In situ synthesis and characterization of polyaniline/ nickel oxide composites

Sneh Lata Goyal[a*], Smriti Sharma[a], Deepika Jain[a], D. Kumar[b] and N. Kishore[a]

[a]Department of Applied Physics, Guru Jambheshwar University of Science and Technology, Hisar, Haryana, India
[b]Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar, Haryana, India
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ABSTRACT

In situ polymerization of aniline was carried out in presence of nickel oxide (NiO) to synthesize polyaniline/nickel oxide (PANI/NiO) composites using chemical oxidation method. The method of synthesis is based on chemical oxidative polymerization of aniline doped with various wt % of nickel oxide by using ammonium persulphate as an oxidant. PANI and PANI/nickel oxide composites were characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermal analysis and DC conductivity. FTIR and XRD results reveal the presence of NiO in the composites. Thermal stability of polymer composites has been analyzed by TGA-DTG and corresponding thermal kinetic parameters were calculated. Thermal analysis exhibits the increase in thermal stability as compared to PANI with increasing concentration of dopant up to 30 wt% and thereafter it decreases. The DC conductivity of these composites has been investigated as a function of temperature and doping concentration and results have been compared with pure PANI. DC conductivity increases with increase in temperature. The variations in DC conductivity with increase in concentration of NiO in composites have been discussed here. PANI/ NiO composites show lower DC electrical conductivity as compared to PANI. For future actions, this work opens new perspectives for the use of PANI/NiO composite as a conducting material because it has higher DC conductivity as compared to NiO.

Keywords: Conducting polymer, XRD, DC conductivity, Thermal analysis
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INTRODUCTION

` Conducting polymers have emerged as a very important class of materials because of their unique electrical, optical and chemical properties leading to the wide range of technological applications. Conducting polymers provide fabulous scope for tuning of their electrical conductivity from semiconducting to metallic region by way of doping [1, 2]. Semiconducting and metallic polymers are the fourth generation of polymeric materials. Conductive polymers with polyaromatic backbone including polypyrrole, polythiophene, polyaniline, etc. have received a great deal of attention in the last two decades [3]. Among them PANI has been the subject of various studies due to its oxygen and moisture stability and potential applications in many fields. PANI is one of the most promising electrically conducting polymer and used in batteries [4], sensors [5, 6], electronic devices [7], super capacitors [8] and corrosion protection in organic coatings [9-11] due to its physical and chemical properties, good electrical conductivity (p-type), high environmental stability, low cost and facile fabrication [12–14]. PANI can also provide good network for inorganic components and modify their properties and stability [15].

Nickel (II) oxide is a notable and well-studied material among various transition metal oxides because of its unique advantage in terms of properties and applications such as p-type transparent conducting film, electro chromic devices, gas sensors, spin valve devices, cathode in alkaline batteries etc [16]. NiO is an anti ferromagnetic transition metal oxide which is considered to be a semiconductor with p-type conductivity and band gap 3.51 eV [17]. Also, NiO particles have excellent thermal stability and are capable of improving the thermal stability of PANI. Our aim in this study is to synthesize PANI and composites of PANI/NiO and to see the changes in structural, electrical and thermal properties after doping. PANI/NiO composites were prepared by in situ

polymerization of aniline monomer with different wt% of NiO. The characterizations of all these samples have been performed and discussed here. The variation in DC conductivity of these composites has been studied as a function of temperature and doping concentration.

MATERIALS AND METHODS

Sample Preparation
All the chemicals used in this investigation were procured from Sigma Aldrich and used as received. To prepare PANI, 0.2 M aniline hydrochloride and 0.25 M ammonium persulphate (APS) solutions were prepared. Both solutions were left to cool for 2-3 hours. APS was added drop wise in aniline hydrochloride solution, maintained at a temperature 0-4 ^{0}C in an ice bath, stirred for 2 hours for oxidization and left for 24 hours at rest to polymerize in refrigerator. Next day PANI precipitate was collected on a filter paper and washed with 1M HCl and acetone till the filtrate became colorless. PANI (emeraldine) hydrochloride powder was dried in air and then in vacuum at 45^{0}C. PANI prepared under these conditions was taken as standard sample.

The samples of PANI/nickel oxide composites were prepared by adding 0.1M solution of 10, 20, 30, 40 and 50 weight percentage of nickel oxide to 0.2 M Aniline hydrochloride (Aldrich) solution in distilled water with vigorous stirring for 1 hour and then cooled for one hour. The pre-cooled aqueous solution of APS (0.25M) was added drop wise in this solution, maintained at a temperature of 0-4 ^{0}C in an ice bath, stirred for 2 hours for oxidization and left for 24 hours at rest to polymerize in refrigerator. Next day PANI/nickel oxide composite precipitate was collected on a filter paper and was washed with the 1M HCl and acetone till the filtrate became colorless. Precipitate was dried in air and then in vacuum at 45^{0}C. Following this procedure, five different samples of PANI/nickel oxide composites named as N1, N2, N3, N4 and N5 were synthesized.

