Thermal analysis and conductivity of Polyaniline nanofibers-Y₂O₃ Nanocomposites

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Abstract: *In the current trend the contribution of conducting polymer composite materials in the field of Direct current conductivity of the composite is vital. Knowing this importance, in this paper Polyaniline nanofiber/Y₂O₃ (Pani/Y₂O₃) are characterized by thermogravimetric analysis,Differential Thermal Analysis and Differential Scanning Calorimetry. ScanningElectron Microscopic studies of the composites shows the nanofiber nature. Obtained results are used to analyse the Direct current conductivity of the composites in the range of room temperature to 180 ^{0}C.The result infers that, the conductivity increased with doping, as well as the crystallinity increased when compared to undoped sample.*
Keywords: *Thermalanalysis, Yttrium oxide, Differential Thermal analysis, Differential Scanning Calorimeter, Direct current conductivity, Polyaniline nanofibre composites.*

I. INTRODUCTION

Thermal characterization of conducting polymer composite materials are useful in guiding the materials to decideproperties for suitable applications. Polyaniline Polystyrenesulphonicacid(PSSA) composites cross linking is confirmed through the thermal anlaysis.Increasingthe loading of PSSA into the Pani and its thermal stability are due to cross linking or oxidative reaction starts at higher temperature[1].The amount of HCl released during the aging increases with heating time and temperature strongly suggest the dedoping leading to the decrease in conductivity[2]. Cross linking reactions of the amine and imine group in the polyaniline resulting in redoping after aging. Such a cross linking reactions and corresponding morphology responsible for the increase in glass transition temperature of the composites. Kumar and Chandra explains the polyaniline synthesized by HCl and Polyaniline Toluene Sulfonic Acid(PTSA) as a dopant shows the TG curves with three step weight loss curves indicating one for water second for the dopant and degradation of the polyaniline. They also shown thermal stabilityupto 234 ^{0}C for the polyaniline doped with PTSA is more than inorganic HCl dopant[3].Such conducting composites find application in conventional thermoplastics. Mallikarjunaetal. shows the polyaniline nanofibers have higher thermal stability and high degree of crystallinity[4] than the polyaniline. Such a crystalline polyaniline nanofibers exhibits the high dielectric constant and low dielectric loss opens the high ability applications for energy storage devices, capacitors and fuel cell membranes etc. In the polyaniline,polypyrrole composites are compared the thermal decomposition of the pani-ppy copolymer synthesized film form and the pani-ppy blend are mechanically mixed such a polymers are also subjected for the TGA. Total ion current curve recorded during the pyrolysis mass spectra of 0.5M Pani/PPy physical blend show high adsorption of water is very effective due to hydrogen bonding. It also show that evolution of CO_2 is diminished at high temperature is due to reaction of polymer with dopant not occurred during the synthesis but probably may takes place during the storage condition. Such analysisgive the percentage of residue of the pure pani and PPy in the composite and blend using TGA and its improved thermal stability are also accounted[5].

In view of the metal oxide polymer composites Polyaniline-V_2O_5 composites also show the two step weight loss one is explained with the water and second weight loss 100-900°C is explained due to the oxidative degradation of the anilinium and Pani in the V_2O_5 network[6]. The thermal stability of polyaniline extracted from aged (PANI)x $V_2O_5nH_2O$ is better than that extracted from fresh samples. The room temperature conductivity of

aged samples is always greater depending on the degree of polymerization. Depending on the polymer content and the degree of polymerization room temperature thermoelectric power is negative and varies(-30 to 200 íV/K).

Continuous weight loss from 100 to 700 also explained due to the aged π -phase of the polyaniline.Sashtry et al discussed the panidoped CSA shows higher decomposition temperatureof the polymer doped CSA have200-700. Due to strong intermolecular interactions with Pani-doped CSA than the Panidoped CSA with tungsten oxide[7].Venugopalbaire gives the presence of the metal oxides in the polymerized pani doped with tannin sulfonic acid[8]. Higher thermal stability of the Panidoped DBSA/ZnO than Pani doped DBSA. Higher thermal stability is explained on the basis of hydrogen bonding in the composites[9].

