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Synthesis and characterization of poly(1-vinyl-1,2,4-triazole) (PVTri)–barium hexaferrite nanocomposite

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ABSTRACT

We present a method for the fabrication of PVTri–$BaFe_{12}O_{19}$ nanocomposites by in-situ polymerization of PVTri in the presence of synthesized $BaFe_{12}O_{19}$ nanoparticles. Nanoparticles, polymer and nanocomposite were analyzed by XRD, FTIR, TGA, TEM, NMR, GPC and conductivity techniques for structural and physicochemical characteristics. Crystallographic analysis revealed the phase as hexaferrite and X-ray line profile fitting yielded a crystallite size of 17 ± 5 nm. Conjugation of PVTri to nanoparticle surface was assessed to be via carbonyl groups on the polymer. TG analysis revealed that 45 wt% of nanocomposite is inorganic phase ($BaFe_{12}O_{19}$). It was found out that the ac conductivity of nanocomposite under a certain frequency increases with temperature.

1. Introduction

In last few decades barium hexaferrite ($BaFe_{12}O_{19}$), also named as magnetoplumbites, has received great scientific and technological interest, due to its low cost, excellent high-frequency response, large magnetocrystalline anisotropy, large magnetization, high Curie temperature, high chemical stability and corrosion resistivity [1]. Barium hexaferrite and its derivatives can be used for permanent magnets, magnetic-recording media and microwave applications because of their specific magnetic properties. As a result of their high anisotropy fields hexaferrites can be used at much higher frequencies than spinel ferrites or garnets [2–4]. Therefore, M-type hexaferrites that possess uniaxial magnetocrystalline anisotropy can also be used for mm-wave applications.

There are various techniques to synthesize Ba-M-type ferrites, including the ceramic sintering, sol–gel [5], co-precipitation [6], microwave plasma [7], ultrasound irradiation [8], laser pyrolysis [9], etc.

Recently, conducting polymer composites with both electrical and ferromagnetic properties have received tremendous attention, and study on this kind of composites has become one of the most active and promising research areas [10–13]. It is well known that conducting polymers can effectively shield electromagnetic waves generated from an electric source, whereas electromagnetic waves from a magnetic source can be effectively shielded only by magnetic materials. Thus, the incorporation of magnetic constituents and conducting polymeric materials into multifunctional composites opens new possibilities for the achievement of good shielding effectiveness for various electromagnetic sources [14,15].

Poly(1-vinyl-1,2,4-triazole) is readily soluble in H_2O and DMSO, nontoxic ($LD_{50} > 3000$ mg/kg), biocompatible and thermally stable, and has a controllable molecular weight (10^4–10^6 Da) [16,17].

In this study, we report on the synthesis of barium hexaferrite, polyvinyl triazole (PVTri–$BaFe_{12}O_{19}$) nanocomposite, where $BaFe_{12}O_{19}$ is the magnetic core, and PVTri is the conductive polymeric shell. PVTri, a new system with triazole units that are directly linked to polymer chain and free from cross-link and aggregation, was synthesized by our group.

2. Experimental

2.1. Chemicals and instrumentation

All chemicals (1-vinyl-1,2,4-triazole (> 97%, Fluka), toluene (> 99%, Merck), azobisisobutyronitrile (AIBN, Merck), $Fe(CH_3COO)_2$ (from Merck)) were used as received without further purification. X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Laboratory diffractometer operated at 40 kV and 35 mA using Cu K_α radiation ($\lambda = 1.54059$ Å). Fourier transform infrared (FTIR) spectra of the samples were recorded with a Perkin-Elmer BX FTIR infrared spectrometer in the range of 4000–400 cm^{-1}. Transmission Electron Microscopy (TEM) analysis was performed in order to investigate the microstructure of

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the sample, using a FEI XL40 Sirion FEG Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to TEM analysis. The thermal stability was determined by thermogravimetric analysis (TGA, Perkin-Elmer Instruments model, STA 6000). The TGA thermograms were recorded for 5 mg of powder sample at a heating rate of 10 °C/min in the temperature range of 30–800 °C in nitrogen atmosphere. The electrical conductivity of the PVTri and PVTri–$BaFe_{12}O_{19}$ nanocomposite was studied in the range of 20–120 °C with 10 °C steps. The samples were used in the form of circular pellets of 13 mm diameter and 3 mm thickness.

2.2. Synthesis of $BaFe_{12}O_{19}$ NPs and PVTri–$BaFe_{12}O_{19}$ nanocomposite

For the citrate sol–gel synthesis of $BaFe_{12}O_{19}$ nanoparticles, stoichiometric amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ba(NO_3)_2$ were dissolved in a minimum amount of deionized H_2O by stirring at 50 °C with Fe/Ba ratio of 12. Citric acid was then added to the mixture solution of Ba^{2+} and Fe^{3+} to chelate these ions. The molar ratio of citric acid to metal ions used was 1:1. Ammonia was added to adjust the pH value to 7. The clear solution was slowly evaporated at 80 °C under constant stirring, forming a viscous gel. By increasing the temperature up to 200 °C, the gel precursors were combusted to form brown loose powders. The precursor was precalcined at 450 °C for 4 h, then sintering at 1100 °C for 1 h was followed. The hexaferrite $BaFe_{12}O_{19}$ particles were thus obtained.

Azobisisobutyronitrile (AIBN, Merck) was recrystallized from THF prior to use. PVTri–$BaFe_{12}O_{19}$ nanocomposite was produced by free radical polymerization of 1-vinyl-1,2,4-triazole in toluene and certain amount of hexaferrite using AIBN (1 mol%) as initiator. The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 85 °C for 2 h. The resulting sample was filtered and washed several times with toluene, dried in vacuum and stored in glove box.

