

Bulk and nano-structured polyaniline: synthesis, characterization, thermal behaviour and dc conductivity

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Abstract- This study reports the synthesis of conducting polyaniline (PANI) in presence of aqueous hydrochloric acid (HCl) as doping agent and ammonium persulfate (APS) as oxidizing agent by chemical oxidative polymerization at room temperature. Different recipes have been used to tailor the particle sizes in both bulk and nano dimensions. Scanning electron microscopy (SEM) was used to characterize the morphology of the PANI. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy and UV-Vis spectroscopy were used to characterize the synthesized PANI. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to measure the thermal behaviour of the samples. FTIR analysis revealed the formation of PANI and the change in polymer structure due to the change in polymerization recipe. This was confirmed by SEM. Results of TGA indicates that bulk PANI-HCl and nano-structured PANI-HCl exhibited similar weight loss pattern while nano-structured PANI-HCl exhibited slightly lower weight loss below the decomposition temperature. The measured electrical conductivity of the two PANI samples at room temperature show that nano-structured PANI-HCl displayed much higher conductivity (0.478 S/cm^{-1}) than bulk PANI-HCl (0.127 S/cm^{-1}).

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

1. INTRODUCTION

Polymers were originally considered to be electrically pure insulating materials until Shirakawa et al. in 1977 [1] discovered a significant electrical conductivity in polyacetylene (PA) after its oxidation in the presence of iodine vapour. Conducting polymers are organic polymers that conduct electricity. They possess electrical properties like that of metals (metallic conductivity) and semiconductors. They display several other characteristics of organic polymers such as lightweight, lower cost, resistance to corrosion and chemical attack, flexibility and greater workability [2-6]. Electrical conductivity of conducting polymers can be tuned from insulating to metallic through adequate doping process or from bulk to nano-structures. They have a conjugated structure with alternate σ and π bonds, which is delocalized throughout the entire polymer network, resulting in an enhanced electrical conductivity [5, 6]. The conductivity of almost all conjugated polymers can reach up to the order of 10^{-3} – 10^3 S/cm after doping [2, 7]. They are widely used in many electrical/electronic devices and for a myriad of applications. Among different conducting polymers, polyaniline (PANI) is the most versatile polymer owing to its low cost and desirable properties such as low

specific mass, thermal/chemical stability and high conductivity [8]. Polyaniline occurs in 3 different states namely leucoemeraldine base (LEB) - which is the fully reduced state, pernigraniline base (PNB) - which is the fully oxidized form and emeraldine base (EB) - which is the partially oxidized form. Emeraldine salt (ES) occurs as a doped (protonated) form of emeraldine base (EB) and it is the only one that is electrically conducting [6]. It is desirable to make a distinction between the properties of bulk and nano-structured PANI. This work describes the preparation of PANI in bulk and in nano dimensions through chemical oxidative polymerization of aniline using HCl as dopant and APS as oxidant. The prepared bulk and nano sized PANI were characterized and its thermal and electrical properties were studied.

2. MATERIALS AND METHODS

2.1 Materials

Chemicals and solvents: Ammonium persulphate (APS) and aniline obtained from Sigma Aldrich Chemical Company were of very high purity (99.9%). Hydrochloric acid (HCl) 98%, and acetone were obtained from Spectrochem Pvt. Ltd, Mumbai, India. Aniline was distilled before use. All other materials were used without any pre-processing.

2.2 Methods

2.2.1 Synthesis of polyaniline (PANI)

Polyaniline was prepared by chemical oxidative polymerization of aniline monomer in the presence of 1 M HCl as dopant using ammonium persulfate as redox initiator at room temperature for 12 hrs with constant stirring. The polymer formed was washed with distilled water, dilute HCl solution and finally with acetone to remove excess HCl, oxidant, aniline and oligomers until the filtrate becomes colourless. 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 bulk PANI-HCl.

Polyaniline was also prepared in nano dimension by polymerizing 0.2g 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.

2.2.2 Characterizations

The morphology of the samples was examined by JEOL Model JSM - 6390LV SEM. 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. Thermo gravimetric analysis (TGA) was performed on a Perkin Elmer STA 6000 thermogravimetric analyzer to determine decomposition and transition temperatures and thermal stabilities of the samples. 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 glass transition and melting behavior of the samples. The electrical properties of the PANI samples were measured by four probe technique (D.C conductivity) using sensitive digital electrometer type Keithley Agilent 616.

