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Thermal, dielectric and microwave absorption properties of polyaniline–$CoFe_2O_4$ nanocomposites

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ABSTRACT

The present paper deals with the synthesis of conducting ferromagnetic polyaniline–$CoFe_2O_4$ (PC) nanocomposites via one-step chemical oxidative polymerization of aniline in the presence of $CoFe_2O_4$ nanoparticles (30–40 nm). These nanocomposites of PC have been characterized by high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM). Extended thermal analysis has revealed that the activation energy of these nanocomposites varies from 75.3 to 84.3 kJ/mol as compared to the activation energy of 50.3 kJ/mol for polyaniline-DBSA. In addition, dielectric and microwave absorption properties of the nanocomposites have been measured in the frequency range of 12.4–18 GHz (Ku-band) which demonstrate that more than 99% attenuation of microwaves (SE_A = 21.5 dB) has been achieved using these nanocomposites. Systematic investigations reveal that the $CoFe_2O_4$ nanoparticles in the polyaniline matrix have phenomenal effect in determining the microwave absorption properties of the nanocomposites.

1. Introduction

Electronically conducting polymers are the novel class of synthetic metals with wide spread application in number of technological devices like EMI shielding and electrostatic charge dissipation [1,2], sensors [3,4], organic light emitting diodes [5,6] and polymer solar cells [7,8]. Similar to inorganic semiconductors, the conductivity of conjugated polymers can be tuned by several orders of magnitude. Polyaniline is the most attractive conducting polymer due to its low cost, high environmental stability, good electrical conductivity and potential applications in molecular electronics. The electrical properties of polyaniline could be modified by the addition of inorganic fillers [9–11]. Nanoscale ferrimagnetic fillers are the most attractive due to the intriguing properties arising from the nanosize and large surface area. The insertion of ferrimagnetic nanoparticles may improve the magnetic and dielectric properties of host materials. Therefore, conjugated polymers combined with magnetic nanoparticles to form ferromagnetic nanocomposites provide an exciting system to investigate the possibility of exhibiting novel functionality. Composites with nanosize ferromagnetic particles can be useful as microwave absorbers since nanoparticles exhibit distinct magnetic properties compared to bulk materials. In the ferromagnetic polymer nanocomposite, the ferromagnetic inclusions (nanoparticles) do both, reduce impedance mismatch at the front interface of the absorber and increase absorption of electromagnetic wave.

The main problem in designing an electromagnetic absorber is related to the choice of the materials with good control over some magnetic and dielectric properties. Both, the magnetic and electrical properties of the materials, must be matched with the frequency of the radiations, where a broadband of frequencies must be covered. The materials must be designed so that their magnetic and dielectric properties vary with frequency in a precise fashion [12]. In fact, there are four electromagnetic parameters (the real and imaginary parts of permittivity and permeability) that must be independently manipulated [13]. Magnetic absorption materials made by dispersing magnetic fillers in an insulating matrix continue to play a leading role in the investigation and application of microwave absorption materials [14]. Many studies have been carried out to investigate the effects of ferrite materials and their volume percentage in the composite on the absorption of microwave and the influence of the addition of conducting fiber on the microwave absorbing properties [15,16]. Some attempts have been made to verify the correlation between the material constants, ε_r and μ_r, and microwave absorption in the sintered ferrites that contain divalent metal ions [17]. Extensive study has been carried out on new absorption materials to develop microwave-absorbing materials with a high efficiency [18,19]. Due to moderate

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conductivity and high dielectric losses, these polymer composites found its application as microwave absorber.

The present paper reports the synthesis of polyaniline nanocomposites having high dielectric and magnetic losses, by the incorporation of cobalt ferrite nanoparticles in the polyaniline matrix. To achieve this goal, nano-sized cobalt ferrite particles have been synthesized and embedded in the polyaniline matrix via *in situ* emulsion polymerization using dodecyl benzene sulfonic acid (DBSA) as dopant, which also act as a surfactant. These polymer composites have been characterized using various techniques. The interaction of ferrite particles with the polymer has been visualized using the high-resolution transmission electron microscope (HRTEM), FTIR and extended thermal analysis. Complex permittivity, permeability and microwave absorption performance of the composites have been studied in 12.4–18 GHz frequency range. The effects of cobalt ferrite content on the properties of the composites have been investigated by different measurement techniques to ensure the fabrication of the proper material for the commercial applications.

2. Experimental

2.1. Material

Aniline (An), ammonium peroxydisulfate $(NH_4)_2S_2O_8$ (APS), Isopropyl alcohol, citric acid and ammonium hydroxide solution have all been procured from Merck India. Cobalt nitrate and ferric nitrate have been obtained from Qualigen (India). Dodecyl benzene sulfonic acid (DBSA) has been purchased from Acros organics (Belgium). The monomers aniline has been purified by distillation in vacuum before use while all other chemicals have been used as such.