Pellet Formation
The powders of polyaniline and polyaniline/NiO composites have been crushed finely in agate pestle mortar. This powder is pressed to form pellets of 12 mm diameter and thickness $\approx$ 1 mm by applying pressure of 100 Kg/cm^2 in a hydraulic press. The pellets of polyaniline and its composites so obtained are coated with silver paste on both sides to obtain better contacts.

Measurements and Characterization
The samples were characterized by Fourier Transform Infrared (FTIR) Spectroscopy, X-ray diffraction (XRD), and Thermal Gravimetric Analysis (TGA) technique. DC conductivity measurements were also made. FTIR analysis was done by using Shimadzu IR affinity-18000 FTIR spectrometer by mixing the powder sample with dry KBr. X-ray diffraction studies of the samples were performed by using Rigaku Table-Top X-ray diffractometer. TGA analysis was performed by TA instrument, model no. SDT Q600 in nitrogen atmosphere with a heating rate of 10ºC/minute. DC conductivity measurements were made by using Keithley 6517B electrometer.

RESULTS AND DISCUSSION

FTIR Analysis
The FTIR spectrum of pure PANI, PANI/NiO and pure NiO are shown in Figure 1. PANI spectrum has characteristic bands at 520 cm^{-1}, 815 cm^{-1}, 1163cm^{-1}, 1317 cm^{-1}, 1495 cm^{-1} and 1589 cm^{-1}[18]. The bands at 520 cm^{-1} and 815 cm^{-1} are due to C-H out of plane bending vibration and para-disubstituted benzene rings, respectively. A band appearing near 1317 cm^{-1} represents the C-N stretching vibration. C-N and C-C stretching mode of vibration for the quinoid and benzenoid units of PANI are shown by 1495cm^{-1} and 1589cm^{-1}. Bands at 1163 cm^{-1} represents in plane bending vibration in C-H. Non-symmetric C_6 ring stretching modes are shown by the bands present in the range of 1450-1600 cm^{-1}. The broad band observed at 2400-2750 cm^{-1} is due to aromatic C-H stretching vibrations while the band at 2950-3300 cm^{-1} is due to N-H stretching of aromatic amines. The characteristic peak at 704 cm^{-1} in the spectra of NiO, ascribed to the bending vibrations of the NiO crystal lattice was also observed in PANI/NiO composites. From the results, it is observed that FTIR spectra of PANI/NiO composites contain contributions from both the NiO particles and PANI. However, some bands of PANI have shifted due to interactions with NiO particles.

XRD Analysis
The XRD patterns of pure PANI, nickel oxide and PANI /NiO composites, synthesized by doping during polymerization method are shown in Figure 2(a & b). Perusal of the figure shows the presence of broad band of PANI at a value of 2θ about 25 degrees. Sharp peak of nickel oxide having maximum intensity at 43.29° along with certain other peaks of low intensity is also observed. The observed 2θ values of the peaks are consistent with the standard JCPDS values (JCPDS No. 78-0643). The average crystallite size of NiO and PANI/NiO composites have been calculated by using the Scherer's formula [18]

$$D = \frac{K\lambda}{\beta Cos\theta}$$

..… (1)

