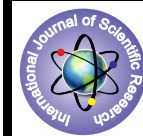


γ -Fe₂O₃ Dispersed Polyaniline Nanocomposite



Engineering

KEYWORDS: Polyaniline, γ -Fe₂O₃, nanocomposites.

Anilkumar Kodge

Singhania University, Rajasthan, India

Arunkumar Lagashetty

Appa Institute of Engineering & Technology, Gulbarga, Karnataka, India

ABSTRACT

Materials at nano dimension in polymer dispersion constitute conventionally filled polymer enhances the material science and technology. Dispersion of nano magnetic material (γ -Fe₂O₃) in to Polyaniline (PANI) matrix composite (γ -Fe₂O₃ -PANI) were prepared by employing interfacial polymerisation. Ammonium persulphate is used as an oxidising agent for oxidation of aniline with gamma iron oxide. The simultaneous oxide addition and aniline polymerisation process leads to the complete composite polymer. Crystallinity of the prepared composite were well studied by X-ray diffraction (XRD), bonding by infrared (IR) and morphological images of composite is viewed by scanning electron micrograph (SEM) tool respectively. Thermogravimetric (TGA) and differential (DTA) analysis were carried out to know thermal stability of the (γ -Fe₂O₃ -PANI) composite.

1.0 Introduction

Polymer nanocomposite materials represent a new alternative to conventionally nanoscopic inorganic materials filled polymers [1-2]. Filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites, because of their nanometer sizes [3-4]. Properties include increased modulus and strength; outstanding barrier properties improved solvent, heat resistance and decreased flammability. Researcher have attempted to enhance the desired properties of Polymer nanocomposites and, thus to extend their utility by reinforcing them with nanoscale materials to drive improved properties compared with to the more conventional particulate-filled microcomposites [5-6].

Polymer nanocomposites, also presently known as nanostructure materials, are materials in which nanoscopic inorganic particle, typically 10-100nm in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the performance properties of the polymer [7]. Nanocomposite materials based on nanosized inorganic materials have been of great interest to researchers due to their applications [8-9]. Metal oxides dispersed polymer nanocomposites have been extensively studied since they exhibit interesting properties with many applications such as quantum electronic devices, magnetic recording materials, sensors, capacitors, smart windows, toners in photocopying, conducting paints and rechargeable batteries [10-14]. These composites are often prepared by dispersing nanomaterials in a non-conducting polymer matrix [15]. The present investigation is the gamma iron oxide dispersed PANI nanocomposite material, which is prepared by insitu polymerization of aniline. The as prepared composite were characterized by different characterization techniques and thermal and electrical study of the PANI composite is under taken.

2.0. Experimental

2.1 Materials, Methods

All chemicals used in the experiment are of AR grade. Insitu polymerization method is adopted for the synthesis of PANI composite.

2.2. Preparation of γ -Fe₂O₃-polyaniline nano composite powder (γ -Fe₂O₃ -PANI)

Insitu polymerization method adopted for the preparation of γ -Fe₂O₃ dispersed polyaniline composites film. The preparative procedure follows; 10 g of aniline was dissolved in 100 ml of distilled water and is acidified with hydrochloric acid (10 ml) and 0.1g of γ -Fe₂O₃ was added to the same and then thoroughly stirred. The solution was cooled under ice water to 0 OC. Add 12 ml 1M (NH₄)₂S₂O₈ to the reaction mixture, which was stirred for 30 minutes and allowed to stand for a further period of 60 minutes. The resultant product obtained was filtered out, washed thoroughly with water, and dried until constant weight at 40 OC. Figure 2.6.shows optical image of as prepared

iron oxide dispersed polyaniline composite. This image shows the dispersion of oxide particles in to the polyaniline.

