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Change in Electrical Conductivity of Polymers: Study showing Effect of Dopant Concentration and Temperature

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Abstract-Here, in this article, an effect on electrical conductivity of Polyaniline (PANI) and Poly (metatoluidine) (PMT) has been studied by formation of nanocomposites with some doping agents like magnesium perchlorate, TiN, copper (I) salt and its complex. The polymers are synthesized by usual method of oxidative polymerization using ammonium persulfate as an oxidizing agent. Increase in conductivity is noticed to a large extent and it is also verified by noting change in band gap with increase in concentration of dopant and temperature as well. Such approach can be used to develop composite structures using some suitable dopant aiming at various electrical applications.

Index Terms: nanocomposites, conductivity, band gap, doping, polymerization.

1. INTRODUCTION

There is a wide scope for the enhancement of electrical conductivity by combining organic materials with inorganic counterparts to form organic-inorganic composite/nanocomposite [Li (2004), Ali *et al.* (2005), Schnitzler *et al.* (2003), Parvatikar *et al.* (2007)]. Organic-inorganic nanocomposites are advanced class of materials due to their extraordinary properties within a single molecular composite; organic polymeric part of the composite provides mechanical, electrical and chemical stabilities whereas inorganic part supports the thermal stability and also increases the electrical conductivity. Various organic-inorganic nanocomposites prepared in laboratory have shown excellent ion exchange behavior, electrical conductivity, high stability, reproducibility, selectivity for heavy toxic metal ions and sensing material for various organic vapors, hazardous gases and humidity [(Khan and Khan (2007), Khan and Akhtar (2008), (Khan and Khan (2009), Khan and Khalid (2010),Khan *et al.* (2010), Khan and Baig (2013)]. Electrically conductive polymer composites have been widely applied in anti-static materials [Li *et al.* (2006)], electromagnetic interference shielding (EMI), chemical sensors [Kachoosangi (2009)], fuel cells [Wu and Shaw (2005)] etc.

On examination, it was observed that the electrical conductivity of the nanocomposites increases with increase in temperature. This increase in conductivity with increase in temperature is the characteristics of thermal activated behavior [Parvatikar *et al.* (2006)]. To explain the conduction mechanism in the conducting polymers, the concept of polaron and bipolaron was introduced. Low level of oxidation of the polymer gives polaron and higher level of oxidation gives bipolaron. Both polarons and bipolarons were mobile and could move along the polymer chain by the rearrangement of double and single bonds in the conjugated system. Conduction by polarons and bipolarons was supposed to be the dominant factors which determine the mechanism of charge transport in polymers with non-degenerate ground states.

2. EXPERIMENTAL DETAILS

Electrical conductivities of the samples are determined by most satisfactory four-probe method. The current–voltage data so generated by a four-in-line probe DC electrical conductivity measuring instrument was processed for calculation of resistivity (ρ). The magnitude of the conductivity was determined by the number of charge carriers available for conduction and the rate at which they move, i.e. mobility. In conducting polymers, which could be considered as semiconductors, the charge carrier concentration increased with increasing temperature. Since the charge carrier concentration was much more temperature dependent than the mobility, therefore it was the dominant factor and conductivity increased with increase in temperature. DC conductivity of the pellets was measured by mounting them between steel electrodes inside a specially designed sample holder. The temperature was measured with a calibrated copper-constantan thermocouple mounted near the electrodes. The samples were annealed to avoid any effect of moisture absorption. The model of DC instruments is Keithley 2401A with a least count of 10 pA(picoAmpere).A stabilized voltage of 50V was applied across the sample and the resultant current was measured with a pico-ammeter, which gives DC conductivity within ±1% of accuracy [Khan *et al.* (2004)].

Conductivity measurements were made using the four-probe technique (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50kN. The error in resistance measurements made under galvanostatic conditions with a Keithley model 220 programmable current source and a Keithley model digital 195A voltammeter was less than 2%.

Conductivity is measured by using Ohm's law as shown by Eq. (1).

$$\mathbf{V = I\,R} \qquad (1)$$

where, I is the current (in Amperes) through a resistor R (in Ohms) and V is the drop in potential (in Volts) across it. The reciprocal of resistance (R) is called conductance (C).

