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Structural and magnetic characteristics of PVA/$CoFe_2O_4$ nano-composites prepared via mechanical alloying method

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ABSTRACT

In this research, polyvinyl alcohol/cobalt ferrite nano-composites were successfully synthesized employing a two-step procedure: the spherical single-phase cobalt ferrite of 20 ± 4 nm mean particle size was synthesized via mechanical alloying method and then embedded into polymer matrix by intensive milling. The results revealed that increase in polyvinyl alcohol content and milling time causes cobalt ferrite particles disperse more homogeneously in polymer matrix, while the mean particle size and shape of cobalt ferrite have not been significantly affected. Transmission electron microscope images indicated that polyvinyl alcohol chains have surrounded the cobalt ferrite nano-particles; also, the interaction between polymer and cobalt ferrite particles in nano-composite samples was confirmed. Magnetic properties evaluation showed that saturation magnetization, coercivity and anisotropy constant values decreased in nano-composite samples compared to pure cobalt ferrite. However, the coercivity values of related nano-composite samples enhanced by increasing PVA amount due to domain wall mechanism.
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1. Introduction

In the last decade, synthesis and properties of polymeric magnetic nano-composites composed of organic polymer and magnetic materials in nano-metric dimensions have intensively attracted scientific and technological interests [1,2]. Combination of desired physical and chemical inherent features of these components not only provides multifunctional nano-composites with remarkable properties but also improves the sum of their individual properties [3,4]. For instance, encapsulation of magnetic nano-particles within non-magnetic polymer matrix improves the intrinsic properties of magnetic particles such as their chemical stability and dispersibility, prevents the aggregation of magnetic particles and reduces toxicity [5–7].

Among various types of magnetic materials, spinel cobalt ferrite with a chemical formula of $CoFe_2O_4$ is emerging as one of the most promising magnetic materials in terms of high coercivity, moderate saturation magnetization, excellent chemical stability, mechanical hardness and large magneto-crystalline-anisotropy compared to other spinel ferrites [8,9]. These properties make it a remarkable candidate for applications in high density magnetic recording medium, catalysts, ferro-fluid [10,11] and particularly in biomedical fields, including magnetic resonance imaging (MRI), targeting drug delivery, magnetic separation, biosensors and hyperthermia [6,12].

Polyvinyl alcohol (PVA) is semi-crystalline, non-toxic, biocompatible, biodegradable polymer with an excellent chemical resistance which is extensively used for biomedical applications [9,13]. Therefore, embedding $CoFe_2O_4$ nano-particles in PVA matrix due to their significant potential applications have been investigated earlier and the effects of polymer matrix and the synthesis methods on size, shape and magnetic properties of cobalt ferrite particles have been studied [7,9,14,15]. However, no effort has been made to preparation and characterization of this nano-composite by mechanical alloying so far.

Generally, two methods are being used for formation of polymer matrix nano-composites. In the first method, known as ex-situ synthesis, previously formed nano-particles are incorporated and mixed into a polymer matrix while in the second route, nano-composites prepared by in-situ synthesis of nano-particles and the polymerization of the monomers [16,17]. Even though it is possible to obtain very homogenous dispersion with the second method, this method is mostly expensive, bases on complex solution or melting process and obtaining homogenous dispersion with high load of filling particles is infeasible. One sustainable alternative to overcome these thermal and solvent problems is using solid-state mixing method such as mechanical alloying [3,4,16]. Mechanical alloying is a well-established technique with

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many advantages including low cost, high yield, good ecological stability, no limitations on the material and low temperature synthesis [16], which is being successfully used to synthesize novel materials at the nano-scale [11].

For the first time, Shaw et al. [18] reported that the mechanical alloying could be employed in preparation of polymer matrix composites. Up to now, some investigations in the case of polymer/magnetic metal [3,4,19] and polymer/soft magnetic ferrite nano-composites [17,20] have been done by applying this method. However, to the best of our knowledge, no detailed study has been carried out on preparation of polymer/hard magnetic ferrite nano-composite by mechanical alloying technique.

In the present work, the mechanical alloying method is applied for synthesis of PVA/$CoFe_2O_4$ nano-composite and the effects of milling time and various amounts of magnetic nano-particles on the characteristics of nano-composite samples are investigated in detail. The results would be helpful for the further studies on physical and biocompatibility properties of these nano-composites for applying in biomedical field.

2. Experimental procedure

2.1. Materials and methods

Hematite (α-Fe_2O_3, Merck), cobalt carbonate ($CoCO_3$, VWR) and polyvinyl alcohol (PVA, $(-C_2H_4O)_n$, Merck) with a molecular weight of 72,000 LR were used as starting materials without further purification. To synthesize $CoFe_2O_4$ nano-particles, iron oxide and cobalt carbonate powders were mixed according to Eq. (1) and then milled in a high energy planetary ball mill PM2400 with a rotation speed of 400 rpm and ball to powder weight ratio of 30:1 rpm for 25 h at room temperature.

$$\alpha\text{-}Fe_2O_3 + CoCO_3 \rightarrow CoFe_2O_4 + CO_2 \quad (1)$$

The vial and balls were both made of hardened chromium steel. Details of synthesis and reaction mechanism of $CoFe_2O_4$ nano-particles were reported in our previous work [21]. The synthesized $CoFe_2O_4$ nano-particles and PVA powders were mixed with different weight ratios of magnetic nano-particles, i.e. 20, 50 and 80%. The mixed powders were milled up to 30 h without using any surfactant/capping agent under air atmosphere. The rotation speed and ball to powder ratio were 300 rpm and 15:1, respectively. To avoid excessive heating, periodic interruption in milling was set for 10 min, twice an hour. Cobalt ferrite and the corresponding nano-composites containing 20, 50 and 80 wt.% cobalt ferrite nano-particles were labeled as CF, PVA/CF2, PVA/CF5 and PVA/CF8, respectively.