Rajive Arora et al. discuss the DSC of the Pani and its salts in a TiO_2composites showes the Tg for the Pure Pani and Pani PVA composites that of the Pani TiO_2 not shown the Tg indicating the degradation of the polyaniline salts before the melting temperature due to interactions of the Pani with TiO_2[10].Pani and its composites are further supported by three step decomposition of the TGA are further supported by DTG in weight loss quantities. Four stage degradation of the Pani/CuO composites are discussed as TGA and DTG for the loss water, loss of NH_4^+obligmer, polymer chains and pani backbone[11]. Endothermic peak of the DSC in the Pani/$WO_3$is due to the bondscissoring which is compensated by bond formation with the exothermic peak[12].

Conductivity of the Pani/ZnO and Pani shows the enhanced conductivity of the Pure Pani than the Pani composites due to the hindrance of the electron/charge flow in the conjugated pani/composites[13]. PPY/flyash composites show the increase in the dc conductivity as the temperature in increased. 40% weight percentage of the PPy/fly ash composites shows the highest coductivity[14].

In this work Polyaniline nanofibers/Y_2O_3 composites are chemically synthesized as reported elsewhere[15]and thermal stability of the composites are discussed using thermal analysis. Effect of temperature on the Pani nanofiber/Y_2O_3 composites with TGA/DTG are discussed. Morphology of the composites are also discussed. Temperature dependent dc conductivity of the Pani nanofiber /Y_2O_3 composites are also discussed within the range of room temperature to 120 ^{0}C.

II.   MATERIALS AND METHODS:

Synthesis of Y_2O_3 by using Agaricusbissporous as a fuel leads to the nanoparticlesare depicted in earlier work[15]. Same Y_2O_3 nanoparticles are mixed in different weight percentages with polyaniline nanofiber by insitu method to form polyaniline nanofiber/Y_2O_3 composites[16]. Obtained Pani nanofiber/1Y_2O_3Paninanofiber /3 Y_2O_3,Pani nanofiber/5Y_2O_3andPani nanofiber/7Y_2O_3composites are subjected for the SEM analysis and Thermal analysis and Dc conductivity are discussed in this paper.

SEM analysis is carried out using the Hitachi-3000. DTA/DTG studies for the above samples were also carried out by using a Perkin Elmermodel TGA 7 instrument. Initial scan was taken 50 to remove the thermal history effects, then cooled to 50°C under nitrogen atmosphere. Data collected at 20°/min, in the range of 40–750°C showed typical sample size for pure Panias 7.92 mg, and that of the composite, 11.964mg, 5 mg, 8 mg and 6 mg for Paninanofiber/ 1Y_2O_3,Pani nanofiber/3Y_2O_3,Pani nanofiber /5Y_2O_3 and &Pani nanofiber/7Y_2O_3 composites respectively.

Direct current conductivity: Finally powder form of the polyaniline nanofiber composites are compressed to form the pellet. Pressure applied during the pellet preparation is 95 Mpa with the dimension range from 1 to 2.3 mm thickness with a diameter of 1cm. Dc conductivity measurements are made by using two probe technique using Multimeter and temperature range from room temperature to 120 ^{0}C. Fixed voltage applied during the dc conductivity measurement is 0.1 V with a current of 100 μA.

III.   RESULTS AND DISCUSSION:
SEM of the composites:

Figure 1 shows the SEM images of the a)Pani nanofiber b) Pani nanofiber/1Y_2O_3 c)Paninanofiber/3 Y_2O_3 d) Paninanofiber /5Y_2O_3 e) Paninanofiber /7Y_2O_3 composites. In the figure 1 a plate shows the small nanofiber formation of the Pani and in the composites due the Presence of the Y_2O_3 shows blend of Y_2O_3 and pani nanofiber with a suitable magnifications are depicted in the figure.

