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Studies on Synthesis, Characterization and Transport Properties of Ta_2O_5 Doped Polyaniline Composites

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ABSTRACT

Polyaniline (PANI) and PANI/Ta_2O_5 composite samples were prepared using chemical oxidative polymerization technique in the presence of hydrochloric acid (HCl) at room temperature. The effect of Ta_2O_5 on surface morphology and structural changes have been investigated and evaluated by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. The XRD pattern of the PANI and PANI/Ta_2O_5 confirm the formation of PANI and its composite. The average crystallite size of the PANI is 2.86 nm which is increased to 46.80 nm when Ta_2O_5 was doped in the PANI matrix. SEM micrographs of the composite confirm the morphological changes in the composite materials. In the electrical conductivity studies, ac conductivity was carried as function of frequency and dc conductivity was studied as a function of temperature. Further to describe the dielectric properties of the PANI and composite, dielectric constant and dielectric loss was studied as a function of frequency.

1. Introduction

The polymer composites with conventionally filled were described as the new class of materials which enhances the performance, strength, heat resistance, conductivity of the materials [1]. When polymer was doped with inorganic particles in an organic polymer matrix which improves the physical properties of the polymer such as conductivity/resistance [2,3]. The polymer with metal oxide doped composites dramatically showing interest to the researchers due to the surprising hybrid properties derived from the polymer and metal oxide [4,5]. Conducting polymers were attracted towards researcher due to their numerous industrial application such as electrical and use of polymers in electronic devices. The desired properties of the polymer can be prepared by doping suitable composition in the polymer matrix [6-8]. One of the great importance in the polymer application is to know how the prepared composites behave in the presence of electric and magnetic field which is a longstanding problem in the field of conducting polymer. However, the interest in the polymer research was increased to know the enhancement of the electrical conductivity of the conducting polymer when doped and undoped.

Polyaniline is one of the conducting polymers and widely studied in view of their unique properties such as dielectric behavior, electrical conductivity, optical and opto-electrical properties. Also, the polyaniline is well known for the environment stability [9]. The insulated emeraldine base of the polyaniline can be made conductive and the conductivity can be enhanced by doping with protonic acids. By doping with protonic acids with polyaniline, which can enhance the conductivity of the composite by more than 10 orders of magnitude. The enhancement of the conductivity usually depends on the strength of the acids [10,11]. This work is aimed to prepare undoped polyaniline and doped polyaniline with Ta_2O_5. Further the prepared composites were characterized using XRD and SEM analysis in addition with electrical conductivity studies.

2. Experimental Methods

Chemicals used to prepare polyaniline are aniline, hydrochloric acid (HCl), ammonium persulfate, Ta_2O_5 of analytical grade and synthesized by employing chemical oxidative polymerization method.

2.1 Preparation of Polyaniline

Initially 0.2 M aniline was prepared and mixed with 1 N hydrochloric acid. The mixer was carried out at room temperature using magnetic stirrer for 2 hours at constant RPM for the completion of the reaction. The solution of 0.25 M ammonium persulfate was added drop wise into the mixer. This reaction mixer was continuously stirred in magnetic stirrer for 8 hours at room temperature. The precipitate formed and separated out by filtering and washed with deionised water followed by acetone. The obtained final suspension was dried at hot air oven at 50 °C for 24 hours. The final product was grinded into fine powder.

2.2 Preparation of Ta_2O_5/PANI

Initially 0.2 M aniline was prepared and mixed with 1 N hydrochloric acid. The mixer was carried out at room temperature using magnetic stirrer for 2 hours at constant RPM for the completion of the reaction. The solution of 0.25 M ammonium persulfate was added drop wise into the mixer. Ta_2O_5 powder for different additive weight percentage (5%, 10%, 15% 20% and 25%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the Ta_2O_5 homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. After 8 hours the precipitate was separated out by filtering and washed with deionised water and then with acetone. The obtained final suspension was dried at hot air oven at 50 °C for 24 hours and grinded into powder.

3. Results and Discussion

3.1 X-Ray Diffraction Analysis

A typical X-ray diffraction pattern of the undoped polyaniline (PANI) is shown in Fig. 1. The broad diffraction peak was observed between diffracted angle 2θ ranges from 26°-30° which is the characteristic peak of polyaniline suggests the amorphous nature of the prepared PANI. The broad diffraction peak with d spacing d=3.29 corresponds to the reflection (200) due to parallel and perpendicular periodicity of the polymer (PANI) and no extra diffraction peaks are observed.

