Surface Morphology Studies and Thermal analysis of V_2O_5 doped polyaniline composites

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Abstract

In situ polymerization of aniline was carried out in the presence of V_2O_5 to synthesize polyaniline / V_2O_5 composites. The XRD patterns of the PANI-V_2O_5 composite do not show sharp peaks characteristic of crystalline materials and suggest generally an amorphous nature to all the PANI- V_2O_5 composite samples. From the FTIR studies on polyaniline/ V_2O_5 composites indicates the peak at 1122 cm^{-1} is considered to be measure of the degree of electron delocalization, 1487 cm^{-1} is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration. The surface morphology of these composites was studied with SEM. The dc conductivity has been studied in the temperature range from 40–180^{0}C and supports the one-dimensional variable range hopping (1DVRH) model proposed by Mott. The TGA-DSC curves indicates that the stability of the composites increase with increase in V_2O_5 percentage in polyaniline. The results obtained for these composites are of scientific and technological interest.

Key words: Polyaniline; Vanadium pentaoxide; Composites; Scanning electron microscopy, DSC-TGA analysis

I. Introduction

The composites of metal–polymer or metal oxide– polymer are expected to be an important class of materials in the area of nanotechnology. Recently, conductive polymer-inorganic nanocomposites with different combinations of the two components had received more and more attention, because they have interesting physical properties and many potential applications in various areas [1]. V_2O_5 is a typical n-type semiconductor as well as an important electronic and photonic material with many potential applications such as field effect transistors, ultra-sensitive nanosized gas sensors, resonators, cantilevers, UV detector, piezoelectronic materials, catalysts, hydrogen storage materials, chemical sensors, and biosensors [2-9].

Polyaniline is one of the typical conductive polymers which are usually considered as p-type material used in making lightweight battery electrode, electromagnetic shielding device, anticorrosion coatings, and sensors [10-14]. In the recent past the conducting polymer-based nanocomposite have drawn attention in their application as gas sensing application [15-19]. Therefore, PANI- V_2O_5 composites have been most intensively studied among various composites, because it could combine the merits of PANI and crystalline V_2O_5 within a single material, and are expected to find applications in electrochromic devices, sensor, nonlinear optical system, and photoelectrochemical devices. Ammonia is one of the important industrial exhaust gases with high toxicity. With the increasing of the human awareness of environmental problems in industrial gases, the requirement of detecting these gases has greatly increased. Composite based sensors have been demonstrated for the detection of LPG under ambient conditions [20-21].

In present work, attempts have been made to synthesize approximately uniform V_2O_5 particles and PANI- V_2O_5 composite. The characterization had been carried out by x-ray diffraction, fourier transform infrared spectroscopy and scanning electron microscopy, and the conductivity measurement by two probes.

II. Materials and Method

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ($(NH_4)_2S_2O_8$), Hydrochloric acid (HCl), and Vanadium pentaoxide (V_2O_5) were procured from sigma and were used as received.

III. Synthesis of Polyaniline

The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volumes of aniline and hydrochloric acid) was dissolved in distilled water in a volumetric flask to 100 mL of solution. Ammonium peroxydisulfate (0.25M) was dissolved in water also to 100 mL of solution. Both solutions were kept for 1 hour at room temperature

(25°C), then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 300-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in vacuum at 60°C to achieve the constant weight.

IV. Synthesis of Polyaniline / V_2O_5 Composites

0.1 mole aniline monomer is dissolved in 1 mole nitric acid to form polyaniline hydronitride. Fine graded pre-sintered V_2O_5 (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 5, 10, 15, 20 and 25 is added to the polymerization mixture with vigorous stirring in order to keep the V_2O_5 powder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 4 hrs at temperature 5^0C. Polymerization of aniline takes place over fine grade vanadium pentaoxide particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any uncreated aniline. After washing, the precipitate is dried under dynamic vacuum at 60^0C for 24 hrs to get resulting composites [22]. In this way five different polyaniline / V_2O_5 composites with different weight percentage of vanadium pentaoxide (5, 10, 15, 20 and 25) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

V. Preparation of Pellets

The powders of polyaniline and polyaniline – V_2O_5 composites so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press. The pellets of polyaniline and its composites so obtained from above mentioned techniques are coated with silver paste on either side of the surfaces to obtain better contacts.