The composites shows the more fibrillary structure for Pani nanofiber/1Y_2O_3 andPani nanofiber/7Y_2O_3 but other two Pani nanofiber/3Y_2O_3 and Pani nanofiber/5Y_2O_3 composites shows less fibrillare structures withyttrium. Due to the nanofiber nature thermal stability is expected to be more and thermal conductivity also more as it provides the skeletal structure.
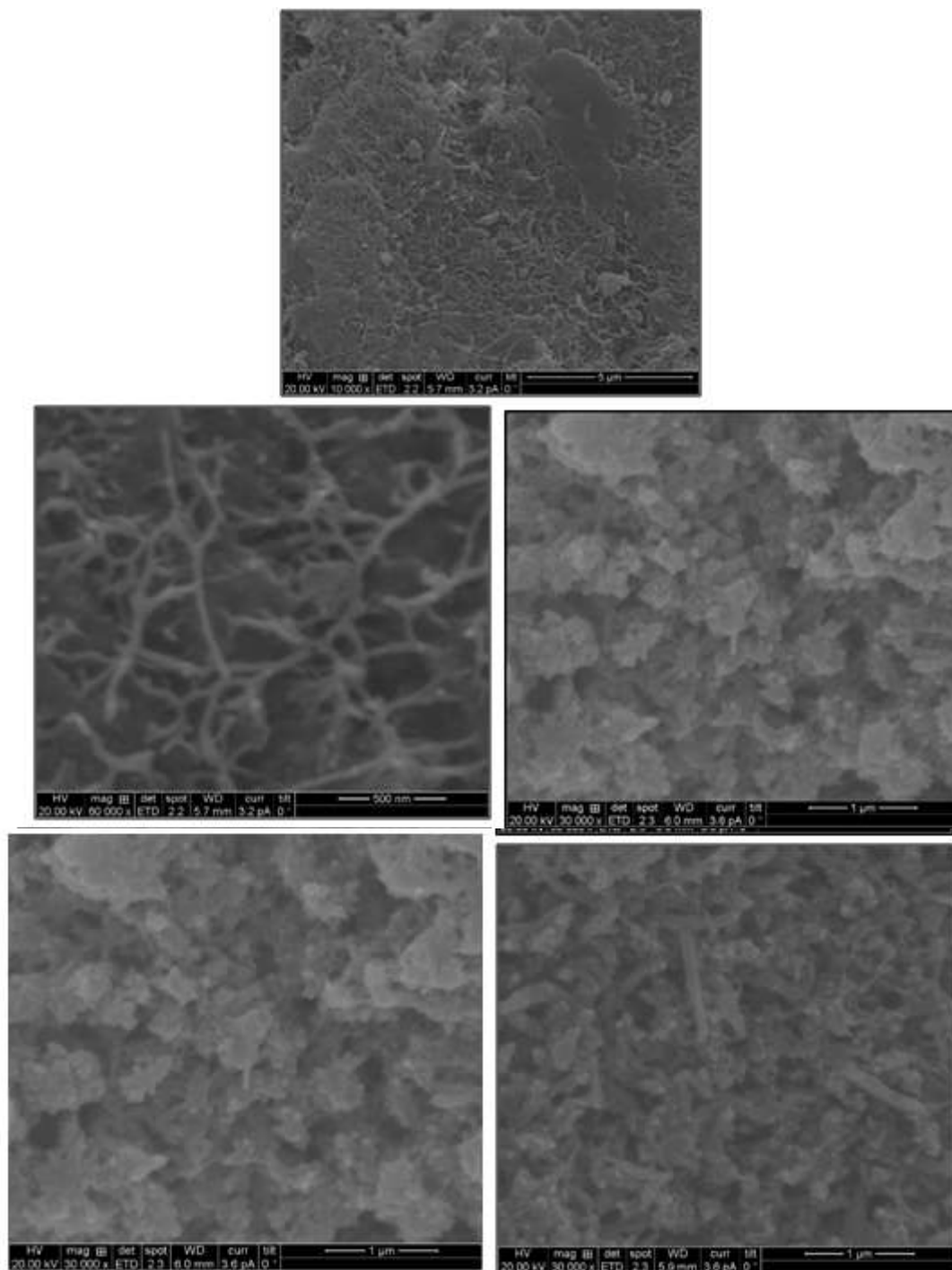
Figure1: SEM of the a) Paninanofiber   b)Pani nanofiber /1%Y_2O_3 c) Paninanofiber/3% Y_2O_3
d) Paninanofiber /5%Y_2O_3 e) Paninanofiber /7%Y_2O_3 composites

Thermal stability of the composites: Thermal degradation of the polymer composites establishes the stability of the composites. Thermal stability of the composites are mainly depends on the structure and morphology of the composites and intermolecular interactions present between the two moieties. Such a study also explains the impact of conductivity of the polymer composites on the polymer stability.

