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MAGNETIC POLYSACCHARIDES

F. Llanes and C. Diaz
Biomaterials Center, University of Havana,
Havana, Cuba

D. H. Ryan
Department of Physics, McGill University, Quebec, Canada

R. H. Marchessault
Pulp and Paper Research Centre and Department of Chemistry,
McGill University, Quebec, Canada

Magnetic composites with superparamagnetic properties has developed a great scientific interest in the last years by their potential application in drug delivery and cell sorting systems. Alginate, starch and chitosan were used as polymeric matrixes in order to obtain magnetic nanostructured composites. Magnetic nanocrystalline particles of iron oxide were formed inside the matrix by an in situ alkaline oxidation of iron (II) ions. The total iron content was determined in each composite. X-Ray Diffraction, Magnetometry and Mössbauer Spectroscopy were used to examine the composites. The magnetic materials exhibits high magnetic response, absense of hysteresis in the magnetization curves and a centered paramagnetic doublet in the Mössbauer spectra indicating the presence of nanocrystalline particles with a superparamagnetic behavior. X-Ray diffractograms show peaks that correspond to maghemite.

Keywords: alginate, starch, chitosan, iron oxides, superparamagnetism, magnetic nanocomposites

INTRODUCTION

Composites are natural or synthetic multiphase materials in which one of the phases, the matrix, is continuous and cover one or more dispersed phases. A magnetic composite is a particular case of composite in which the matrix is a polymer and the dispersed phase are magnetic particles.

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Address correspondence to F. Llanes, Biomaterials Center, University of Havana, Ave. Universidad entre Ronda y G, Vedado 10400, Havana, Cuba. E-mail: paco@biomat.uh.cu

Magnetic composites with nanometric particles have a superparamagnetic behavior, *i.e.*, they display little or no remanence and coercivity while keeping a very high saturation magnetization. Such materials have potential applications in medical diagnostic technologies, magnetic drug delivery and cell-sorting systems [1, 2].

Nanostructured magnetic composites have been obtained by *in situ* synthesis of iron oxides inside a synthetic or natural polymeric matrix following a procedure proposed by Ziolo [3] based in a cation exchange of the sulfonate or carboxilate groups, already present or synthetically generated in the monomer unit, with iron (II) ions, followed by the precipitation of iron (II) hydroxide in alkaline media and finally performing a carefull oxidation with hydrogen peroxide or oxygen [4, 5]. Bacterial cellulose was used also as polymeric matrix to prepare magnetic membranes without introducing any other functional group [6, 7].

Alginate

Alginate, the major structural polysaccharide of marine brown algae, is a (1 → 4)-linked copolymer of β-D-mannopyranuronosyl (M) and α-L-gulopyranuronosyl (G) residues.

Seaweed species characteristically differ from each other in their relative proportions (M/G ratios) of these two constituents sugar acids, as well as in their sequencing within the polymer chain [8 – 11].

G sequences of alginate have a buckled minimum energy conformation and the crystalline packing forms an array of cavities simulating the "egg box" [12]. G sequences organize by selectively binding Ca^{2+} and other divalent ions such as Fe^{2+}, to form ordered domains which are responsible for gelation.

Since M sequences in the chain do not form an "egg box", the content of G in the alginate determines the properties of the gels. Alginates with high content of G produce rigid gels, while alginates with high content of M form more elastic gels [13].

Starch

Starch is the principal food-reserve polysaccharide in the plant kingdom. The starch granules can be separated into two distinctly different components. The two components amylose and amylopectin, vary in relative amount among the different sources, from less than 2 per cent to about 80 per cent, but the majority of starches contains between 15 and 35 per cent amylose [14].

The characteristic features of amylose and amylopectin are chains (1 → 4)-linked α-D-glucopyranosyl residues with, in the case of amylopectin, 1,4,6-tri-O-substituted residues acting as branch points [15].

Crosslinking of Starch

The chemistry of crosslinking polysaccharides is well known and there are a variety of agents to crosslink hydroxyl groups of polysaccharides. Crosslinking is performed by treating granular starch with multifunctional reagents capable of forming ether or ester linkages with hydroxyl groups in the starch [16].

