

Nanocomposites Based on Chitozan and Carbon Nanotubers with Iron Oxides Formed by *in situ* Precipitation

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Composites which contain iron oxide nanoparticles and unmodified or aminated silica were synthesised by *in situ* precipitation of ferrous salts in chitozan or glucose solution. Nanocomposites based on oxidized or aminated carbon nanotubers were obtained by immobilizing oxide nanoparticles in surface layer during salt precipitation in water dispersion. The metal-containing phase was obtained by the Elmore reaction using different ratios of ferrous ammonium sulfate hexahydrate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). The composites obtained were characterized using FTIR spectroscopy. In addition for selected samples XRD, DSC, and specific surface area measurements were carry out. The analysis results indicate that *in situ* co-precipitation of iron oxide precursors in chitosan or glucose allows producing Fe_3O_4 particles with the average size ca. 5-7 nm. The presence of silica leads to particles size decrease which can be controlled, along with iron oxide particles location, by changing the silica surface functionality. Characteristics and location of iron oxide nanoparticles in nanotubers modified layer are strongly depended from nature of the groups attached to surface.

Keywords: Nanocomposites, Iron oxide nanoparticles, Silica, Multiwalled nanotubes, Chitozan structure.

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1. INTRODUCTION

Many researchers are looking for various methods for preparation of chitosan- Fe_3O_4 nanocomposites. However, not only magnetite particles size but also the structure of matrix determines the properties of a composite. However, very little is known about the effect of nanoparticles on the rheological properties of these systems which have been proven to be crucial for biopolymer composites. For example, addition of silica nanoparticles invariably impairs the gelation process, as viewed by the reduction of gel strength and decrease of gelation and melting temperatures. On the other hand, formation of Fe_3O_4 nanoparticles in the presence of a biopolymer promoted the gelation process and led to an increase of the gel viscoelastic moduli and gelation temperature [1]. As has been demonstrated [2], high chitosan concentrations prevent formation of magnetite due to the slow diffusion of the alkali species through the viscous medium provided by chitosan. But the presence of magnetite nanoparticles increases the elastic modulus which results in reinforcement of the chitosan ferrogels. As both the filler and polymer have significant influence on composite inner structure and, hence, on material properties; that is why in present study we discuss mutual influence of a carrier surface nature (silica particles or nanotubers), polymer matrix, and magnetite prepared via *in situ* precipitation in biopolymer solution.

This paper describes the synthesis of iron oxide nanoparticles accomplished by *in situ* co-precipitation of ferrous and ferric cations by aqueous ammonia in solu-

tions. The study aims to investigate, on one hand, the influence of concentration and type of iron oxide precursors on formation and characteristics of magnetite nanoparticles and, on the other hand, the effect of the magnetite nanoparticles on the chitosan structure. Also, the influence on magnetite particles formation the silica or nanotubers surface (contained hydroxyl groups or aminated) in this process are discussed.

2. EXPERIMENTAL SECTION

2.1 Materials

Chitosan (CTS) (DD 85 %, 220 kDa) was obtained from shrimp shells by a known method that includes a demineralization in HCl and deacetylation in alkaline solution under heating. Glutaraldehyde (GA) 25 % solution was purchased from Acros Organics (Belgium) and glucose (Gl) was purchased from Fluka. All other chemicals purchased from commercial sources were analytical grade: Mohr's salt (ferrous ammonium sulfate hexahydrate $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$), ferric chloride hexahydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, aqueous ammonia (25 wt %), glacial acetic acid, toluene. All the chemicals were used as received without additional pre-processing. Fumed silicon dioxide (A-300) with the specific surface area of 300 m^2/g was provided by Kalush Research Plant, Ukraine. Aminated silica (A-NH₂) was produced by modification of A-300 with γ -aminopropyltriethoxysilane (Fluka) in toluene at mild conditions. The concentration of the attached amino-groups determined by means of acid-base titration was 0.36 mmol/g.

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Multiwalled carbon nanotubes (MWCNTs) were synthesized by pyrolysis of propylene on the ferruginous catalyst (ISC NASU production). Nanotubes oxidation was performed in hydrogen peroxide 50 % solution at 80 °C for 48 h. Oxidized nanotubes surface modification was carried out from toluene solution of γ -aminopropyltriethoxysilane.

2.2 Synthesis of Iron Oxide-Containing Composites

Composites based on chitozan and metal-containing phase were synthesized by the Elmore reaction using the Mohr salt (ferrous ammonium sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) via in situ precipitation at mild conditions without and in presence of the silicas as stabilisers for the growing particles of a magnetite. The materials composition is represented in Table 1.