3. RESULTS WITH DISCUSSION

DC conductivity of pure PANI increases exponentially with temperature, exhibiting semiconductor behavior. The doping of conducting polymers implies charge transfer, the associated insertion of a counter ion and the simultaneous control of Fermi level or chemical potential. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into π-electron system through doping. At low doping levels these charge carriers are self–localized and form non-linear configuration. Because of large interchain to be principally along the conjugated chains, with interchain hopping as a necessary secondary condition [Scrosati (1993)]. transfer integrals; the transport of charge is believed In PANI, there are nearly degenerate ground states, the dominating charge carriers are polarons and bipolarons. It has been observed that doped PANI is showing charge carriers formation with linear configuration; as a result conductivity changes substantially.

The proposed composite materials contain two components viz. inorganic and organic. The inorganic components of the composites are the efficient ion-exchange materials whereas organic components, PANI and PMT are good conducting polymers. In general, a high electrical conductivity of conductive polymers is attained by dopant, which stabilizes the polaron and bipolaron states as counter anions [Fukuyama *et al.* (1993), Thieblemont *et al.* (1995), Thompson *et al.* (1994)].

It is found that DC conductivity of doped PANI and PMT samples changes with changing the concentration of dopant as well as with the temperature and is shown in the form of Tables 1-4 given below.

The conductivity decreases with decrease of temperature that indicates the semiconducting behavior for samples of all the compositions. To investigate the charge transport mechanism, the temperature-dependence of the electrical conductivity was studied with change in the temperature. The temperature dependent DC conductivity for different samples are shown in the form of Tables and Figures (1-4) given below.

3.1. I-V characterization of PANI with different dopants and at different dopant concentration and Temperature

Values of conductivity (σ) for all the samples are given in ($\times 10^{-5}$) (Ω^{-1} cm^{-1}or S cm^{-1}).

Table 1. Conductivity of doped samples of PANI with [$Cu(AN)_4ClO_4$].

Temp.(^{0}C)	Undoped PANI	5% doped	10% doped	20% doped	40% doped
35	0.0208	0.0285	2.28	7.012	120.19
40	0.0341	0.0341	2.85	5.883	122.62
45	0.0480	0.0542	3.51	5.369	123.74

Table 2. Conductivity of doped samples of PANI with [Mg $(ClO_4)_2$].

Temp. (^{0}C)	Undoped PANI	5% doped	10% doped	15% doped
35	0.0208	5.719	6.41	676.85
40	0.0341	6.159	6.71	1604.52
45	0.0480	6.261	7.63	1976.43

3.2. I-V characterization of PMT with different dopants and at different dopant concentration and Temperature

Values of conductivity (σ) for all the samples are given in ($\times 10^{-5}$) (Ω^{-1} cm^{-1} or S cm^{-1}).

Table 3. Conductivity of doped samples of PMT with [$Cu(AN)_4$ ClO_4].

Temp. (^{0}C)	Undoped PMT	5% doped	10% doped	20% doped	40% doped
35	0.00612	0.00656	0.0156	0.226	0.371
40	0.00655	0.00656	0.0351	0.269	0.436
45	0.00721	0.01092	0.0740	0.370	0.488

Table 4. Conductivity of doped samples of PMT with [Mg $(ClO_4)_2$].

Temp. (^{0}C)	Undoped PMT	10% doped	15% doped	20% doped
35	0.00678	17.8	21.4	475.2
40	0.00765	19.5	22.8	1126.6
45	0.00809	19.9	24.5	1387.7

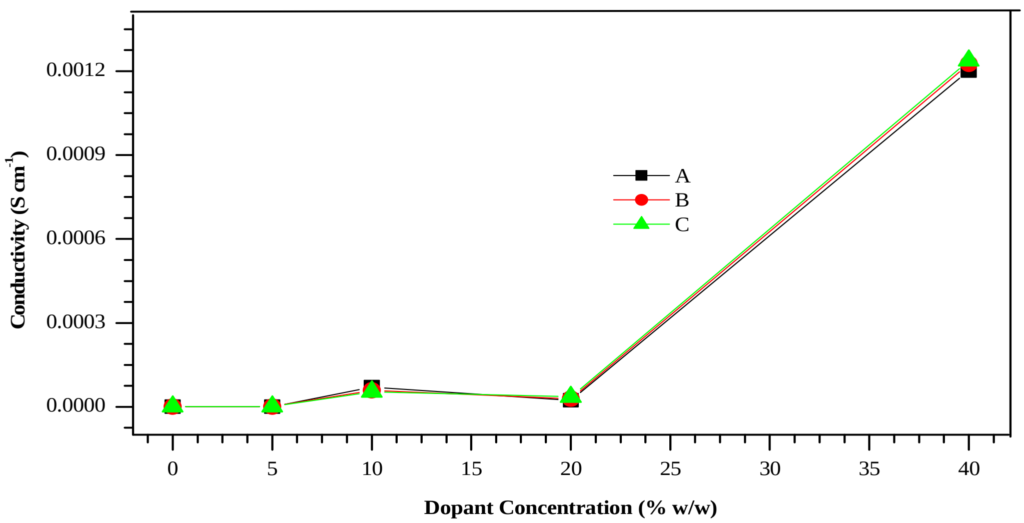

Fig. 1. DC conductivity of undoped and 5, 10, 20 and 40% (w/w) [Cu(AN)$_4$ ClO$_4$] doped samples of PANI at 35^{0}C (A), 40^{0}C (B) and 45^{0}C (C) temperature.

