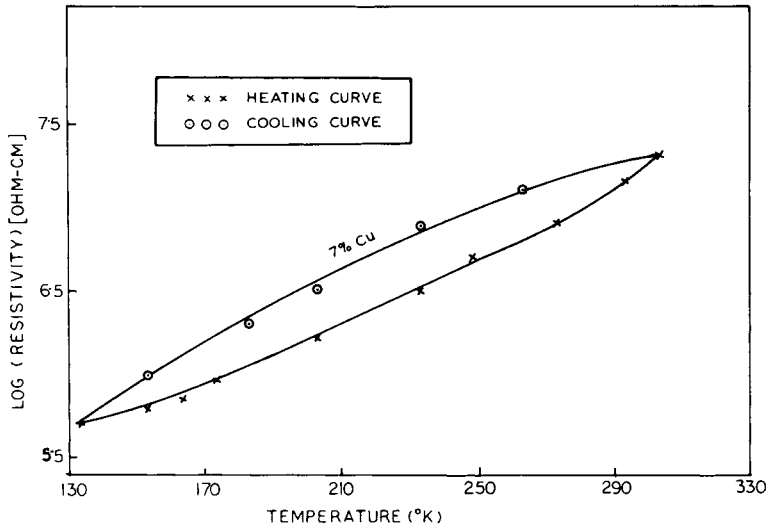


Fig. 1. The DC resistivity as function of temperature. Oxide level of filler particles is negligible: (x) heating curve; (o) cooling curve.

## RESULTS AND DISCUSSIONS

### DC Resistivity at Low Temperatures

The dc resistivity at different temperatures in the range of 77–303 K is shown in Figures 1 and 2. The temperature coefficient of resistivity is positive, indicating metallic-type conduction. Similar observations were also made by Gul and co-workers<sup>9</sup> while studying metal-filled epoxy films in the glassy state of the polymers containing nickel and silver. The heating and cooling curves in our systems exhibit a hysteresis which is due to the lag between the sample tem-

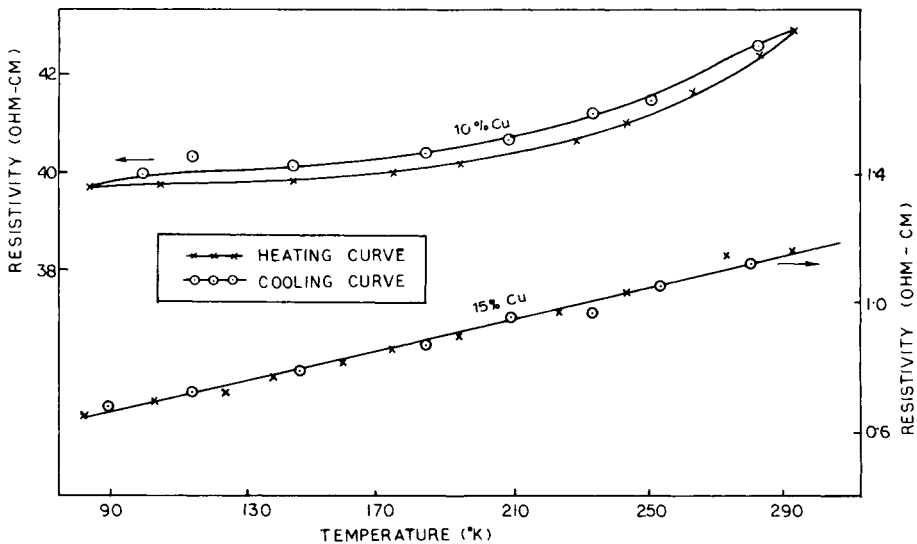


Fig. 2. The DC resistivity as function of temperature. Oxide level of filler particles is negligible: (x) heating curve; (o) cooling curve.