Chitosan solution was prepared by dissolving a target quantity (Table 1) of chitosan powder in 50 ml of 3 % acetic acid solution. GA 2.5 % solution was prepared by dilution of initial reagent. Required quantities of magnetite precursors were dissolved in 5 ml 3 % solution of acetic acid and then poured into flask with chitosan solution at mechanical stirring. The mixture was covered with toluene and heated to 60-65 °C. After 5-10 min the aqueous ammonia was quickly added until acidity of the reaction mixture reached pH 11. When the mixture became black, the dispersion pH was reduced to 7 by adding acetic acid and 2.5 % GA solution (5 ml) was introduced. A cross-linked magnetite-containing polymer composite was precipitated with centrifugation (4000 rpm for 15 min), and rinsed with ethanol and distilled water for three times. Finally, the material prepared was subject to drying for 48 h at room temperature. The same procedure was applied for synthesis of silica filled composites; the only difference was that the silica was introduced into the solution before heating. Samples 9 and 10 were obtained by mixing iron-containing salts with glucose (Gl) aqueous solution followed by chemical co-deposition, washing, and drying at the abovementioned conditions. Immobilisation of iron oxide nanoparticles on carbon nanotubes was performed from aqueous salts solution with pH correction during synthesis procedure at 70 °C.

3. RESULTS AND DISCUSSION

3.1 Effect of Iron Oxide Precursor's Nature on Composite Structure

The structure of polymer matrix with in situ formed iron-containing nanoparticles will strongly differ from the pure CTS. FTIR spectrum of the Sample 2, corresponding to pure CTS, testify formation of a material with larger amount of amino groups; confirm the low intermolecular interaction in the polymer matrix but testifies chemical interaction of the system components. The use as iron oxides precursors the ferrous ammonium sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Sample 3) results in more stable magnetite phase forming. There are both individual Fe_3O_4 nanoparticles and Fe_3O_4 -chitosan composite. Obtained results testify the formation of a

complex between the surface charged Fe_3O_4 nanoparticles and cationic CTS matrix; the Fe_3O_4 nanoparticles are coated by (or embedded into) chitosan and a high cross-linking degree of chitosan via formation of azomethyne groups ($\text{C}=\text{N}$) as was followed from FTIR spectra. Consequently, if only Mohr's salt is used as the source for iron, the chitosan-based composite formed will have low resistance to oxidation of the metallic particles and weakly cross-linked polymer matrix. Using both Mohr's salt and ferric chloride as the precursors allows producing a composite with a more stable magnetite phase and high cross-linking degree of the polymer matrix.

3.2 Effect of Silica Fillers on Composite Structure

The formation of the composite structure in case of A-300 presence depends on interaction of the system components with silica surface. The interaction of silica with iron oxide particles is confirmed, in particular, by the presence of the characteristic band (817 cm^{-1}) which is specific for silica/iron oxide systems and can be attributed to vibration of Si-O bond in terminal groups. This band decreases as the degree of surface modification increases. According to obtained spectrum the Sample 4.1 contains $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ particles with Fe-OH groups on their surface. After cross-linking the polymer with glutaraldehyde (Sample 4.2) a several types of binding of silica and composite components take place. The narrowing of the peak attributed to the Fe-O stretching vibration in tetrahedral site testifies a change of the crystallite structure due to availability of the silica surface. Thus, we can assume that the formation of oxide phase occurs on the silica surface and the interaction of magnetite and polymer is realized during chitosan cross-linking with glutaraldehyde. The complex compounds of iron oxides with chitosan are formed on the surface of silica particles in Composite 4.2. Magnetite, however, is present in the composite, but either its amount is small or very small magnetite particles are formed, which complicates their identification. The findings also imply that the magnetic nanoparticles located on silica surface have a chitozan coating adsorbed on them.

Change of the silica surface nature significantly affects the structure of the final composite. Namely, the influence of the modifying silica layer on the macromolecular packing of the polymer matrix was observed. Analysis of the results suggests that the Composite 5 has the magnetite particles distanced from the silica surface, and aminopropyl groups on the silica surface facilitate compaction of the adsorbed chitozan layer with iron oxide particles embedded. DSC was used to determine if the change in the polymer microenvironment occurs in the presence of magnetite and unmodified or aminated silica. For samples 3-5 the exo-effect peak ascribed to amino groups destruction becomes more intense. The excessive amounts of -COOH groups promotes formation of a pseudo-crystalline phase due to the intermolecular hydrogen bonding. The emergence of this effect on the DSC curves is a proof of the existence and the emergence (or degradation) in the course of the experience of different supramolecular structures. It's likely that microdomain structures with