Among the crosslinking agents used to crosslink starches the most common is epichlorohydrin (1-chloro-2,3-epoxypropane). This reagent react with the hydroxyl groups in starch in alkaline media to form a chemical gel [17].

Chitosan

Chitosan is a linear copolymer of β-(16 4)-linked 2-amino-2-deoxy-D-glucose residues, which is readily prepared from chitin by chemical N-deacetylation.

Chitin is currently obtained in large scale from the shells of crabs, shrimps and lobsters.

The chemical and biochemical reactivity of chitosan is higher than those of chitin because chitosan have free primary amino groups distributed regularly in its chain. Therefore, chitosan is soluble by salt formation because the primarily amine can be protonated by certain selected acids [18].

In this paper we report the synthesis and properties of magnetic composites using alginate, crosslinked starch and chitosan as polymeric matrixes. The products were examined by, Magnetometry, X-ray Diffraction and Mössbauer Spectroscopy.

EXPERIMENTAL

Materials

Alginate extracted from *Sargassum* with an average molecular weight of 34000 g/mole [20] and a M/G ratio of 0.6 [21] was obtained from the Biomaterials Center of the University of Havana, Cuba. High amylose starch samples crosslinked with epichlorohydrin were kindly provided by Y. Dumoilin from University of Montreal, Canada. Chitosan (84% deacetylated) and all other reagents were obtained from commercial sources.

Methods

In Situ Synthesis

In situ synthesis of alginate magnetic composite followed a modified Ziolo three steps procedure [3], using hydrogen peroxide as oxidizing agent.

Iron (II) Alginate Beads

A solution of 0.75 g of alginate in 25 mL of distilled water was added dropwise to a degassed ferrous chloride tetrahydrated solution (250 mL, 0.5 mole/L) to form ferrous alginate beads. The solution was gently stirred during the whole addition and remained stirred for 30–45 minutes. The ferrous alginate beads were separated by filtration and washed several times with methanol/water 1 : 1. The ferrous alginate beads were placed in 250 mL of methanol/water 1 : 1 and an aqueous solution of sodium hydroxide (200 mL, 0.5 mole/L) was added stirring for 30 minutes. At last, the suspension was placed in a 65 ± 5°C water bath and a solution of hydrogen peroxide (10 mL, 10% weight %) was added dropwise. The suspension was stirred at 65 ± 5°C for 60 minutes. Nitrogen was bubbled in the suspension before the hydrogen peroxide addition. The final product was separated and washed several times with methanol/water 1 : 1 by centrifugation and freeze-dried to obtain a reddish-brown powder.

Nitrogen was continuously bubbled in the suspension before the hydrogen peroxide addition to prevent undesirable oxidation.

Crosslinked Starch Magnetic Composite

A suspension of 0.75 g of crosslinked high amylose starch in 25 mL of distilled water was prepared with constantly stirring. This suspension was slowly added to a degassed ferrous chloride tetrahydrated solution (250 mL, 0.5 mole/L). The solution was gently stirred during the addition and remained stirring for 2 hours. The embedded starch was washed with distilled water by centrifugation and suspended in 250 mL of distilled water. An aqueous solution of sodium hydroxide (200 mL, 0.5 mole/L) was added, the suspension was placed in a 65 ± 5°C water bath and a solution of hydrogen peroxide (10 mL, 10% weight %) was added dropwise. The suspension was stirred at 65 ± 5°C for 60 minutes. Nitrogen was constantly bubbled in the suspension before the hydrogen peroxide addition. The final product was separated and washed several times by centrifugation and freeze-dried to obtain a reddish-brown powder.

Nitrogen was continuously bubbled in the suspension before the hydrogen peroxide addition to prevent undesirable oxidation.

