

PREPARATION, CHARACTERIZATION, THERMAL BEHAVIOUR AND DC CONDUCTIVITY OF NANO-STRUCTURED POLYANILINE DOPED WITH HCL OR TSA: A COMPARATIVE ANALYSIS

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ABSTRACT- Polyaniline (PANI) in nano dimension was prepared in the presence of aqueous hydrochloric acid (HCl) or toluene sulfonic acid (TSA) as doping agent and ammonium persulfate (APS) as oxidizing agent by chemical oxidative polymerization at room temperature. The morphology, microstructure and thermal decomposition behavior of the PANI materials were investigated by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffractometry (XRD), uv-visible spectroscopy, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). FTIR analysis confirmed the formation of PANI and change in polymer structure due to the different doping agents. The dc electrical conductivity of the PANI was measured by four-probe technique. The electrical conductivities of the two PANI samples show that nano-structured PANI doped with TSA has higher conductivity of 0.824 Scm^{-1} compared to PANI doped with HCl with the value of 0.478 Scm^{-1} . The nano-structured PANI doped with TSA is slightly thermally more stable compared to the one doped with HCl.

Keywords: Chemical oxidative polymerization; nano-structured polyaniline; thermal stability; electrical conductivity.

1.0 Introduction

Conducting polymers are organic polymers that conduct electricity as they possess electrical properties like that of metals (metallic conductivity) and semiconductors. They display several characteristics of organic polymers such as lightweight, lower cost, resistance to corrosion and chemical attack, flexibility and greater workability [1-5]. They are commonly used in many electrical/electronic devices and for a myriad of applications. Among different conducting polymers, polyaniline (PANI) is the most versatile owing to its low cost, low specific mass, thermal/chemical stability and high conductivity [6, 7]. Polyaniline is particularly attractive for electronic applications due to its simplistic synthesis, environmental stability, distinctive electronic properties and simple acid/base doping/dedoping interaction. Chemical oxidative polymerization among different methods is one of the most important methods developed to prepare PANI through the incorporation of dopants into aniline monomer during synthesis. Varieties of organic and inorganic acids capable of doping activities, such as hydrochloric, sulfuric, nitric, phosphoric, perchloric, acetic, formic, tartaric, methylsulfonic, ethylsulfonic, camphorsulfonic, dodecyl sulfonic, toluenesulfonic acid, etc. are commonly used [8]. The type, size and amount of the dopants play an important role in influencing the morphology of conducting polymers. The acid has significant effect on the morphology and size of the polyaniline nanotubes [9]. By simply changing the volume ratio of dopant to aniline could change the structure of PANI from bulk to nano dimensions. Many techniques such as stirring, static placement, sonication, emulsion polymerization, etc., have been used to synthesize PANI nanostructures [8]. The investigation of nanostructured conducting polymers has great importance for both scientific and technological points of view due to their unique properties and favorable prospective in nanodevices applications.

In this work we report the synthesis of PANI in nano dimensions through chemical oxidative polymerization of aniline using HCl or TSA as dopants and APS as oxidant. The prepared nano-structured PANI materials were characterized FTIR spectroscopy, SEM, TEM, XRD, uv-visible spectroscopy, DSC and TGA. Their thermal and electrical properties were studied and compared.

2.0 Materials and Methods

2.1 Materials

Chemicals and solvents: Ammonium persulfate (APS), toluene sulfonic acid (TSA) and aniline monomer of 99.9% purity were obtained from Sigma Aldrich Chemical Company. Hydrochloric acid (HCl) 98% and acetone were obtained from Spectrochem Pvt Ltd, Mumbai, India.

The aniline was distilled before use. All other materials were used without any pre-processing.

