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Thermal, morphological and impedance behavior of Polydiphenylamine-Vanadium pentoxide nanocomposites

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ABSTRACT

PDPA-V_2O_5 nanocomposites containing PDPA and V_2O_5 nanoparticle were synthesized through chemical oxidation method using potassium periodate. The PDPA-V_2O_5 nanocomposites were characterized using UV-VIS, FTIR, XRD, SEM, TG/DTA and DSC studies. The incorporation of V_2O_5 nanoparticles in polydiphenylamine matrix was confirmed by FTIR results. The size of nanocomposites was estimated to be < 100nm from XRD studies. Good dispersion of V_2O_5 nanoparticles in the polydiphenylamine matrix was confirmed by SEM micrograph. Difference of oxidation peak potential (820 mV) and reduction peak potential (600mV) of polydiphenylamine and oxidation peak potential (425mV) and reduction peak potential (540 mV) of polydiphenylamine - Vanadium pentoxide nanocomposites were deduced by analysis of volatammogram. TG/DTA and DSC studies revealed good thermal stability of the polymer metal composites. Impedance spectroscopy showed that the capacitance of PDPA-V_2O_5 nanocomposites can be used as an electronic material.

Key words: *polydiphenylamine, vanadium pentoxide, nanocomposite, capacitance*

I. INTRODUCTION

A nanocomposite is a nanomaterial consisting of two or more phases with at least one phase having crystals (grain) 0.01 to 0.1 micron in size. Composites of polymers are materials that utilize conjugated polymers and at least one secondary component that can be inorganic or organic materials or biologically active species.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

Nano inorganic materials with special physical properties are combined with polymers to form polymer nanocomposites whose chemical and physical properties differ from those of the component materials significantly [1-3].

The nanostructured metal oxides are promising new materials for blending with polymers for obtaining low weight nanocomposites with excellent mechanical, electrical, thermal, and multifunctional properties. The creation of nanocomposites based on electro-conductive polymers and nanostructured metal oxides, i.e. incorporation of inorganic filler into polymer matrixes, can dramatically improve their processibility [4-6].

Among the PANI class, polydiphenylamine (PDPA) a polymer of N-aryl substituted aniline has attracted now-a days [7-10]. Many properties of PDPA that include electrochemistry, conductivity, luminescence and electrochromism are found to be different from PANI and also from polymers of other N-substituted aniline derivatives.

Polymers containing vanadium pentoxide (V_2O_5) have attracted our interest in respect of their potential applications in gas sensing materials, memory and switching devices [11-20].

This paper reports the synthesis of polydiphenylamine - Vanadium pentoxide nanocomposites and its characterization using UV-VIS, FTIR, XRD, SEM, TG/DTA and DSC studies.

II. EXPERIMENTAL METHODOLOGY

2.1. Chemicals used

Diphenylamine, ammonium sulfate, vanadium pentoxide, ammonium hydroxide, ethanol, potassium periodate, sulphuric acid, acetic acid, sodium hydroxide.

2.2. Synthesis of V_2O_5 nanoparticles

For the synthesis of V_2O_5 nanoparticles, a solution of 1.5 M ammonium sulfate which consisted of 0.75 M vanadium pentoxide was used. The total volume of 50 mL in aqueous solution was heated at 75 ºC and maintained at the same temperature for 90 min. After that, ammonium hydroxide solution (2.5 M) was added drop-wise under high speed stirring. The precipitate was collected, repeatedly washed with distilled water and ethanol and dried at 50-55ºC. After being calcined at 400°C for 4 hours, the sample was slowly cooled at room temperature.

2.3. Synthesis of PDPA

Exactly 0.5g of diphenylamine was added to 7.5 ml 1M H_2SO_4 with constant stirring for 15 min at room temperature. For the polymerization of diphenylamine, dilute solution of potassium periodate (2.25mL, 0.02M) was added drop-wise with constant stirring. After 24 h, the reaction mixture was filtered and dried in vacuum oven at 60 ºC for 24 h.

2.4. Synthesis of PDPA-V_2O_5 nanocomposites

Exactly 0.5g of diphenylamine was injected to 7.5 ml 1M H_2SO_4 containing 25 mg nano- V_2O_5 with constant stirring for 15 min at room temperature. For the polymerization of diphenylamine, dilute solution of potassium periodate (2.25mL, 0.02M) was added drop-wise with constant stirring. After 24 h, the reaction mixture was filtered and dried in vacuum oven at 60 ºC for 24 h.

2.5. Analytical techniques

The UV-Visible spectra of the nano composites were recorded on JASCO V-530 UV-Visible spectrometer. FTIR measurements were performed on the nano composites using KBr pellets by a SHIMADZU FTIR 8400S spectrometer. The average grain size was determined by XRD performed using X-ray diffractometer. The polymer film surface morphology was studied by computer controlled Hitachi S300 H SEM. Thermal analysis of nano composites were carried out using Perkin Elmer Diamond TG/DTA and Pyris 6 DSC. The electrochemical measurements were made by electrochemical analyzer, CH instruments electrochemical workstation model 760C.