Table 1 – Materials used for syntheses of samples

Samples	CTS	Gl	Mohr's salt	FeCl3	A-300	A-NH2	GA
	Quantity (g)						
1	0.75	–	–	–	–	–	0.132
2	0.75	–	0.2	–	–	–	0.132
3	0.375	–	0.3	0.42	–	–	0.066
4.1	0.375	–	0.3	0.42	0.182	–	–
4.2	0.375	–	0.3	0.42	0.182	–	0.066
5	0.375	–	0.3	0.42	–	0.182	0.066
6	0.375	–	0.6	0.3	–	–	0.132
7	0.375	–	0.6	0.3	0.182	–	0.132
8	0.375	–	0.6	0.3	–	0.182	0.132
9	–	1	0.6	0.3	–	–	–
10	–	1	0.3	0.3	–	–	–

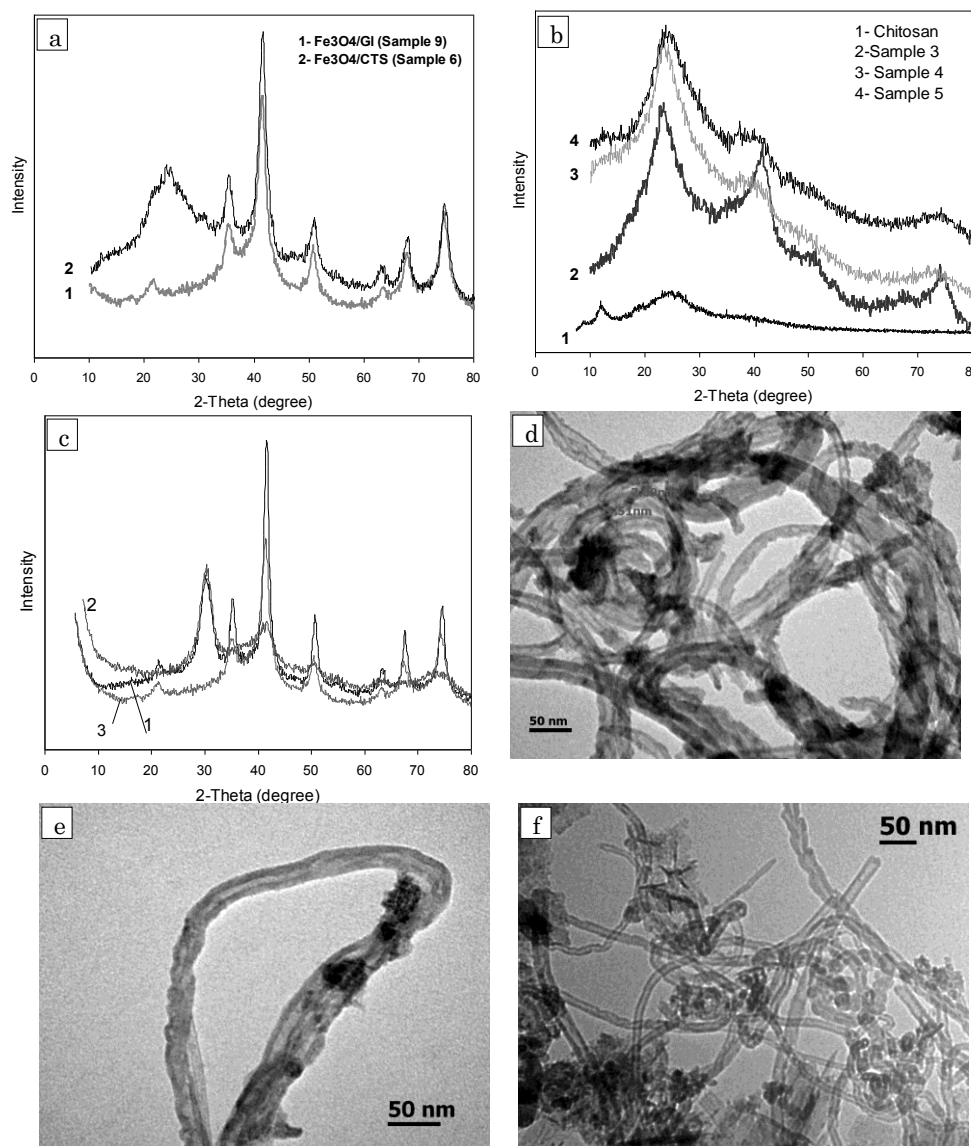


Fig. 6 – (a) – XRD patterns of Fe₃O₄ / Gl (1) and Fe₃O₄ / CTS (2) (samples 9 and 6, respectively); (b) – XRD patterns of the chitosan (1) and iron oxide-containing composites without silica (2) and filled with A-300 (3) or A-NH₂ (4) (Samples 3-5, respectively); (c) – XRD patterns of magnetite / carbon nanotubers that were oxidized (1) and with attached amino group (2) and pure Fe₃O₄ obtained without nanotubers at the same conditions (3); (d-f) – TEM micrographs of composites based on magnetite particles and oxidized, aminated and modified with chitosan nanotubers, respectively.