2.3.Characterization

The powder X-ray diffraction pattern of cobalt oxide and γ -Fe₂O₃ -PANI nanocomposite film was obtained from GEOL JDX-8P X-ray diffractometer using CoK α radiation. The morphology of the nanocomposite film was obtained from Leica Cambridge-440 scanning electron microscope. nanocomposite material was recorded on a Perkin-Elmer FTIR spectrometer [model 100] in the range 3000-300cm⁻¹. The thermal traces were obtained from Perkin-Elmer instrument.

2.4.Preparation of the pellets

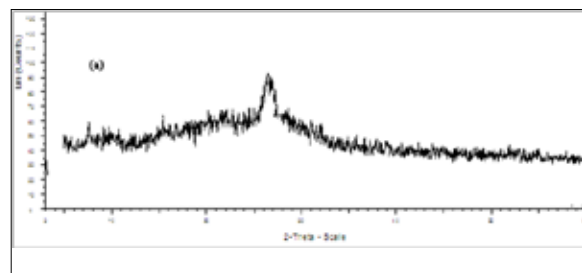
The powders were crushed and ground finely. A few drops of polyvinyl alcohol (PVA) binder was added to the powder and pressed into pellets of 12 mm diameter and 1-2 mm thickness for conductivity and dielectric measurements by applying a pressure of 70 MPa. For the thermal expansion studies of the powder polymer, the pellet size was 8 mm diameter and 8-12 mm thick (length). The binder burn off was carried out by a slow heating at a rate of 3 K/minute to 373 K, soaking time being an hour.

3.0.Results and Discussion

3.1. X-ray diffraction

Figure 1 (a-b) shows the X-ray diffraction pattern of pure PANI and γ -Fe₂O₃ -PANI, respectively. Pure PANI shows the broad peak at about 2 θ value about 27oC is the characteristic peak of PANI. This is ascribed to the periodicity in parallel and perpendicular directions of the polymer chain. The highly intense peaks are observed in the composite pattern are due to the presence of γ -Fe₂O₃ and are indexed in the composite pattern as given in the figure 1(b). The indexed peaks (311) and (400) and (440) belongs to γ -Fe₂O₃ (Peaks matches well with JCPDS in the γ -Fe₂O₃-PANI composite) reflects the composite formation with development of crystallinity in the PANI matrix. From these XRD results one may conclude that, the addition of γ -Fe₂O₃ into the polymer matrix results in the decrease in degree of crystallinity of γ -Fe₂O₃.

3.2.SEM study



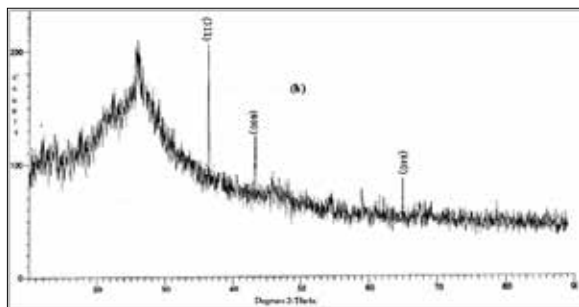


Figure 1: XRD pattern of a) pure PANI b) γ -Fe₂O₃-PANI composite

Figure 2 (a-b) shows the SEM images of as prepared PANI and γ -Fe₂O₃-PANI composite respectively. Pure PANI shows less crystalline nature due to particle agglomeration in the image. However, composite shows the presence of some fibrous morphology is seen on the particle surface when PANI content in the composite is high and this fibrous nature on decreases with increase in γ -Fe₂O₃ wt %. Figure 2(b) shows globular structure due to compact and irregular morphology confirms the formation of composite. This nature for decrease in fibrous nature can arise from the fact that γ -Fe₂O₃ particles of their nanosize and high surface area possibly act as sites for polymerisation process. During polymerisation one end of the polymer gets anchored on the γ -Fe₂O₃ particles and other was the growing end, which could project extensively out of the surface.