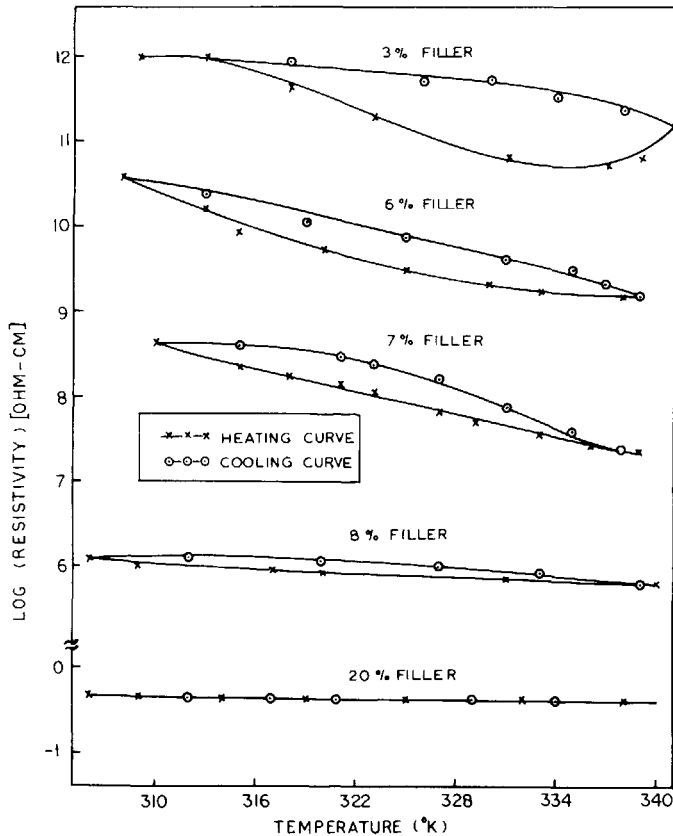


Fig. 3. The DC resistivity as function of temperature. Oxide level of filler particles is 47% by weight: (x) heating curve; (o) cooling curve.

perature and the Dewar temperature. This effect tends to disappear at higher metal loadings, presumably due to better heat transfer through the metallic contacts. A similar hysteresis effect has also been observed in carbon black-filled silicon rubber<sup>10</sup> and nickel-filled epoxy resin.<sup>9,10</sup>

### DC Resistivity at High Temperatures

The dc resistivity of the composites with fillers containing intermediate level of oxide is shown in Figure 3. In contrast to Figure 1, resistivity of these composites shows a negative temperature coefficient, indicating a semiconducting

TABLE I  
Activation Energy Values Calculated from Heating Curves Using<sup>12</sup>  $\sigma = \sigma_0 e^{-E/kT}$

Filler volume, %	Oxide level	Activation energy $E$ , eV
3	47% by weight	0.22
6	—do—	0.23
7	—do—	0.20
8	—do—	0.05
13.5	pure copper oxide	0.16
20	—do—	0.18

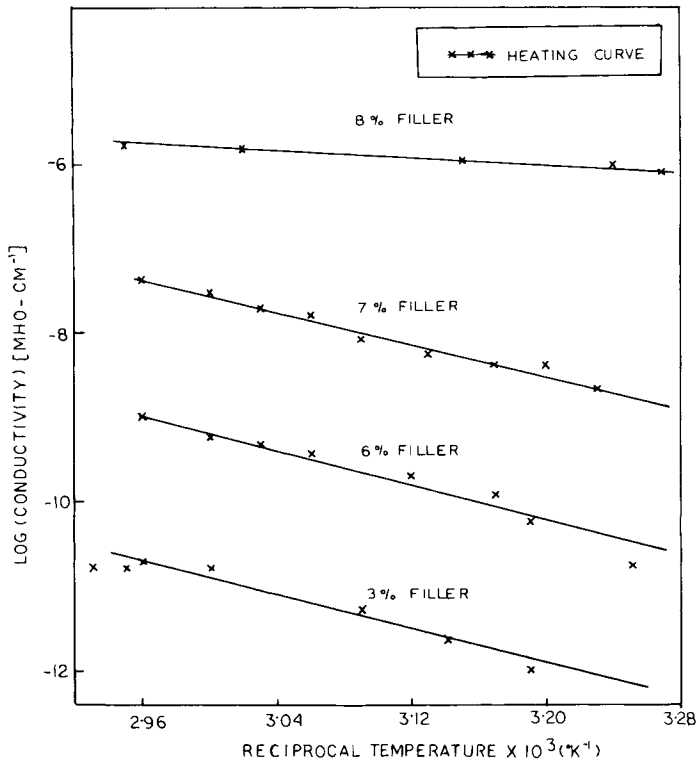


Fig. 4. The DC conductivity as function of reciprocal temperature. Oxide level of filler particles is 47% by weight: (x) heating curve.