3.1 TGA/DTG
Figure 2 shows TGA of the Pani nanofiber between the range of room temperature to 30^0- 720^0C. The pure pani undergo three step weight loss which can be observed from the figure 2 inset.The first degradation commences at 39.5^0 to 100^0 may be due to removal of moisture that can be further quantized by DTG curve with average weight loss of 0.565mg within the 150 sec. It is well match with the literature values[5-7]. Further second

weight loss occurred from 150 to 220^0 may be due to loss of dopantHCl quantised as 0.41mgand third weight loss noticed between the 250 to 295^0 with weight loss 0.296 mg may be due to surfactant DBSA. And fourth weight loss may be due to the degradation of the polyaniline chain which commences from 400^{0}to 486^0 within 80^0 (approximately) weight lossoccurred is 0.768 mg but final degradation has reached up to the 740^0 it is higher than the reported 650^0 polyaniline fiber by Mallikarjuna etal. They used only one APS oxidant along with acetic acid. We used both FeCl$_3$+ APS as a composite oxidant in the polymer preparation as a result four step degradation. Rest of the polymer of about 5.986 mg is finally decomposed to Figure 2
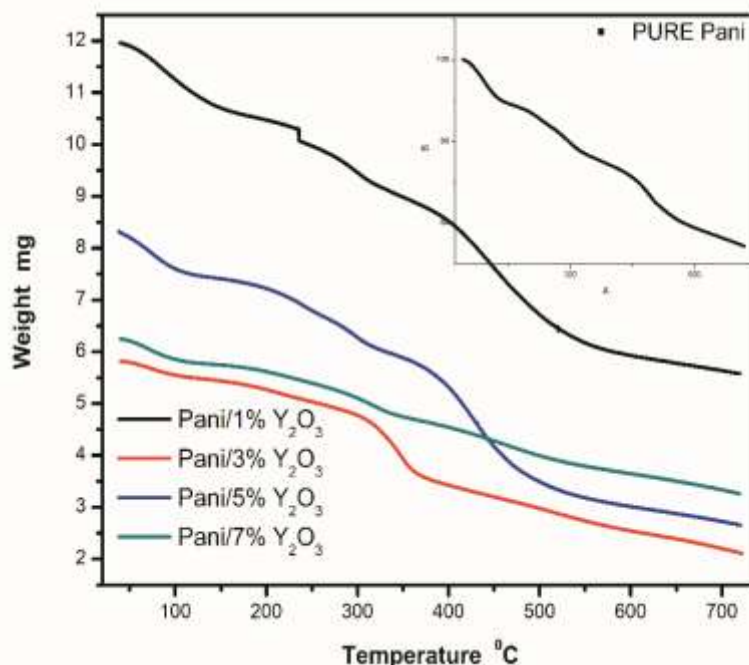

Figure 2:

