Electrical Conductivity of Nickel-Poly(acrylate divinylbenzene)

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ABSTRACT

The electrical conductivity of nickel-poly(acrylate divinylbenzene) has been studied over a wide range of temperatures. Poly(acrylic acid-divinylbenzene) was doped with nickel acetate to prepare samples containing 5.35, 9.73 and 25.0% (w/w) nickel and current-voltage relationship was studied as a function of concentration and temperature. There is a linear variation of electric current with applied voltage. The slopes of ln(I) vs ln(V) plots being equal to one which suggests the ohmic behaviour of charge carriers. The conductivity has a strong concentration and temperature dependence and is non-monotonic. The conductivity is considered to be due to thermal hopping motion of localized charge carriers which are believed to be polarons.

Key Words: electrical conductivity, poly(acrylate divinylbenzene), nickel, concentration, thermal stability

INTRODUCTION

The use of polymers as insulators is very common because of their high resistivity but now the researchers are engaged in converting insulating polymers to conducting materials due to their strength, toughness, frictional resistance, plasticity, elasticity and corrosion resistance. The advantage of using polymers as conductors is that they are light weight, low cost materials and can easily be shaped into fibres and films through known procedures.

The doping of polymers provides an easy method for making conducting materials.

Among highly conducting polymers are doped samples of polyacetylene which have conductivities comparable to metals when doped with iodine and other dopants [1, 2]. In the recent years interest has grown in the use of polymers as semi-conductors in electronic devices [3, 4]. Treatment of insulating polymers with oxidizing or reducing agents also make them good conductors [5].

Polyacrylic acid [6] and polymethacrylate [7] when doped with certain metal salts become conductor. For example, polyacrylic acid when doped with chromium acetate becomes more conductive than polyacrylic acid. The electrical conductivity in this case is dependent both on concentration and temperature. In the present work a copolymer of acrylic acid and divinyl benzene has been doped with nickel acetate and then DC conductivity of doped polymer is measured as a function of nickel concentration, temperature and applied voltage.

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EXPERIMENTAL

Chemical Used and Physical Methods
Poly(acrylic acid-divinylbenzene), 100–200 mesh granules (Fluka), nickel (II) acetate 99% (E. Merck), and methanol 99.5% (E. Merck), were used. Spectroscopic grade potassium bromide was used to prepare KBr pellets for IR studies.

Infra-red spectra were recorded on Hitachi IR spectrometer model 270–50. Beckman R11C model KB–0112 dye (1.3 cm diameter) was used to prepare pellets for conductance studies. Autoranging picoameter model 485 (Kiethly) was used for current measurements. A power supply lZS–5/71 was used.

Synthesis of Nickel-Poly(acrylate divinylbenzene), Ni-PADVB
Two grams of poly(acrylic acid-divinylbenzene), PADVB, was soaked in 25 mL of methanol and stirred for 30 min. One gram of nickel acetate dissolved in 50 mL of methanol was added to soaked polymer and stirred for 2 h. The nickel doped polymer was filtered and soaked in 50 mL of methanol to dissolve any unreacted nickel acetate. The polymer was filtered again, washed three times with methanol and dried under vaccum. The nickel-polyacrylate thus formed contained 9.73% nickel as estimated by atomic absorption spectroscopy. Similarly nickel-polyacrylate samples containing 5.35 and 25.0% nickel were also prepared.

Electrical Conductivity
The circular shape pellets of the doped polymer having mass 0.2 g with a diameter 1.3 cm were prepared for current measurements. The DC conductivity of the doped polymer was calculated by measuring resistance of the polymer. The measuring technique and circuit diagram are reported in literature [8].

RESULTS AND DISCUSSION

In the present work poly(acrylic acid-divinylbenzene) was doped with nickel acetate and its DC conductivity was measured as a function of nickel concentration, temperature and applied voltage.

The infra-red spectrum of PADVB shows characteristic carbonyl peak at about 1700 cm⁻¹. On doping PADVB with nickel acetate a new peak appeared at 1635 cm⁻¹ due to the formation of carboxylate ion. The appearance of similar new IR peak due to the formation of carboxylate ions, in case of palladium doped polyacrylic acid is already reported in literature [9]. The intensity of carboxylate ion peak increased with increase of nickel concentration while the intensity of carboxylic acid peak decreased. The presence of both peaks in IR of Ni-PADVB indicate that some of carboxylic acid groups in polymer matrix are changed to carboxylate ions and are bonded to nickel. Thus PADVB has both nickel and hydrogen ion pendant groups.