VI. Characterization

X-ray diffraction studies were performed by using Philips X-ray diffractometer with CuKα□ as the radiation source. The morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope. The FTIR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, powders are mixed with KBr in the ratio 1:25 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness. Temperature dependent electrical conductivity was measured by two probe technique using laboratory made setup.

Thermal studies (TG/ DSC measurements) were performed on Linseis STA PT-1600 (Germany) Thermal analyzer.10mg of completely dried sample is taken in a clean alumina crucible and heated up to 50^oC - 700 ^{o}C in the nitrogen atmosphere at the rate of 10^o C/min.

VII. Results and discussion

X-rays diffraction

Figure 1(a) Shows X-ray diffraction pattern of Polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has amorphous nature with a broad peak centered on $2\theta \approx 26.40^0$.

VIII. Vanadium pentaoxide and Polyaniline / V_2O_5 composites

The pure V_2O_5 diffraction pattern (figure 1(b)) was indexed for orthorhombic crystal symmetry. The X-ray diffraction analysis is also a powerful tool to determine the structure and crystallization of polymer matrices. The effect of V_2O_5 addition in the PANI and its composites were analyzed through the same XRD technique. The respective diffraction patterns of pure V_2O_5, PANI and its composite blends with different V_2O_5/monomer weight ratio and PAni-V_2O_5 composite weight fractions are shown in Figures 1(c). Just like the regular rigid polymers that own lots of benzene rings, the XRD pattern of PANI obtained is very similar to previous reports where the orientation of the polymer has been taken on the basis of a pseudo orthorhombic cell. As reported in most literature, most of the forms of PANI essentially amorphous and show the presence of broad high-angle asymmetric scattering peak stretching from 2θ between 15 – 25^o. The main peak of the synthesized PANI itself seems to be comprised with one broad peak situated at approximately 25.24^o, corresponding to d-spacing of 3.5256 Å, indicate a low degree of crystallinity of the polymer and consistent with those reported by D. Djurado et al. and M. Laridjani et al. The pure V_2O_5 reveals peaks at 2θ = 20.39, 26.21. 31.09, 34.41, which corresponding to d = 4.35 Å, 3.39 Å, 2.87 Å and 2.60, respectively. Nevertheless, it is noted that these peaks become broader and the intensity is reduced in the composites, possibly owing to the low V_2O_5 content in PANI composite and the amorphous nature of PANI. For PANI-V_2O_5 the peaks corresponding to V_2O_5 disappears which are attributed to the disorder ness in the composites.

The XRD patterns of the PANI-V_2O_5 composite do not show sharp peaks characteristic of crystalline materials and suggest generally an amorphous nature to all the PANI- V_2O_5 composite samples.