Figure 1shows TGA of the Paninanofiber /Y$_2$O$_3$ nanocomposites,inset of the figure shows the TGA of the Pure Pani.It can be seen that TG curve of pure PANI shows a two-step weight loss process. The first step corresponds to loss of moisture up to temperatures 120 C. This step can be attributed to the expulsion of water molecules. The second-step weight loss occurs between 120 and 400 C, which is due to the degradation of PANI chains and the dopant DBSA form PANI chains. An interesting observation is that the TG curve of the pure PANI corresponding to the second-step weight loss of the TG curve shows two minima rather than one. The first minimum is due to the loss of surfactant DBSA, while the second is the result of degradation of the polymer. The trend of degradation of the composite is similar to that of pure PANI and also shows a two-step weight loss process. The minimum in the TG curve for pure PANI and Pani/1yttria is at 500 C (for DBSA), but the temperature of the minimum in the case of the PANI/3 Y$_2$O$_3$ and Pani/5 yttriacomposite is significantly shifted to a lower value of 350 and 480 ^{0}C respectively. This result indicates that the composite systems are more thermally stable for pure PANI and Pani/1yttria, which may be rationalized in terms of interaction between PANI and Y$_2$O$_3$ restricting thermal motion of the PANI in the composite shows its thermal stability matches with literature (26). Fig. 2 also shows TG curves of PANI/Y$_2$O$_3$ composites as a function of DBSA anion. The sample with higher weight percentage of yttriashows lower thermal stability of polyaniline/ yttriacomposites.
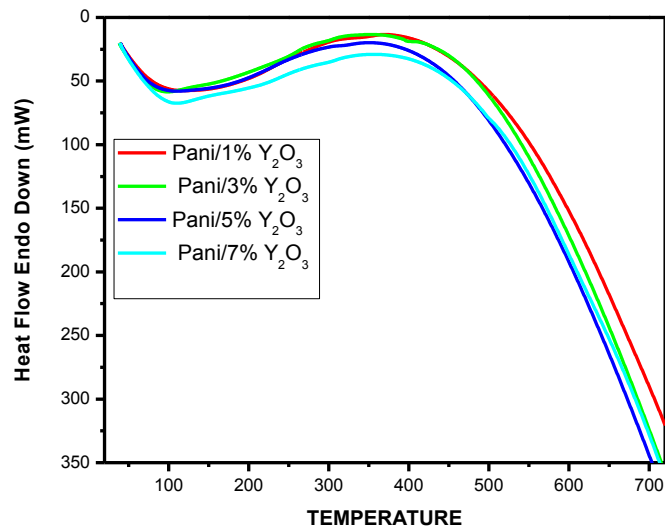
3.2 DTA

Firuge 3:

      Figure 3shows DTA of the Pani nanofiber /Y_2O_3 nanocomposites, inset of the figure shows the DTA of the Pure Pani. DSC thermos gram of the polyanilineand shows an endothermic peak at 50-140^0 and an exothermic peak at 300-450^0. The first peak is most likely attributed to the removal of water and the second peak may be related to the cross-linking reaction [21]. In comparison to polyaniline Pure form, the composite materials in different compositions show thermogram is further confirm from the DSC in figure 4.

3.3 **DSC:**

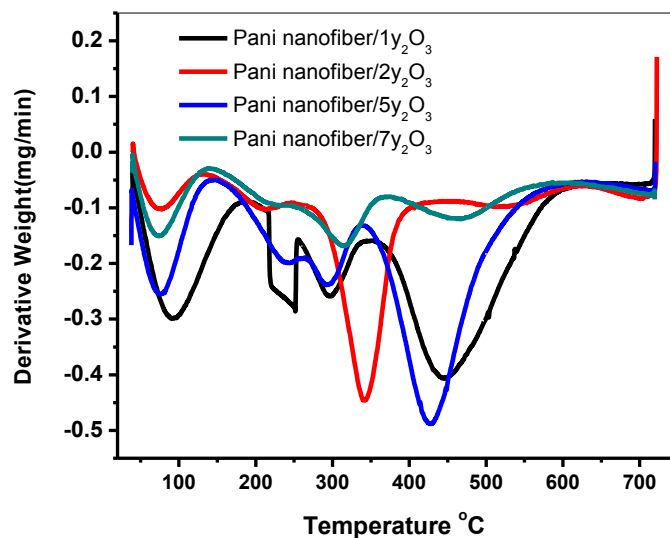**Figure 4 shows the DSC of Paninanofiber/Y_2O_3 composites.**

Figure 4: DSC curves of the Paninanofiber with the Y_2O_3 composites

3.4 Temperature Dependent Conductivity:

      The variation of DC conductivity with temperature for pure PANI and the PANI/Y_2O_3composites (with different wt%) is shown in Figure 3. Arrhenius plot of DC conductivity shows straight line behaviour. The DC conductivity of pure PANI increased exponentially with doping, exhibiting semiconductor characteristics. The relation between conductivity and temperature can be represented by the equation

