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Dielectric study of Polyaniline–Ta_2O_5 Polymer Composites

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Abstract

Polymers with oxide materials constitute a new class of polymer composite materials, that integrates materials science and technology. Chemical oxidation of aniline is carried out for Polyaniline (PANI) and in-situ polymerization for Polyaniline-Ta_2O_5 (PANI-Ta_2O_5) composite materials. Characterization tools such as SEM, XRD and IR were used. The dielectric behavior is investigated in the frequency range 10^2–10^7 Hz at room temperature. It is observed that, the Ta_2O_5 particles in the PANI matrix have a greater influence on the dielectrics

Keywords: In Situ, Dielectric Constant, Polyaniline, Ta_2O_5

INTRODUCTION

Research on polymer composite materials integrates the science and technology of polymeric materials. Polymers containing metal oxides constitutes polymer composites are well studied for its properties (1-3). Conducting polymers have a variety of applications in the Industrial, Scientific and Medical (ISM) fields. Applications like anticorrosion, static coating electromagnetic shielding etc comes under first generation. Second Generation of electric polymers have applications such as transistors, LEDs, solar cells batteries etc. Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world (1-5).

The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use for practical applications. One of the most widely studied conducting polymers; Polyaniline can be obtained chemical or electrochemical route. Polymeric materials has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices (4-6). Polyaniline has received much attention because of its unique reversible proton doping, high electrical conductivity, ease of preparation and cost effective. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing (7, 8). Metal oxides dispersed polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. Ta_2O_5 is one of the examples of oxide material, which is known for functional oxide materials with prominent applications (6-11).

Conducting PANI containing such metal oxide materials called PANI composite with variable compositions my lead to desirable properties. These materials are especially important owing to their bridging role between the worlds of conducting polymers (12-15).

However, in this paper we report the synthesis technique of PANI and PANI-Ta_2O_5composites. The characterization of Ta_2O_5, PANI and PANI-Ta_2O_5 were carried out by characterization tools and studied the dielectric properties of the prepared samples.

MATERIALS AND METHODS

Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl), aniline and Tantalum oxide (Ta_2O_5) used were of AR grade. Double distilled water is used as a solvent for chemical synthesis process. Polyaniline is prepared by oxidative method and its composites were prepared by insitu polymerization aniline with dispersion of Ta_2O_5.

Synthesis of Polyaniline-Ta_2O_5 Composites

0.1M of aniline was dissolved in 1M HCl to form Polyaniline (PANI). Tantalum oxide (Ta_2O_5) is added in the weight percent of 10, 20, 30, 40 and 50 to PANI solution with vigorous stirring in order to keep the Tantalumoxide (Ta_2O_5) suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate $[(NH_4)_2S_2O_8]$ which acts as the oxidant was added slow and steadily with continuous stirring for 4 – 6 hrs at 5^0C temperature. The precipitated powder recover was vacuum filtered and washed with deionizer water. Finally the resultant precipitate was dried in an oven for 24 hrs to achieve a constant weight. In this way five different polyaniline -Ta_2O_5 composites with different wt % of Ta_2O_5 (10, 20, 30, 40 and 50) in polyaniline has been synthesized.

RESULTS AND DISCUSSION

Figure1 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 $2\theta \approx 26.40^0$.

Figure 2 shows the X-ray diffraction pattern of polyaniline / Ta_2O_5 composite with 50 wt % of Ta_2O_5 in polyaniline. It is seen that the peaks of Tantalum oxide indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of PANI, the prominent peaks corresponding to 2 θ = 22.819^0, 28.244^0 28.733^0 and 36.614^0 are due to (010), (411), (102) and (121) planes of Ta_2O_5. By comparing the XRD patterns of the composite and JCPDS of Ta_2O_5 No. 79-1375, it is confirmed that Ta_2O_5 has retained its structure even though it is dispersed in PANI during polymerization reaction.