III. RESULTS AND DISCUSSION

3.1. UV-VIS spectroscopy of PDPA-V_2O_5 nanocomposites

The UV-Vis spectral studies were carried out for the PDPA and PDPA-V_2O_5 nanocomposites in dichloromethane. Figure 1b shows the UV-Vis spectra of the PDPA-V_2O_5 nanocomposites. A shoulder around 390nm corresponds to the π-π* transition of the benzenoid rings and a band around 500nm corresponds to polaron band of DPA. The absorption at 506 nm (Fig.1a) for PDPA and 509nm for PDPA-V_2O_5 (Fig. 1b) are due to the polaron bands. The red shift indicates the formation of complex between polymer and V_2O_5 nanoparticles.

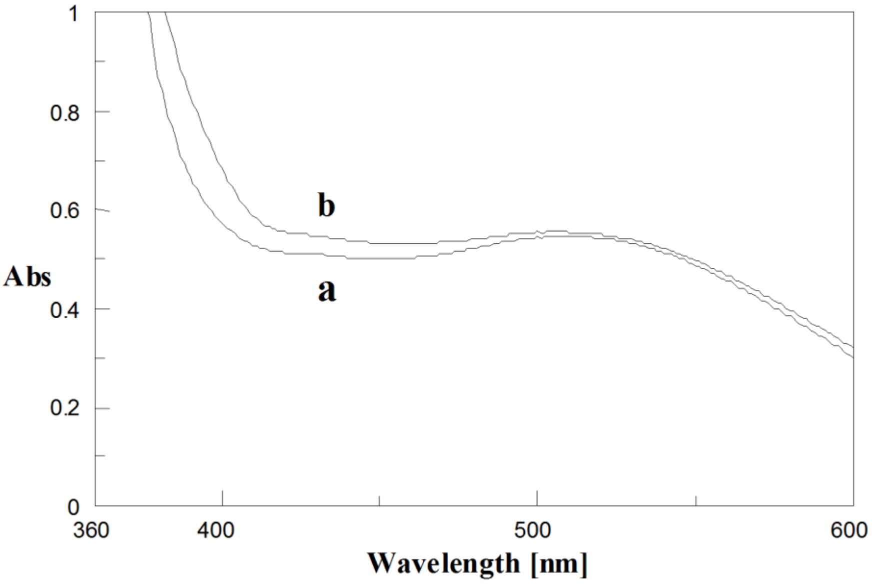

Fig.1. UV-VIS spectra of (a) PDPA and (b) PDPA-V_2O_5 nanocomposite

3.2. FTIR behavior of PDPA-V_2O_5 nanocomposites

FTIR spectra of PDPA, V_2O_5 nanoparticles and PDPA-V_2O_5 nanocomposite are shown in fig 2-4. In PDPA, the band at 3383cm $^{-1}$ is attributable to N-H stretching of the secondary amine. The bands at 1595 & 1492 cm^{-1} corresponds to quinoid and benzenoid structure of PDPA respectively. Also the band at 1315cm^{-1} assigned to C-N stretching of the secondary aromatic amine. All the above characteristic bands are seen in FTIR of PDPA-V_2O_5 nanocomposites. Since vanadium is a transition metal it has a tendency to form coordination compound with nitrogen atom in DPA polymer molecules. This interaction may weaken the bond strengths of C=C and C-N in DPA polymer molecule. These results confirmed the formation of nanocomposites.