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right), \qquad (1)$$

where (ΔE) is the activation energy for the DC conduction mechanism, "k" is the Boltzmann constant, and "σ_0" is the pre exponential factor. The activation energy (ΔE) has been calculated from the slope of Figure 5 for pure PANI and the PANI/3. The DC conductivity of undoped PANI is measured to be 3.58×10^{-9}S/cm. After doping with different weight % of $Y_2O_3$the conductivity was found to change from $10^{-7}$to 10^{-9}S/cm, attaining a maximum value at 30 weight % of $Y_2O_3$and then reduced at 40 weight % of Y_2O_3. 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. Through doping, electronic and optical properties of conducting polymers can be controlled over a long range.
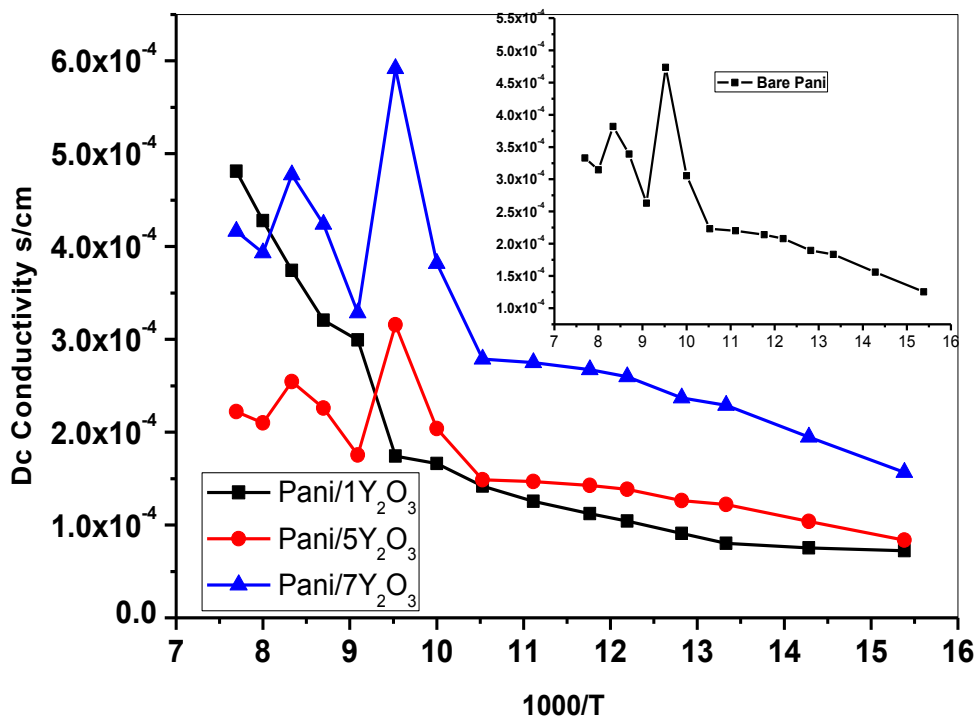
The electrical conductivity of conducting polymers results from mobile charge carriers introduced into the π-electronic system through doping. At low doping levels these charge carriers are self-localized and form nonlinear configurations. Because of large interchain transfer integrals, the transportof charge is believed to be principally along the conjugated chains, with interchain hopping as a necessary secondary condition [28–31]. When the polymer is heavily doped (40 weight %), the wave functions are delocalized over many lattice constants along the polymer chain. In PANI, sincethere are nearly degenerate ground states, the dominating charge carriers are polarons and bipolarons [32]. When PANI is doped with Y_2O_3hydrochloric acid, the charge carriers form nonlinear configurations, and as a result the conductivity does not change substantially. The nonlinear formation may be more in the case of heavy doping of 40 weight%of Y_2O_3, due to which it exhibits lesser conductivity than 30 weight % doped polymer.

IV.   CONCLUSIONS:
A series of PANI nanofiber/Y_2O_3 composites have been prepared by insitupolymerization with different weight percentage of Y_2O_3. The DC conductivity of polyaniline and PANI/Y_2O_3 composites and in the temperature range of 300–550 K. The conductivity measured is in the range 10^{-7}–10^{-9}S/cm at a temperature 302K. The conductivity increased with doping, as well as the crystallinity increased when compared to undoped sample. Indirect transition ($m = 2$) is found most suitable to calculate band gap. The optical band gap (Eg)

increases as the concentration of Y_2O_3 increases; it shows that the disorderliness reduces and defect state density decreases. Dielectric behavior is possible for application in conductive paints, rechargeable batteries, sensors, MOS devices, and so forth.

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