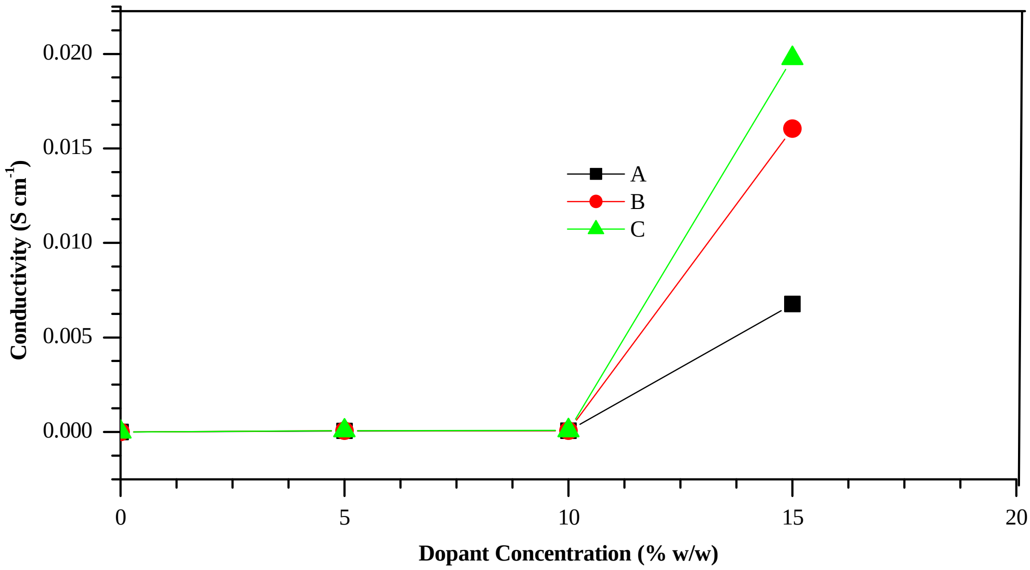

Fig. 2. DC conductivity of undoped and 5, 10 and 15% (w/w) [Mg(ClO$_4$)$_2$] doped samples of PANI at 35^{0}C (A), 40^{0}C (B) and 45^{0}C (C) temperature.

The effect of dopant concentration and temperature on values of DC conductivity can also be shown with the help of graphs as given below.

Fig. 1 shows effect of doping of [Cu(AN)$_4$ ClO$_4$] and temperature on conductivity values of PANI. There is increase in conductivity values on increasing concentration of dopant and with temperature as well. It is also clearly seen from Table 1. At 40% concentration of dopant there is abrupt increase in values of conductivity.

Fig. 2 shows effect of doping of [Mg(ClO$_4$)$_2$] and temperature on conductivity values of PANI. There is increase in conductivity values on increasing concentration of dopant and with temperature as well and it is also shown in Table 2. The effect of increase of temperature is clearly shown in graph**. Fig. 3** shows effect of doping of [Cu(ClO$_4$)].4AN and Fig. 4 shows effect of doping of [Mg (ClO$_4$)$_2$] temperature on conductivity values of PMT.

All these plots (Fig. 1–4) indicate an increase in conductivity with temperature that may be due to a hopping mechanism between coordinating sides, local structural relaxations and segmental motions of the polymer. These plots follow Arrehenius behaviour, initially, the conductivity increases slowly, while with increase in dopant concentration, it increases at a higher rate. The later may be due to a change in phase from an amorphous to a semi-crystalline.

The polymer chain acquires faster internal modes for which bond rotations produce segmental motion. This favors hopping of ions within and between chains and therefore the conductivity becomes high [Reddy *et al*. (1998)].