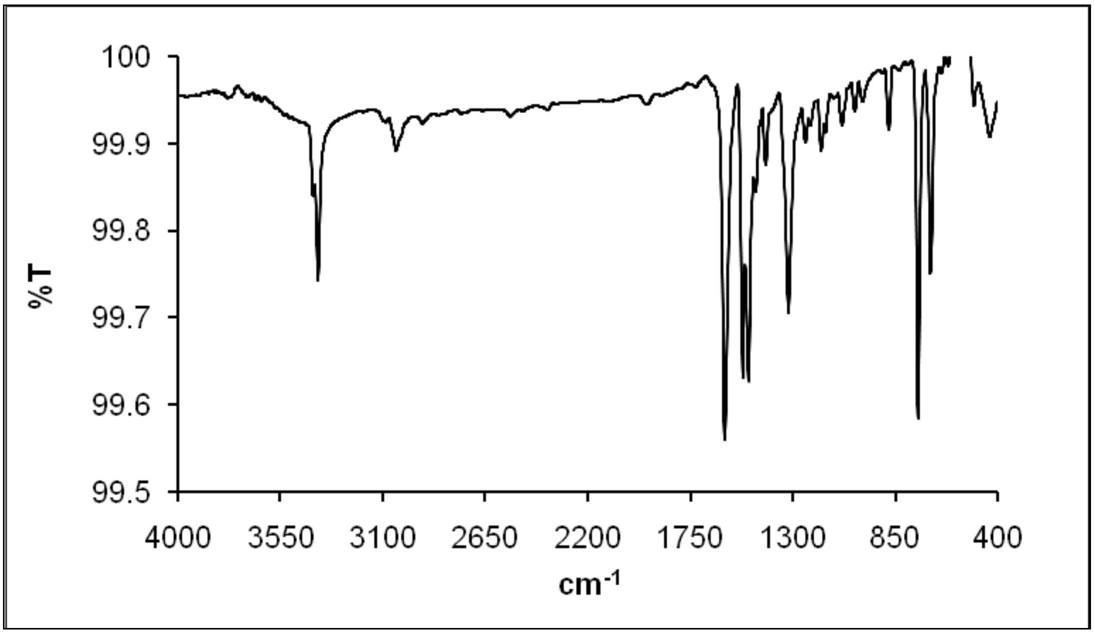

Fig.2. FTIR spectrum of PDPA

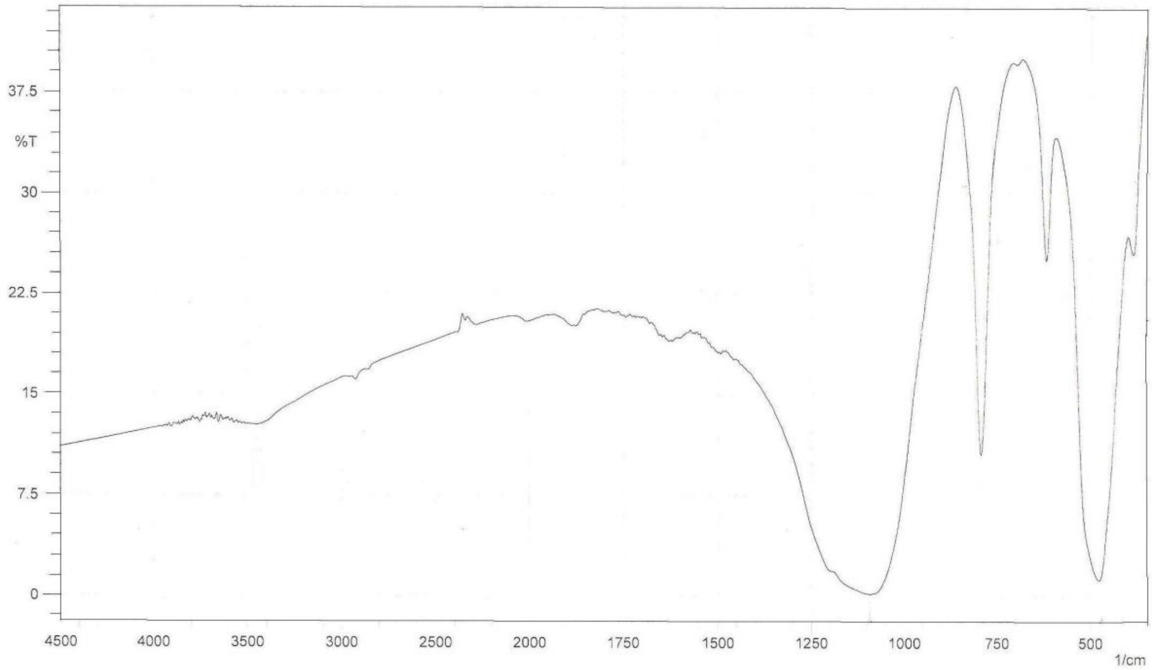

Fig.3. FTIR spectrum of V_2O_5 nanoparticle

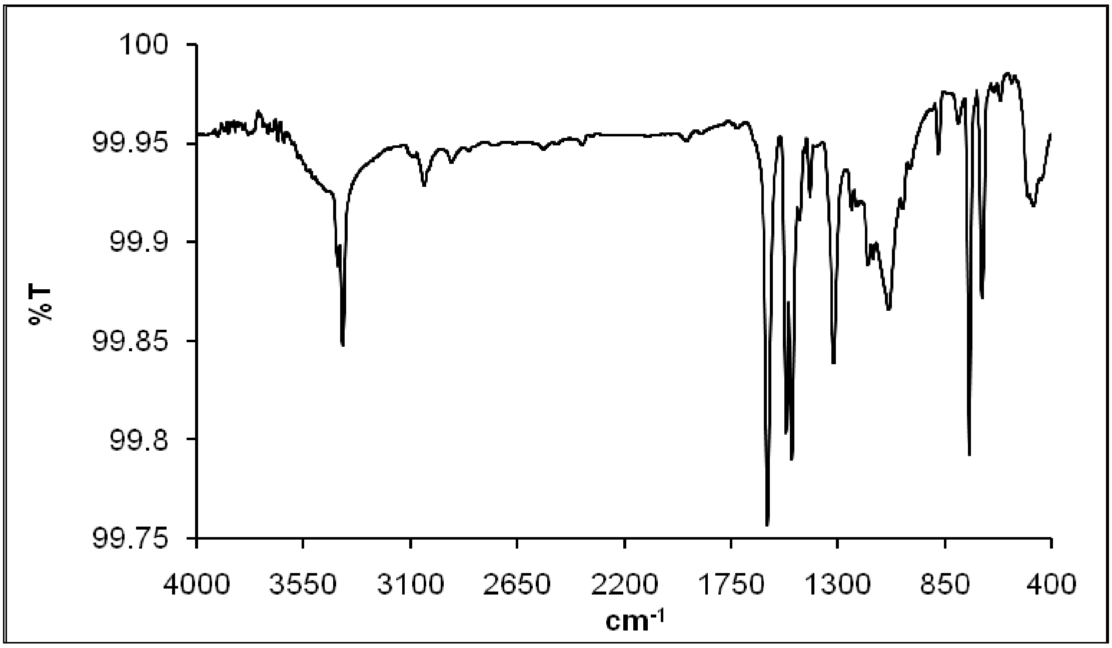

Fig.4. FTIR spectrum of PDPA-V_2O_5 nanocomposite

3.3. XRD studies of PDPA-V_2O_5 nanocomposites

Fig (5-7) show the X-ray diffraction pattern for PDPA, V_2O_5 nanoparticle and PDPA-V_2O_5 nanocomposite. The XRD behavior of PDPA-V_2O_5 nanocomposites exhibit crystalline nature and the particle size also nanometer range. The particle size of PDPA, V_2O_5 nanoparticle and PDPA-V_2O_5 nanocomposite are 74.66, 31.69 and 66.38nm respectively.