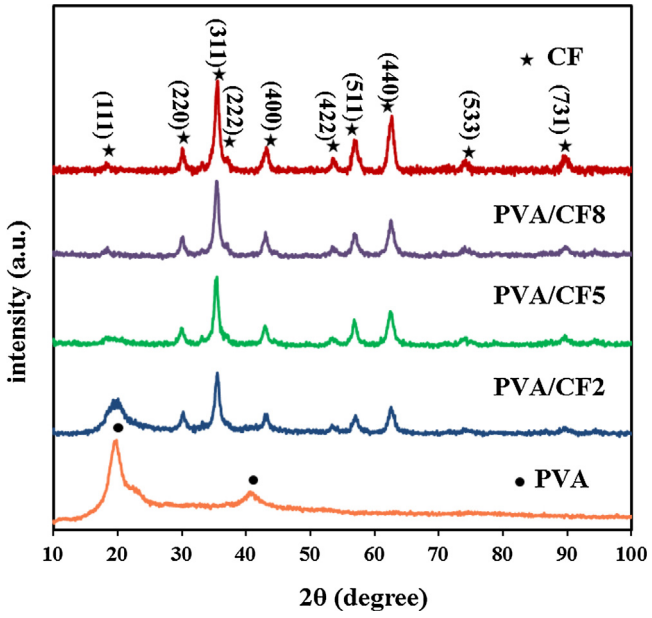

Fig. 1. XRD patterns of PVA, pure CF and their corresponding nano-composites milled for 10 h.

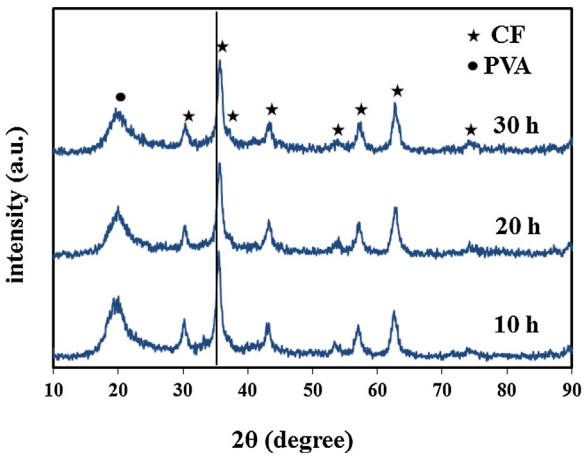

Fig. 2. XRD patterns of PVA/CF2 sample milled for various periods of time.

2.2. Characterization

The phase identification of the samples was investigated by X-ray diffraction (XRD) at room temperature using a Philips PW-3710 diffractometer with Cu-Kα radiation (λ = 0.15406 nm) in a 2θ range between 10 and 100° and step size of 0.02°. The mean crystallite size and the lattice strain of the milled samples were estimated by XRD peak broadening analysis using Williamson-Hall equation [22,23].

Morphology and chemical composition of milling products were examined by both field emission scanning electron microscope (FESEM, Hitachi S4160) and high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100, operating at 200 kV) equipped with an energy dispersive spectrometer (EDS) point chemical analysis. Also, the particle size of cobalt ferrite was analyzed by MIP (Microstructural Image Processor) software. Formation of cobalt ferrite nano-particles and corresponding

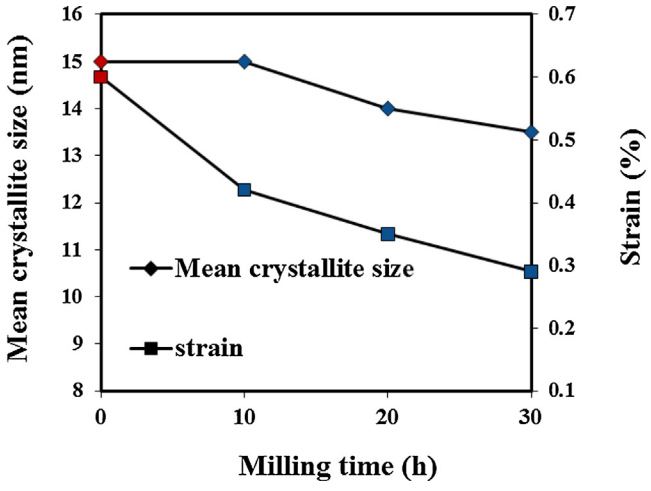

Fig. 3. Mean crystallite size and strain changes as a function of milling time in PVA/CF2 sample (the data of 0 h is related to CF sample).

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