3. RESULTS AND DISCUSSIONS

3.1 Scanning Electron Microscopy (SEM).

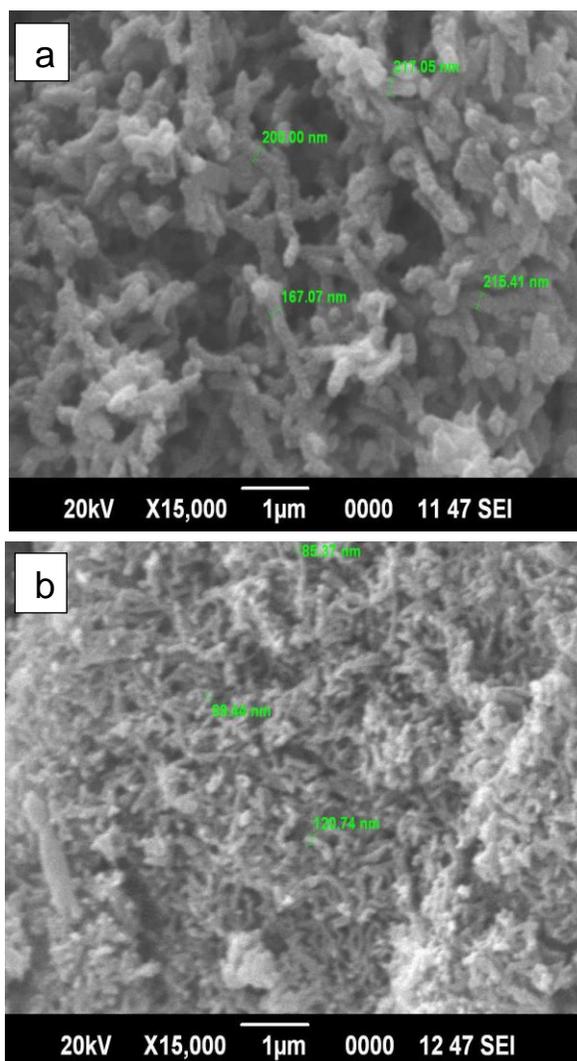


Fig. 1 SEM micrographs of PANI: (a) Bulk PANI-HCl and (b) Nano-structured PANI-HCl

Figures 1a and 1b show the SEM micrographs of bulk PANI-HCl and nano-structured PANI-HCl respectively. The micrographs reveal the irregular granular morphology of the synthesized polyaniline. Bulk PANI-HCl has a porous structure with particle size of 217 nm. The micrographs of nano-structured PANI-HCl reveal that the synthesized polyaniline comes under nanodimension of an average particle size of 85 nm with more compact and oriented structure.

3.2 Fourier Transform Infrared (FTIR) Spectroscopy

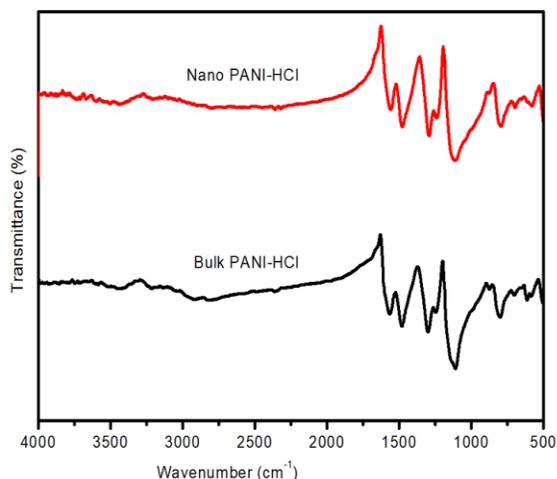


Fig. 2 FTIR Spectra of Bulk PANI-HCl and Nano-structured PANI-HCl.

The FTIR spectra of PANI (bulk PANI-HCl and nano-structured PANI-HCl) is presented in Figure 2. The respective bands at 1566 cm^{-1} and 1482 cm^{-1} observed in bulk PANI-HCl and 1560 cm^{-1} and 1480 cm^{-1} observed in the case of nano-structured PANI-HCl are attributed to the C=C stretching of quinoid (Q) and benzenoid (B) rings indicating the oxidation state of emeraldine salt of PANI [9-12]. The peaks at 1301 cm^{-1} and 1245 cm^{-1} for bulk PANI and 1293 cm^{-1} and 1240 cm^{-1} for nano PANI are attributed to the bending vibration of C-N for aromatic amines/imines and C-N stretching vibrations in the polaronic structures (displacement of π electrons) owing to differing conformation or charge configuration suggesting the presence of protonated conducting PANI induced by acid doping of the polymer [6, 13, 14]. The strong bands at around 1111 cm^{-1} are assigned to C-H in plain bending and vibration mode of -NH associated with the charged polymer units $\text{Q}=\text{NH}^+-\text{B}$ or $\text{B}-\text{NH}^+-\text{B}$, thus indicating the existence of positive charges on the chain of quinonoid and benzenoid rings. This is considered to be the extent of the degree of delocalization of electrons and thus it is the characterized peak of doped PANI [15, 16, 17]. The observed band at 878 cm^{-1} , 769 cm^{-1} and 801 cm^{-1} , 697 cm^{-1} 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 506 cm^{-1} and 500 cm^{-1} [11, 12].