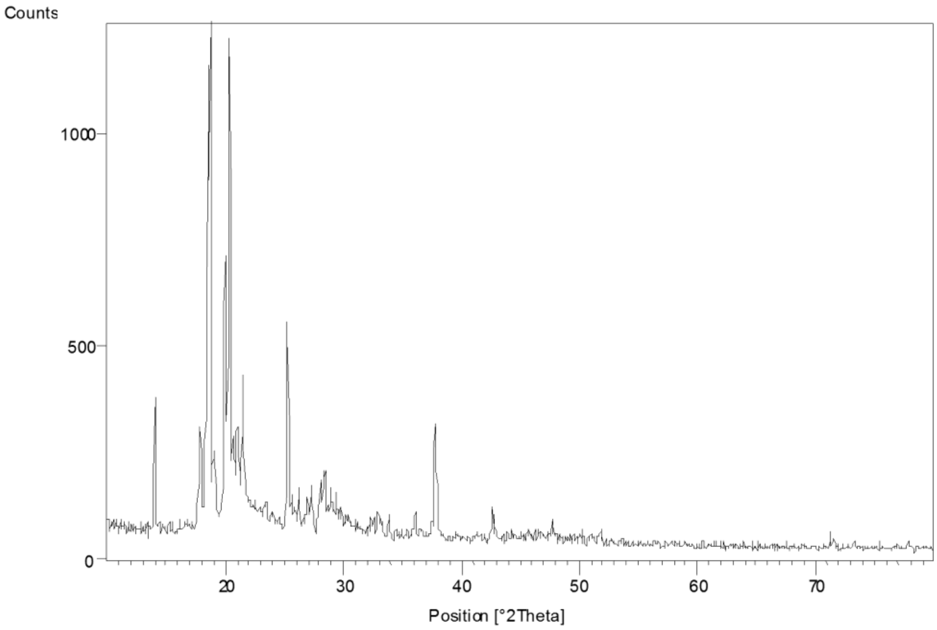

Fig.5. XRD behavior of PDPA

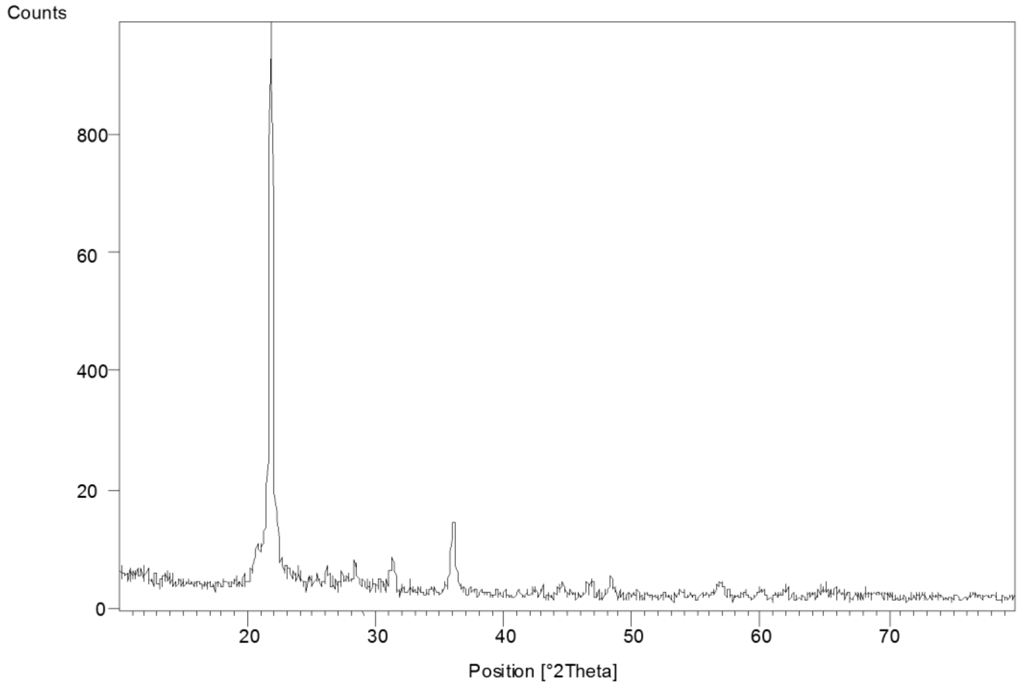

Fig.6. XRD behavior of V_2O_5 nanoparticle

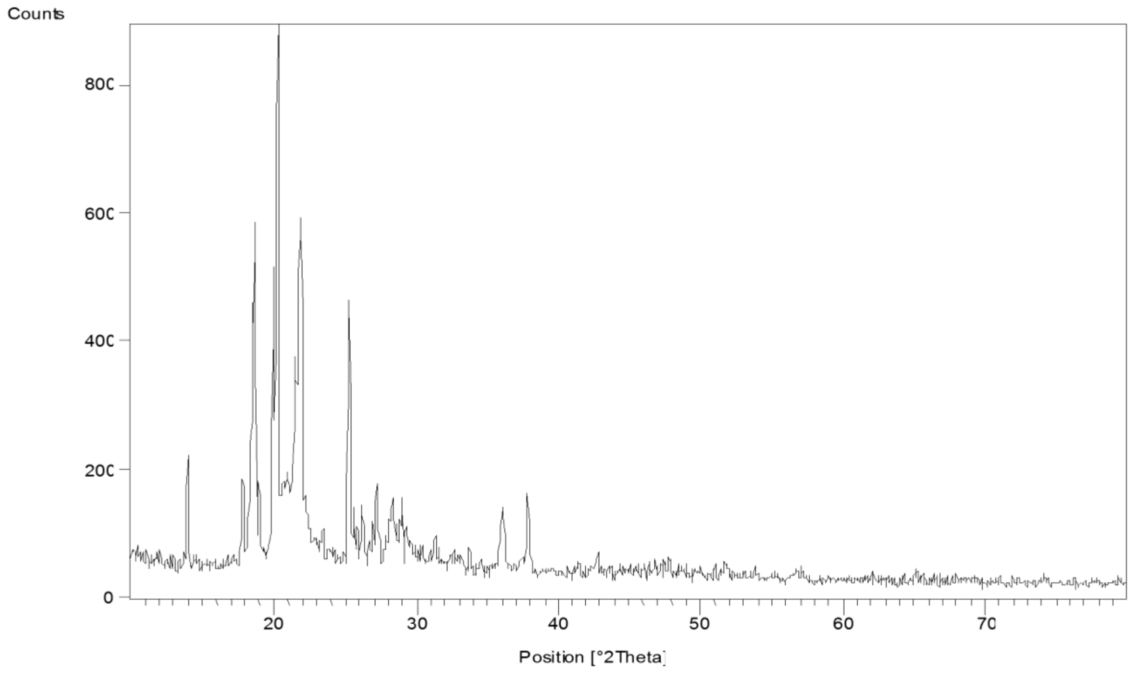

Fig.7. XRD behavior of PDPA-V_2O_5 nanocomposite

3.4. SEM behavior of PDPA-V_2O_5 nanocomposites

The surface morphology of PDPA exhibits spongy like structure (Fig 8). The surface morphology of PDPA-V_2O_5 nanocomposites exhibits mixed structure of spongy and granular (Fig 9). According to fig 9 the SEM micrograph of the PDPA-V_2O_5 nanocomposites confirms the good dispersion of V_2O_5 nanoparticles in the polydiphenylamine matrix.