2.2 Methods

2.2.1 Synthesis of polyaniline (PANI)

Nano polyaniline was prepared by chemical oxidative polymerization of 200 μl aniline using 0.66g of ammonium per sulfate dissolved in 1.8 ml water as initiator in the presence of 40 mL aqueous solution of 1M HCl at room temperature for 12 hrs. The polymer formed was washed with distilled water, dilute HCl solution and finally with acetone until the filtrate becomes colourless

to remove excess HCl, oxidant, aniline and oligomers. The green coloured precipitate was then dried in vacuum oven at 50 °C for 24 hours. The dried mass was ground to fine powder using mortar and pestle. The prepared polyaniline is designated as nano PANI-HCl. In order to determine the influence of the novel polymerization formulation on the dimensions of the synthesized nano PANI-HCl, polyaniline was also prepared in bulk dimension by polymerizing 20 ml aniline using 66g of ammonium per sulfate dissolved in 180 ml water as initiator in the presence of 400 ml aqueous solution of 1M HCl with stirring at room temperature for 12 hrs and designated as bulk PANI-HCl. To check and be sure of the dimensions, the morphology of both the nano and bulk PANI-HCl were analyzed using SEM.

The reaction recipe of nano PANI-HCl was repeated with 1 M TSA as dopant keeping all other reactants the same and designated as nano PANI-TSA.

2.2.2 Characterizations

The morphology and microstructure of the samples was examined by JEOL Model JSM - 6390LV SEM and JEOL/JEM 2100 TEM. The Fourier transform infrared (FTIR) spectra of samples were recorded from KBr sample pellets using a Thermo Nicolet Avatar 370 FTIR spectrometer. The compositional state of the samples was determined using X-Ray Powder Diffractometry (XRD - Bruker AXS D8). The optical absorption by the sample in the UV and visible region was measured with Varian Cary 5000 UV-Visible spectrophotometer in the spectral range 225-1000 nm. Differential Scanning Calorimetry (DSC) was carried out on a Mettler Toledo DSC 822e to measure the amount of heat energy absorbed or released by a sample, as it is heated, cooled or held at a constant temperature in order to study the thermal behavior of the samples. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer STA 6000 thermogravimetric analyzer to determine decomposition and transition temperatures, and thermal stabilities of the samples. The electrical properties of the PANI samples were measured by four probe technique (D.C conductivity) using sensitive digital electrometer (Keithley Agilent 616).

3.0 Results and discussions

3.1 Scanning Electron Microscopy (SEM)

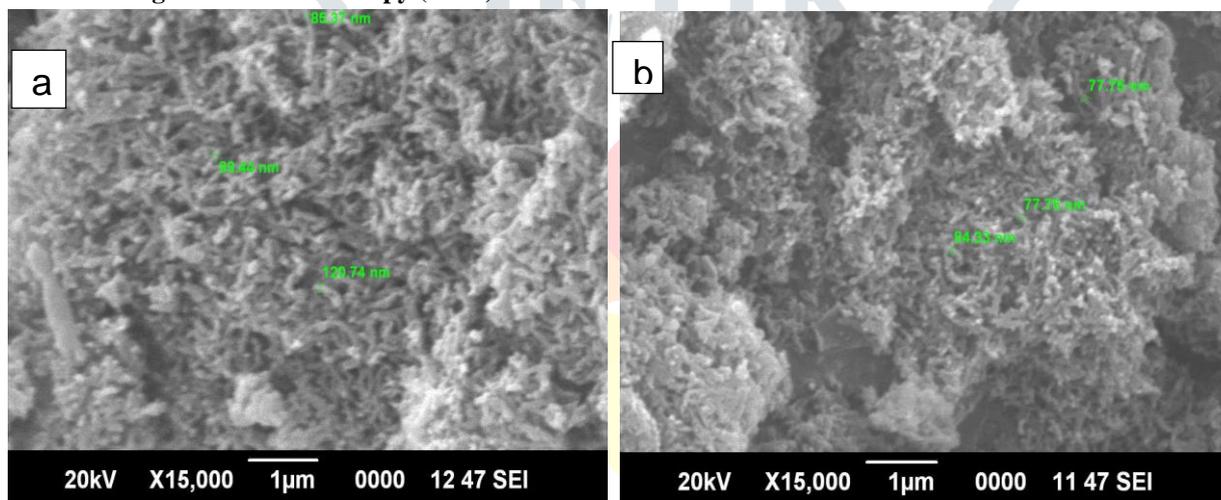


Fig 1. SEM micrographs of PANI: (a) Nano-structured PANI-HCl and (b) Nano-structured PANI-TSA