The average crystalline size of the PANI was calculated by using Debye -Scherrer formula and found to be 2.86 nm. Fig. 2 shows the XRD pattern of PANI/Ta_2O_5 composite (5%, 10%, 15%, 20% and 25%) and investigated the presence and effect of different weight percent of the Ta_2O_5 in the PANI matrix. The X-ray diffraction peaks at angle 2θ =23.08, 27.52, 37.36, 46.4, 55.5, 64.46 degree with d spacing d=3.84, 3.23, 2.40, 1.95, 1.65, 1.44

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corresponds to the reflection planes (001), (100), (101), (002), (102), (201) respectively (25%) revealed the Ta_2O_5 phase to have an orthorhombic structure according to the standard diffraction data JCPDS Card No. 25-0922 and 89–2843. The crystallite size was estimated at around 33.90 nm for the full width half maximum peak (001). The average crystalline size of the PANI is estimated as 46.80 nm (D) calculated from Debye-Scherrer formula. Moreover, the crystallite size of the undoped PANI is obtained as 2.86 nm (25%). In the presence of the Ta_2O_5, crystallite size of the composite increased from 2.86 of PANI to 46.80 nm of composite. It is also observed that, the intensity of the peaks is increased from 600 counts to approximately at around 3000 counts as doping concentration increased from 5% to 25%. This increase in the intensity of the XRD peak may suggest that, Ta_2O_5 oxide dispersed in the polyaniline matrix.

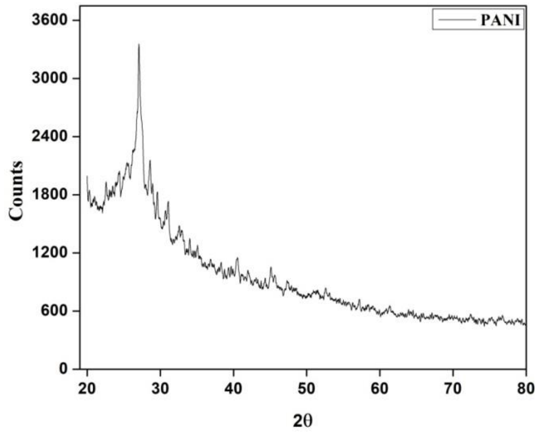

Fig. 1 XRD pattern of pure PANI

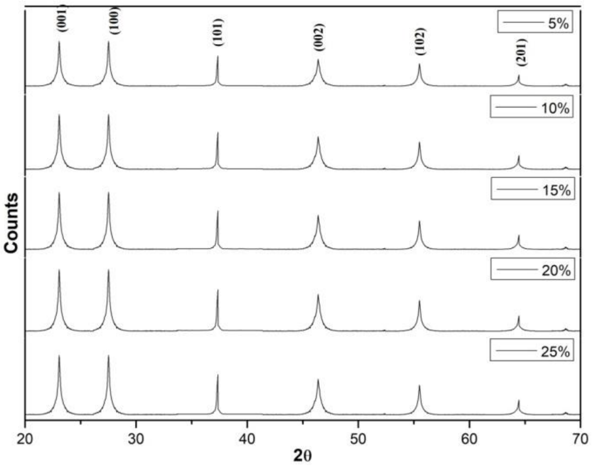

Fig. 2 XRD pattern of PANI/Ta_2O_5 composite

3.2 Scanning Electron Microscope

Scanning electron microscope was used to investigate the surface morphology of the prepared sample and lead the idea to identify the presence of dopant particles. Fig. 3 shows the SEM micrograph of the PANI and PANI/Ta_2O_5 composite. The SEM image of PANI shows uniform morphology with semi-crystalline structure. The SEM image of PANI/Ta_2O_5 reveals that the dopant particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. It can be observed that the Ta_2O_5 particles appear uniform sphere-like shape. The SEM micrograph of the PANI indicates the big globular agglomeration with smooth surface. It is noticeable that the SEM micrograph of PANI/Ta_2O_5 composites shows different morphology as compared with the PANI particles [12,13].