where D is crystallite size of particle, λ is the X-ray wavelength of Cu K_{α} used in the present study, K=0.89 is the shape factor, $Cos\theta$ is the cosine of the Bragg angle(θ) and β is the full width at half height of peak of diffraction in radians.
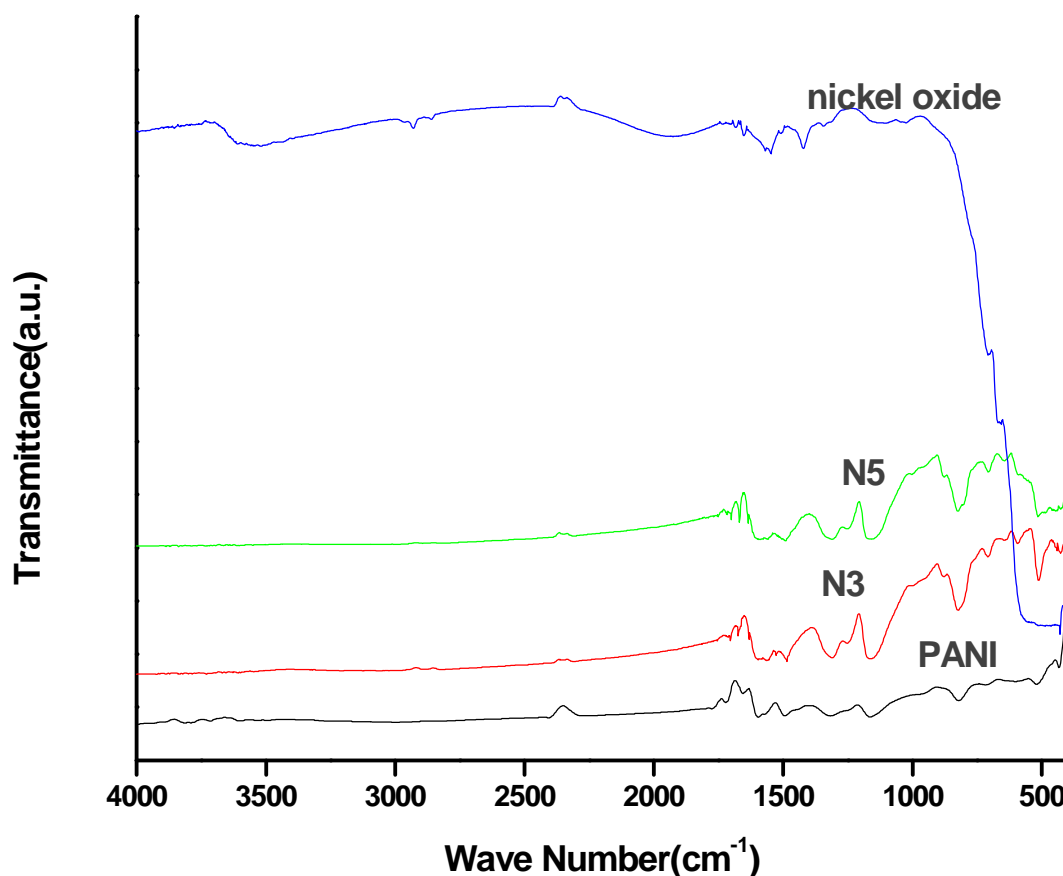

Figure 1: FTIR of PANI, PANI/NiO composites and NiO

The above equation when applied for the characteristic (200) plane, peak of NiO and its composites with PANI leads to an average size of about 27 nm. It is observed by comparing the XRD pattern of composites with that of NiO, the prominent peaks corresponding to $2\theta=37.26°$, $43.29°$, $62.89°$, $75.43°$ and $79.43°$ are due to (111), (200), (220), (311) and (222) planes of NiO respectively.