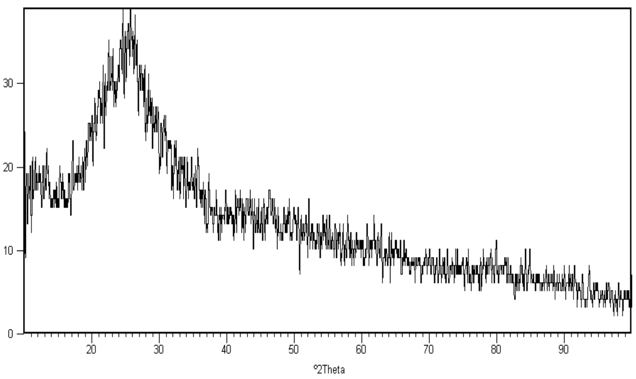


Figure 1(a) X-ray diffraction pattern of polyaniline

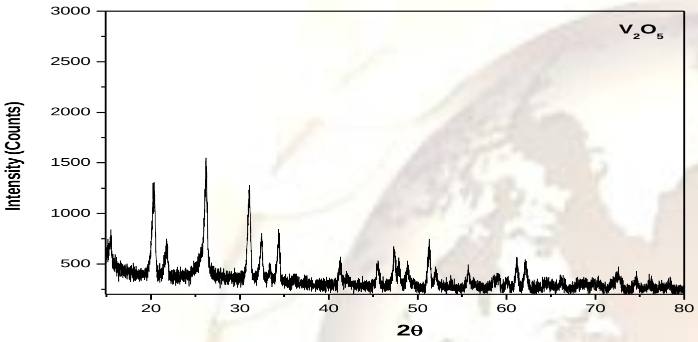


Figure 1(b) X-ray diffraction pattern of V_2O_5 composite

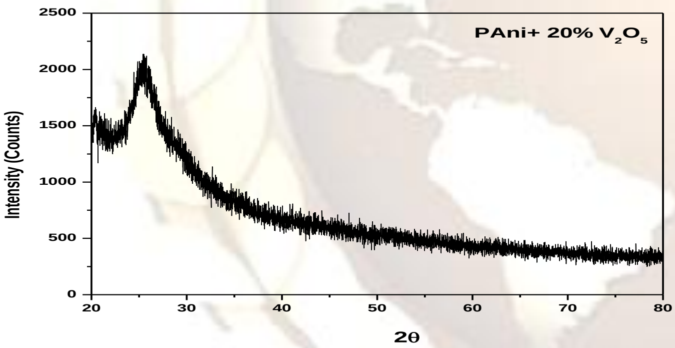


Figure 1(c) X-ray diffraction pattern of Polyaniline – V_2O_5 composite

IX. FTIR Spectroscopy

Figure 2(a) shows FTIR spectra of pure polyaniline. The characteristic vibration of polyaniline is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of PANI shows vibrations around 499, 592, 617, 814, 1024, 1122, 1240,1300, 1487, 1556, 2860, 2924, 3447cm^{-1}. The band at 499 is stretching out of plane, 592 corresponds to aromatic ring, 617 is for metal oxygen stretching, 814 is plane bonding of C-H bonding aromatic ring, 1024 is S-O vibration, 1122 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1303 is C-N aromatic amines, 1487 is C=C stretching of benzonoid ring, 2860 and 2924 are C-H stretching, 3447 is N-H stretching vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline.

Figure 2(b) shows FTIR spectra of 5 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline/V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 509, 580, 698, 808, 879, 1140, 1238, 1304, 1485, 1558, 2922cm^{-1}. The band at 509, 580, 698 are metal oxygen stretching, 808 corresponds to plane bonding of C-H bond aromatic ring, 879 is C-H bond, 1140 is C-O-C stretching excess oxidant, 1238 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1485 is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration, 2922 is C-H stretching. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 2(c) shows FTIR spectra of 15 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 507, 594, 700, 804, 871, 1140, 1240, 1304, 1475, 1558cm^{-1}. The band at 507, 594, 700 are metal oxygen stretching, 804 corresponds to plane bonding of C-H bond aromatic ring, 871 is C-H bond, 1140 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1475 is C=C stretching of benzonoid ring , 1558 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

Figure 2(d) shows FTIR spectra of 25 wt% polyaniline/V_2O_5 composite. The characteristic vibration of polyaniline /V_2O_5 composite is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of the composite show vibrations around 507, 590, 704, 806, 875, 1134, 1240, 1304, 1479, 1556cm^{-1}. The band at 507, 590, 704 are metal oxygen stretching, 806 corresponds to plane bonding of C-H bond aromatic ring, 875 is C-H bond, 1134 is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1304 is C-N aromatic amines, 1479 is C=C stretching of benzonoid ring , 1556 is C=N quinonoid stretching mode of vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline/ V_2O_5 composite.