3.3 X-Ray Diffractometry (XRD)

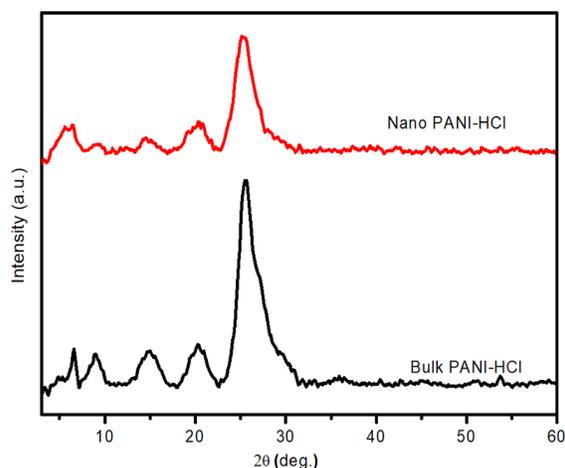


Fig. 3 XRD Pattern of Bulk PANI-HCl and Nano-structured PANI-HCl.

Figure 3 shows the XRD pattern of bulk PANI-HCl and nano-structured PANI-HCl. The diffraction pattern of bulk PANI-HCl showed medium sharp peaks at $2\theta = 6^\circ$ and 25° while for nano-structured PANI-HCl the peaks were 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. This is more obvious in the bulk PANI-HCl. The sharp peak at $2\theta = 25^\circ$ obtained for both PANI samples is the characteristic peak of PANI indicating the extent of π conjugation in the polyaniline and sharpness of the peak reveals the degree of order of π conjugation.

3.4 UV-Visible spectroscopy (UV-Vis)

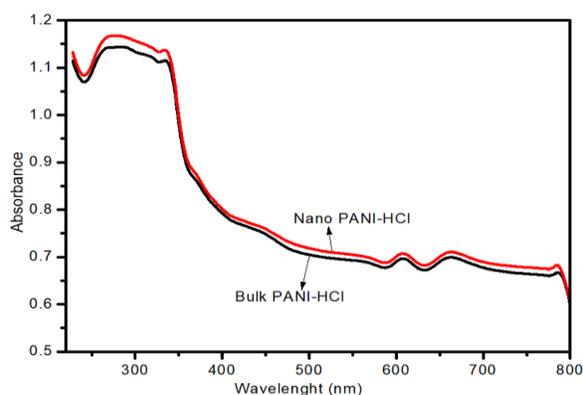


Fig. 4 UV-Visible Spectra of Bulk PANI-HCl and Nano-structured PANI-HCl.

Electronic absorption of conducting polymers is a useful tool in investigating the oxidation and doping state of the polymer. The UV-Visible spectra of PANI (bulk PANI-HCl and nano-structured PANI-HCl) are shown in Figure 4. Two absorption bands at 277–288 nm and 608–663 nm were obtained for both samples. The band at 277–288 nm is due to π - π^* transitions in the benzenoid rings of polymer backbone while the band at 608–663 nm is due to exciton absorption of quinoid rings (n - π^*) (inter-band charge transfer associated with excitation of benzoid (HOMO) to quinoid (LUMO)) moieties). A small shoulder-like band at 335 nm is attributable to the formation of polaronic/bipolaronic transitions resulting in the protonation of the polymer indicating that the resulting PANI are in the doped state [18-26]. The continuous absorption peak at 780-790 nm shows free carrier tail, confirming the presence of conducting emeraldine salt phase of the polymer [12, 13, 14, 20, 24]. The slight difference in the absorption bands observed for the two PANI samples might be due to the difference in dimension of the particles resulting to the slight shift in absorption values. The bulk PANI with comparatively larger particles as seen in SEM micrograph may induce more specular reflection, hence lower absorption and vice versa. This could also influence the conductivity of the samples.

3.5 Thermogravimetric analysis (TGA) of Polyaniline

The thermogravimetric analysis (TGA) of PANI (bulk PANI-HCl and nano-structured PANI-HCl) was conducted to ascertain their thermal stability. The results are presented in Figure 5.