By comparing the XRD patterns of the composites and NiO, it is confirmed that NiO retains its structure even though it is dispersed in PANI during the polymerization reaction. This indicates that PANI undergoes interfacial interactions with NiO crystallites and the presence of NiO in PANI matrix strongly affects the structural behavior of the formed PANI.
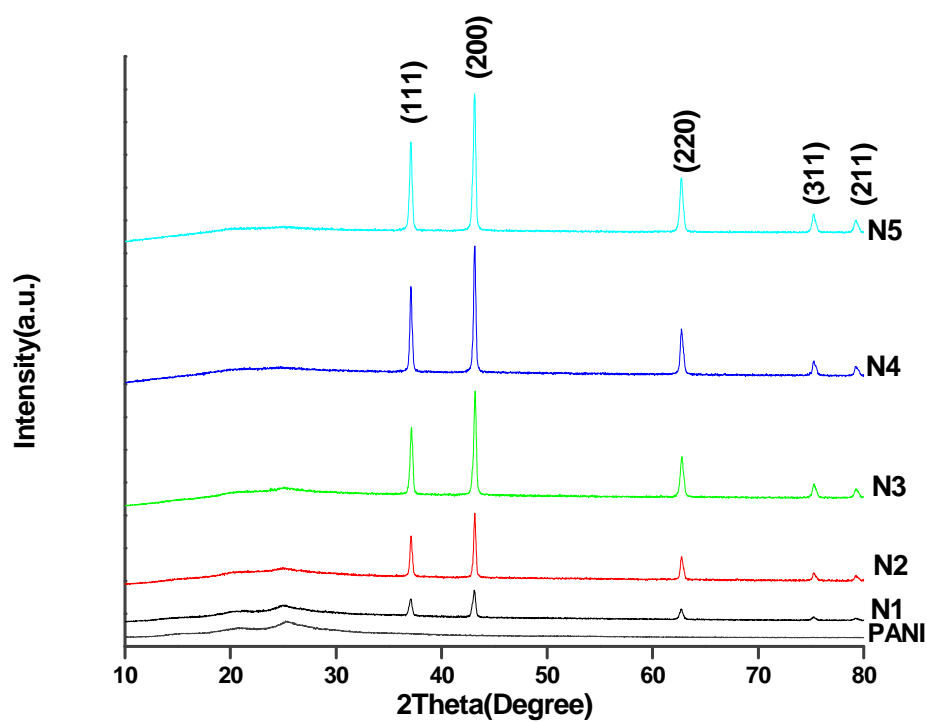
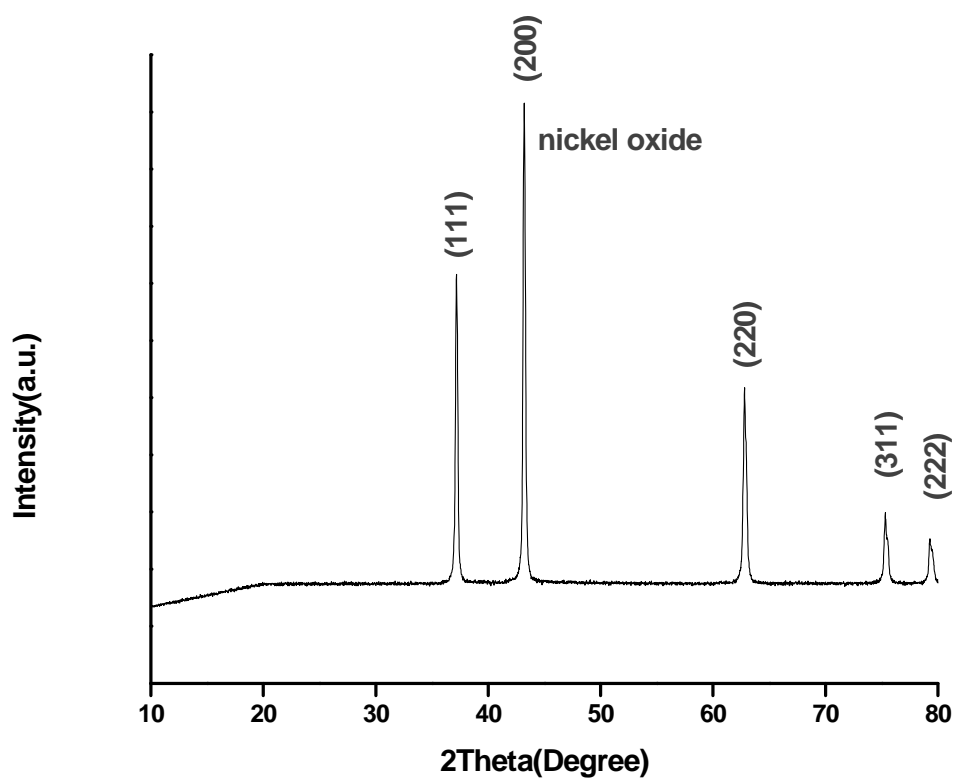**Figure 2(a): represents XRD of PANI and PANI/NiO Composites**

Figure 2(b): XRD of pure NiO

Thermo Gravimetric Analysis (TGA)

Thermal degradation is a very important process which helps in determining the influence of the polymer morphology on the thermal stability, the optimum temperature of operation and the activation energies related to the degradation processes [19, 20]. Several studies have also been made on the thermal stability of PANI/inorganic composites [21–24]. TGA curve of pure PANI shows three step weight losses: the first step loss at 100°C can be attributed to the loss of water, the second step loss around 230–380°C is due to loss of the dopant from the polymer matrix and the third major weight loss at 400–600°C is attributed to the degradation and decomposition of the polymeric backbone. The results indicate that more thermally stable inorganic particles improve the thermal properties of PANI by the interaction between them. Thermo gravimetric analysis has been proved to be reasonably rapid and precise method for the determination of such kinetic parameters related to the degradation processes [25].
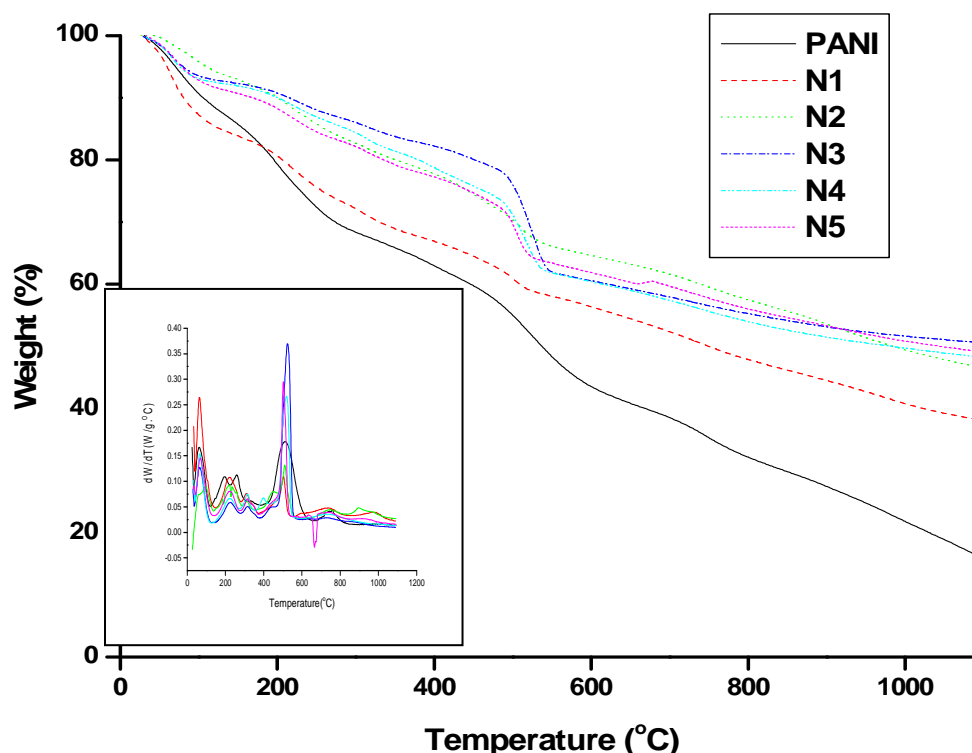