low branching but high amount of carboxyl groups are formed in this case.

Analysis of the curves suggests that the thermal stability of the composites is higher compared with that

of pure chitosan. Preparation of magnetite nanoparticles *in situ* facilitates formation of structures which have destruction temperatures above 380 °C. The presence of magnetite and silica promotes formation of a discrete regular globular structure with varying packing density of surface layers of the polymer. In addition, amino groups on silica surface provide for cross-linking of adsorbed chitosan macromolecules.

3.3 Effect of Stabilizer Nature on Iron-Containing Phase Composition

The change of the stabilizing agent with the precursor mixture ratio unchanged (0.6 : 0.3) affects composition of the iron-containing phase. The FTIR spectrum of sample 9 indicates that magnetite is dominant in the composite, unlike the composite based on chitosan (sample 6). The spectrum profile indicates that glucose interacts with the nanoparticles.

Less amount of Mohr's salt in the precursor mixture (Sample 13) results in higher amount of Fe₂O₃ in the sample, as well as, a compaction of the stabilizer molecules' packing. Obtained results points on Fe-OH groups presence and uniformity of the iron oxides lattice. Most probably, magnetite is located in facets of glucose crystals or on their surface. It's worthwhile to note that owing to the composite fine dispersion it is hard to be cleaned from excessive stabilizer and requires long drying times. Higher amounts of Mohr's salt (sample 9) result in formation of a more loose structure of the adsorbed stabilizer layer. Compared to the spectrum of sample 10, the Fe₃O₄ dominates in sample 9, and nanoparticles are covered by the stabilizer. It's likely that the excess of Mohr's salt facilitates compatibility of the iron-containing and organic phases.

3.4 Effect of Matrices Nature on Characteristics of Iron Oxides Particles

In order to confirm the presence of Fe₃O₄, the structure of same samples was characterized by XRD (Fig. 1). The average sizes of iron oxide particles were estimated from XRD patterns using the Scherrer's formula [3]. Diffraction patterns of both chitosan- and glucose-stabilized magnetite nanoparticles (Fig. 1a) contain six diffraction peaks at $2\theta = 21.5$ (111), 35.4 (220), 41.6 (311), 50.8 (400), 63.2 (422), 67.9 (511), 74.4 (440) which can corre-

spond to either crystalline magnetite or maghemite with the spinel structure (JCPDS PDF 85-1436 or 39-1346, respectively). According to the IR spectroscopy results, nanoparticles produced are comprised of either magnetite (if glucose is used) or both magnetite and maghemite (in case of chitosan matrix). Co-precipitation of iron oxide precursors in either chitosan or glucose solution allows obtaining particles with the size of coherent scattering zones ca. 5-7 nm, respectively.

The higher is content of Mohr's salt in the precursor mixture, the larger particles are formed (compare patterns of samples 3 and 6, Fig. 1). Quite weak and noised diffraction peaks of sample 3 suggest that Fe₃O₄ particles are coated by amorphous chitosan.

The structure of magnetite nanoparticles in samples 4 and 5 seems to be greatly affected by silica, Fig. 1(B). The broad peak at ca. 23° was assigned to CTS [3]. Peaks of Fe₃O₄ are weaker and broader than in case of sample 3 due to decrease in the crystallite size of the particles obtained. The average size of coherent scattering zones are estimated as 1-2 and 2-2.5 nm for samples 4 and 5, respectively. It should be noted that the change of polymer structure is reflected by the disappearance of characteristic chitosan peaks at $2\theta = 12.55^\circ$ and 19.25° along with a shift of the main peak at 25.7° . This is caused by interaction between the CTS and inorganic components. Thus, the composite materials display different structural patterns since the degree of polymer crystallization is smaller in them compared to that of pure chitosan.

Found that the charge on the surface of nanotubes affects the size of magnetite particles formed *in situ*, whereas modifying layer architecture causes the particle distribution in the sample

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