Figures 1a and 1b respectively show the SEM micrographs of nano PANI-HCl and nano PANI-TSA. All the micrographs reveal the irregular granular structures of the synthesized polyaniline. The micrographs of nano PANI-HCl and nano PANI-TSA reveal that the synthesized polyaniline comes under nano dimension with an average particulate size of 85 nm and 77 nm respectively.

3.2 Transmission Electron Microscopy (TEM)

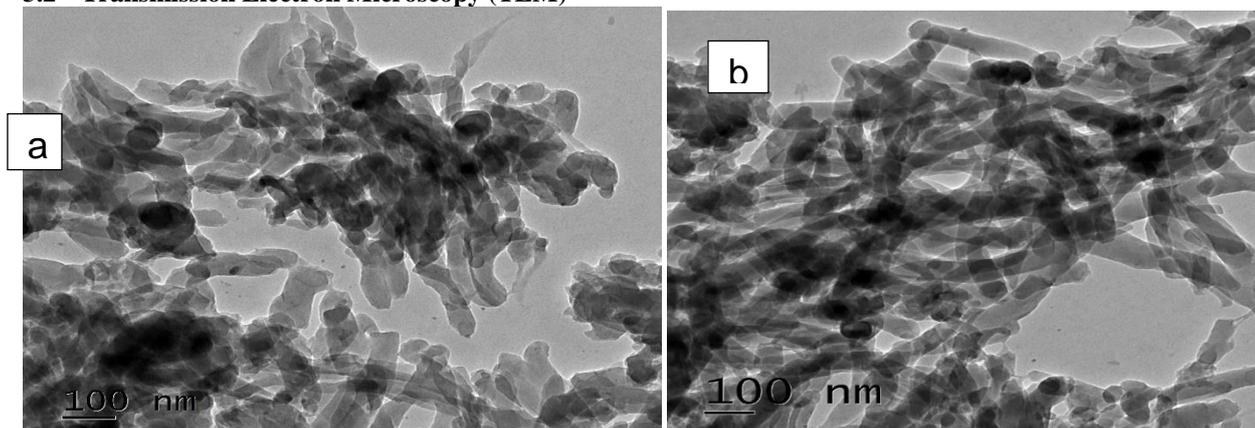


Fig 2. TEM micrographs of PANI: (a) Nano-structured PANI-HCl and (b) Nano-structured PANI-TSA

The transmission electron micrograph (TEM) images of nano PANI-HCl and nano PANI-TSA are shown in Figures 2a and 2b respectively. The TEM images clearly show a fibrous like structure with a diameter of 2 nm in the form of hollow nanorods.