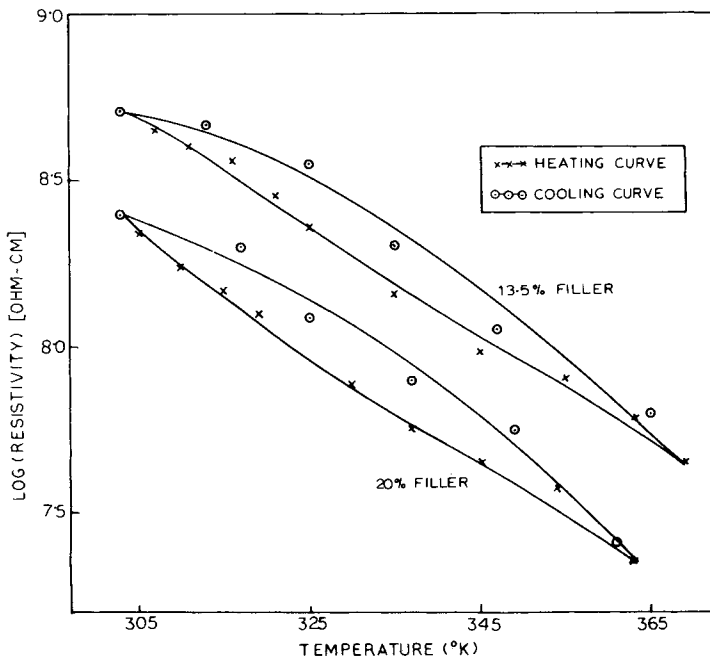


Fig. 5. The DC resistivity as function of temperature. Pure copper oxide is used as filler: (x) heating curve; (o) cooling curve.

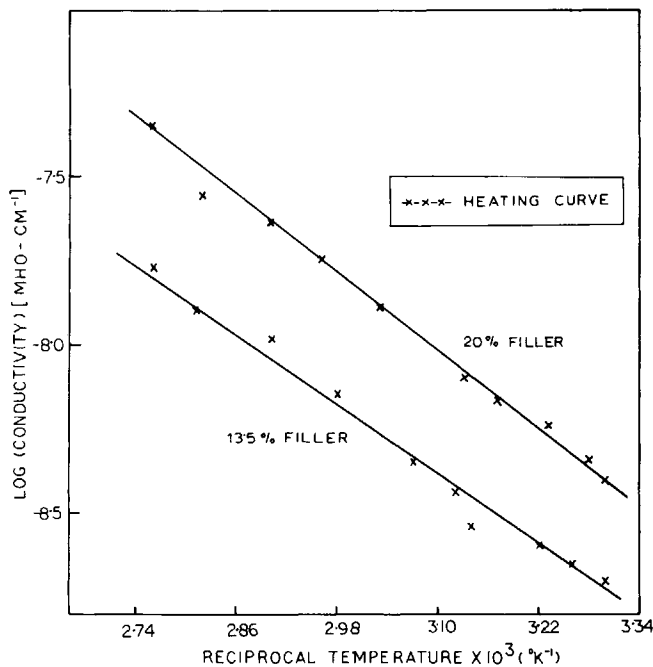


Fig. 6. The DC conductivity as a function of reciprocal temperature. Pure copper oxide is used as filler: (x) heating curve.

behavior. Plots of log conductivity versus reciprocal temperature (Fig. 4) yield activation energy values in the range of 0.16 to 0.23 eV (Table I). In this set of composites the area of the hysteresis curves decreases markedly with increasing metal concentration.