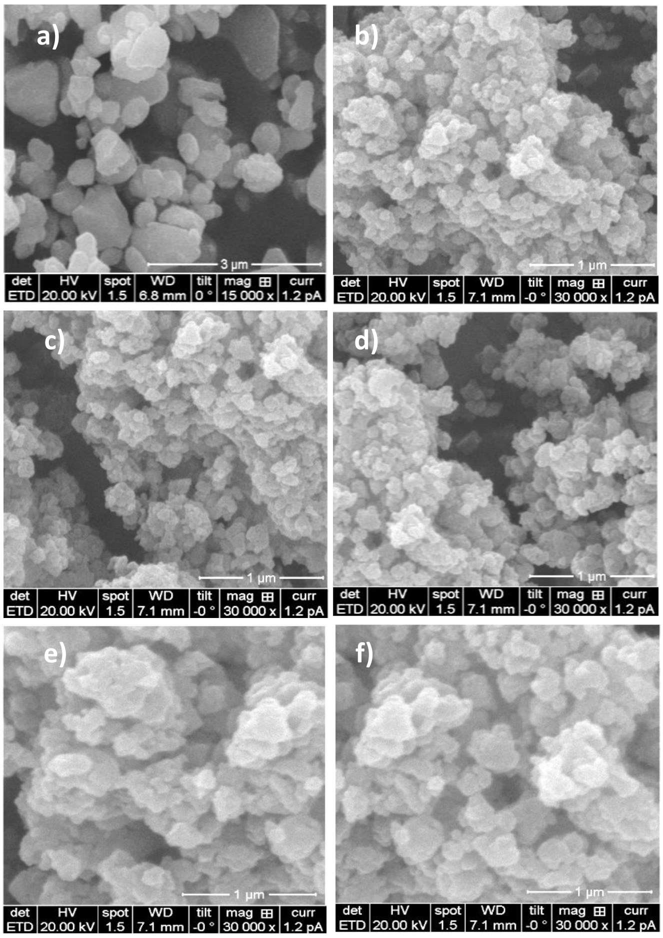

Fig. 3 SEM micrograph of a) PANI, b) PANI/Ta_2O_5 (5%), c) PANI/Ta_2O_5 (10%), d) PANI/Ta_2O_5 (15%), e) PANI/Ta_2O_5 (20%) and e) PANI/Ta_2O_5 (25%) Composite

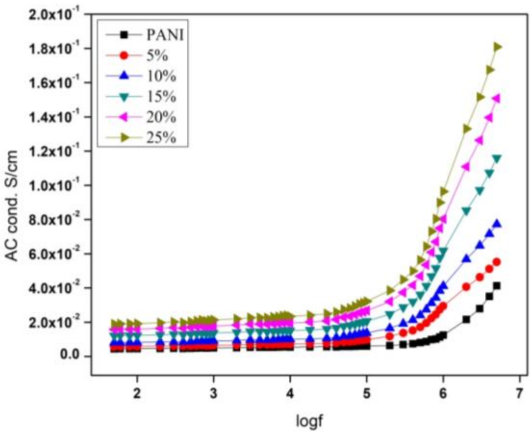

Fig. 4 AC conductivity of PANI and PANI/Ta_2O_5 composites

3.3 AC Conductivity

Fig. 4 shows the ac conductivity (σ_{ac}) of undoped PANI and PANI/Ta_2O_5 composite as function of measured frequency range 50 Hz to 1 MHz. The conductivity of the disorder materials such as polymer as a function of frequency is mainly due to the interfacial polarization at contacts and grain boundaries of the sample [14,15]. The conductivity of the PANI and composites increases with increase with frequency. The increase in the conductivity as function of frequency indicates that there may be charge carriers which can be transported by hopping through the defect sites along the polymer chain [16]. The conductivity of the PANI/Ta_2O_5 composite is higher than that of the conductivity of the PANI. The reduced conductivity of the PANI compared to the composite may due to the low level of protonation of the PANI chains [17]. The enhancement in the conductivity of the PANI/Ta_2O_5 composite is may due to the presence of the Ta_2O_5 particles in the PANI matrix. It can also be seen that the conductivity of the PANI/Ta_2O_5 composite increases with increase of Ta_2O_5 content in the PANI matrix which may due to the increase in effective dispersion of Ta_2O_5 particles. The ac conductivity of polyaniline exhibit two phases in the frequency range 50 Hz (1.69 logf) to 10^6 Hz (6.69 logf). For the frequency between 50 Hz (1.69 logf) to 10^5 Hz (5 logf), the conductivity values are almost constant. The conductivity increases suddenly in the frequency range 10^5–10^6 Hz (6.69 logf). Lattice polarization around a charge in localized state may be responsible for multiple phases of conductivity [18].

3.4 DC Conductivity

To investigate the effect of Ta_2O_5 on dc conductivity of the PANI was studied as a function of temperature. Fig. 5 shows the electrical dc conductivity (σ_{dc}) of undoped PANI and PANI/Ta_2O_5 composite as the

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function of measured temperature range 40 °C to 200 °C. The dc conductivity of the PANI and PANI/ Ta_2O_5 composite increases with increase in temperature suggests that the semiconductor characteristics of the PANI and composite. It is evident that the conductivity of the PANI/Ta_2O_5 composite is higher than the conductivity of PANI. Also, the conductivity increases with increase in Ta_2O_5 concentration into the PANI matrix suggests that the increasing electrical conductivity property of the PANI due to the interaction between the PANI and Ta_2O_5 particles [19].