3.1 Fourier Transform Infrared (FTIR) Spectroscopy

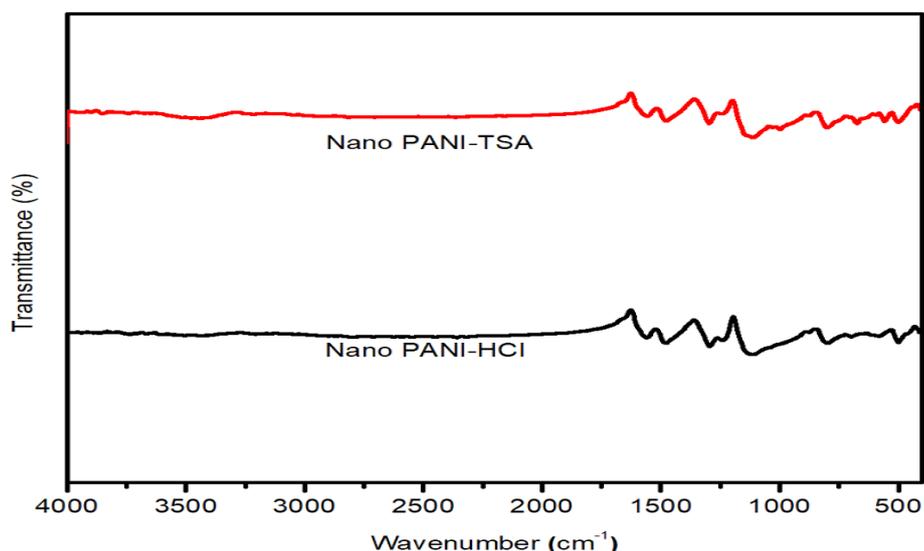


Fig. 3 FTIR Spectrum of Nano-structured PANI-HCl and Nano-structured PANI-TSA

The FTIR bands of nano PANI-HCl and nano PANI-TSA are presented in Figure 3. The respective bands at 1560cm^{-1} and 1557cm^{-1} for the PANI doped HCl and 1480cm^{-1} and 1477cm^{-1} for the PANI doped with TSA are attributed to the C=C stretching of quinoid and benzenoid rings indicating the oxidation state of emeraldine salt PANI [10-13]. The characteristic peaks at 1293cm^{-1} and 1296cm^{-1} , and 1240cm^{-1} and 1233cm^{-1} for PANI-HCl and nano PANI-TSA respectively are attributed to the bending vibration of C-N for aromatic amines/imines and C-N⁺ stretching vibrations in the polaronic structures due to divergent conformation or charge structure signifying the presence of protonated conducting PANI prompted by acid doping of the polymer [6, 14, 15, 16]. The strong bands at around 1111cm^{-1} are assigned to vibration mode of C-H in-plane bending vibration is considered to be the extent of the degree of delocalization of electrons and hence the characterized peak of PANI [11]. The observed bands at 769cm^{-1} and 878cm^{-1} , nano PANI-HCl and 697cm^{-1} and 800cm^{-1} for nano PANI-TSA respectively can be assigned to the aromatic ring out-of-plane deformation vibration bending of C-H bond in the benzene ring and para-distributed aromatic rings indicating polymer formation [14]. Out of plane bending deformation of C-H is observed at 506cm^{-1} and 500cm^{-1} . The peak at 997cm^{-1} in nano PANI-TSA can be assigned to SO_3^- group of the dopant TSA bound to the aromatic rings [12, 13]. The weak and broad signal observed at 3448cm^{-1} in nano PANI-TSA also is assigned to N-H bond stretching indicating the presence of a secondary amine. This peak is broad and weak such that it is not visible in the nano PANI-HCl spectrum.

