

Some Studies on Structural, Morphological, Electrical & Dielectric **Property of Vanadium Pentoxide Doped Polyaniline [V₂O₅/PANI]**

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Abstract: Vanadium pentoxide doped with polyaniline (V₂O₅/PANI) composites have been prepared using chemical oxidative polymerization techniques using aniline, ammonium per sulphate & V_2O_5 as feed products. Frequency-dependent conductivity operation of V_2O_5 / PANI composites has been studied. The structure of PANI & V₂O₅/PANI composites with respect to structural & micro-structural material characteristics has been examined by XRD and SEM methods. DC electrical conductivity of pure polyaniline as well as its derivatives was determined in the range of temperature from of 30°C to 180°C. In addition to a small variance in the lower frequency spectrum as well as an increase in the concentration of V_2O_5 , the variance of σ_{ac} with respect to the change in frequency obeys the power law.

Key words: AC-Conductivity; DC-Conductivity; Scanning Electron Microscopy; X-Ray Diffraction; Polyaniline; V₂O_{5.}

1. INTRODUCTION

The synthesis of polymers has been the key element of advanced technology due to their possible uses in several technical fields. Cp's offered a possibility of a new era for polymeric material possessing the optical and electrical properties of materials as electronic components as well as possessing the desirable mechanical properties and manufacturing benefits of polymers leading to a wide variety of technical applications. [1-4]. Among polymers, the polyaniline family have drawn a significant interest from scientists around the world due to its ease of synthesis, its specific charge transfer process, its significant ecological sustainability through the presence of air or oxygen and water, its relatively inexpensive, its compact size as well as its high sensing capability[5-6]. They often show an extremely redox reaction nature, which is also very useful in many areas. Abundance of research shows that major achievements were formed by scholars everywhere across the nation in enhancing the conducting capability of polyaniline through different doping methods, with little more information about dielectric properties of the conductive polymers identified mostly with conduction

mechanism [7-9]. Upon doping, such conjugate polymers exhibits extremely high electrical conductivity comparable to metals.

Although sometimes they can be just called synthetic metals. The incorporate the electrical, physical and mechanical properties of a metal with the benefits of polymers as with lower weight, optimized reliability, resistance to corrosion as well as cheaper [10]. Another very interesting features of conductive

polymers will be in television screens, mobile phones, vehicle dashboard screens and simulated cockpit panels, light emitting devices (led's), photovoltaic panels, flexible cells, LED's, actuators, resistance to corrosion agents, sensors as well as organic electronic devices[11]. In this research, the possibilities of enhancing the conductance of PANI is through doping it with molecules V205/PANI composites with 'Chemical Oxidation Polymerization' method. The electrical properties of the V₂O₅/PANI composites were also reviewed.

2. Materials and Methods

2.1 Materials and Method:

Chemicals are used to prepare polyaniline as aniline, hydrochloric acid (HCl), ammonium persulfate $(NH_4)_2S_2O_8$ of analytical grade and synthesized using chemical oxidative polymerization process using as monomer and in existence of HCl(hydrochloric acid) as catalyst with (NH₄)₂S₂O₈ (ammonium persulfate) as an oxidizer.

2.2 Preparation Of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. These mixers were stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2M of (NH₄)₂S₂O₈ (ammonium persulfate) were added drop wise into the mixer. The above reaction mixers were vigorously stirred at room temperature for 8 hrs. The precipitate formed and separated out by filtering then cleaned with acetone or de-ionized. The obtained final suspensions were dried for about 24 hours in oven at the temperature of 50° C... The obtained products were crushed into powder.

2.3. Preparation Of V₂O₅/Polyaniline:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M ammonium persulfate $(NH_4)_2S_2O_8$ was added drop by drop into the mixer. Vanadium Pentoxide (V2O5) powder for various mass fractions (10%, 20%, 30%, 40% & 50%) is dissolved in the different weight percentage to the above mixture with constant stirring so as to keep the V₂O₅ uniformly dispersed in the mixture and stirring of final solution was continued for another 8 hours at room temperature. After 8 hrs the precipitate has been extracted by filtering and rinsed with de-ionized water with acetone. The obtained final suspension was dried in hot air furnace about 24hrs at the temperature of 50°C. Then obtained product was grinded into powder.



Figure-1: Flow chart of preparation composite.

3. Result And Discussion:

3.1. X-Ray Diffraction (XRD):

Figure.2 illustrate the X-ray diffraction configuration of composites V205 /PANI (10%, 20%, 30%, 40% & 50%) respectively influenced by ammonium persulphate. Generally the presence of wide peak in the pattern shows the amorphous behavior of the given material and it is known as amorphous peak. If there is a presence of sharp peak throughout the pattern indicates polymer has crystallinity. The spectrum is the addition of crystalline peak and an amorphous peak.

Figure shows the common room temperature XRD spectra of the oxidative polymerization synthesized pure polyaniline and V2O5 doped PANI composite (V2O5-Polyaniline). The oxide dispersed PANI shows characteristic peaks of PANI and some broad peak may be due to masking of crystalline oxide into the polymer chain. As well as the sharpness of the peak in the pattern may be the dispersed of the V2O5 particles into the PANI matrix. Additional V2O5 peaks may be observed in the pattern. This confirms the formation of the composite. It is likewise seen that, the intensity of the peaks is expanded from approximately 100 to 900 counts as doping increased from pure to 50%. This suggests the V2O5 is distributed in the polyaniline chain.