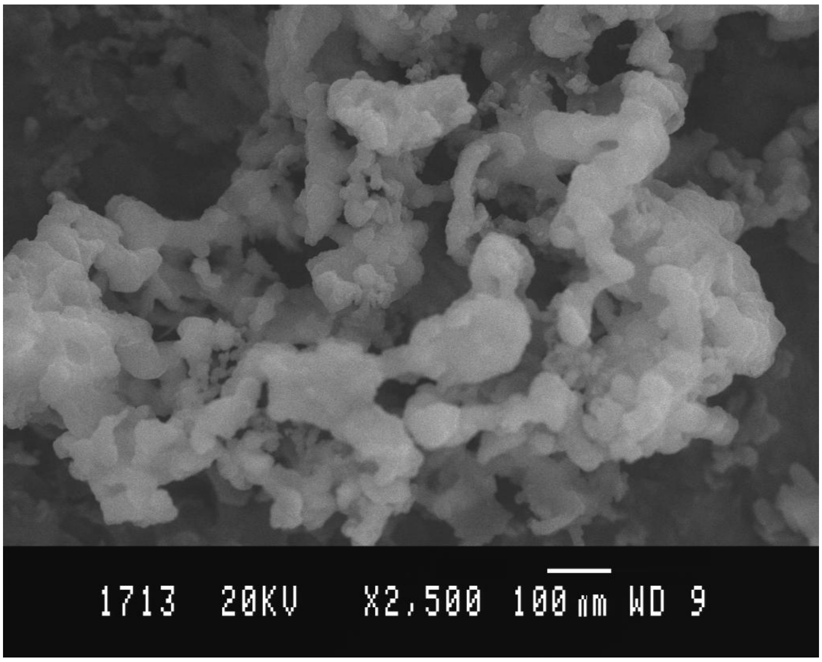

Fig.8. SEM behavior of PDPA

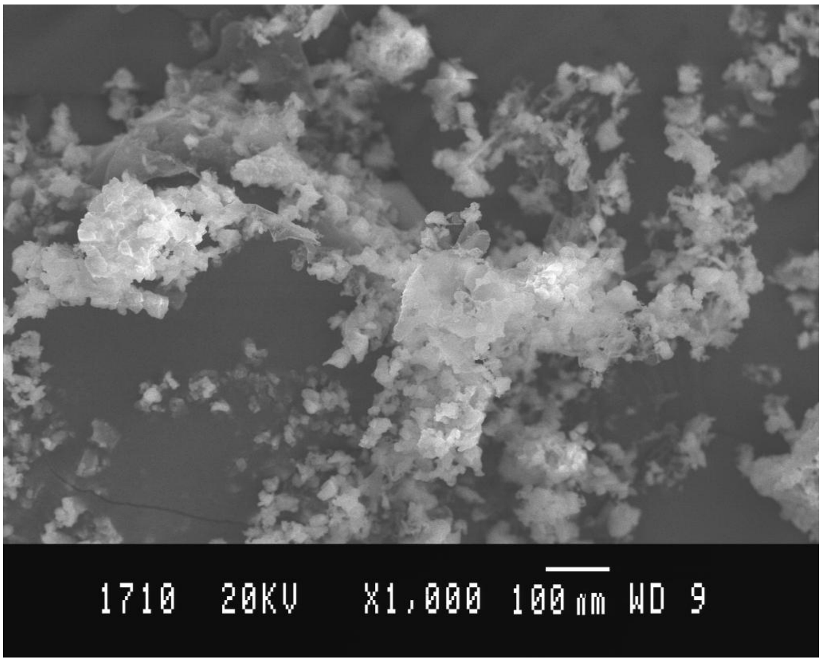

Fig.9. SEM behavior of PDPA-V_2O_5 nanocomposite

3.5. Cyclic Voltammetric Behavior

The polymer and polymer-V_2O_5 nanocomposites were coated as thin film on the surface of glassy carbon electrode and the cyclic voltammetric behavior of the PDPA and nanocomposites were studied. The volatammogram is cycled between –200 and 1200 mV in 0.1M H_2SO_4 at scan rate 100 mVs^{-1}. The voltammogram of polymer (Fig 10) shows one oxidation and reduction peak at 820 and 600mV respectively. Similar manner polymer-V_2O_5 nanocomposites are also carried out. Here also one oxidation and one reduction peak observed around 425 and 540 mV. The oxidation and reduction peak potentials were different from polymer. These behaviors might be DPA combined with V_2O_5 to form polymer-V_2O_5 nanocomposite. This behavior is further confirmation of nanocomposite formation.

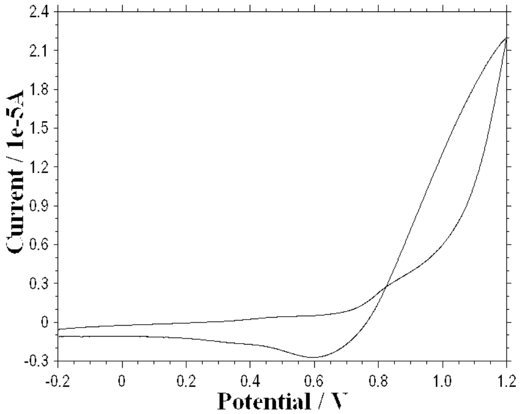

Fig. 10. Cyclic voltammetric behavior of PDPA in 0.1M H_2SO_4 at scan rate of 100 mV/s.

