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Optimization of multiroute synthesis for polyaniline-barium ferrite composites

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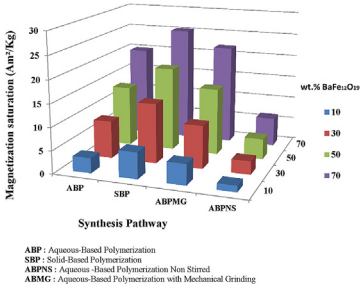
HIGHLIGHTS

- Different pathways are compared for preparation of Polyaniline-barium ferrite composites.
- Magnetic data are used to calculate the volume fraction and loading of ferrite in the composites.
- Solid-based polymerization yielded to composites with the highest volume fraction and loading.
- Mechanical stirring reduced the ferrite particles dissolution by acid-attack during aqueous-based polymerization.

GRAPHICAL ABSTRACT



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ABSTRACT

A comparative study of physicochemical and magnetic properties of Polyaniline-$BaFe_{12}O_{19}$ composites prepared by Solid-Based Polymerization (SBP) and by Aqueous-Based Polymerization (ABP) is carried out. The composites obtained by the latter method underwent a grinding to study the influence of shear stress. Thus, in a systematic approach, an investigation of stirring effect was done by synthesizing these composites using aqueous-based polymerization but without mechanical stirring. Different mass ratio of $BaFe_{12}O_{19}$ was used to explore their impact on composites properties. X-ray diffraction, FTIR, SEM, TGA, conductivity and vibrating sample magnetometer measurements were performed. Structural and morphological investigations confirmed the presence of polyaniline and barium hexaferrite phase, which were in interaction in the composites regardless the polymerization route. The powder obtained by solid-based pathway revealed distinct particles with uniform distribution for various compositions (wt. %) of $BaFe_{12}O_{19}$ in Pani, while the composites obtained by aqueous-based polymerization presented agglomerated nanostructures. Thermogravimetric analysis exhibited an improved thermal stability for Pani-$BaFe_{12}O_{19}$ obtained by solid-based route. The electric conductivity has displayed decreasing trend of DC conductivity with the increase of $BaFe_{12}O_{19}$ particles in the polymer matrix. Magnetic studies showed a ferromagnetic behaviour for all composites. The saturation magnetization monotonously increased with the increasing of $BaFe_{12}O_{19}$ amount. The magnetic properties of the powders were mainly related to the hexaferrite loading which was determined using measured magnetic data. These results revealed that magnetization saturation was dependant of volume fraction of ferrite in the composites which was significantly affected by the reaction medium and mechanical stirring. The powders obtained by solid-based polymerization manifested enhanced magnetic characteristics. The solventless reaction medium contributed to the increase of volume fraction of ferrite in the composite compared to the aqueous

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reaction medium. Moreover, the mechanical stirring during aqueous-based polymerization had an important influence on the volume fraction of ferrite since it prevented the dissolution of $BaFe_{12}O_{19}$ particles.

1. Introduction

Hybrid materials, composed of both organic and inorganic units, offer wide opportunities for new materials with increased functionalities relative to that achievable with organic and inorganic materials alone [1–4]. Advances in composites consisting of conducting polymer have been widely investigated, specifically polyaniline (Pani) with various nanomaterials such as carbon nanomaterials, metal nanoparticles and inorganic compounds [5–12].

Over decades, numerous researches have been devoted to the study of polyaniline for its molecular structure, mechanism formation and different application as electronic-conducting polymer [13]. One of the particular features of Pani is the presence of intrinsic redox states. The term Pani usually denotes the family of aniline-based polymers of the following general formula $[(-B-N-H-B-NH-)_y (B-N=Q=N-)_{1-y}]_x$, in which B and Q denote respectively the C_6H_4 rings in the benzenoid and the quinoid rings.

In polyaniline the neutral intrinsic redox states can vary from that of the fully oxidized pemigraniline ($y = 0$) to completely reduced leucoemeraldine ($y = 1$), through the half-oxidized form, named emeraldine ($y = 0.5$) [14]. The emeraldine form of Pani can be doped with protonic acid to produce emeraldine salt (ES) [15].

One of the most prevalent types of these composites is composed of Pani and ferromagnetic barium hexaferrite ($BaFe_{12}O_{19}$), with a general chemical formula BaO-6 Fe_2O_3, used for potential application in antennas [16], radar absorbers [17,18], tunable filters [19], electromagnetic shielding materials for low and high frequencies [20].