The average crystalline sizes of the PANI are estimated to be approximately 10-20nm are calculated by using 'Debye – Scherrer's' formula

$(D=K\lambda/(\beta \cos\theta))$

Where,

'D' \rightarrow correspond to the standard crystalline size,

' λ ' \rightarrow indicates the wavelength of the X-ray,

'K' \rightarrow indicates the crystallite shape factor a good approximation is 0.9,

' β ' \rightarrow correspond to the full width at half the maximum (FWHM) of the X-ray diffraction peak as well as 2 θ represents the Braggs' angle (deg.) and lattice strain was estimated to be 0.0088.





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Figure-2: XRD pattern of PANI as well as V₂O₅/PANI composites. (10%,20%,30%,40% & 50%)

3.2. Scanning Electron Microscope (SEM):

Figure-3 confirms the electrical conductivity (σ_{ac}) for all polyaniline composites with respect to change in the frequency of specific wt. % was carried out. In all cases, the AC electrical conductivity increases as frequency increased over the considered range of frequency. Conductivity tends to increase by increasing frequencies at higher frequencies around 10⁶ Hz agreeing with the fundamental principle of 'Power Law'. The conductivity will be nearly stable up to 106 Hz after which conductivity will change due to the addition of polarons. Increased conductivity at higher frequencies has been correlated with the migration of charge-carriers in crystal domains, enabling their existence for both isolated polarons as well as bipolarons through these domains. Compared to the polyaniline and the composite shows high conductivity. The expansion in the ac electrical conductivity for the composite may be due to dipole polarization.



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Figure-3: SEM pattern of PANI and V₂O₅/PANI composites.

3.3. AC Conductivity:

Figure-4 suggests the AC conductivity (σ_{ac}) of pure PANI, V₂O₅/PANI composites with respect to frequency. In all cases, the AC conductivity increases as frequency increased over measured frequency range. At specific frequencies around 10⁶ Hz, conductivity changes at higher frequencies, obeys the of Universal Power Law. The conductivity is essentially constant up to 10⁶ Hz and afterwards the conductivity continues to increase due to the addition of the polarons. Enhanced conductivity at specific frequencies is due to charge vibration within crystal lattice, which promotes the existence of isolated polarons and bipolarons in the field. [12-13]. Compared to the polyaniline and the composite shows high conductivity. The increase in the ac electrical conductivity for the composite may due to dipole polarization.



Figure-4: AC conductivity of PANI and V₂O₅/PANI composites.

3.4. DC Conductivity:

The temperature dependence of dc-conductivity (σ_{dc}) for PANI, V205/PANI composites in a temperature range between 30 to 180°C is represented in Figure-5. It is noticeable from the figure which the conductivity estimations for the examined composite polymers are lower than that found for pure PANI. The σ dc increases gradually with temperature exhibiting semiconductor behavior up to a temperature 180°C and it is the characteristic property of materials [14].

In all cases the dc conductivity increases in two phases. In the first phase, the dc conductivity almost found to be constant in the range 30°C to 140°C. In the second phase, the dc conductivity increase suddenly up to 180°C. The first phase conductivity is almost constant because of movement of the charge transporter, i.e., jumping of charge carriers across the polymer matrix but it is usually seen at transitional temp. However, at higher temp region, (phase two) there is an abrupt increase in the conductivity with increase in temp because of movement of the charge carriers across the polymer lattice, which could be explained by the conduction band phenomenon and is usually seen at higher temp as described by authors in their past work [15-17].



Figure-5: DC conductivity of PANI and V₂O₅/PANI composites.

3.5 Dielectric Constant (ε'):

Figure-5 illustrates the variation of DC (ϵ ') measured with respect to change in the frequency which seem to be a real part of DC for polyaniline & V2O5/ PANI contents. The graph shows that, if the frequency increases the dielectric constant decreases. At low frequency the significance result of DC (ϵ ') is quite increases and reduces for a change in frequency with all polymer composites. At greater frequencies the significance of DC (ϵ ') remains steady with all the composite materials at a frequency 106 Hz shows lower value level, which is due to Debye-type relaxation [18]. All the composite materials were found to be greater value of dielectric constant compared to the PANI and oxides.



Figure-6: Dielectric constant of PANI and V₂O₅/PANI composites.



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4. Conclusions:

The present works was attempt to synthesize pure polyaniline and V_2O_5 doped polyaniline with different concentration (10%, 20%, 30%, 40% & 50%) and are characterized by different techniques like structural (XRD) & micro structural (SEM).

We have reviewed more number of literatures of pure polyaniline and doped polyaniline apart from them V_2O_5 is finalized for the substitution in polyaniline. Stoichiometric amount of aniline, hydrochloric acid, ammonium persulphate, V_2O_5 are weighed and mixed in a proper proportion like 0.2M aniline, 0.2M ammonium persulphate, 1N hydrochloric acid, 10%, 20%, 30%, 40% & 50% of V_2O_5 .

Structural analysis of polymer samples were carried out by XRD, amorphous peak of polyaniline were found in the range 25-28 degree. As we increase the composition V_2O_5 from 10% to 50% it shows that crystallinity of the PANI. These micro structural images clearly demonstrate the formation of agglomeration and irregular shaped V₂O₅ doped PANI. A non-uniform morphology and chemical homogeneity observed. No other impurity peaks are observed. SEM shows agglomeration and irregular shapes of PANI and V₂O₅ doped PANI. It is confirmed that the V_2O_5 particles were equally distributed throughout the matrix material of polymer. The AC conductivity value of the PANI as well as the entire composite increased as frequency increased. The DC conductivity value of the composites rises exponentially with temperature. The decrease in the values of dc conductivity of all the wt% of the composite is attributed to substantial knocking of charge carriers. These were investigated that the real dielectric constant (ϵ '), in case of polyaniline and composite materials decreases with respect to frequency.

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