3.2 X-Ray Diffractometry (XRD)

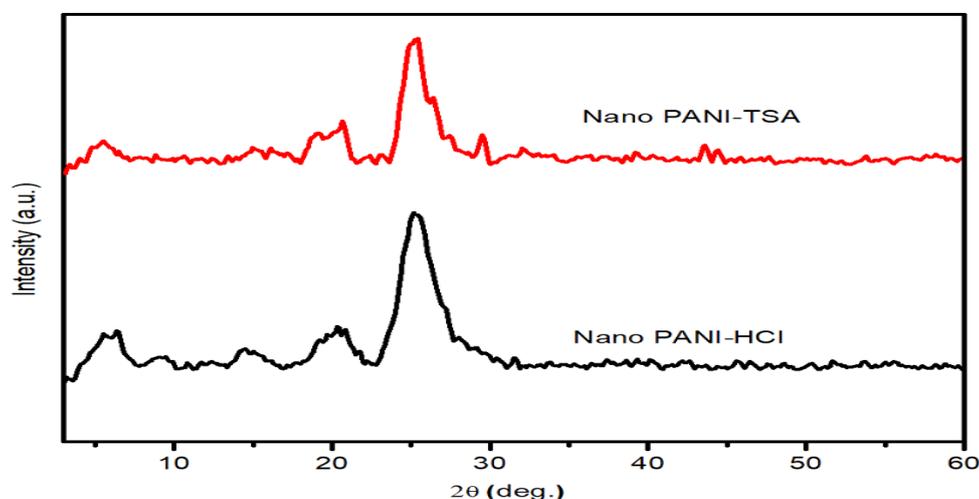


Fig. 4 XRD Pattern of Nano-structured PANI-HCl and Nano-structured PANI-TSA

Figure 4 shows the XRD pattern of nano PANI-HCl and nano PANI-TSA. The diffraction pattern of nano PANI-HCl are obtained at $2\theta = 6^\circ$, 25° and 31° . The peaks give evidence for the partially crystalline nature of HCl doped PANI with conducting metallic islands separated by large amorphous regions. The diffraction pattern of the para-toluene sulphonic acid (TSA) doped nano PANI with sharp peaks at $2\theta = 20^\circ$, 25° , 28° , 43° and 44° also indicate the partial crystallinity of the sample. The sharp peak

at $2\theta = 29^\circ$ is a characteristic peak indicating the inflexibility and regular nature of some portion of the PANI sub chains due to interchain packing between poly-cation and TSA anion [5, 10, 17, 18, 19]. The sharp peak at $2\theta = 25^\circ$ obtained for the two PANI samples is a characteristic peak of PANI showing the extent of π conjugation in the polyaniline. The sharpness of the peak reveals the degree of order of π conjugation.

3.3 UV-Visible spectroscopy (UV-Vis)

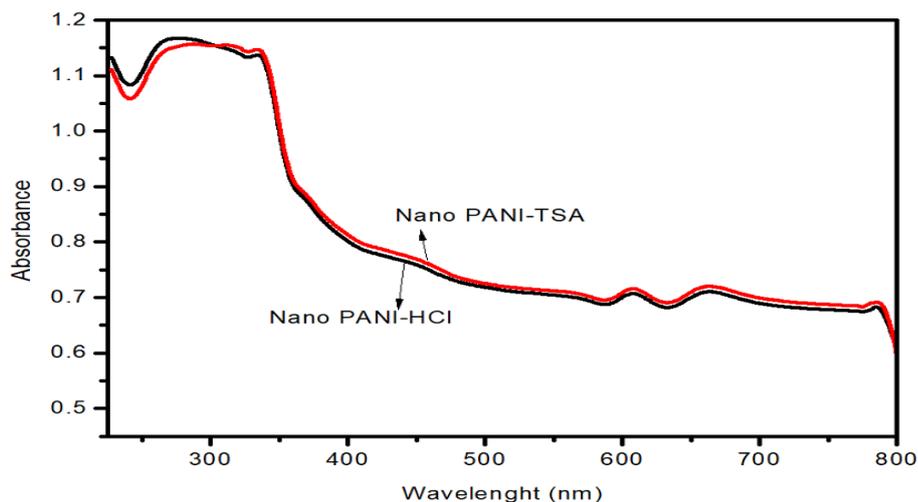


Fig. 5 UV-Visible Spectra of Nano-structured PANI-HCl and Nano-structured PANI-TSA