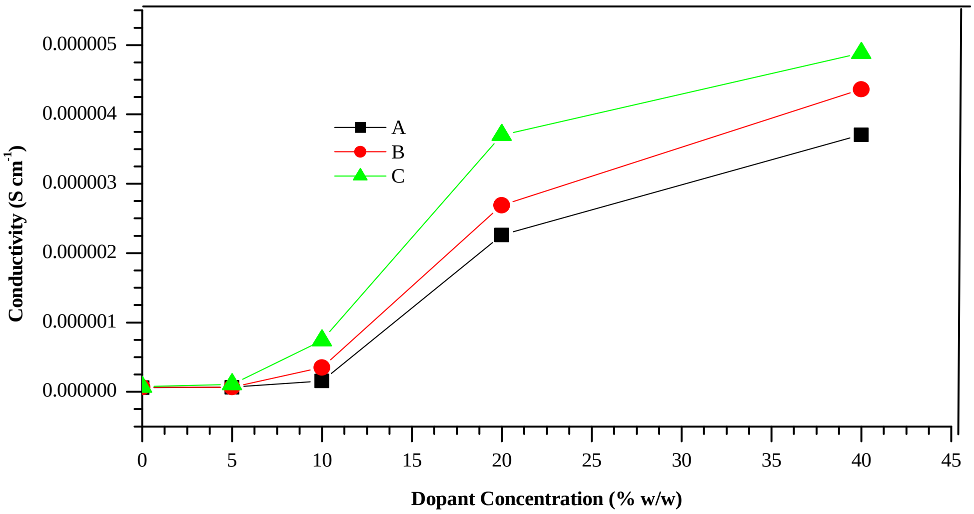

Fig. 3. DC conductivity of undoped, 5, 10, 20 and 40% (w/w) [$Cu(AN)_4$ ClO_4] doped samples of PMT at 35^{0}C (A), 40^{0}C (B) and 45^{0}C (C) temperature.

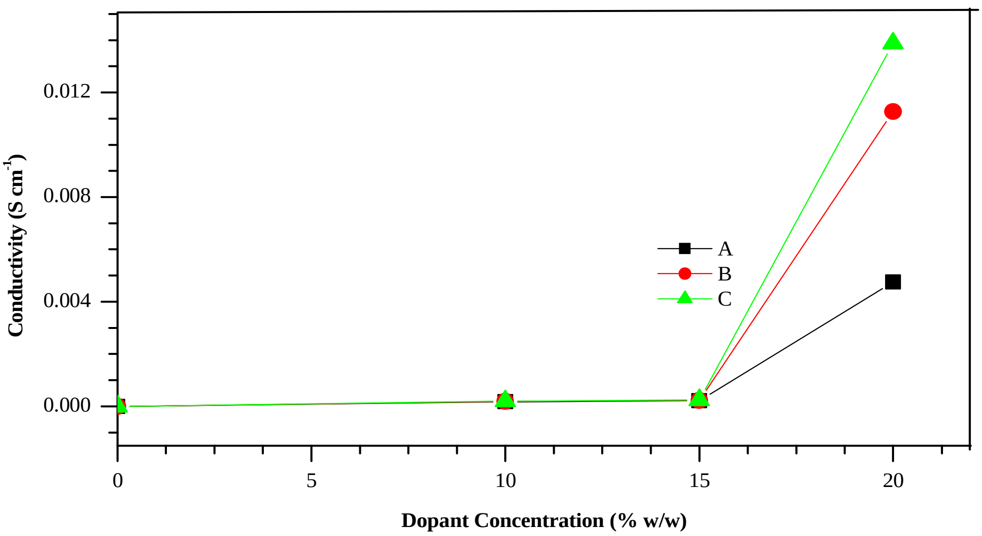

Fig. 4. DC conductivity of undoped, 10, 15 and 20% (w/w) [$Mg(ClO_4)_2$] doped samples of PMT at 35^{0}C (A), 40^{0}C (B) and 45^{0}C (C) temperature.

4 .CONCLUSION

However, conducting polymer based organic-inorganic nanocomposites are identified as good candidates for practical applications, since they are compatible to oxides and ceramics and also they can be used at room temperature [Li *et al.* (2001), Somani *et al.*(2001)].

The behavior of the doped materials so prepared was suitable for use in electrical and electronic applications under an ambient atmosphere.

The increase in electrical conductivity is also explained on the basis of decrease in value of Band Gaps. The optical band gap of 3.73 eV in the undoped PANI decreased to 3.57 eV after doping and is found to decrease with further increase of dopant concentration. This reduction may be due to the protonation of the quinoid rings in the polymer backbone [Barman and Pal (2013)].
Similar is the case for PMT, although its conductivity is very less than that of PANI but found to increase with increase in dopant concentration.

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