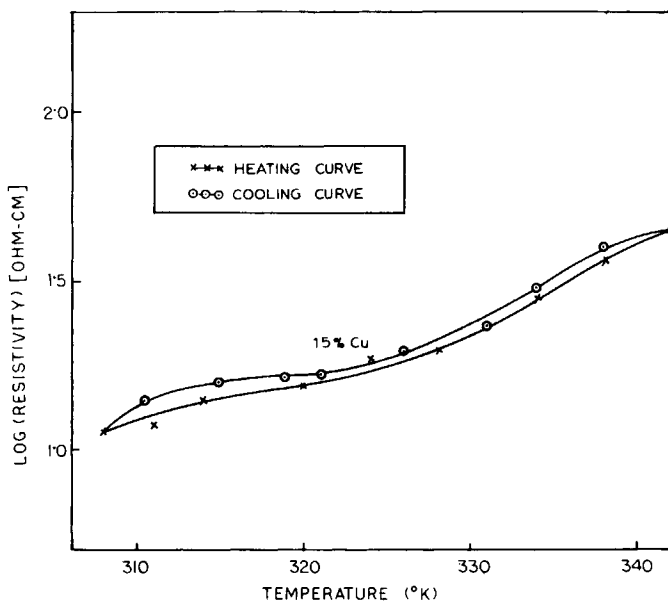


Fig. 7. The DC resistivity as function of temperature. Oxide level of filler particles is negligible: (x) heating curve; (o) cooling curve.

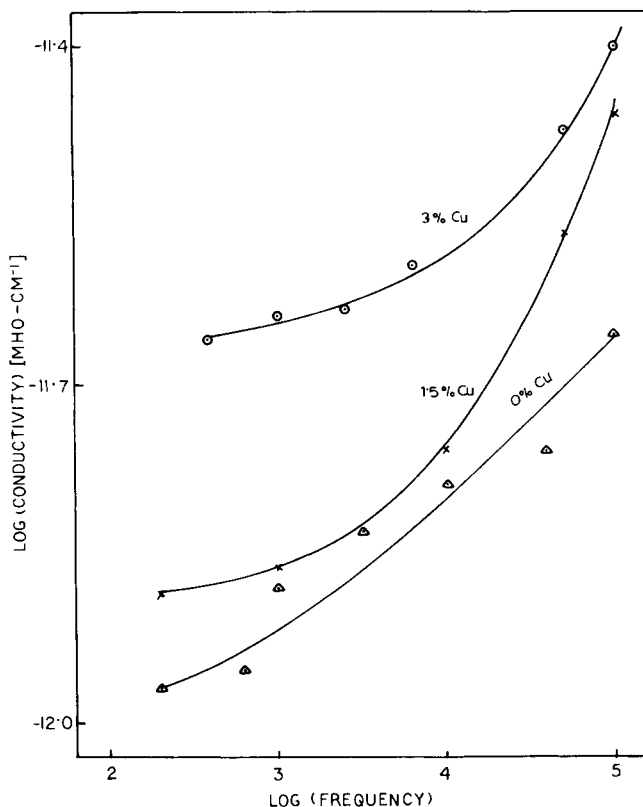


Fig. 8. The AC conductivity as function of frequency. Composites used are in the insulating region.

The experiments with composites containing pure copper oxides instead of metallic copper also reflect the semiconducting nature (Figs. 5 and 6). The activation energy obtained from Figure 6 is close to the values for intermediate oxide level (Table I). It is also to be noted that composites with metallic copper containing negligible oxides show positive temperature coefficient of resistance in this temperature range (Fig. 7).

### AC Resistivity

For composites with filler concentration below the critical loadings (that is, in the insulating region), the ac conductivity has been studied as a function of frequency. Plots of log conductivity versus log frequency show the hopping-type conduction (Fig. 8). Conductivity varies with  $f^n$ , where  $f$  represents frequency. It appears that there are two regions of frequency dependence of conduction up to  $10^4$  Hz and beyond. Rastogi and Chopra<sup>11</sup> obtained a similar change in frequency dependence of resistivity of poly(vinyl chloride) around  $10^5$  Hz.

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