Several studies have focused on developing Polyaniline-barium hexaferrite composites to investigate their structural and electromagnetic properties. Nanocomposites of polyaniline charged with barium ferrite particles have been prepared using various methods. Pani-$BaFe_{12}O_{19}$ was synthesized by *in situ* chemical polymerization process with either mechanical stirring [21] or ultrasonic approach [22]. The nanocomposites showed a colloidal structure for potential microwave absorbers application. In addition, the emulsion polymerization method [23], with an easy and low cost preparation, was also used to fabricate conductive Polyaniline-ferrite composites. However, few papers have intended to study the effect of the elaboration method of these composites and their resultant physicochemical properties.

The present work aimed at synthesizing Polyaniline-$BaFe_{12}O_{19}$ composites following different pathways: aqueous-based polymerization (acidic environment) and solid-based polymerization (solvent less environment). The impact of each preparation method and consequently the calculated ferrite-loading using magnetic data on the magnetic properties and electrical conductivity was reported. The effect of mechanical stirring and shear stress caused by grinding on the formed nanocomposites and the following physicochemical properties was also discussed.

2. Experimental

2.1. Materials

Aniline monomer (Ani, analytical grade, Merck) was distilled twice under reduced pressure and stored in the refrigerator. Iron (III) nitrate nonahydrate $Fe(NO_3)_3$, $9H_2O$, barium nitrate $Ba(NO_3)_2$, sodium hydroxide (NaOH), aniline chloride (AnCl), ammonium persulfate ($(NH_4)_2S_2O_8$, APS) and hydrochloric acid (HCl) were all of analytical purity purchased from commercial sources, and used directly without further purification.

2.2. Synthesis of $BaFe_{12}O_{19}$ particules (HF)

$BaFe_{12}O_{19}$ powder was prepared by the hydrothermal process using an autoclave introduced into a shaked furnace. A mixture of $Fe(NO_3)_3$, $9H_2O$ and $Ba(NO_3)_2$ were added to 2.5 mol L^{-1} NaOH solution according to desired stoichiometries. The mixture was then poured into the autoclave and heated at 220 °C during 8 h. The resulting powder was repeatedly washed with distilled water and dried at 80 °C. Then, it was calcined at 900 °C for 2 h inside a muffle furnace.

2.3. Synthesis of polyaniline-$BaFe_{12}O_{19}$ composites by solid-based polymerization (SBP)

Polyaniline-$BaFe_{12}O_{19}$ composites were obtained by Solid-Based Polymerization (Fig. 1a) as follows: the synthesis was carried out in an agate mortar by grinding an appropriate amount of An-Cl and $BaFe_{12}O_{19}$ for 10 min. Then APS was added to the mixture and ground for 20 min until the colour turned dark green. Different mass ratios of $BaFe_{12}O_{19}$ were used: 10, 30, 50, and 70 wt % with respect to aniline monomer and the samples were marked as 10SBP, 30SBP, 50SBP and 70SBP, respectively. The polymerization lasted for 24h at room temperature. The dark green product was filtered, washed by HCl (0.2 M) until the filtrate became colourless then dried in vacuum at 60 °C for 24 h. Throughout the experiment the molar ration of aniline to APS was maintained at 1.25.

2.4. Synthesis of Polyaniline-$BaFe_{12}O_{19}$ composites by aquous-based polymerization (ABP)

Likewise, Polyaniline-$BaFe_{12}O_{19}$ composites were prepared by Aqueous-Based Polymerization of aniline in the presence of $BaFe_{12}O_{19}$ particles using APS as oxidant, as shown in Fig. 1b. In a typical procedure, a certain amount of $BaFe_{12}O_{19}$ particles was added to 0.2 M aqueous solution of hydrochloric acid containing aniline monomer sonicated in an ultrasonic bath for 30 min. Then, 5.71 g APS dissolved in 0.2 M HCl solution was then added to the above mixture under mechanical agitation. The polymerization was carried out with the same barium hexaferrite and reagent ratios as above for 24h at room temperature. The products were isolated by filtration, thoroughly washed with HCl for removal of inorganic residues, then dried in vacuum at 60 °C for 24 h. The composites were called as 10ABP, 30ABP, 50ABP and 70ABP, respectively.

For further investigation, mechanical stirring was studied by preparing Pani-$BaFe_{12}O_{19}$ composites following the same procedure as described before in aqueous-based polymerization, but without mechanical agitation called ABPNS (Aqueous-Based Polymerization Non Stirred). The samples ratios of $BaFe_{12}O_{19}$ in weight (wt %) were identical: 10 (10ABPNS), 30 (30ABPNS), 50 (50ABPNS) and 70 (70ABPNS), respectively.

In addition, to examine the effect of shear stress caused by grinding during solid-based polymerization on Pani-$BaFe_{12}O_{19}$