It is observed from the Fig. 5 that, conductivity of PANI and composite is observed in two phases i.e., the conductivity in the range 30 °C – 125 °C and 125 °C – 200 °C. The first phase conductivity is almost constant which may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is a sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually observed at high temperatures as reported by few researchers in their work [20,21].

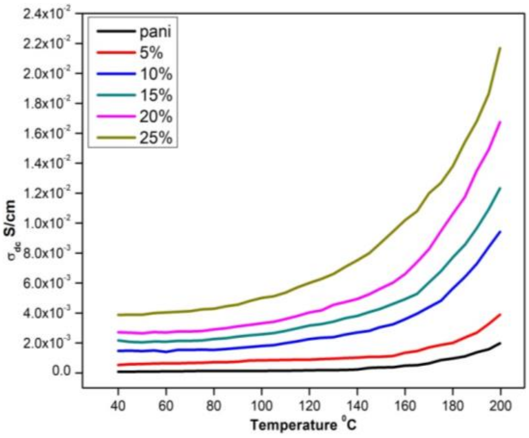

Fig. 5 DC conductivity of PANI and PANI/Ta_2O_5 composite

3.5 Dielectric Constant

Frequency dependent dielectric constant has been determined using different values of equivalent parallel capacitance, dissipation factor, and parallel equivalent resistance are measured using LCR meter as function of frequency. Dielectric parameters have been calculated using the following equations,

$$\varepsilon' = \frac{C_p}{C_0} \,\&$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{or} \quad \varepsilon'' = \varepsilon' \tan\delta$$

Fig. 6 shows the frequency dependent dielectric constant (ε') of the PANI and PANI/ Ta_2O_5 composite. The dielectric constant of the PANI and PANI/ Ta_2O_5 composite decreases with increase in measured frequency. The high dielectric constant was observed at lower frequency range and low dielectric values at higher frequency range. The higher dielectric constant at lower range frequency may attribute due to the PANI samples interfacial effects and also occurrence of periodic reversal of the electric field at higher frequency range. Further the decrease in the dielectric constant at higher range frequency may attribute to polarization due to decrease in the charge accumulation [22].

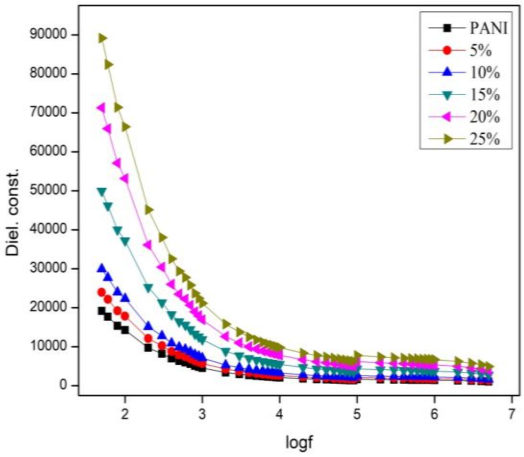

Fig. 6 Dielectric constant of PANI and PANI/Ta_2O_5 composite

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4. Conclusion

PANI/Ta_2O_5 composite were successfully prepared using chemical oxidative polymerization method with different content of Ta_2O_5 in the PANI matrix. The structural and morphology studies of PANI/Ta_2O_5 support the efficient interaction of Ta_2O_5 particles. The broad peak in the XRD pattern confirms the existence of PANI and XRD pattern of composite confirms the successful formation of PANI/Ta_2O_5 composite. The average crystallite size of the PANI is 2.86 nm which is increased to 46.80 nm when Ta_2O_5 is doped in the PANI matrix. SEM image of PANI shows uniform morphology with semi-crystalline structure. The SEM image of PANI/Ta_2O_5 reveals that the dopant particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. The ac conductivity of PANI and composite increases with increase in frequency. The conductivity of the PANI/Ta_2O_5 composite is higher than that of the conductivity of the PANI. The dc conductivity of the PANI and PANI/ Ta_2O_5 composite increases with increase in temperature suggests the semiconductor characteristics of the PANI and composite. It is evident that the conductivity of the PANI/Ta_2O_5 composite is higher than the conductivity of the PANI. The dielectric constant of the PANI and PANI/ Ta_2O_5 composite decreases with increase in measured frequency. The high dielectric constant was observed at lower frequency range and low dielectric values at higher frequency range.

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