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Magnetic behaviour of Polyaniline/BaFe$_{12}$O$_{19}$ composites synthesised by two different pathways

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ABSTRACT—Polyaniline/BaFe$_{12}$O$_{19}$ composites synthesised by two different polymerization pathways: chemical polymerization and solid-state polymerization, were studied. The influence was explored by the type of polymerization synthesis on the microstructure and on the magnetic properties of the composites. Structural, morphological and magnetic properties of the nanocomposites were performed by XRD, FTIR, SEM and VSM measurements, respectively. XRD analysis revealed the inorganic phase as bariumhexaferrite and FTIR analysis indicated an interaction between hexaferrite particles with Polyaniline regardless the synthesis method. The powder morphologies obtained from SEM revealed very similar particle sizes for the two routes while the extent of agglomeration was higher for the chemical polymerization method. Polyaniline/BaFe$_{12}$O$_{19}$ composites exhibited a ferromagnetic behaviour. The powders obtained by solid-state polymerization presented better magnetic characteristics (for 70% Polyaniline/BaFe$_{12}$O$_{19}$ composite, saturation magnetization 25.37 emu/g) than those obtained by chemical polymerization.

KEY WORDS: Polyaniline, barium hexaferrites, chemical polymerization, solid-state polymerization, magnetic measurements.

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].

Recently, a great attention has been focused on the synthesis of composites consisting of conducting polymer, specifically Polyaniline (Pani) with various inorganic nanomaterials such as oxide, sulphide, nitride, metal and clay [5-7]. One of the most prevalent types of these composites is composed of Pani and ferromagnetic barium hexaferrite (BaFe$_{12}$O$_{19}$) which have potential application in antennas [8], radar absorbers [9], tunable filters [10], electromagnetic shielding materials for low and high frequency [11].

Several studies have investigated the structural and magnetic properties of the obtained composite. However, few papers focused on the way of elaborating these composites and its influence on these properties. Barium hexaferrite with a general chemical formula BaO.6Fe$_2$O$_3$ has been coated with Pani by chemical oxidative polymerization [12-14]. The magnetic properties of the obtained composite were influenced by the coating of hexaferrite by the polymer which is explained as a result of electronic interaction between Pani at the interface of ferromagnetic particles.

The present work was aimed at comparing the structural and magnetic properties of Polyaniline/BaFe$_{12}$O$_{19}$ composites synthesized following chemical and solid state polymerization processes at room temperature.

2. EXPERIMENTAL

2.1. Materials

Aniline (analytical grade, Merck) was distilled twice under reduced pressure and stored at the refrigerator. Iron (III) nitrate nonahydrate (Fe (NO$_3$)$_3$.9H$_2$O), barium nitrate (Ba (NO$_3$)$_2$), sodium hydroxide NaOH, aniline chloride (AnCl), ammonium persulfate (APS) and hydrochloric acid (HCl) were all of analytical purity and used without further purification.

2.2. Synthesis of BaFe$_{12}$O$_{19}$particles

The 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$_2$O and Ba(NO$_3$)$_2$ were added to 2.5 M NaOH solution according to desired stoichiometries. The mixture was then poured into the autoclave and heated at 220°C during 8 h. The resulting powders were repeatedly washed with distilled water and dried at 100°C. Then, the obtained powder was calcined at 900°C for 2 h.

2.3. Synthesis of Polyaniline/BaFe$_{12}$O$_{19}$ composites by solid-state polymerization (SP)

Polyaniline/BaFe$_{12}$O$_{19}$ composites were obtained by solid-state polymerization (Fig.1a) as follow: 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, 70% with respect to aniline monomer and the samples were marked as 10SP, 30SP, 50SP and 70SP, respectively. The polymerization lasted for 24 h at room temperature. The dark green product was filtered, washed by HCl 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 chemical polymerization (CP)

Likewise, Polyaniline/BaFe$_{12}$O$_{19}$ composites were prepared by chemical polymerization of aniline in the presence of BaFe$_{12}$O$_{19}$ particles using APS as oxidant (Fig. 1b). In a typical procedure, a certain amount of BaFe$_{12}$O$_{19}$ particles was added to 0.2M aqueous solution of hydrochloric acid containing aniline monomer sonicated in an ultrasonic bath for 30 min. Then, 5.71 g APS dissolved in 0.2M HCl solution was then added to the above mixture under agitation. The polymerization was carried out with the same barium hexaferrite and reagents ratio 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 24h. The composites were named as 10CP, 30CP, 50CP and 70CP, respectively.