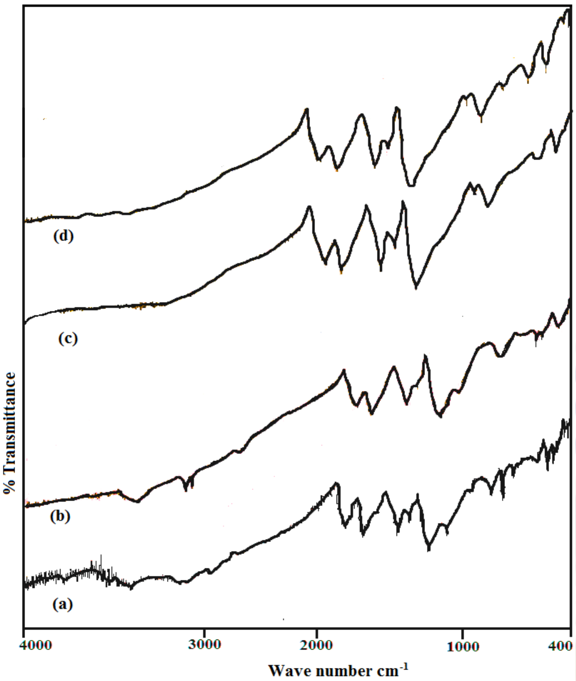


Figure 2(a-d) shows the FTIR spectra of PANI/V_2O_5 composites of different weight percentage.

Scanning Electron Microscopy (SEM)

Figure 3(a) shows that Scanning Electronic Micrograph (SEM) image of pure polyaniline. Highly agglomerated granular in shape and has amorphous nature. The average grain size was found to be 2 to 4µm. The grains are well interconnected with each other which indicate that they have enough binding energy to combine with neighbor grains or molecules.

The SEM image of 10 wt % of PANI/ V_2O_5 composites shown in figure 3(b). The grains are highly agglomerated, irregular in shape but they are well interconnected each others. The average grain size was found to be 0.22µm.

Figure 3(c) shows the SEM image of 20 wt % of PANI/ V_2O_5 composites. The grains are irregular in structure, some of them are elongate and some are spherical in shape. The particles are individual and are separated with each other. The average grain size was found to be 0.37µm.

The SEM image of 30 wt % of PANI/ V_2O_5 composites shown in figure 3(d). It is observed from the image that all grains are irregular in structure arranged one above the others. The average grain size was found to be 0.43µm.

Figure 3(f) shows the SEM image of 40 wt % of PANI/ V_2O_5 composites prepared at room temperature. It is seen from the image the grains are clustered, have low porosity. The average grain size was found to be 0.47µm.

Figure shows the SEM image of 50 wt % of PANI/V_2O_5 composites prepared at room temperature. It is found that from the image the grains are high agglomerated, have porosity and good interconnectivity between the particles. The average grain size was found to be 0.53µm.

By comparing the figure (a-f), it can be conclude that the gradual increase in granular size and change in morphology helps the transportation of charge particles through the carbon back-bone of polymer chains [23].

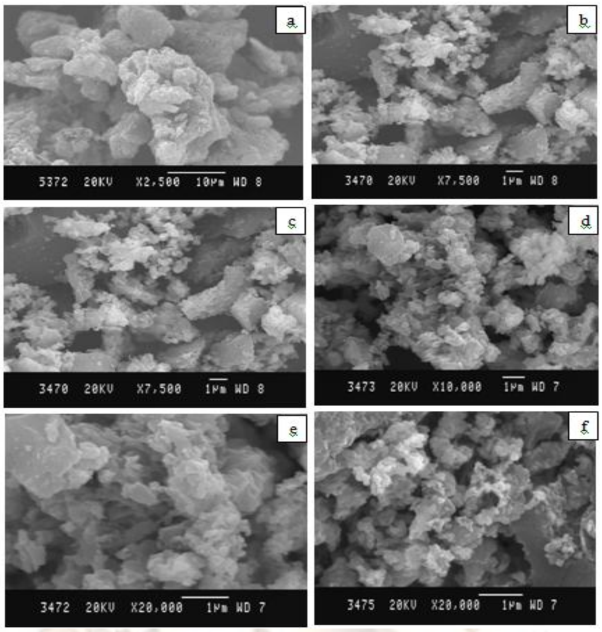


Figure 3 (a-f) show the SEM image of PANI and PANI/V_2O_5 composites of different weight percentage (5, 10, 15, 20 and 25 wt %)

