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# New nanocomposite based on poly(lactic-co-glycolic acid) copolymer and magnetite. Synthesis and characterization

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ABSTRACT

The study presents the preparation of the new magnetic nanocomposite based on PLGA and magnetite. The PLGA used to obtain the magnetic nanocomposites was synthesized by the copolymerization of lactic acid with glycolic acid, in the presence of tin octanoate [Sn(Oct)$_2$] as catalyst, by polycondensation procedure. Magnetite was obtained by co-precipitation from aqueous salt solutions $FeCl_2/FeCl_3$. The particles size of magnetite was 420 nm, and the saturation magnetization 62.78 emu/g, while the PLGA/magnetite nanocomposite size was 864 nm and the saturation magnetization 39.44 emu/g. The magnetic nanocomposites were characterized by FT-IR, DLS technique, SEM, VSM and simultaneous thermal analyses (TG–FTIR–MS). The polymer matrix PLGA acts as a shell and carrier for the active component, while magnetite is the component which makes targeting possible by external magnetic field manipulation. Based on the gases resulted by thermal degradation of PLGA copolymer, using the simultaneous analysis TG–FTIR–MS, a possible degradation mechanism was proposed.

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## 1. Introduction

Poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and their copolymers PLGA are biocompatible, biodegradable and bioabsorbable materials, that can be degraded to metabolites (lactic and glycolic acid) by hydrolysis of the ester links in the human body [1–3]. High molecular weight PLA and PLGA copolymers are non-immunogenic and widely utilized in the medical field as sutures, bone fixation devices, bone tissue engineering based on PLLA and nano-hydroxyapatite, drug-delivery systems [4–6]. Also, these aliphatic polyesters can be completely biodegraded into $CO_2$ and $H_2O$ and are friendly products, wholly nontoxic to the environment. Magnetic nanoparticles (MNPs) have attracted intensive attention for their wide applications as biomaterials in the biomedical and pharmaceutical field. The biomedical application of MNPs mainly focuses on four particular areas: magnetic separation, drug delivery, hyperthermia treatments, magnetic resonance imaging (MRI) contrast enhancement [7–9]. Magnetic targeting of therapeutic agents to the specific sites in the body enjoys certain advantages over other drug delivery methods. One advantage is that magnetic colloids can be injected into the bloodstream and guided to the targeted area with external magnetic fields [10,11]. Encapsulation of MNPs into biocompatible polymeric microcapsules can combine their advantages to serve as dual contrast agent for both magnetic resonance imaging and ultrasound contrast imaging [12,13]. Due to different surface properties of MNPs, encapsulating methods and the corresponding encapsulation efficiency will be different [14,15]. The hydrophobic magnetite nanoparticles can be coated with phospholipids, silica, or amphiphilic polymers as shells to display good solubility and biocompatibility *in vivo* [16]. Oleic acid-coated MNPs are commonly used for their high saturation magnetization. Their hydrophobicity facilitates the mixing with hydrophobic monomers for polymerization and their encapsulation efficiency is relatively high. However, the hydrophobic surface of oleic acid-coated MNPs limits to some extent their applications in the biomedical field. On the contrary, hydrophilic MNPs [17] are more suitable for biomedical applications due to their compatibility with aqueous medium. Polymers and inorganic coatings, monomeric organic stabilizers, can also be used to stabilize nanoparticles in aqueous solutions [18,19]. Coating agents that are physically adsorbed (by electrostatic interactions or hydrogen bonding) show limited stability in comparison to coating agents which are chemically adsorbed. The most common coatings for biocompatible magnetite suspensions are polymers such as derivatives of dextran [20], starch, polyethyleneglycol, siloxane, PLA, poly(ε-caprolactone) [21,22], polyvinyl alcohol (PVA), Due to their good in water solubility and biocompatibility, polysaccharides are among the most commonly used coatings for the magnetite stabilization. This coating has terminal groups that allows further functionalization by chemical reactions with certain drugs.

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The study presents the synthesis and characterization of PLGA copolymer matrix (80/20) and preparation of the PLGA/magnetite nanocomposite by the double emulsion method between the aqueous and organic phase (w/o/w).

## 2. Experimental

### 2.1. Materials and methods

The monomers D,L–lactic acid (LA) aqueous solution 90 wt.%, 1.21 g cm$^{-3}$ density, glycolic acid (GA) powder, 1.27 g cm$^{-1}$ density, tin octanoate [Sn(Oct)$_2$], as catalyst from Sigma Aldrich Chemie were analytical grade reagents and used without further purification. Magnetite was obtained in laboratory by co-precipitation from aqueous salt solutions $FeCl_2/FeCl_3$ (molar ratio 1/2), with the addition of a base (pH = 10–12), under inert atmosphere ($N_2$), at 60 °C according a method described in the literature [23], with particle size of about 420 nm. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) non-ionic amphiphilic block copolymer (Pluronic F127), as stabilizing agent for $Fe_3O_4$ nanoparticles, was used. Poly(vinyl alcohol) (40–98), from SC Romacryl SA (Romania) with Mn = 18000, hydrolysis degree 98%, saponification index 140 ± 30 mg KOH/g. Dichloromethane, methanol, from Chimopar S.A. (Romania) were analytical grade reagents.

