Synthesis of Nickel and Cobalt Ferrite Nanopowders and Selected Properties of Polycarbonate Composites with Nickel Ferrite

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Abstract. NiFe₂O₄ and CoFe₂O₄ have been synthesized by sol-gel self-combustion method and high frequency plasma chemical synthesis. Structure and magnetic properties of the synthesized products have been characterized. All the synthesized ferrites are nanocrystalline single phase materials with specific surface area of 30–40 m²/g and calculated particle size of 30–40 nm. Ni and Co ferrites synthesized by high-temperature plasma route are characterized by saturation magnetization $M_S$ of 44.2 emu/g and 75.4 emu/g, remanent magnetization $M_r$ of 10.0 and 32.0 emu/g and coercivity $H_c$ of 74 Oe and 780 Oe, respectively. NiFe₂O₄ (2 - 10 wt. %) has been introduced in a polycarbonate (PC) matrix by melt compounding. Magnetic as well as elastic properties of PC matrix nanocomposites are increased along with growing NiFe₂O₄ content.

1. Introduction

Ferrites are widely applied in life sciences, biochemical processes (magnetic liquids, hyperthermia etc.) and special coatings (antistatics, electromagnetic interference shielding). The effectiveness of the spinel ferrites in most of these applications can be increased, if their dimensions are in nanolevel, i.e., below single domain sizes [1]. Properties of ferrites, can be tailored also depending on it morphology and nanostructure. Consequently, it is important to analyse the effects of manufacturing methods/conditions on structural features of ferrite nanoparticles. Several liquid phase and gas phase synthesis have been developed to synthesize ferrite nanoparticles – hydrolysis, hydrothermal synthesis [2], pyrolysis, microwave synthesis [3], co-precipitation method [4], sol-gel method [5], combustion [6], and plasma synthesis [7]. In this research, synthesis of nickel and cobalt ferrite nanopowders have been performed by using sol-gel self-combustion method (liquid phase reaction) and high frequency plasma synthesis (gas phase reaction).

Application potential of synthesized ferrite nanostructures can be increased by their introduction in suitable matrix materials. Consequently the aim of the current research is to find out the effects of the nanofiller type and concentration on certain structural, mechanical and thermal characteristics of the polycarbonate based composites.
2. Experimental

Two distinct ferrite types (NiFe$_2$O$_4$ and CoFe$_2$O$_4$) are obtained by using high frequency plasma chemical synthesis and sol-gel self-combustion method. Plasma synthesized ferrites are synthesized by using the technological equipment, developed in RTU Institute of Inorganic Chemistry [7]. The synthesis of aforementioned ferrite nanostructures has been realized by evaporating commercial metal and metal oxide (Ni, Co, NiO, CoO and FeO) powders in high frequency plasma. Sol-gel self-combustion method synthesized ferrites have been obtained by using reagent grade chemicals: Co(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, glycine, nitric acid.

All samples have been analysed by using X-ray diffractometer Advance 8 (Bruker AXS). Crystallite sizes have been determined by using Scherer’s equation. Magnetic properties of the synthesized ferrites and nanocomposites have been analysed by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM). Specific surface area (SSA) has been measured with the BET single point method. Measurements were made at the boiling point of liquid nitrogen (−196 °C), the adsorbing gas was Ar (~7 % Ar gas mixture in He gas).

Plasma synthesized NiFe$_2$O$_4$ nanoparticles in the amount of 2 to 10 wt. % have been introduced in a polycarbonate (PC) matrix (Trirex 3022IR) by using two-roll mill technique. Specimens for tensile tests have been manufactured by injection moulding. Specimens for dynamic mechanical thermal analysis, density characterization and magnetic property determination have been manufactured by compression moulding. Density has been determined at 23 °C by hydrostatic weighting. Room temperature (23 °C) tensile properties have been determined by using Zwick/Roell BDO020 universal testing machine. Dynamic mechanical thermal analysis have been performed by using TA Instruments TA Q800 apparatus.

3. Results and discussion

The characteristics for synthesized ferrite products are given in Table 1 and in Figures 1-3. It is found that all the synthesized ferrites are nanocrystalline single phase materials with specific surface area of 30–40 m$^2$/g and calculated particle size of 30–40 nm.

![Figure 1. XRD patterns of ferrite nanopowders.](image1)

![Figure 2. Microstructure of plasma CoFe$_2$O$_4$.](image2)

Analyzing XRD patterns there are slight differences between relative intensities and width of reflexes comparing ferrite samples depending on synthesis method which indicates to the differences of crystallite size. The sol-gel self-combustion method gives nanopowders with smaller crystallite size (Table 1). One should however consider rather broad particle size distribution of the synthesized ferrites (in range 10 - 100 nm with some particles of 200 nm) as shown in Figure 2 for plasma synthesized CoFe$_2$O$_4$. 
The magnetic properties (saturation magnetization $M_S$, remanent magnetization $M_r$, emu/g and coercivity $H_c$, Oe) (Table 1, Figure 3) of nanopowders obtained by using sol-gel self-combustion method differ from those, obtained by plasma synthesis. Probably, it is attributed to the differences in particle sizes of the synthesized nanopowders. It is interesting to note that although all of the nanoparticles, synthesized within the framework of this research, have particle sizes below the critical single-domain limit (ca. 70 nm [8, 9]), quasi-supermagnetic behavior is observed only in the case of plasma synthesized NiFe$_2$O$_4$ nanoparticles.