DC conductivity studies

Polyaniline

Figure 4 shows the variation of dc conductivity as a function of temperature for polyaniline. The conductivity increases with increase in temperature. The dc conductivity of polyaniline exhibit three phases in a temperature range 40 ^{0}C to 200^{0}C. In temperatures between 40 – 100 ^{0}C, the conductivity values are almost constant and increases suddenly in the temperature range 100 – 180 ^{0}C. In stage III, between temperatures 180 – 200 ^{0}C, a linear increment in the conductivity values is observed.

Polymers can exist in different states depending upon the temperature. At low temperature they are hard, glassy materials. At a temperature referred as glass transition temperature T_g, they undergo transition to rubber like state.

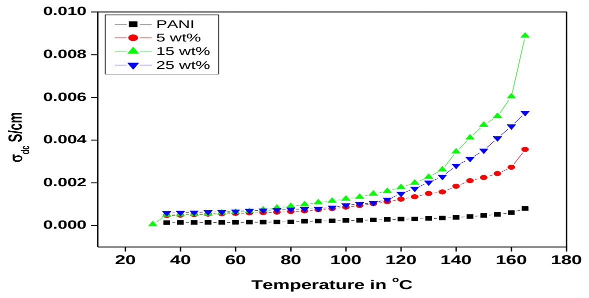
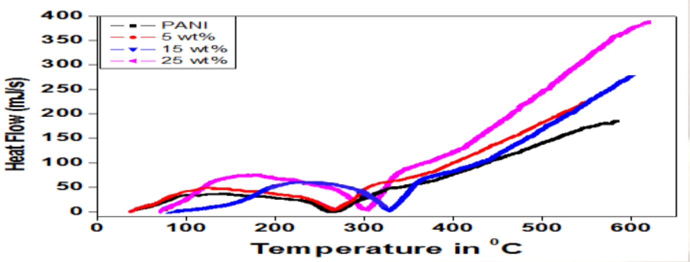


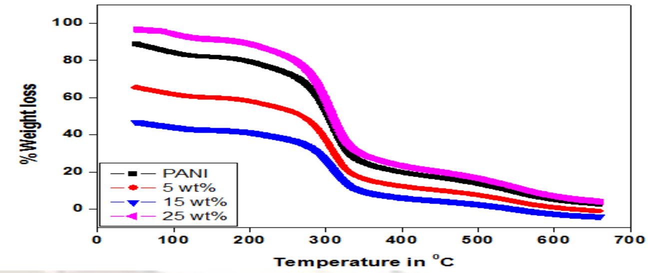
Figure 4 shows the □$_{dc}$ conductivity of PANI and PANI/ V_2O_5 composites as function of temperature of various weight percentages.

From X-ray diffraction pattern and SEM micrograph of polyaniline employed in the present investigation shows semi crystalline behavior. Under such conditions a uniform crystallite is surrounded by amorphous regions. The crystalline contains some defects but by and large has a regular array of molecules. The localized states that forms extended band like structures may act in trapping the carriers from extended states of crystalline region. Lattice polarization around a charge in localized state may be responsible for multiple phases of conductivity in polyaniline.

Among all the composites 15wt. % of PANI/ V_2O_5 shows high conductivity followed by pure PANI, 10 and 25 wt. % of PANI/ V_2O_5 composites and is within percolation limit. It is suggested that the thermal curling effects of the chain alignment of the polymer, leads to the increase in conjugation length and that brings about the increase of conductivity. Also, there will be molecular rearrangement on heating, which make the molecules favorable for electron delocalization [24].