### 2.2. Poly(lactic-co-glycolic acid) synthesis

Poly(lactic-co-glycolic acid) (PLGA) was synthesized by the melt polycondensation reaction of lactic acid with glycolic acid (molar ratio 80/20), in presence of tin octanoate as catalyst, according to some methods (slightly modified) presented in the literature [24]. Synthesis of the PLGA copolymer was done in a glass reaction vessel (250 mL) equipped with a mechanical stirrer, thermostated oil bath, Dean–Stark distillation device, funnel dosing reagents and vacuum valve. Firstly, 4.5 g GA were dissolved in 19.8 mL LA aqueous solution 90 wt.% (21.6 g pure LA). The monomer mixture was maintained under stirring at 110 °C, for 2 h to remove the water present in the LA solution. After water removal, the temperature was lowered to about 70 °C, then 0.143 g Sn(Oct)$_2$ (0.54 wt.% reported to the reaction components), were added. Next, the temperature was raised to 160–170 °C, and the reaction was kept for 16 h under vacuum to remove the reaction by-products (about 4.5 mL water, unreacted monomer, oligomers), by means of the Dean–Stark device. Drying of the reaction product was carried out 48 h under vacuum, at 80–90 °C. The copolymer purification was achieved by dissolution in dichloromethane and precipitation in a nonsolvent mixture of $CH_3OH/H_2O$ (1/3), decantation, centrifugation, drying under vacuum at 70 °C for 24 h to remove the organic solvent and finally freeze drying for 48 h at −20 °C. The yield of the copolymer was 88%.

### 2.3. Nanocomposite fabrication

Synthesis of PLGA/magnetite nanocomposite was done by the double emulsion method between aqueous and organic phase (w/o/w). Firstly, 0.6 g PLGA were dissolved under stirring in 40 mL methylene chloride. Separately, 0.5 g $Fe_3O_4$ were dispersed in 20 mL bidistilled water by sonication, then 1 mL Pluronic F127 as stabilizing agent for the magnetite nanoparticles, was added. The magnetite solution was added dropwise to the previously prepared PLGA solution and dispersed by stirring 40 min, with a mechanical stirrer at 1400 rpm speed. After dispersal and homogenization of the components, the PLGA/magnetite dispersion was added by slow dripping in 200 mL aqueous solution of PVA 1 wt.% concentration and stirring at 1400 rpm. Further, the obtained mixture was left to low stirring, at room temperature for several hours to remove the organic solvent ($CH_2Cl_2$). Subsequently, the obtained mixture was decanted on a permanent magnet and the aqueous phase removed. Then, 200 mL ultra pure water were added, ultrasound two times about 5 min, decanting on a permanent magnet and washing the obtained magnetic nanoparticles This washing operation with ultra pure water was repeated of 2–3 times. Finally, PLGA/magnetite nanoparticles were dried under vacuum at 40–50 °C. Magnetic nanocomposites are kept dry until use, because in aqueous solution occurs oxidation of the magnetite.

### 2.4. Characterization

Fourier transform infrared (FT-IR) spectra of were recorded on a Vertex 70 spectrophotometer (Bruker–Germany) on KBr pellet (2 mg sample in 500 mg KBr). The vibrational transition frequencies were reported in wavenumbers (cm$^{-1}$) and FT-IR spectra recorded on the 400–4000 cm$^{-1}$ domain, with a resolution of 4 cm$^{-1}$.

Vibrating sample magnetometer (VSM). The magnetite and PLGA/magnetite nanocomposites were analyzed with Lakeshore VSM 7410 system, to estimate the magnetization (M, emu/g), measured at the applied magnetic fields (H) ranging from −20,000 to 20,000 Oe, at room temperature (25 °C). To avoid vibration of the particles, the samples were mixed with molten bees wax, cooled to form a spherical solid sample of 8 mm.

The particle size distribution was determined by dynamic light scattering (DLS) technique, using a Zetasizer Nano-ZS device, ZEN-3500 model (Malvern Instruments-England). The measurement was carried out using a red laser He–Ne (633 nm) as light source, at a fixed angle of 173°. The hydrodynamic diameter and polydispersity index (PDI) were determined using noninvasive backscatter (NIBS) technology, which allows sample measurement in the range of 0.6 nm–6 μm. The following parameters were used for measurements: water as dispersant medium with refractive index 1.330, viscosity 0.887 cP and dielectric constant 79. For measurements, the samples were dispersed in twice distilled water at a concentration of 1 g/L. The apparent hydrodynamic diameter ($D_H$) of the samples is determined using the formula $D_H = \frac{kT}{3\pi\eta D}$ where: $D_H$ is the hydrodynamic diameter, $k$ – the Boltzmann constant, $T$ – temperature, $\eta$ – the dispersant medium viscosity, $D$ – the diffusion coefficient. The hydrodynamic diameter is related to the intensity means, being calculated from the signal intensity. DLS experiments present high reproducibility, with a deviation from the average diameter of 5%. For each determination five measurements at 25 °C temperature were done.

Morphological studies of the PLGA/magnetite nanocomposites and magnetite were performed using an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 20 kV with secondary electrons, in low vacuum mode (60–100 Pa) with LFD detector. The Quanta 200 microscope is equipped with an Energy Dispersive X-ray system for qualitative and quantitative analysis. The ESEM studies were performed on samples fixed on copper supports.

Thermogravimetric (TG) analysis of the samples were evaluated in dynamic conditions using STA 449 F1 Jupiter apparatus (Netzsch–Germany), in nitrogen atmosphere, at 10 °C min$^{-1}$ heating rate, on the temperature interval 30–650 °C. Samples of 7–10 mg weight were placed in $Al_2O_3$ crucibles. The thermal fragmentation behavior of PLGA and PLGA/magnetite, which appear in the thermal decomposition of samples, was analyzed using online connected FT-IR apparatus (Vertex 70) and Aëolos QMS 403C mass spectrometer (Netzsch–Germany). The released gases during the thermal decomposition processes are transferred by two isothermal transition lines to FT-IR spectrophotometer and mass spectrometer. The FT-IR transfer line is carried out of polytetrafluorethylene (1 m

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