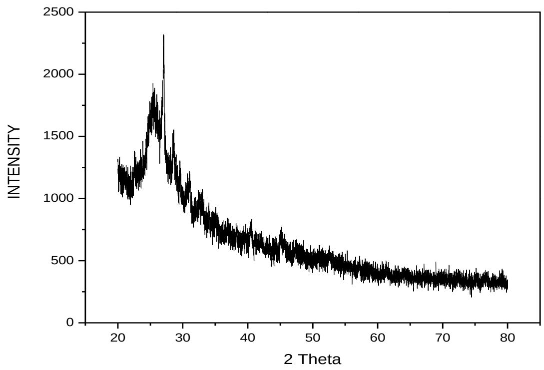

Figure 1. X-ray diffraction pattern of Polyaniline

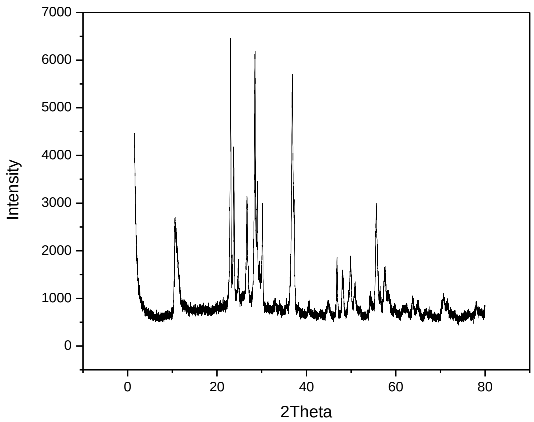

Figure 2. X-ray diffraction pattern of Polyaniline – Ta_2O_5 composite

Figure 3 shows the IR spectra of polyaniline where the transmittance is plotted as a function of wave number (cm^{-1}). Careful analysis of the spectra reveals the presence of intensity peaks 3417.58cm^{-1}, 2923.26cm^{-1}, 1574.77 cm^{-1}, 1489.81 cm^{-1}, 1300.17 cm^{-1}, 1118.23 cm^{-1}, 817.61 cm^{-1} and 502.12 cm^{-1}. The spectra show the presence four intense bands at 1574.77 cm^{-1}, 1489.81cm^{-1}, 1300.17 cm^{-1} and 1118.23 cm^{-1}. The peak at 3417.58 is due to secondary amine, 2923.26 is CH_2 a symmetric stretching. The peaks at 1574.77 cm^{-1} and 1489.81 cm^{-1} may be attributed due to the presence of quinoid (N=Q=N) and benzenoid (N=B=N) ring stretching. 1300.17cm^{-1} is due to N-H deformation,

Figure 4 shows the IR spectra of pure Ta_2O_5. The important peaks are observed at 831.01cm^{-1}, 747.34 cm^{-1} and 607.26 cm^{-1}are due to metal oxygen (Ta-O) vibrational modes. The peaks below1000 cm^{-1} confirm the formation of metal oxide composite

The IR spectra of polyaniline – Ta_2O_5 composite (50 wt % of Ta_2O_5 in PANI) is shown in figure 5. The prominent peaks that are observed in polyaniline – Ta_2O_5 composite are 3434.06cm^{-1}, 2923.64 cm^{-1}, 1580.26 cm^{-1}, 1489.84 cm^{-1}, 1303.60 cm^{-1}, 1144.97 cm^{-1}, and 507.61 cm^{-1}. By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The data suggest that, there is also a Vander walls kind of interaction between the polymeric chain and Ta_2O_5.The important peaks observed in case of polyaniline, Ta_2O_5 and polyaniline / Ta_2O_5 composites are given in the table-1.

Table 1. FTIR data of PANI, Ta_2O_5 & PANI-Ta_2O_5

Sample	**Observed band due to (cm^{-1})**
Pure Polyaniline	3417.58, 2923.26, 1574.77 , 1489.81 , 1300.17, 1118.23, 817.61 and 502.12
Pure Ta_2O_5	831.01, 747.34 and 607.26
PANI – Ta_2O_5	3434.06, 2923.64, 1580.26, 1489.84, 1303.60, 1144.97, and 507.61

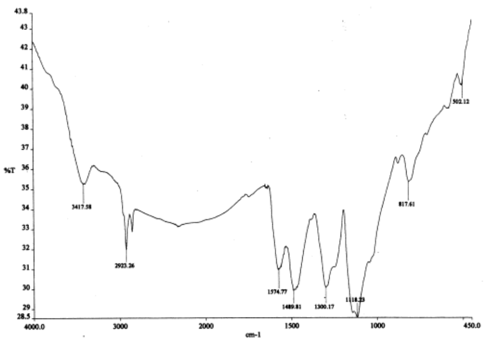

Figure 3. FTIR spectra of Polyaniline

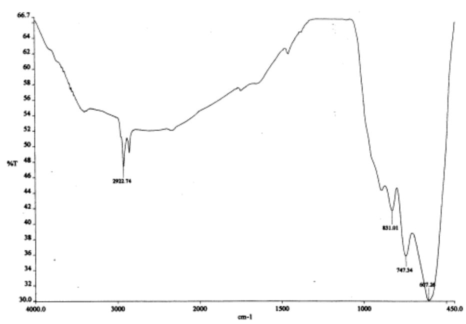

Figure 4. FTIR spectra of Ta_2O_5

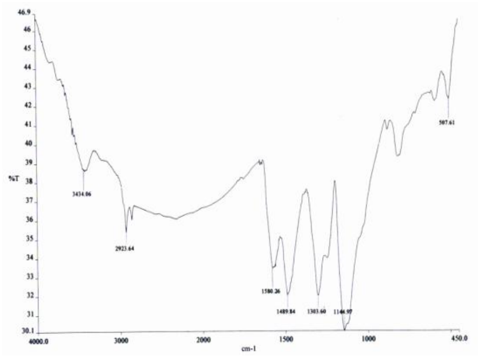

Figure 5. FTIR spectra of Polyaniline – Ta_2O_5 composite (50 wt %)