2.5. Characterization

X-ray diffraction (XRD) patterns were recorded on a X’Pert PRO, PANalytical diffractometer using Co K$_\alpha$ radiation (\(\lambda = 2.29\)Å) in the range of 2 \(\theta = 5°-80°\) with 0.002° increment. Scanning electron microscopy (SEM) images were taken on a VP-SEM S-3400N scanning electron microscope. Fourier transform infrared (FTIR) spectra were collected on a Perkin Elmer FTIR spectrometer using pressed KBr discs. The FTIR spectra were recorded with a resolution of 1 cm$^{-1}$ over the range of 4000-400 cm$^{-1}$. Magnetic properties of the samples were measured at room temperature on vibrating sample magnetometer VSM Lake Shore 7400 model.

3. RESULTS AND DISCUSSION

3.1. Structure, composition and morphology

Fig. 2 shows the XRD spectra of the Pani/BaFe$_{12}$O$_{19}$ and BaFe$_{12}$O$_{19}$ powders. All the peaks of the prepared BaFe$_{12}$O$_{19}$ marked in Fig. 1 can be indexed to (101), (102), (110), (107), (114), (203), (205), (206), (217), (2011), and (220) planes of hexagonal BaFe$_{12}$O$_{19}$ (space group P63/mmc, JCPDS cards 74-1121). The as-prepared BaFe$_{12}$O$_{19}$ have the hexagonal crystal magnetoplumbite structure. As seen in Fig. 1a and b, diffraction peaks position and intensity of the Polyaniline/BaFe$_{12}$O$_{19}$ composites synthesised by chemical and solid-state polymerization are similar to those of pure barium hexaferrite [15]. The crystal phase of magnetic particles is well maintained after the synthesis process, based on the fact that there is no change in peak position between BaFe$_{12}$O$_{19}$ and the composite. In addition, there is a wide peak in the range of 20° = 20°-30° which is attributed to the characteristic diffraction peak of Pani and proves the existence of the polymer [16]. However, the intensity of Pani peak decreased with increasing the amount of hexaferrite in the polymer.
Further investigations of the crystalline transitions and interactions between Polyaniline and hexaferrite in the composites were performed using FTIR spectroscopy. The aim was to obtain an improved understanding of the formation mechanisms and existing interactions of the composites. FTIR spectra were recorded from 4000 – 400 cm\(^{-1}\) for the different samples, however figures show only expanded view in wavenumber region 400-2000 cm\(^{-1}\), where major changes are observed as shown in Fig. 3. The absorption at 578 cm\(^{-1}\) and 430 cm\(^{-1}\) for barium hexaferrite (Fig. 3a), correspond to the intrinsic vibrations of tetrahedral and octahedral sites for the prepared BaFe\(_{12}\)O\(_{19}\), respectively [17].

In Fig. 3 b and c, Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites spectra obtained by the two syntheses exhibit the characteristic peaks of Paniemeraldine salt [18, 19]. The band 1564-1573 cm\(^{-1}\) can be associated mainly to C=N and C=C stretching of the quinoidiimineunit, while the band near 1484-1489 cm\(^{-1}\) is assigned to the C-C aromatic ring stretching of the benzoidiamine unit. The C-N stretching of the secondary aromatic amine and aromatic C-H out of plane banding vibration, respectively, are attributed to the bands at ~1297-1303 cm\(^{-1}\) and ~806-817 cm\(^{-1}\). However, it can be observed that the two bands at 572 and 429 cm\(^{-1}\) corresponding to the Fe-O band of BaFe\(_{12}\)O\(_{19}\)red shift and decrease clearly with the decrease in weight percentage of hexaferrite in the composite. This shift reveals a strong interaction between Polyaniline on the surface of barium hexaferrite [20, 21].

Scanning electron microscopy was used to examine the morphology of the prepared barium hexaferrite and the different Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites obtained by chemical and solid-state polymerization (Fig. 4, 5 and 6). As seen in Fig. 4, BaFe\(_{12}\)O\(_{19}\) particles exhibit a platelet like shape and that the average size is estimated at 300 nm. Agglomeration appears due to interactions between magnetic particles. SEM micrographs of the composites consist of irregularly shaped and aggregated particles due to the coating of BaFe\(_{12}\)O\(_{19}\) by Polyaniline in the two syntheses. Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites obtained by chemical synthesis present much more morphological heterogeneity in terms of particle size than those obtained by solid-state polymerization (Fig. 5 and 6). In fact, Wang et al. [22] have shown that in acidic solution, there is an electrostatic force between hydrogen of amine groups of Polyaniline backbone and oxygen atom of the metal oxide in ferrite, and supported by the chloride ions which are attracted by the positive charges of ferrite and could be adsorbed by Polyaniline cations. Whereas, the solid-state polymerization present a smaller particle size composites compared to chemical polymerization due to the less contact between the monomer and oxidant according to Bahadra et al. [23]. In addition for the both syntheses, with the increase cotenant of Polyaniline in the composites, a bigger segregation of the magnetic grain is produced which can be...