Figure 3: TGA graph of PANI and PANI/NiO composites

A TGA thermo gram of PANI and PANI/NiO composites in nitrogen atmosphere is shown in Figure 3. It shows that the trend of   degradation of PANI/NiO composites is similar to that of the pure PANI but thermal stability of the composites has changed. From TGA thermo grams, various kinetic parameters viz. activation energy (E$_a$), frequency factor (A), entropy of activation (ΔS) and free energy of activation (ΔG) of degradation reaction have been determined by adopting most commonly used method of Horowitz–Metzger [21, 26-30] and are listed in Table1. While calculating these parameters, for the sake of calculations, the central linear region between 400-600°C was considered for all samples which is the main region for polymer degradation.

The activation energy (E$_a$) for the thermal degradation process was calculated using equation,

$$\ln\left[\ln\left(\frac{w_0-w_f}{w-w_f}\right)\right] = \frac{E_a\theta}{RT_s^2} \qquad \text{.......... (2)}$$

where w_0 is the initial weight, w is the remaining weight at temperature T, w_f is the final weight, E$_a$ is the activation energy, R is gas constant and $\theta = T-T_s$ with T$_s$ as the reference temperature corresponding to $\left(\frac{w_0-w_f}{w-w_f}\right)$ = 1/e.

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Table1: Values of various kinetic parameters for PANI and PANI/NiO composites

Sample	E_a(KJ/mol)	A(s^{-1})	ΔS(J/mol/K)	ΔG(KJ/mol)
PANI	123.30	0.0040E+8	-335.89	393.02
N1	154.479	2.07E+8	-29.805	378.358
N2	205.795	4.677E+11	-111.961	292.789
N3	637.217	1.3489E+39	498.53	248.863
N4	401.674	3.930E+24	217.856	228.742
N5	343.076	3.097E+20	139.174	231.597
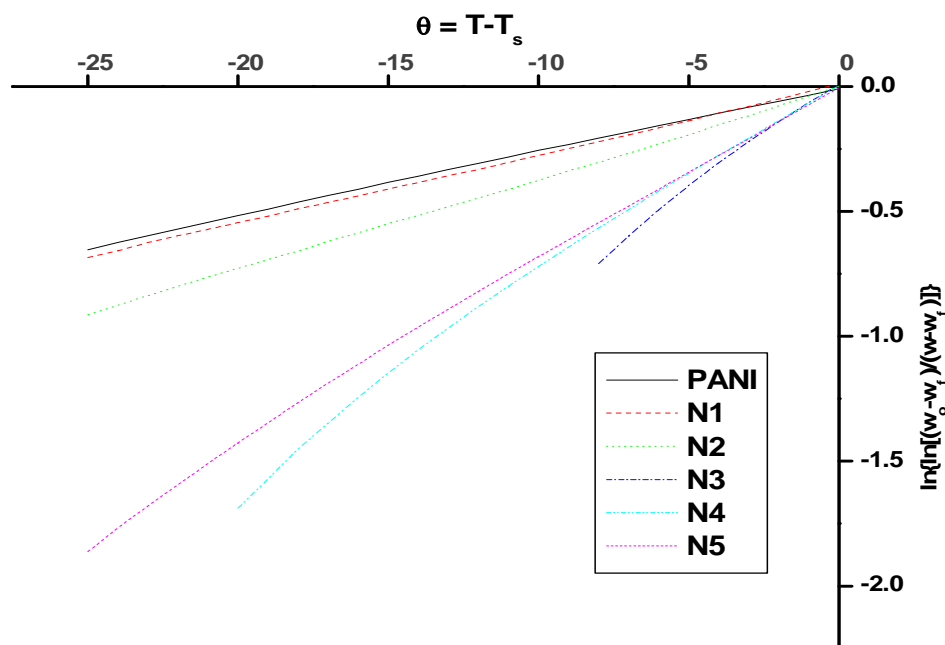
Figure 4: Graph between θ =T-T$_s$ and ln[ln(w$_o$-w$_f$/w-w$_f$)]