The possibility of absorption of electrons by conducting polymers is a useful tool in investigating the oxidation and doping state of polymers. The UV-Visible spectra of nano PANI-HCl and nano PANI-TSA are shown in Figure 5. Two absorption bands at 277–288 nm and 608–663 nm are obtained for both the samples. The band at 277–288 nm in the nano PANI-HCl and nano PANI-TSA spectra are due to π - π^* transitions in the benzenoid rings of the polymer backbone. The band at 608–663 nm is due to exciton absorption of quinoid rings due to n - π^* transition in the inter-band charge transfer associated with excitation of benzoid (HOMO) to quinoid (LUMO) moieties. The small shoulder-like band at 335 nm is attributable to the formation of polaronic/bipolaronic transitions resulting in protonation of the polymer indicating that the resulting PANI samples are in the doped state [5, 14, 15, 16]. The continuous absorption peak at 780–790 nm shows free carrier tail, confirming the presence of conducting emeraldine salt phase of the polymer [20]. The slight difference in the absorption bands observed in the two PANI samples might be due to the molecular interaction of the dopants with imine nitrogen of PANI [35] resulting in the slight shift in absorption values. The PANI with somewhat larger particles as seen in SEM micrograph may induce more specular reflection, hence lower absorption and blue shift. This could likewise influence the conductivity of the samples.

3.4 Thermogravimetric analysis (TGA) of Polyaniline

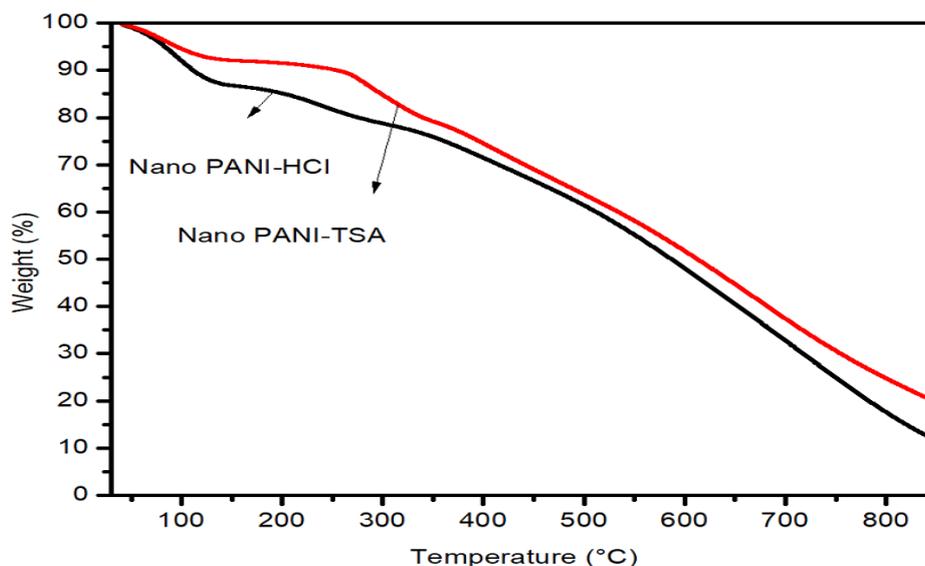


Fig. 6 TGA thermogram of Nano-structured PANI-HCl and Nano-structured PANI-TSA

Figure 6 shows the TGA thermogram of nano PANI-HCl and nano PANI-TSA. In the first step, approximately 10% and 6% weight loss respectively at the temperature up to 105°C can be seen in the thermogram of nano PANI-HCl and nano PANI-TSA respectively. This is attributable to the loss of water molecules, unreacted organic monomers and the free acid trapped in the

PANI structure [11, 19, 21]. The second weight loss of about 14% and 9% at temperature in the region of 220°C may be due to the evaporation of dopant acids in PANI samples while the third step of weight loss was marked out at between 500°C and 800°C with 38% and 36% weight loss and residues respectively for PANI doped HCl and 18% and 25% weight loss and residues respectively for PANI doped TSA. This probably represents the oxidative degradation of the PANI samples which could be an indication of chemical structure decomposition causing possible chain scission [22]. The thermal stability of PANI is highly dependent on the dopant acid anion attached to the backbone of the polymer. PANI doped with TSA (organic dopant) is more stable than the PANI doped with HCl (inorganic dopant)