![Fig. 2 X-Ray diffraction patterns of Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites obtained by: a) chemical polymerization and b) solid –state polymerization.](image1)

![Fig. 3 FTIR Spectra of a) BaFe\(_{12}\)O\(_{19}\); b) Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites obtained by chemical polymerization and c) Polyaniline/BaFe\(_{12}\)O\(_{19}\) composites obtained by solid –state polymerization.](image2)
explained by a secondary nucleation of Pani growing on the existing Pani [24].

3.2. Magnetic properties

The hysteresis loops of barium hexaferrite and the composites at room temperature at a maximum applied field at 2T are shown in Fig.7 and 8. The magnetization under applied magnetic field for the as-prepared Polyaniline/barium hexaferrite composites exhibits clear hysteresis behaviour.
coercivity field (Hc) as obtained from the curves at Fig. 7 and 8 are listed in Table 1.

Table 1 Magnetic properties of BaFe<sub>12</sub>O<sub>19</sub> and Polyaniline/BaFe<sub>12</sub>O<sub>19</sub> composites prepared using chemical and solid-state polymerization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis pathway</th>
<th>Ms (Am&lt;sup&gt;2&lt;/sup&gt;/Kg)</th>
<th>Mr (Am&lt;sup&gt;2&lt;/sup&gt;/Kg)</th>
<th>Hc (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 CP</td>
<td>Hydrothermal</td>
<td>66.65</td>
<td>29.91</td>
<td>0.1118</td>
</tr>
<tr>
<td>30 CP</td>
<td>CP</td>
<td>0.55</td>
<td>0.35</td>
<td>0.1212</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>5.77</td>
<td>2.19</td>
<td>0.1083</td>
</tr>
<tr>
<td>50 CP</td>
<td>CP</td>
<td>8.25</td>
<td>3.5</td>
<td>0.1117</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>13.18</td>
<td>5.57</td>
<td>0.1094</td>
</tr>
<tr>
<td>70 CP</td>
<td>CP</td>
<td>13.36</td>
<td>5.76</td>
<td>0.1026</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>18.52</td>
<td>7.64</td>
<td>0.1030</td>
</tr>
</tbody>
</table>

The real content of barium hexaferrite in the composites after each synthesis was determined using the magnetic parameters. The weight fraction of BaFe<sub>12</sub>O<sub>19</sub> in the composites were converted into volume fractions by using densities of barium hexaferrite ρ<sub>f</sub> = 5.32 g/cm<sup>3</sup> and Polyaniline, ρ<sub>p</sub> = 1.45 g/cm<sup>3</sup>. The density of barium hexaferrite and Pani are written as follow:

\[ \rho_f = \frac{m_f}{v_f} \quad (1) \]

\[ \rho_p = \frac{m_p}{v_p} \quad (2) \]

where \( m_f \) and \( v_f \) are the weight and the volume of barium hexaferrite, respectively, \( m_p \) and \( v_p \) are the weight and volume of Polyaniline, respectively.

The weight fraction of hexaferrite \( f_{wf} \) is given by

\[ f_{wf} = \frac{m_f}{m_f + m_p} \quad (3) \]

Introducing Eq. (1) and (2) into Eq. (3) leads to

\[ \frac{v_p}{v_f} = \frac{1 - f_{wf} \rho_f}{f_{wf} \rho_p} \quad (4) \]

In the same way, volume fraction of hexaferrite \( f_v \) is written:

\[ f_v = \frac{v_f}{v_f + v_p} \quad (5) \]

To convert weight fraction to volume fraction, Eq. (4) is introduced in Eq. (5).

\[ f_v = \frac{\rho_f f_{wf}}{\rho_p f_{wf} + \rho_f (1 - f_{wf})} \quad (6) \]

The weight and volume fractions of Polyaniline/BaFe<sub>12</sub>O<sub>19</sub> composites were calculated using the magnetic parameters obtained from VSM measurements then listed in Table 2.