From Eq. (2), the activation energy E_a can be calculated from the slope of the linear fitted line between $\{\ln[\ln(\frac{w_o - w_f}{w - w_f})]\}$ and θ as illustrated in Figure 4, for Pure PANI and PANI/NiO composites.

The values of frequency factor (A), entropy of activation (ΔS) and the free energy of change of decomposition (ΔG) were calculated using the following equations [28, 30],

$$A = \frac{\beta E_a}{RT_s^2} \exp\left(\frac{E_a}{RT_s}\right)$$ ------ (3)

$$\Delta S = 2.303 \, R \log\left(\frac{Ah}{kT_s}\right)$$ ------ (4)

$$\Delta G = E_a - T_s \Delta S$$ ----- (5)

where, h-Planck's constant, β-constant rate of heating and k-Boltzman constant. The activation energy, frequency factor, entropy of activation, free energy of change of decomposition of pure PANI and PANI/NiO composites have been deduced and shown in table 1. It is clear from table 1 that the value of activation energy increases with increasing content of nickel oxide up to 30 wt% and then decreases further up to 50 wt%. It signifies that 30 wt% is the most thermally stable amongst all the composites. Thermal stability of PANI/NiO composites is higher than that of the pure PANI, which indicates that some interaction exists between NiO particles and PANI backbone.

It is clear from table 1 that corresponding to the values of activation energy, the values of frequency factor changes. This change in the frequency factor shows that there is a change in the rate of reaction corresponding to A. The value of entropy of activation of NiO composites increases as compared to pure PANI which in turn suggests the increase in the rate of reaction.

Positive values of entropy of activation suggest that reaction is too fast and disorderness is more in the case of NiO (30, 40, 50 wt %) composites. This positive value of ΔS is probably due to the value of logarithm A > 13.2 for these composites as reported in literature [31]. ΔG determines the spontaneity of the reaction. The positive values of ΔG signify the non spontaneity of the degradation reaction [32].

DC Conductivity
Current (I) - Voltage (V) characteristics of PANI and its composites with NiO at temperature are shown in Figure 5. The current increases non-linearly with applied voltage. The mechanisms of electrical conductivity in conducting polymers are well studied and DC conductivity of conducting polymers depend on their morphology and certain other factors such as type of monomer, doping level, degree of crystallinity etc [1]. Conductivity can be measured by the equation

$$\sigma = \frac{I \; X \; L}{V \; X \; A}$$

---------- (6)

where, I is the current, L is the thickness, V is the voltage and A is the area of cross section of the sample. For all the composites, conductivity of all the samples is lower than pure PANI (10^{-4} S/cm) but greater than conductivity of NiO (10^{-7} S/cm) at temperature 313K. This decrease in DC conductivity as compared to PANI is due to blocking of charge carrier upon doping. Due to doping, charge carriers are unable to hop between favorable localized sites and hence conductivity decreases [33]. DC conductivity for the composites, observed from Table 2 shows that DC conductivity of composites decreases for 10, 40, 50 wt% and increases for 20, 30 wt%. Increment in conductivity for 20 and 30 wt% of NiO composites may be due to extended chain length of polyaniline in which the charge carriers possess sufficient energy to hop between various favorable localized sites [34]. To learn more about the mechanism of electrical conductivity, the functional dependence of the conductivity on temperature must be determined. It was seen that the conductivity increases with increase in temperature as shown in Fig. 6. This can simply be associated to the contribution of charge carrier mobility. In this case, polarons or bipolarons might move with higher diffusion velocity when the temperature increases and thus increases the conductivity [35].

The models for thermally activated and Mott's variable range hopping (VRH) is given by Equation (7)

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma}\right]$$

-------- (7)

where, σ is the conductivity, T the temperature, and σ_0 the conductivity at characteristic temperature T_0. The exponent $\gamma = 1/(1+d)$ determines the dimensionality of the conducting medium. The possible values of γ are 1/4, 1/3 and 1/2 for three, two and one-dimensional systems respectively [36]. Conductivity varies with various values of the exponent (e.g. $T^{-1/4}$, $T^{-1/3}$, $T^{-1/2}$ and T^{-1}) which have been reported to interpret the data. The values of $\ln\sigma_0$ obtained from the intercept is obtained from the above mentioned plots and shown in Table 3.