SEM micrograph of conducting polyaniline synthesized by chemical oxidative method is shown in figure 6. It is clearly seen that the micrograph of polyaniline is branched and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen. The polymeric amorphous netting can also be observed in the image

The SEM micrograph of pure Ta_2O_5 is shown in figure 7. Most of the molecules are stacked together to form a porous big clustered image. The irregular shaped particles with globular arrangement is observed, the morphological image clearly showing the crystalline nature of the oxide material, The SEM micrograph of polyaniline/Ta_2O_5 composite with 50 wt% of Ta_2O_5 in polyaniline is shown in figure 8.

The composites possess grains and porous structure. Further the composites have capillary pores connected by pores. Such composites are likely to facilitate the absorption of water vapors or gas due to the large surface area and capillary pores. One can observe fine dispersion of theTa_2O_5 spherical particles in the amorphous sheet. Most of the particles are irregular shape with surface blockage in polymer matrix. Crystalline behavior is observed in the composite image due to close assembly of the particles.

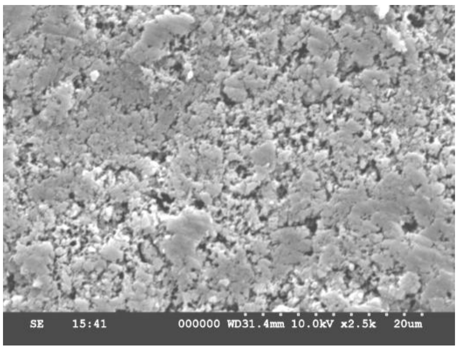

Figure 6. SEM Micrograph of Polyaniline

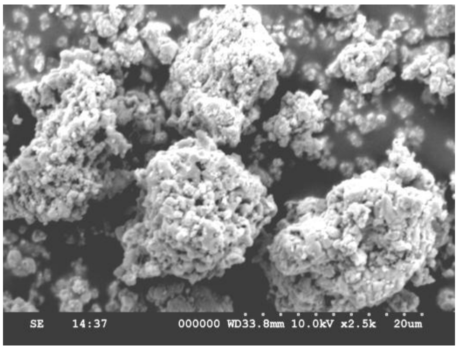

Figure (7) SEM Micrograph of Ta_2O_5

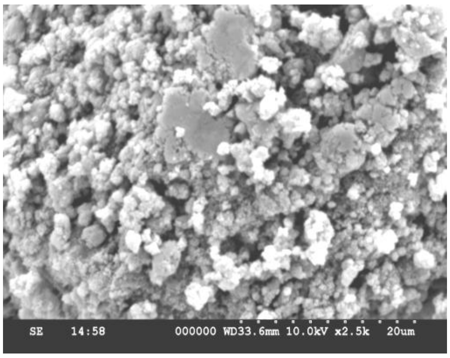

Figure 8. SEM Micrograph of Polyaniline – Ta_2O_5

Figure 9 shows the variation of dielectric constant (ε') as a function of frequency for polyaniline –Tantalum oxide composites (different wt %). In all the cases it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to the Debye relaxation mechanism taking place in these materials.

Figure 10 represents the variation of ε' as a function of wt% of Ta2O5 at room temperature and at three different frequencies. It is observed that the values of dielectric constant increases up for 20, 30 & 50 wt% and then decreases for 10& 40 wt% of Ta2O5 in PANI. All these results go in accordance with the conductivity behavior.