Table 2 Weight fraction \( f_v \) and volume fraction \( f_v \) of Polyaniline/BaFe<sub>12</sub>O<sub>19</sub> composites prepared using chemical and solid-state polymerization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis pathway</th>
<th>( f_v ) before synthesis</th>
<th>( f_v ) after synthesis</th>
<th>( f_v )</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 CP</td>
<td>CP</td>
<td>0.10</td>
<td>0.008</td>
<td>0.002</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>0.10</td>
<td>0.086</td>
<td>0.025</td>
<td>87</td>
</tr>
<tr>
<td>30 CP</td>
<td>CP</td>
<td>0.30</td>
<td>0.12</td>
<td>0.036</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>0.30</td>
<td>0.19</td>
<td>0.062</td>
<td>66</td>
</tr>
<tr>
<td>50 CP</td>
<td>CP</td>
<td>0.50</td>
<td>0.20</td>
<td>0.063</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>0.50</td>
<td>0.23</td>
<td>0.075</td>
<td>46</td>
</tr>
<tr>
<td>70 CP</td>
<td>CP</td>
<td>0.70</td>
<td>0.30</td>
<td>0.105</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>SP</td>
<td>0.70</td>
<td>0.38</td>
<td>0.143</td>
<td>54</td>
</tr>
</tbody>
</table>

From the Table 1, it is evident that the Ms and Mr for all samples increase with increasing BaFe<sub>12</sub>O<sub>19</sub> content, while Hc changes a little. The saturation magnetization of pure BaFe<sub>12</sub>O<sub>19</sub> was 66.65 Am<sup>2</sup>/Kg at room temperature which is close to the theoretical one calculated for single-crystal barium hexaferrite, i.e. 72 Am<sup>2</sup>/Kg, as reported by Shirk and Buessem [25]. The Ms values for the composites (Fig. 9) are lower than that of pure barium hexaferrite which depends on BaFe<sub>12</sub>O<sub>19</sub> content and uneven distribution in the composite [26]. The calculated weight and volume fraction in Table 2 confirms these values.
In fact, magnetisation saturation $M_s$ is related to the volume fraction of the magnetic ferrite. In Table 2, the different values of weight and volume fraction of particles are depicted together with the yield. The yield is globally between 40 and 50% independently of the chemical route and size of ferrite, except for the lower amount of barium hexaferrite, 10wt%, which correspond to a weight fraction of 0.83% and 8.6% while the volume fraction of 0.02% and 0.25% for chemical polymerisation and for solid-state polymerisation, respectively. This is presumably due to a relative heterogeneity of the mix, so that the sample may not be representative of the mix.

The coercive force of the composites doesn’t show significant change. However, a slight decrease with increasing fraction of ferrite is observed. This may be due to increasing magnetostatic interactions between particles as the distance decrease as the morphology and size of particles doesn’t depend on the mixing method.

4. CONCLUSION

Two types of polymerization methods were studied, namely, chemical and solid-state polymerization, in view of synthesizing Polyaniline/Barium ferrite composites. The particles have irregular shapes and are agglomerated. In fact, the powders produced by the solid-state polymerization exhibited a much higher degree of homogeneity than those obtained by chemical polymerization. The magnetic properties of the samples are mainly related to the weight and volume fraction of ferrite in the composites not the synthesis route. It is thus demonstrated that the solid-state polymerization, which is less complicated and less expensive than the classical chemical polymerization, can be used to prepare powders of Polyaniline/barium hexaferrite nanocomposites with good magnetic properties in view of applications.

5. REFERENCES


Fig. 9 Variation of saturation magnetisation and coercivity of Polyaniline/BaFe₂O₄ composites obtained by: a) chemical polymerization and b) solid-state polymerization.

<table>
<thead>
<tr>
<th>Ferrite content</th>
<th>Ms (Am²/kg)</th>
<th>Hc (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0,104</td>
<td>0.108</td>
</tr>
<tr>
<td>10</td>
<td>0,106</td>
<td>0.110</td>
</tr>
<tr>
<td>15</td>
<td>0,102</td>
<td>0.110</td>
</tr>
<tr>
<td>20</td>
<td>0,106</td>
<td>0.108</td>
</tr>
<tr>
<td>25</td>
<td>0,104</td>
<td>0.108</td>
</tr>
<tr>
<td>30</td>
<td>0,102</td>
<td>0.106</td>
</tr>
<tr>
<td>35</td>
<td>0,100</td>
<td>0.108</td>
</tr>
<tr>
<td>40</td>
<td>0,098</td>
<td>0.108</td>
</tr>
<tr>
<td>45</td>
<td>0,096</td>
<td>0.108</td>
</tr>
<tr>
<td>50</td>
<td>0,094</td>
<td>0.108</td>
</tr>
<tr>
<td>55</td>
<td>0,092</td>
<td>0.108</td>
</tr>
<tr>
<td>60</td>
<td>0,090</td>
<td>0.108</td>
</tr>
<tr>
<td>65</td>
<td>0,088</td>
<td>0.108</td>
</tr>
<tr>
<td>70</td>
<td>0,086</td>
<td>0.108</td>
</tr>
</tbody>
</table>

\[ Ms = \gamma m_s \] (7)