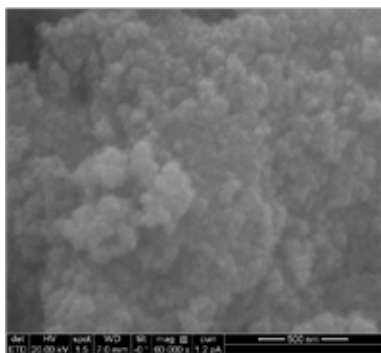
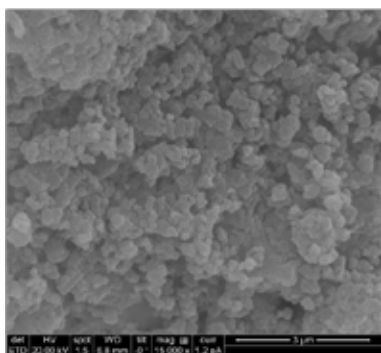


Figure-2: SEM image of a) pure PANI b) γ -Fe₂O₃-PANI composite

3.3. Infrared Study

The infrared spectra of the polyaniline and γ -Fe₂O₃ dispersed polyaniline composite are shown in Figure 3(a-b). The intensities of some of the peaks, for example, 1743, 1537, 1291, 1238, 1022 and 822 cm⁻¹, are affected by the presence of γ -Fe₂O₃ during PANI synthesis. These differences in the IR spectra can



be explained on the basis of constrained growth and restricted modes of vibration in the PANI grown in presence of γ -Fe₂O₃. In such case, the aniline monomer gets adsorbed on the particles which were dispersed in the reaction mixture and polymerization proceeds initially on the surface when (NH₄)₂S₂O₈ was

added to the solution. This leads to adhesion of the polymer to γ -Fe₂O₃ particles and the constrained growth around these particles. Such adsorption and constrained motion of the chains leads to differences in IR spectra.

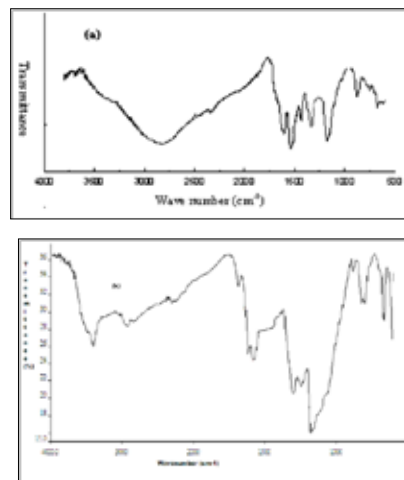


Figure- 3: FTIR of a) pure PANI b) γ -Fe₂O₃-PANI composite

3.4. Dielectric constant

Figure 4(a-b) shows the variation of dielectric constant (ϵ') with respect to frequency (102 to 107 kHz) of pure polyaniline and gamma- polyaniline composite respectively. PANI shows a steep decrease from the initial value of 18 at 102 Hz to 5 at 104 Hz and thereafter the ϵ' , remains constant. The decrease in ϵ' , is more sharp from 2.5 * 10² to 10³ Hz and thereafter the decrease in ϵ' , is quite slow. The dielectric loss (tan δ) also similar trend in the initial loss of 8 and goes steeply to 0 at 107 Hz. These values of ϵ' , and tan δ , are in general agreement with the chemically synthesized non-conducting PANI sample.