**Table 1.** Properties of synthesized ferrite nanopowders

| Sample               | SSA, m$^2$/g | $d_{50}$, nm* | Crystallite size, nm | Phase content | Magnetic properties |
|----------------------|--------------|---------------|---------------------|---------------|---------------------|
| CoFe$_2$O$_4$ (plasma) | 29           | 39            | 40                  | 100% CoFe$_2$O$_4$ | $M_S$, emu/g = 75.4, $M_r$, emu/g = 32.0, $H_c$, Oe = 780 |
| CoFe$_2$O$_4$ (combust.) | 37           | 31            | 20                  | 100% CoFe$_2$O$_4$ | $M_S$, emu/g = 53.4, $M_r$, emu/g = 20.3, $H_c$, Oe = 1170 |
| NiFe$_2$O$_4$ (plasma) | 29           | 38            | 40                  | 100% NiFe$_2$O$_4$ | $M_S$, emu/g = 44.2, $M_r$, emu/g = 10.0, $H_c$, Oe = 74 |
| NiFe$_2$O$_4$ (combust.) | 43           | 26            | 10                  | 100% NiFe$_2$O$_4$ | $M_S$, emu/g = 29.0, $M_r$, emu/g = 6.0, $H_c$, Oe = 140 |

*calculated from SSA

**Figure 3.** Magnetic properties of the ferrites obtained by sol-gel self-combustion method and high-frequency synthesis.

The effects of plasma synthesized NiFe$_2$O$_4$ nanoparticles on the dynamic elastic characteristics, stress-strain properties as well as density are shown in Figures 4-7. As shown in Figure 4, certain magnetic properties are assigned to otherwise diamagnetic PC matrix already at the lowest investigated nanofiller content. It is important to mention that saturation magnetization $M_S$ of PC composition containing 10 wt. % of NiFe$_2$O$_4$ (1.6 emu/g) is more than one tenth from that of as-synthesized nanofiller. Remanent magnetization $M_r$ of the same PC composite, in its turn, is close to zero, which is not surprising by considering low $M_r$ value of neat NiFe$_2$O$_4$. Coercivity $H_c$ of the PC composite with 10 wt. % of NiFe$_2$O$_4$ (190 Oe) is almost 2.6 times higher than that of neat NiFe$_2$O$_4$ (74 Oe). Such behaviour could be connected with certain change in particle dimensions after their introduction in PC matrix.

In addition to magnetic properties elastic behaviour of PC nanocomposites is studied in a broad temperature interval by using dynamic mechanical thermal analysis in a single cantilever mode (Figure 5). It is an effective tool to study not only elastic properties of the materials but also their structural relaxation behaviour.
As one can see, there is considerable increase in storage modulus $E'$ of PC nanocomposite with NiFe$_2$O$_4$ wt. content of 2%, especially at lower temperatures. By increasing temperature, elastic modules of neat PC and the nanocomposite with 2wt. % of NiFe$_2$O$_4$ approach each other and close to glass transition of the polymer matrix have practically the same values. However, it should be mentioned that upon addition of the nanostructured filler, glass transition of the composite is increased, the behavior characteristic for nanocomposite materials and generally explained with stiffening of polymer macromolecules in the proximity of nanostructured filler [10].

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Elastic as well as stress-strain properties of PC/NiFe$_2$O$_4$ nanocomposites more in detail are investigated at room temperatures. As it is demonstrated in Figure 6, tensile modulus $E$ and yield strength $\sigma_Y$ of PC/NiFe$_2$O$_4$ nanocomposites are increased along with increasing nanofiller content up to 10 wt.%. Increase of stress-strain characteristics is the steepest up to the nanofiller content of 2 wt.%. At higher nanofiller contents rise of the aforementioned stress-strain characteristics is somewhat hindered, which most probably could be explained with greater possibility of the formation of NiFe$_2$O$_4$ agglomerates in the PC matrix. At the same time strain at break $\varepsilon_B$ of the nanocomposite decreases in comparison to neat PC matrix. It is, however, worth mentioning that character of deformation remains unchanged for all of the investigated nanocomposites, i.e., nanocomposites deform through yielding,
accompanied with expressed necking, and followed by unexpressed strain hardening until the rupture of the test specimens at specified ultimate deformations.

In addition to magnetic, elastic and stress-strain behaviour, PC/NiFe$_2$O$_4$ nanocomposites are investigated also in respect to their densities, determined experimentally and calculated according to the rule of mixtures (Figure 7). In the calculations it is assumed that densities of polycarbonate matrix and the ferrite nanofiller are 1.18 g/cm$^3$ and 5 g/cm$^3$, respectively. As expected, experimental density of the investigated PC nanocomposite increase along with growing NiFe$_2$O$_4$ content and is lower than that calculated according to the rule of mixtures. Differences between the experimentally detected and arithmetically calculated densities increase by rising the nanofiller content in the polymer matrix (up to 2.2 % for the nanocomposite with 10wt.% of NiFe$_2$O$_4$). This most probably is attributed to the void content in the nanocomposite.

4. Summary
In the current research NiFe$_2$O$_4$ and CoFe$_2$O$_4$, synthesized either by sol-gel self-combustion method or by high frequency plasma chemical synthesis, are characterized in respect to their structure and magnetic properties. In addition, selected structural, magnetic, elastic as well stress-strain properties of the melt compounded PC matrix based nanocomposites, modified with various amounts (0-10 wt. %) of plasma synthesized NiFe$_2$O$_4$ nanoparticles, are characterized.

In general it is shown that (a) high purity nanostructured ferrite fillers with average crystallite sizes between 10 – 40 nm are synthesized, (b) certain magnetic traits are assigned to the investigated polycarbonate nanocomposites already at NiFe$_2$O$_4$ content of 2 wt.%, (c) considerable increase in stiffness of NiFe$_2$O$_4$ modified PC nanocomposites is observed already at the ferrite content of 2 wt. %, (d) gain in the elastic modulus E and yield strength $\sigma_Y$ of the nanocomposites, however, decreases, above the ferrite content of 2 wt. %.

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