3. Results and discussion

3.1. XRD analysis

Phase investigation of the crystallized product was performed by XRD and the diffraction pattern is presented in Fig. 1. The XRD pattern indicates that the product is M-type $BaFe_{12}O_{19}$ and the diffraction peaks are broadened owing to very small crystallite size. All of the observed diffraction peaks are indexed by the cubic structure of $BaFe_{12}O_{19}$ (JCPDS no. 84-0757), revealing a high phase purity of hexaferrite. The mean size of the crystallites was estimated from the diffraction pattern by line profile fitting method using Eq. (1) given in Refs. [18,19]. The line profile, shown in Fig. 1, was fitted for observed 21 peaks with the following miller indices: (1 0 4), (1 1 0), (0 0 8), (1 0 7), (1 1 4), (1 0 8), (2 0 3), (2 0 5), (2 0 6), (1 0 11), (2 0 9), (3 3 0), (2 1 7), (2 0 11), (2 0 12), (2 2 0), (1 1 14), (2 1 11), (2 0 14), (3 0 10) and (2 1 12). The average crystallite of size D and σ was obtained as 17 ± 5 nm as a result of this line profile fitting.

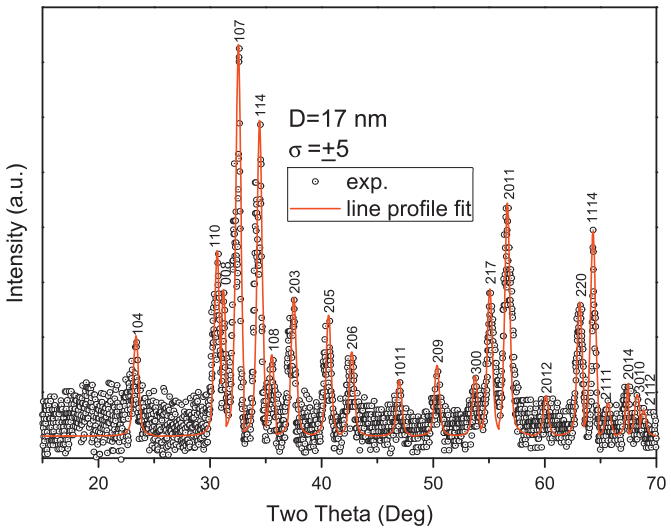

Fig. 1. XRD powder pattern and line profile fitting of PVTri–$BaFe_{12}O_{19}$ nanocomposite.

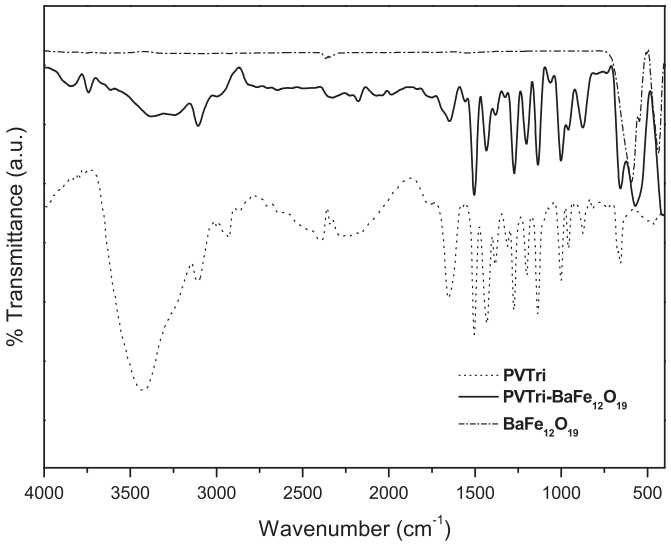

Fig. 2. FTIR spectra of uncoated $BaFe_{12}O_{19}$, PVTri and PVTri–$BaFe_{12}O_{19}$ nanocomposite.

3.2. FTIR analysis

Functional groups exhibited by uncoated $BaFe_{12}O_{19}$, PVTri and PVTri–$BaFe_{12}O_{19}$ nanocomposite are investigated by FTIR spectroscopy and the resultant spectra are presented in Fig. 2. As prepared powder presents characteristic peaks that are exhibited by the $BaFe_{12}O_{19}$ powder: characteristic absorption bands for $BaFe_{12}O_{19}$ at around 450 and 590 cm^{-1} (corresponding to vibrations of the tetrahedral and octahedral sites for $BaFe_{12}O_{19}$) [20,21]. The triazole rings of the pristine polymer PVTri give rise to several medium strong peaks in the 1430–1650 cm^{-1} range due to ring stretching (C–N, C=N) vibrations. The peak at 1270 cm^{-1} is due to the ring N–N stretching [22].

3.3. TG analysis

Dependences of sample weight loss in percent on the temperature are given for the samples of $BaFe_{12}O_{19}$, PVTri and PVTri–$BaFe_{12}O_{19}$ nanocomposite in Fig. 3. PVTri–$BaFe_{12}O_{19}$ nanocomposite undergoes similar decomposition steps as that of PVTri, but it has a greater thermal stability. Such behavior of the nanocomposite sample may be due to the interaction between PVTri and $BaFe_{12}O_{19}$, which restricts the thermal motion of PVTri chains in the nanocomposite sample. This effect is also clearly seen in the DTG curves of such samples. DTG peak temperatures of the PVTri and PVTri–$BaFe_{12}O_{19}$ nanocomposite were not varied. On the other hand, peak width of the derivative