Current-Voltage Relationship
The current(I)-voltage(V) relationship of Ni-PADVB was studied for 5.35, 9.73 and 25.0% (w/w) of nickel. Figure 1 shows a linear variation of electric current with applied voltage (50–500 V) for 290–383 K. The linear variation shows that doped polymer exhibits ohmic conduction. The plot of ln(I) vs ln(V) shown in
Figure 2 supports the ohmic behaviour of the charge carriers. The slopes of the lines are equal to 1.0 and this confirms that ohmic conduction mechanism is operative at all temperatures.

The possibility of Schottky and Poole-Franke type conduction mechanism can be discounted as the current-voltage dependence does not follow: $I \propto \exp[\beta V^{1/2}]$ relationship. Further the possibility of tunneling can also be ignored because the pellets used for measurements were sufficiently thick and the fields relatively low.

**Temperature Dependence of Conductivity**

The temperature dependence of the electrical conductivity of Ni-PADVB is shown in Figure 3. The conductivity initially increases exponentially with increase in temperature from 290–323 K. This increase in conductivity is due to the fact that degree of chemical short-range order in the material initially increases with increase of temperature due to the growth of small crystallites i.e., the formation of local ordered regions in the otherwise disordered amorphous polymer matrix [9]. The local ordered regions degrade on further heating and as a result the decrease in conductivity beyond 323 K is due to disturbance in the conduction domains. The change in conductivity with temperature indicates the development of different discrete phases and metallic character.

Figure 3 shows that change in potentials does not have major effect on conductivity. A small variation in conductivity is observed in 308–353 K region for different potentials but at other temperatures conductivity remains the same.

**Effect of Nickel Concentration on Electrical Conductivity**

To study the effect of concentration on conductivity, polymer was doped with 5.35, 9.73 and 25.0% nickel. A maximum possible metal loading was 9.73%. Attempts to prepare samples of higher nickel percentages did not succeed. To prepare 25.0% Ni-PADVB, the doped polymer was not washed with methanol, and as a result it contained both polymer bonded and unbonded nickel.

Table 1 shows a change in conductivity as a
function of nickel concentration in Ni-PADVB at various temperatures. The results indicate that conductivity is highly dependent on nickel concentration. There is many fold increase in conductivity at 323 K when concentration of nickel is changed from 5.35% (0.22×10^{-11} \text{ mho.cm}^{-1}) to 9.73% (0.73×10^{-10} \text{ mho.cm}^{-1}). It is anticipated that increase in nickel content, increases the effective free volume in the polymer matrix and facilitates the mobility of either ions or molecules in it. A further increase in nickel concentration lowers the conductivity of the doped polymer. For 25.0% Ni-PADVB conductivity is less than that of 9.37% sample. This indicates that in 25% Ni-PADVB there is bonded as well as unbonded nickel in the polymer matrix. The unbonded nickel occupies the spaces in the polymer matrix and offers resistance to the current flow resulting in decrease of conductivity [10].

A comparison of current-voltage characteristics of polyacrylic acid (PA), PADVB and 9.73% Ni-PADVB shows that PADVB is more conductive than PA, but when PADVB is doped with nickel acetate, conduction increases many folds. For example, at 323 K the current flowing through PA, PADVB and 9.73% Ni-PADVB is 3.30×10^{-10}, 2.55×10^{-9} and 1.38×10^{-11} A, respectively. The advantage of using PADVB is that it is thermally much more stable than PA. The enhanced values of conductivity for Ni-PADVB may be explained as due to complex formation which is of donor-acceptor type and the bonding is between COO⁻ and Ni⁺⁺ ions. It has been presumed that polarons are the dominant charge carriers in polymeric materials and a model [11–13] has been suggested to explain conductivity over a wide range of temperature in doped ionic polymers.

### Table 1. Concentration dependence of conductivity (mho.cm⁻¹) of Ni-PADVB at 500 V.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>0.0 (%)</th>
<th>5.35 (%)</th>
<th>9.73 (%)</th>
<th>25 (%)</th>
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<tr>
<td>Ni⁺⁺</td>
<td>Ni⁺⁺</td>
<td>Ni⁺⁺</td>
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<tr>
<td>303</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>363</td>
<td>1.81×10^{-14}</td>
<td>0.11×10^{-11}</td>
<td>0.22×10^{-11}</td>
<td>0.11×10^{-11}</td>
</tr>
</tbody>
</table>

### CONCLUSION

– The electrical conductivity of Ni-PADVB of 9.73% is about hundred times that of PADVB. This may be due to complex formation which is of donor-acceptor type and the bonding is between COO⁻ and Ni⁺⁺ ions.
– The complex Ni-PADVB exhibits ohmic conduction.
– The electrical conductivity has strong concentration and temperature dependence.
– The conductivity varies non-monotonically with rise in temperature.

### REFERENCES