Table 2: DC conductivity of PANI, NiO and PANI/NiO composites at various temperatures at 0.5V

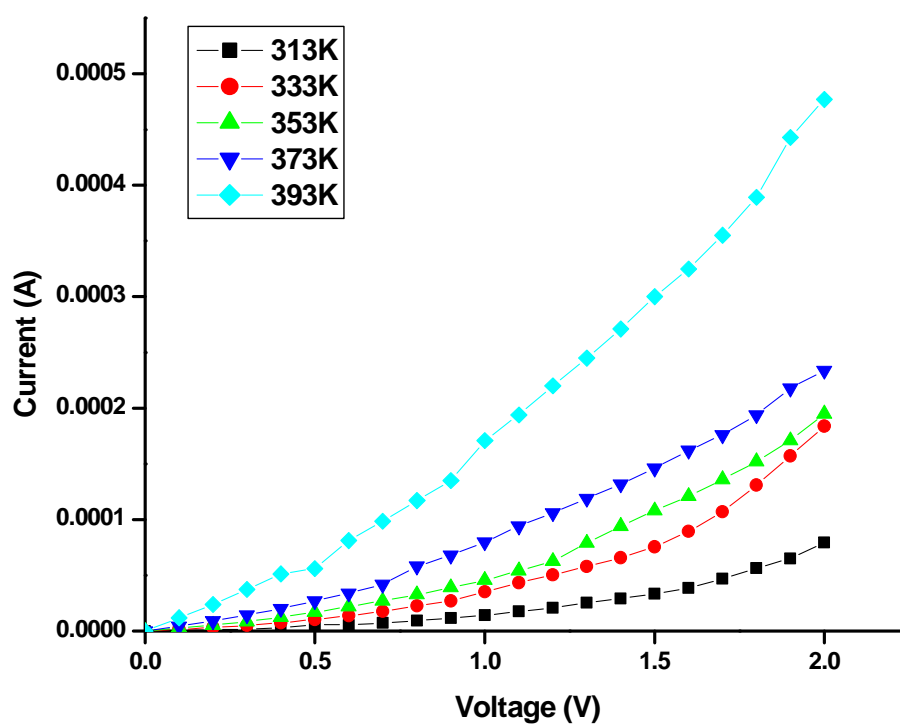| TEMP.	Conductivity (10^{-5} S/cm)						
	PANI	N1	N2	N3	N4	N5	NiO
313	58.8	0.102	0.383	0.559	0.332	0.237	0.028
333	69.7	0.178	0.832	1.12	0.659	0.35	0.059
353	78.1	0.293	1.55	2.53	0.957	0.483	0.108
373	84	0.467	2.97	4.09	1.59	0.716	0.170
393	86.8	0.961	4.17	6.52	2.24	1.21	0.246

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Figure 5: I-V characteristic of N5 at various temperatures