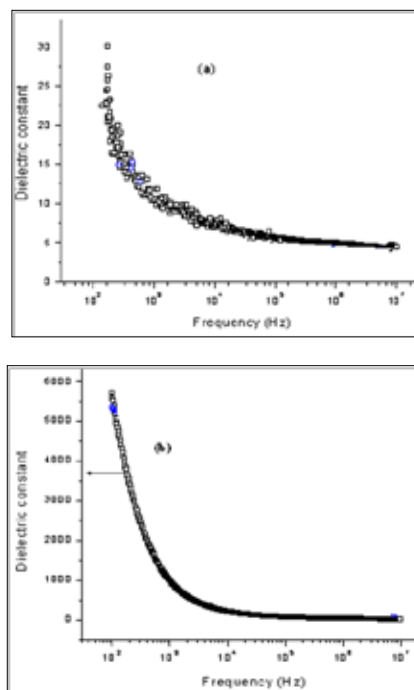


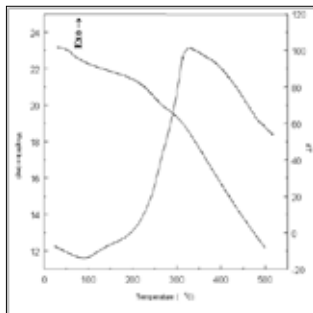
Figure-4: Dielectric constant of a) Pure PANI b) γ Fe₂O₃-PANI composite

To understand the dielectric behavior of the γ -Fe₂O₃-PANI composites, the variation of ϵ' , with respect to frequency and variation of tan δ , with respect to frequency is undertaken. In Figure 4(b) the ϵ' , value falls sharply from 3500 at 102 Hz to 200 at 103 Hz. Thereafter the ϵ' , values remains almost constant. The tan δ , shows an initial value of 3 at 102 Hz and is constant upto 103

Hz thereafter the fall in $\tan \delta$, is a slow and steady process and reaches 0 at 107 Hz.

3.5. Thermal analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) with heating rate 10 °C/min and under static air atmosphere are carried out for PANI and γ -Fe₂O₃ - polyaniline composite sample, and the thermal trace is shown in Figure 5(a-b). The TGA/DTA data for pure polyaniline shows that the decomposition temperature 370 °C, In addition to that the DTA plot shows another additional feature (small hump before decomposition), which corresponds to the $\gamma \rightarrow \alpha$ phase transition. When the wt % of γ -Fe₂O₃ increases this feature remains unaltered, and the decomposition temperature shifts towards higher value. The composite trace shows that the initial weight loss on the TGA trace and the endothermic peak on the DTA trace are due to the loss of moisture present in the sample. The continuous weight loss on the TGA trace and the broad exothermic peak on the DTA trace are due to decomposition of the polymer. Besides, the DTA trace shows another additional feature (small hump before decomposition), corresponding to the $\gamma \rightarrow \alpha$ phase transition. When the wt % of γ -Fe₂O₃ increases this feature remains unaltered, and the decomposition temperature shifts towards higher value.



The differential scanning calorimetry (DSC) analysis with heating rates of 10 °C/min and under nitrogen atmosphere are carried out for γ -Fe₂O₃ -PANI sample, and its trace is shown in Figure 5(c). Composite trace shows presence of two widely separated endothermic peaks one at 250 °C and another above 330 °C. The second endothermic peak would correspond to decomposition of the polymer. The first endothermic peak would then correspond to a phase transition possibly a $\gamma \rightarrow \alpha$ transition. Our statement of the $\gamma \rightarrow \alpha$ transition preceding the polymer decomposition was further substantiated from the DSC traces by observing the shifts in the shoulder. As the γ -Fe₂O₃

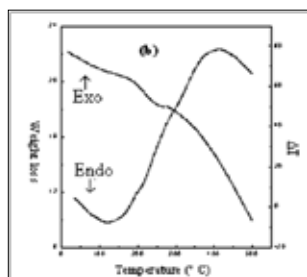


Figure 5(b) TGA/DTA trace of γ -Fe₂O₃-PANI composite

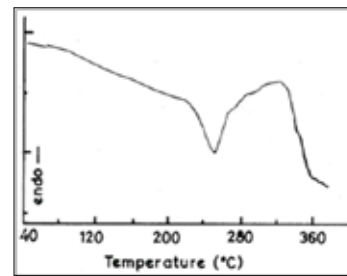


Figure-5(c): DSC trace of γ -Fe₂O₃-PANI composite

content goes on increasing the shoulder peak gets more pronounced and finally separated. Hence, from these observations, it is understood that formation of α -Fe₂O₃ aids in the decomposition of PANI and that the γ -Fe₂O₃ stabilized the PANI composite.