From figure 5(a) it is found that an offset decomposition temperatures of composites were higher than that of pure PANI and shifted towards the higher temperature range as the content of nanostructured V_2O_5 increased whereas the onset value decreases because the small particles changes the rate of reaction and hence the shape of the TG curves also altered. The decomposition starts much earlier and comparatively low temperature of PANI with the samples having nanostructure titanium dioxide. This behavior confirmed the increased thermal stability of composites, as the content of nanostructured V_2O_5 increased that could be attributed to the retardation effect of V_2O_5 as barriers for the degradation of PANI [25-27]. From the graph it is found that the onset temperature is 238.9^{0}C and at the offset point at 344.7^{0}C. The result agrees with the moisture evaporation, which are trapped inside the polymer or bound to the polymer backbone, as evidenced by the first degradation stage of TGA curve [28].



It can be observed from DSC curved (figure 5(b)) that the thermal decomposition of polyaniline and polyaniline/ V_2O_5 composites curve weight percentages shows a three-stage decomposition pattern. For pure polyaniline it shows a large weight loss, occurring below 650^{0}C and can be ascribed to the elimination of water, acetone and HCl. For pure polyaniline three mass losses could be detected in the temperature range of 50−650^{0}C. The first weight loss observed at 80 to 140^{0}C was essentially due to desorption of water absorbed on the doped polymer. The loss of 140 to 200^{0}C can be primarily related to the expulsion of the doped HCl from PANI. The main loss at 200 to 450^{0}C can be ascribed to thermal degradation of skeletal polyaniline chain structure. This curve also indicates that there is a sharp weight loss near 200^{0}C and continues until 650^{0}C, at which PANI almost completely decomposed. The total mass change of PANI at the temperature range from 50 to 660 ^{0}C is about 86.97%. The DSC curve peaks indicates the endothermic processes, where energy is required to break the bonds in the successive elimination of H_2O, CO and CO_2.

The same behavior is observed even for all weight percentage of polyaniline/ V_2O_5 composites. But 30 wt% of polyaniline/ V_2O_5 composites shows a less weight loss, occurring above 650^{0}C and can be ascribed to the elimination of organic moieties, water and HCl in the temperature range of 50−650^{0}C.

In DSC curve generally, the glass transition temperature (Tg) of PANI powders is not evident in the thermographs [29]. The exothermic transition observed at 179.3 - 266.1^{0}C is believed not to be Tg. Instead, it would be attributed to a series of chemical reactions. Basically, bond scissioning followed by a bond formation are involved when the powders are heated. The bond scissioning is endothermic, which is compensated by the generated heat by bond formation and shows an exothermic peak at around 150 - 300 ^{0}C. The decreased peak temperatures from 273 ^{0}C (pure PANI) to 179.7, 238.4, and 264.2^{0}C for the composites filled with a particle loading of 5, 15, and 25 wt%, respectively, further demonstrate the ordered polymer structure as well as a good interfacial interactions between the metal oxide and the polymer matrix.

X. Conclusion

Polyaniline composites with different weight percentages of V_2O_5 in PANI were synthesized by chemical oxidative polymerization of monomer aniline. Characterizations of the composites were carried out using FTIR and SEM techniques. From the FTIR studies on polyaniline/ V_2O_5 composites, the peak at 1122 cm^{-1} is considered to be measure of the degree of electron delocalization, 1487 cm^{-1} is C=C stretching of benzonoid ring, 1558 is C=N quinonoid stretching mode of vibration and its indicates there was the Vander walls interaction between polymer and vanadium pentaoxide. The results of dc conductivity show a strong dependence on the weight percent of V_2O_5 in polyaniline. At higher temperatures, conductivity ($\square_{dc}$) increases because of hopping of polarons from one localized states to another localized states. It is observed from the electrical conductivity studies that the 25 wt % of V_2O_5 in the polymer matrix shows the enhancement of the conductivity of the conducting polyaniline and their values are found to be in the semiconducting range. The TGA-DSC curves confirmed the increased thermal stability of composites, as the content of nanostructured V_2O_5 increased that could be attributed to the retardation effect of V_2O_5 as barriers for the degradation of polyaniline.

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