3.6 Differential Scanning Calorimetry (DSC)

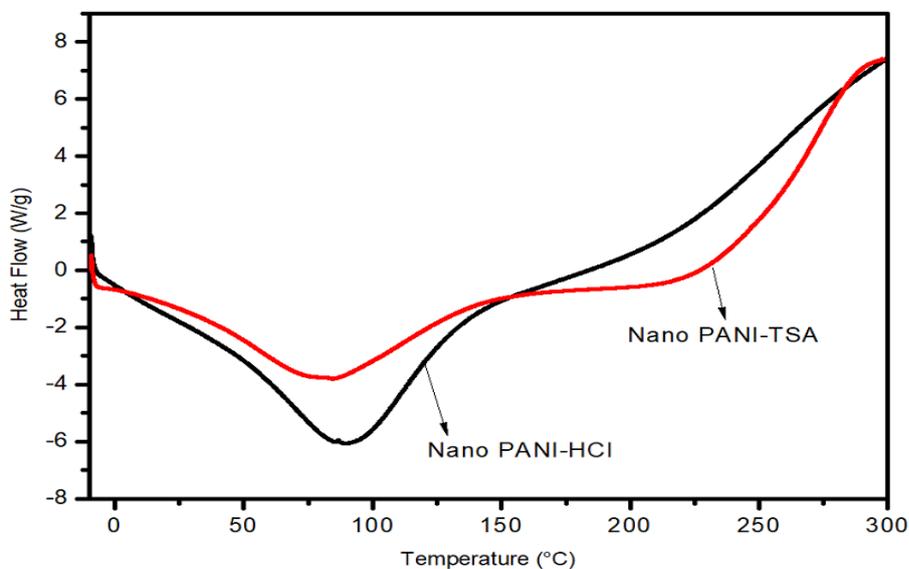


Fig. 7 DSC thermogram of Nano-structured PANI-HCl and Nano-structured PANI-TSA

Differential Scanning Calorimetry (DSC) thermogram of the nano PANI doped HCl shows an endothermic peak in the range 20-136 °C while the nano-structured PANI shows a peak in the range 30-140 °C. These peaks may be attributed to the evaporation of water, loss of HCl and low molecular weight polyaniline material. The peaks displayed in the range 150-265 °C and 155-285 °C for nano PANI-HCl and nano PANI-TSA respectively may be associated with the cross-linking reaction [23-26]. The crosslinking reaction results from a coupling of two neighboring $-N=Q=N-$ groups (where Q represents the quinoid ring), to give two amine $-NH-B-NH-$ groups (where B represents the benzenoid ring) through a link of the N with its neighboring quinoid ring in the PANI structure. The resistance of these links to scission with increase in temperature influences the thermal stability of the PANI. This result is closely related to the TGA result in Figure 6.

3.7 Electrical Conductivity Measurements

The electrical conductivity of pelletized nano PANI-HCl and nano PANI-TSA are found to be 0.478 and 0.824 S/cm⁻¹ respectively. PANI doped with TSA shows the highest conductivity. This is possibly due to the molecular composition of TSA which could have helped to stabilize the bond linking the dopant TSA and the polymer resulting from strong intermolecular interaction between aniline and counteranion molecules through the benzene ring of the dopant anion when TSA is incorporated [27, 28]. This will facilitate the formation of a resonating structure thereby activating electron flow in the form of polaron over the whole structure of the polymer chain. Also, the sulfur content of the TSA dopant anions may have contributed to the molecular interactions resulting in higher conductivity [29].

4.0 Conclusion

PANI in nano dimensions could be prepared through chemical oxidative polymerization of aniline using HCl or TSA as dopants. The SEM and TEM studies show that the PANI materials are in nano dimension. From the TGA data, nano-structured PANI doped with TSA possess relatively better thermal stability compared to the one doped with HCl. Higher conductivity was obtained for PANI-TSA.

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