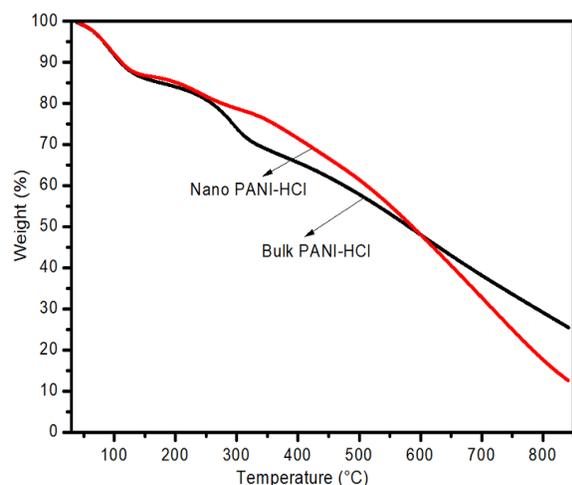


Fig. 5 TGA thermogram of Bulk PANI-HCl and Nano-structured PANI-HCl.

Figure 5 shows the TGA thermogram of PANI (bulk PANI-HCl and nano-structured PANI-HCl). Both the samples exhibited approximately 10% weight loss respectively at the temperature up to 105 °C as evident in the thermogram. This is attributable to loss of water molecules and unreacted organic monomers [10, 20, 27] from the PANI structure. The second weight loss of about 17% and 14% of total weight at temperature in the region of 220°C may be due to evaporation of dopant acids in PANI samples. The third step of weight loss was marked out at between 500°C and 800°C with 42% and 29% weight loss and residues of total weight respectively for bulk PANI-HCl and 38% and 18% for nano-structured PANI-HCl. This possibly represents the oxidative degradation of the PANIs which could be an indication of chemical structure decomposition and the release of organic moieties like C, H and N [28, 29]. The thermal behaviour of both PANI samples are not much different from each other as observed in the thermograms. However, the difference observed in the first two steps may be due to particle dimensional difference affecting the crystallinity of the polymer thereby influencing the thermal stability.

3.6 Differential Scanning Calorimetry (DSC)

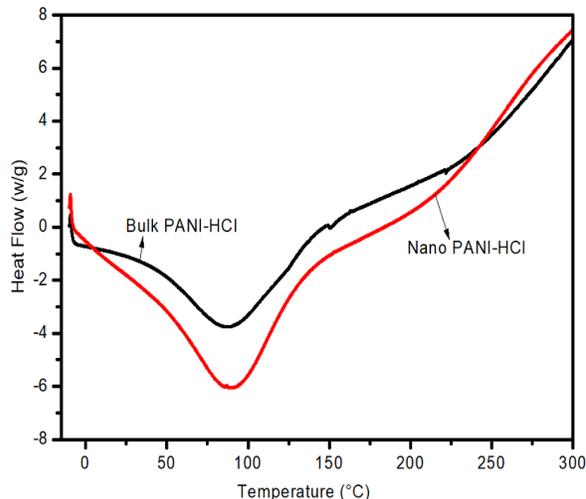


Fig. 6 DSC thermogram of Bulk PANI-HCl and Nano-structured PANI-HCl.

Figure 6 shows the DSC thermogram of PANI (bulk PANI-HCl and nano-structured PANI-HCl). Differential Scanning Calorimetry (DSC) thermogram of the bulk PANI shows an endothermic peak in the range 40-140 °C while the nano-structured PANI shows a peak in the range 20-136 °C. These peaks may be attributed to the evaporation of water, loss of HCl and low molecular weight polyaniline material. The second endothermic

peaks displayed in the range 150-300 °C and 150-280 °C respectively may be related to the cross-linking reaction [30-34] though not very sharp because no obvious moisture is present in the samples at this temperature. 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 [35]. The resistance of these links to scission with increase in temperature influences the thermal stability of the PANI.

3.7 DC Conductivity

The conductivity values of the pelletized bulk PANI-HCl and nano-structured PANI-HCl as detected by the four-probe method are 0.127 and 0.478 S/cm-1 respectively. In the nano-structured PANI-HCl the smaller particle size can pave way for stronger interfacial interactions between aniline monomer and counteranion molecules of the doping acid [36, 37]. This can change the molecular conformation of PANI from amorphous to crystalline conformation and may tend to promote linear conformation necessary for crystallization. As a result, there may be an amplification in the conductivity of nano-structured PANI-HCl. Increasing the crystallinity of polymer can increase the bulk conductivity since the conductivity of conducting polymers depends on their morphology, type of monomer, extent of conjugation, doping level and degree of crystallinity [33].

4. CONCLUSIONS

Conducting PANI in nano dimensions could be prepared through chemical oxidative polymerization of aniline using HCl as dopant by tuning the recipe of aniline polymerization. FTIR analysis revealed the formation of PANI and the change in polymer structure (bulk to nano) due to the change in the polymerization recipe. This was further confirmed by the result of SEM studies. Higher dc conductivity was obtained for the nano-structured PANI and it is relatively thermally more stable compared to the bulk PANI. This is due to stronger interfacial interactions between PANI molecules as a result of change in molecular conformation from compact structure to an expanded structure.

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