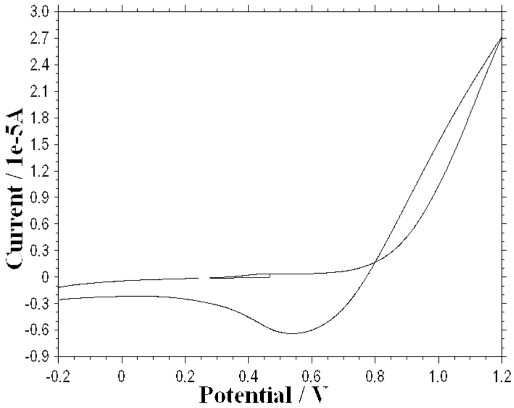

Fig. 11. Cyclic voltammetric behavior of PDPA-V_2O_5 nanocomposite in 0.1M H_2SO_4 at scan rate of 100 mV/s

3.6. Electrochemical impedance spectroscopy

Chemically synthesized PDPA-V_2O_5 nanocomposites were coated on glassy carbon electrode (0.0314 cm^2) as working electrode. The cell is composed by a 1 cm^2 Pt counter electrode, Ag/AgCl as reference electrode. The measurements were made in 0.1 M HCl medium. The depressed semicircles seem to be caused by a distribution of parameter values due to surface heterogeneities and are commonly observed in measurements of systems containing polymers.

The contact phase element (CPE), Q=1/ (jw)^n C$_d$ (w=2pf) is used for determination of the capacitance value. The calculated capacitance values of PDPA and PDPA-V_2O_5 nanocomposites are 0.4538, and 0.6141 nC respectively. The capacitances of chemically synthesized polymer composites are very well used as electronic material.

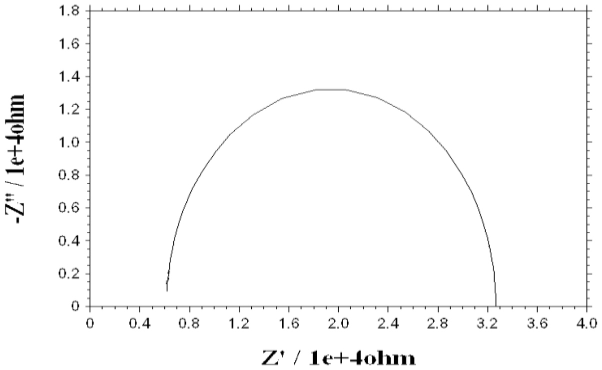

Fig.12. Impedance spectrum of PDPA

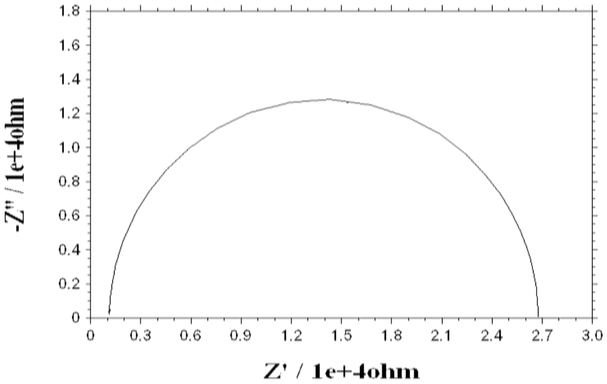

Fig.13. Impedance spectrum of nanocomposite

3.7. Thermal behavior of PDPA and PDPA-V_2O_5 nanocomposites

The thermogravimetric and differential thermal analysis (TG/DTA) of the chemically synthesized PDPA, V_2O_5 nanoparticle and PDPA-V_2O_5 nanocomposite were carried out and the resultant thermograms are presented in fig14-16. Three distinct stages are observed in the TG curve (Fig. 14) of the polymer. The first step, up to 120 ºC, corresponds to the removal of the reversibly bound water, whereas the second step at 250 ºC corresponds to the loss of more strongly bound water between the layers. This is followed by a continuous weight loss up to 550 ºC, which can be attributed to the complete combustion of the organic polymer component, after 550 -580 ºC weight loss is indicates highly bounded polymer molecules, in agreement with the exothermic peak in the DTA curve. A subsequent mass gain up to 250 ºC can be attributed to the formation of polymer. Crystallization of this phase is evidenced from the DTA curve, which showed a relatively sharp endothermic peak at 566 ºC. Similar manner PDPA-V_2O_5 nanocomposite also carried out. Here also two distinct stages are observed in the TGA curve (Fig.16). Crystallization of this phase is evidenced from the DTA curve, which showed a relatively sharp endothermic peak around 564 ºC. In the DTA curve of V_2O_5 nanoparticle, the weight loss at 100 ºC is corresponds to the removal of the reversibly bound water, the weight loss up to 500 ºC is corresponds to the complete combustion of the V_2O_5 nanoparticle, in agreement with the exothermic peak in the DTA curve. Crystallization of this phase is evidenced from the DTA curve, which showed a relatively sharp endothermic peak at 460 ºC.