2.2. Synthesis of cobalt ferrite nanoparticles

The synthesis of cobalt ferrite nanoparticles has been carried out via citrate precursor route. In this method, cobalt nitrate, ferric nitrate and citric acid have been dissolved in distilled water in the molar ratio of 1:1:0.3. Aqueous ammonium solution has been added to maintain the pH of the solution at 7.0. The resulting solution has been heated at 90 °C with continuous stirring to form a viscous gel. The viscous gel thus formed has been dried at 100 °C until it ignited in air. With citric acid as reductant and nitrates as oxidant, the gel so formed has been burnt to form dendrite structure which has been crushed in a pastor mortar resulting in brown colored brittle powder. The precursor so formed has been calcined at 1000 °C for 2 h resulting to form cobalt ferrite ($CoFe_2O_4$). To reduce the particle size, cobalt ferrite powder is further grinded for 6 h using Retsch "PM-400" planetary-ball mill in tungsten carbide jars and balls of 10 mm with balls to powder ratio of 2:1.

$$Co(NO_3)_2 + Fe(NO_3)_2 + C_6H_8O_7 \times \underset{pH7,\ 90^\circ C}{\overset{Stirring}{\rightarrow}} \text{Cobalt ferrite precursor} \underset{1000^\circ C,\ 2\ h}{\overset{Calcined}{\rightarrow}} CoFe_2O_4$$

2.3. Synthesis of polyaniline–$CoFe_2O_4$ nanocomposites

Synthesis of polyaniline–$CoFe_2O_4$ nanocomposites has been carried out by *in situ* emulsion polymerization using DBSA as dopant which also act as surfactant. In this synthesis process, a micro emulsion has been prepared by homogenizing (0.3 M) DBSA along with appropriate amount of $CoFe_2O_4$ in distilled water. A thick paste of cobalt ferrite nanoparticles embedded in DBSA has been formed, in which aniline (0.1 M) has been added and again homogenized for 2 h. The micellar solution of aniline/DBSA containing $CoFe_2O_4$ nanoparticles, has been polymerized at −2 °C by the oxidant ammonium peroxydisulfate, $(NH_4)_2S_2O_8$ (0.1 M) with continuous stirring for 6–8 h. The product so obtained has been demulsified using equal amount of isopropyl alcohol and the product has been filtered, washed repeatedly with distilled water and dried at 60–65 °C in vacuum oven.

A range of formulation of polymer nanocomposites having different weight ratio of monomer to ferrite, aniline:cobalt ferrite; 2:1 (PC21); 1:1 (PC11); 1:2 (PC12) and 1:3 (PC13) have been synthesized in DBSA medium to check the effect of ferrite constituents on the properties. Beside this, for comparison of results, polyaniline doped with DBSA (PD13) without ferrite particles has also been synthesized using emulsion polymerization.

3. Characterization

The particle size and the morphology of cobalt ferrite and polymer composites have been examined using a high-resolution transmission electron microscopy (HRTEM, Technai G20-stwin) instrument operating at an accelerating voltage of 200 kV, having a point resolution of 1.44 Å and a line resolution of 2.32 Å. The presence of cobalt ferrite in the polymer composite has been confirmed by X-ray diffraction (XRD) studies carried out on D8 Advance X-ray diffractometer (Bruker) using Cu Kα radiation (λ = 1.540598 Å) in scattering range (2θ) of 20–70° with a scan rate of 0.02°/s and slit width of 0.1 mm. Fourier transform infrared (FTIR) spectra have been recorded on Nicolet 5700 in transmission mode, wavenumber range 400–4000 cm^{-1}. The spectroscopic grade KBr disks has been used for collecting the spectra with a resolution of 4 cm^{-1} performing 32 scans. Thermo gravimetric analysis (TGA) has been performed by Mettler Toledo TGA 851e in nitrogen atmosphere with a flow rate of 60 ml/min, heating rate at 10 °C/min from 25 to 700 °C. Room temperature conductivity has been measured via four-probe method. Four contacts have been made on the compressed pellet of the composite samples using conducting silver paste. These contacts have been connected to the Keithley programmable current source (model 6221) and nanovoltmeter (model 2182A) and conductivity has been calculated based on ohm's law given by

$$\sigma = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A} (\text{S/cm}) \tag{1}$$

The magnetic measurements have been performed using the vibrating sample magnetometer (VSM) (model 7304 Lakeshore cryotronics Inc. USA), having a maximum magnetic field of 1.2T and the vibrating frequency of 76 Hz. Electromagnetic shielding and dielectric measurements have been carried out on an Agilent E8362B Vector network analyzer in the frequency range of 12.4–18 GHz (Ku-band). Powder samples have been compressed in rectangular pellets (15.8 × 7.9 mm^2) and inserted in a copper sample holder, which has been connected between the waveguide flanges of network analyzer.

4. Results and discussion

4.1. FTIR investigation

The addition of oxidant APS to the micellar solution of aniline and DBSA with $CoFe_2O_4$ lead to the oxidative polymerization of aniline which oxidize to form anilinium radical cations. The anilinium radical cations subsequently combine with another unit to form neutral dimers. The further oxidation of these dimers leads to formation of trimers and finally to polymer nanocomposite. These polymer nanocomposites have conductivity of the order of ~0.2 S/cm, which has been found to be lower, as compared to polyaniline doped with DBSA [20]. The decrease in the conductivity