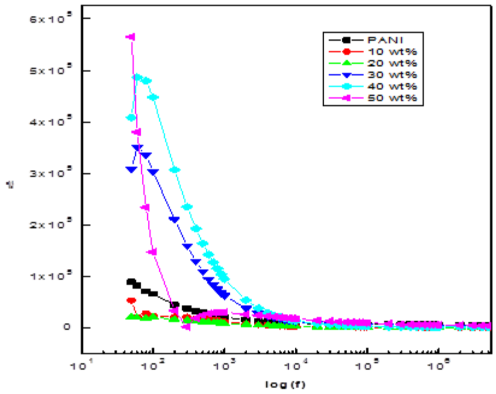

Figure 9. Variation of ε' as a function of frequency for polyaniline –Ta_2O_5 composites

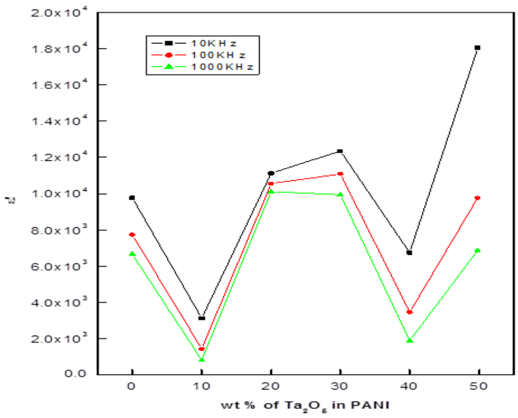

Figure 10. Variation of ε' as a function of wt% of Ta_2O_5

CONCLUSIONS

Insitu polymerization is a simple method for preparation of conducting PANI composites. This method may be used for the preparation of other than PANI composites. Structural changes of pure PANI and pure metal oxide is taken place due to the presence of oxide material in the PANI is observed by XRD pattern. Similarly, morphology and bonding changes is observed in composite material compared to pure PANI and pure metal oxide. The results of dielectric property show a strong dependence on the wt. % of Ta_2O_5 in PANI.

REFERENCES

[1] Devindrappa, Rao U V S, Ambika Prasad M V N Study of dc conductivity and Battery application of PEO/PANI Composites. *Journal of Power sources* 155, (2006). 3689

[2] Sinha R Outline s of polymer technology, New Delhi: Prentice Hall of India

private Limited (2002).

[3] Lagashetty A, Vijayanaand, Basavaraj S, Bedree MD, Venkataraman A. Preparation, characterization and thermal studies of γ-Fe_2O_3 and CuO dispersed polycarbonate nanocomposites. *J. Thermal Analysis and Calorimeter.*99 (2010)577.

[4] Jiang LH, Leu C MWei KH Layered silicates/fluorinated polyamide nanocomposites for advanced dielectric materials applications. *Advanced Materials*. 14 (2002). 963.

[5] Caruso F. Nanoengineering of particle surface. *Advanced Materials*. 13 (2001)11.

[6] Mallikarjuna NN, Venkataraman A and Aminabhavi TM. A study on γ-Fe_2O_3 loaded Poly (methyl methacrylate) Nanocomposites. *Journal of Applied Polymer Science.* 94 (2004) 2551.

[7] Murgendraappa MV, Ambika Prasad MVN. Dielectric spectroscopy of Polypyrrole-γ-Fe_2O_3 composites. *Materials Research Bulletin*. 41 (2006)1364.

[8] Raghavendra SC , Khasim S, Revansiddappa M, Ambika Prasad MVN, Kulkarni AB. *Bulletin of Materials Science*. 26 (7) (2003) 733.

[9] Leu CM, Wu Z, Wei KH. Synthesis and properties of covalently bonded layered silicates/polyimide (BDTA-ODA) nanocomposites. *Chemical Materials*. 14 (2002) 3016.

[10] Lagashetty A, Bhavikatti A M, Mahadevi B and Kulkarni S. Synthesis and characterization of BaTiO3 by thermal decomposition of metal oxalate precursors. *International Journal .Electronics Engineering. Research.* 2(4) (2010) 581.

[11] Parvatikar N, Jain Shilpa, Kanamadi CM, Chougule BK, SV Bhoraskar and Ambika Prasad MVN. Humidity Sensing and Electrical Properties of Polyaniline/Co_3O_4 Composites. *Journal of Applied Polymer Science.* (2007) 653

[12] Mallikarjuna NN, Manohar SK, Kulkarni PV, Venkatarman A and Aminabhavi TM. Novel high dielectric constant nanocomposites of polyaniline dispersed with PANI-Fe_2O_3 nanoparticles. *Journal of Applied Polymer Science.*, 97 (2005)1868

[13] Parvatikar N, Ambika Prasad MVN. Frequency dependent conductivity and dielectric permittivity of Polyaniline/CeO_2 Composites. *Journal of Applied Polymer Science.*100 (2006)1403.

[14] Patil SD, Raghvendra SC, Revansiddappa M, Parvatikar N and Ambika Prasad MVN. Synthesis, Transport and Dielectric Properties of Polyanniline-Cobaltous Oxide – Composites. *Bulletin of Materials Science* 30 (2007) 89

[15] Mahesh B, Basavaraj S, Balaji S D, Shivakumar V, Lagashetty A, Venkataraman A. *Polymer Composites* (2009)1668.