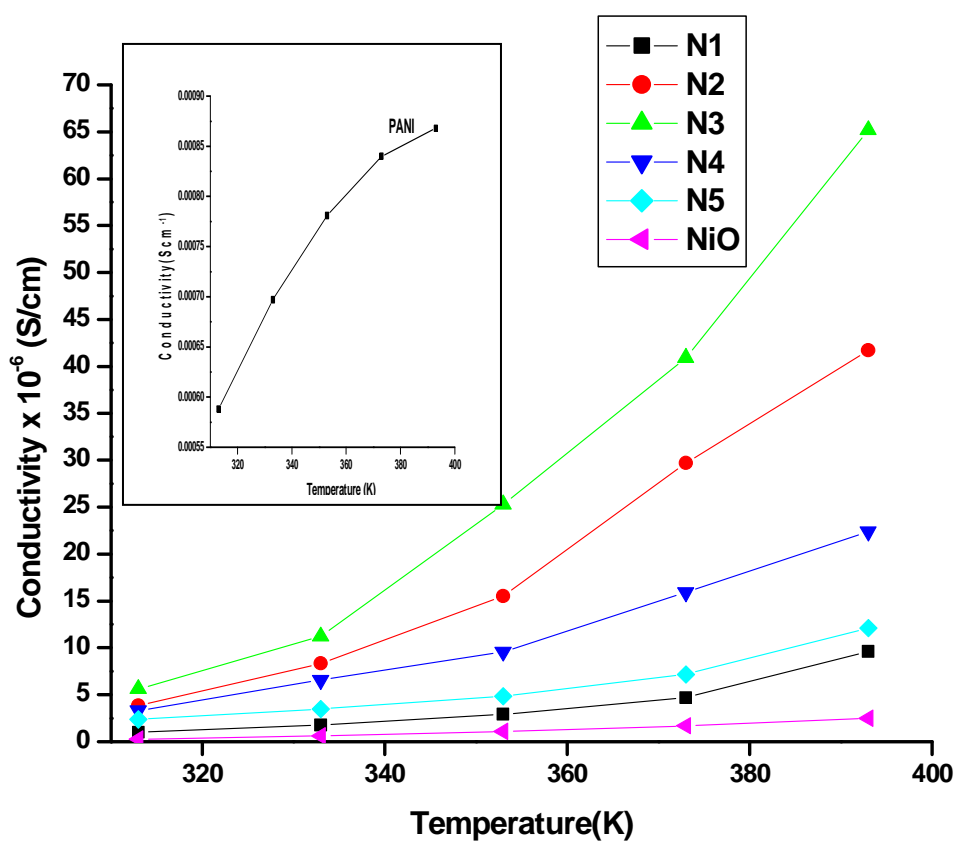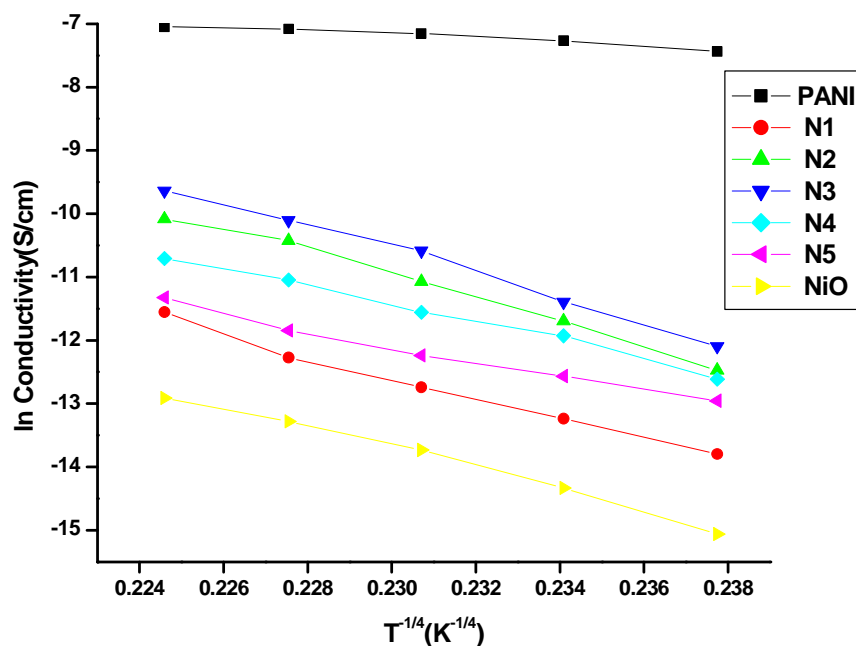**Figure 6: Conductivity vs Temperature curves of PANI (inset), PANI/ NiO composites and NiO**

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Table 3: The values of $\ln\sigma_0$ and T_0

Sample	$\ln\sigma_0$ (S/cm)	T_0 (10^5) K
PANI	-0.5964	6.61
N1	21.256	4.716E+3
N2	33.810	1.428E+4
N3	34.920	1.53E+4
N4	19.567	3.27E+3
N5	13.033	1.429E+3
NiO	23.096	6.54E+3

Figure 7: Graph between ln (σ_{dc}) vs $T^{-1/4}$ for PANI, PANI/NiO composites and NiO

It was suggested by Mott that the pre-exponential factor (σ_0) for conduction in the localized states should be two or three order smaller in the magnitude than for conduction in the extended states, and should become still smaller for conduction in the localized states near Fermi level. The plot of $\ln\sigma$ vs. $T^{-1/4}$ is a straight line as shown in Fig. 7 and indicates that three dimensional (3D) charge transport occurs in all the samples.

CONCLUSION

PANI and PANI/NiO composites were synthesized by means of the oxidative polymerization of aniline hydrochloride in presence of different wt% of NiO with ammonium persulphate. The FTIR results confirm the presence of PANI in the composites. In composites of PANI/NiO, there exists small shifting in frequencies of the bands as observed in PANI. Crystalline nature of the prepared composites has been ascertained by X-ray diffraction pattern. Composites show a higher thermal stability than that of PANI, which can be shown by comparing the values of activation energy. The temperature dependence of the DC conductivity of PANI/NiO, as measured in temperature range (313 to 393 K), has been analyzed in the framework of Mott's model for transition metals and variable range hopping models by Mott. Also DC conductivity of 30 wt% of PANI/NiO composites is maximum among all the composites and correlates with the TGA results. The DC electrical conductivity of PANI and PANI/NiO composites increases with increase of temperature. It is observed that composites of PANI/NiO are good conductors as compared to NiO. Thus, such materials can be used as soft electro-magnetic materials in constructing transformers and cathode materials in batteries instead of NiO.

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