3.6. Electrical Conductivity

Figure 6 shows electrical conductivity of γ -Fe₂O₃ -PANI composite. The room temperature conductivity values are of 10-5S/cm. Initially conductivity of the sample increases slowly up to 80°C and again increases up to 160°C. This is due to the loss of water molecules, then exponential increase with increase in temperature.

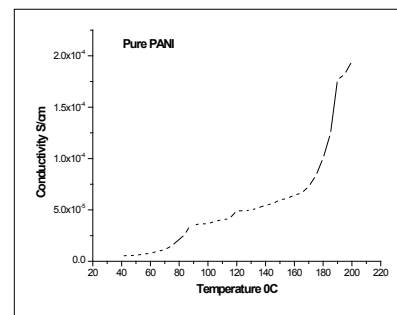


Figure-6: conductivity study of γ -Fe₂O₃-PANI composite

CONCLUSION

Cobalt oxide dispersed poly (methyl methacrylate) composite film was prepared by a simple solvent casting method. The development of crystallinity in PMMA is due to incorporation of cobalt oxides in to PMMA matrix. Presence of cobalt oxide particles in the PMMA matrix changes the morphology of the pure PMMA. Additional reflections and shifted frequencies in the FTIR spectrum confirm the presence of the composite formation. Thermal study concludes the increase in thermal behavior of the polymer composite compared to its pure polymer.

ACKNOWLEDGEMENT

Authors are grateful to Prof. A Venkataraman, Professor and Chairman, Department of Materials Science, Gulbarga University, Gulbarga for useful discussion in spectral analysis. We are also thankful to Sri Guruling, I.I.Sc, Bangalore for providing spectral data. Thanks are due to President and Principal, Rural Engineering College, Bhalki for constant support and encouragement.

REFERENCE

1. J.Richard, P. Spontak and N. P.Patel, Current Opinion Colloid Interf. Sci., 53 (2000) 34. | 2. C. Castro, A. Millan and F.Palocio, J. Mater. Chem. 10(2000) 1945. | 3. A. Lagashetty, H.Vijayanand, S. Basavaraja, M. D. Bedree and A.Venkataraman, J. Therm. Anal. & Cal., 99 (2010)577. | 4. B.Govindraj, N.V. Shastry and A Venkataraman, J Appl Polym Sci., 93(2004) 778. | 5. A.Lagashetty, V. Havanoor, S. Basavaraj, A.Venkataraman, Bull. Mater. Sci., 28(5) (2005)477. | 6. N. N.Mallikarjuna, S.K.Manohar, P. V.Kulkarni, A.Venkataraman, T.M.Aminabhavi, J. Appl. Polym. Sci., 97 1868 . | 7. R. Sinha. Outlines of polymer technology (New Delhi: Prentice Hall of India Private Limited) 2002. | 8. R. D. Shull and L. H.Bennett, Nanostructured Mater. 1 (1992)83. | 9. M.D. Bedre, S.Basavaraj, D. S. Balaji, V. Shivakumar, A. Lagashetty, and. A Venkataraman, Polymer Composites, 30(11) (2009)1168. | 10. C.M.Leu, Z.W. Wu, K. H.Wei, Chem. Mater. 14 (2002)3021. | 11. J. Wang, J. Yang, J. Xie, N. Xu, Adv. Mater. 14(2002)963. | 12. L. H. Jiang, C.M.Leu and K.H.Wei, Adv. Mater. 14 (2002)426 | 13. M. Hughes, M.S. Shaffer, P.A.C. Renouf, C. Singh, G. Z.Che, D.J.Fray and A.H Windle, Adv. Mater., 14 (2002)382. | 14. T.Vossmeier, B.Guse, I. Besnard, R. E Bauer, K.Mullen and A.Yasuda, Adv. Mater., 14 (2002)238. | 15. M P.Lalko, L.Rakesh and S.Hirschi, J. Therm. Anal. Color: 95 (2009)203 |