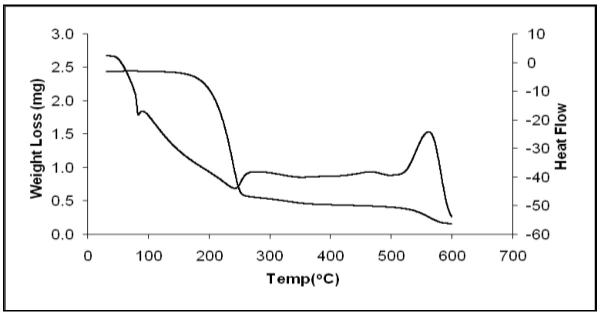

Fig.14. TG/DTA curve of PDPA

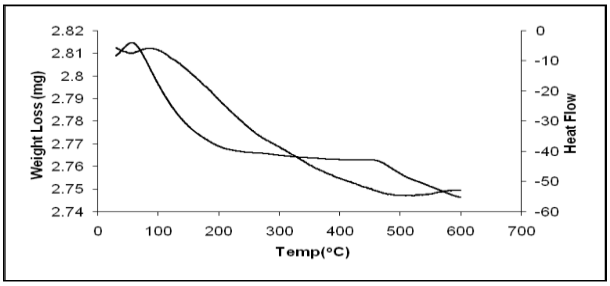

Fig.15. TG/DTA curve of V_2O_5 nanoparticle

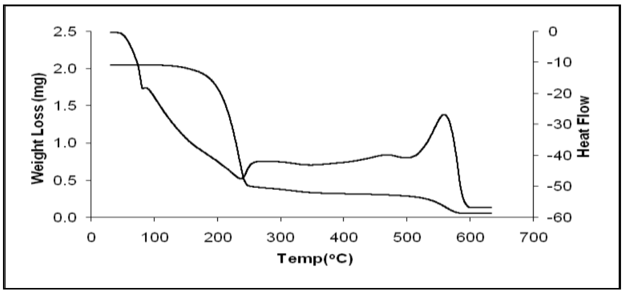

Fig.16. TG/DTA curve of PDPA-V_2O_5 nanocomposite

DSC thermogram of PDPA, V_2O_5 nanoparticle and PDPA - V_2O_5 nanocomposite recorded at the heating rate of 20/min in air is shown in fig 17-19. The glass transition temperature (Tg), crystallization transition temperature (Tc) and melting point (Tm) are determined from the DSC curve. The Tg value of polymer is 26 ºC, the Tc value is 101 ºC and the polymer started melting after 360 ºC. The exotherm, which started from – 55 ºC and extended upto 140ºC is due to the expulsion of free and bounded water.

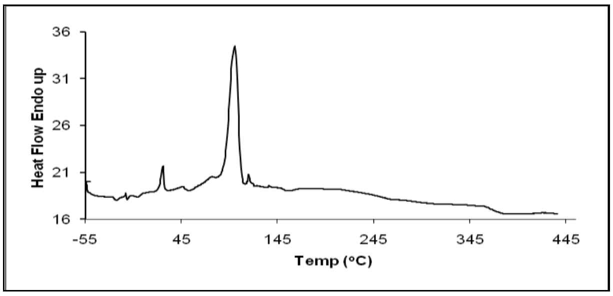

Fig.17. DSC curve of PDPA

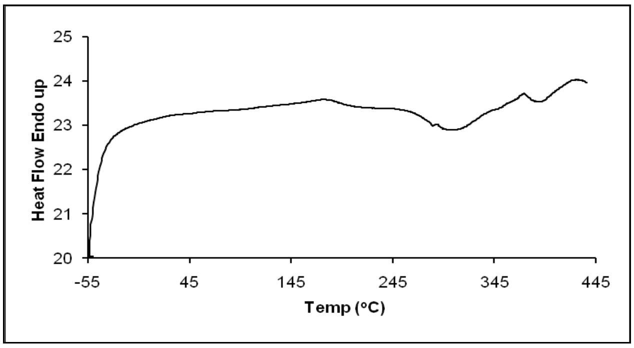

Fig.18. DSC curve of V_2O_5 nanoparticle

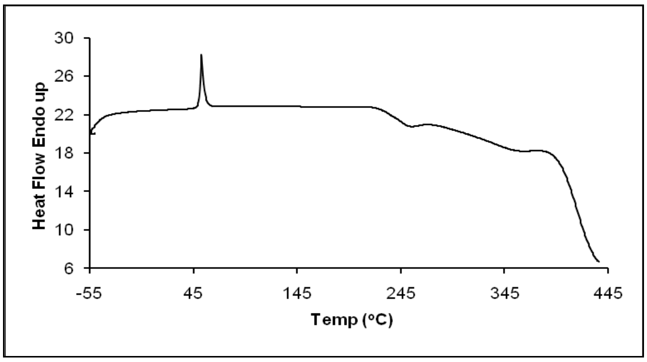

Fig.19. DSC curve of PDPA-V_2O_5 nanocomposite

IV. CONCLUSIONS

PDPA-V_2O_5 nanocomposites containing PDPA and V_2O_5 nanoparticle were synthesized in acid medium through chemical oxidation method using potassium periodate. From cyclic voltammetric studies good reversible redox behavior is observed for polymer and polymer-V_2O_5 composites. The polymer- V_2O_5 composites exhibited good adherent film on electrode surface and good electroactivity. Impedance spectroscopy is employed to study the capacitance of nanocomposites. The capacitance of chemically synthesized polymer composites is very well used as an electronic material. TG/DTA and DSC studies revealed satisfactory thermal stability of the polymer metal composites.

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