Chitosan Magnetic Composite

Chitosan (1 g) was dissolved in 100 mL of acetic acid solution at pH 1 and mixed with a degassed ferrous chloride tetrahydrated solution (100 mL, 0.5 mole/L). A chitosan-iron (II) complex was formed at pH 5–6 after the neutralization of the mixture with a sodium hydroxide solution. The complex was washed several times with distilled water by centrifugation, suspended in 100 mL of distilled water and an aqueous solution of sodium hydroxide (200 mL, 0.5 mole/L) was added. The suspension was placed in a 65 ± 5°C water bath and a solution of hydrogen peroxide (10 mL, 10% weight %) was added dropwise. The suspension was stirred at 65 ± 5°C for 60 minutes. The final product was separated and washed several times by centrifugation and freeze-dried to obtain a reddish-brown powder.

Nitrogen was continuously bubbled in the suspension before the hydrogen peroxide addition to prevent undesirable oxidation.

Total Iron Content

The total iron content of the composites were determined by a plasma technique at Guelph Chemical Laboratories Ltd. Guelph, Ont., Canada.

X-ray Diffraction

Samples were analyzed by Cu K_α X-ray diffraction on a Nicolet-Stöe automated powder diffractometer. The relative intensities as a function of the diffraction angle were recorded.

Magnetometry

Magnetization measurements were made on a Quantum Design PPMS equipped with a 9 Tesla superconducting magnet and operating between 5 K and 300 K. Approximately 20 mg of powder was packed into a gelatin capsule for the magnetic measurements. The magnetization M at room temperature was fitted as being due to the superparamagnetic particles.

Mössbauer Spectroscopy

Room temperature ^{57}Fe Mössbauer spectra were obtained on a constant-acceleration spectrometer using a 1 GBq ^{57}CoRh source. The spectra were fitted using a conventional non-linear least squares routine. A gaussian distribution of quadrupole splittings (mean ~0.65 mm/s, width 0.1–0.3 mm/s) was used to reproduce the slightly broadened lines.

RESULTS AND DISCUSSION

Total Iron Content

The total iron content of the samples (Tab. 1) indicates that the composites from crosslinked starch and *Sargassum* alginate retain much more oxide particles than that from chitosan. These results can be explained by the structural characteristics of the polysaccharides. Crosslinked starch is a

TABLE 1 Total iron content of magnetic composites

Composite	*Iron content* (%)
Crosslinked starch	43.0
Sargassum alginate	31.1
Chitosan	14.6

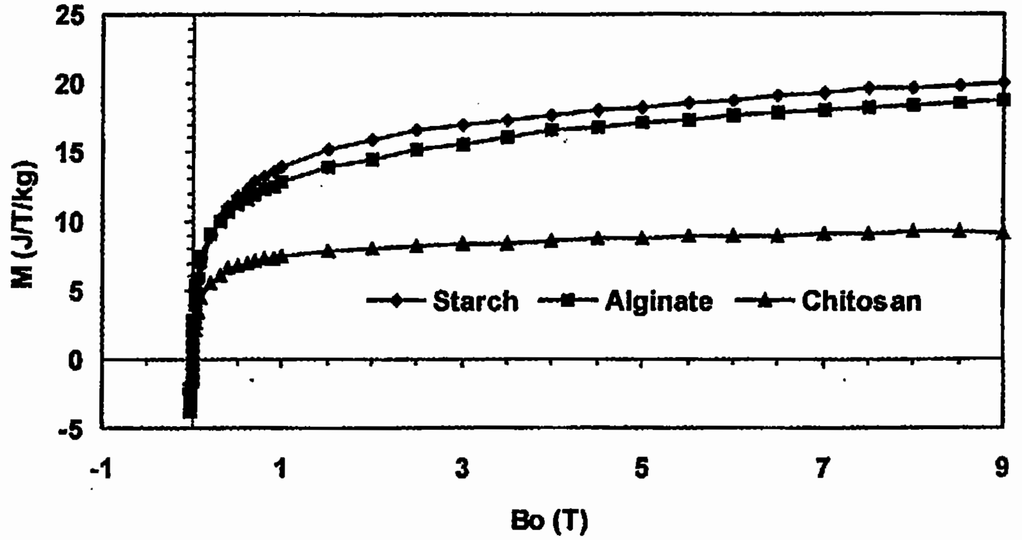

FIGURE 1 Powder X-ray spectra of magnetic composites from (a) alginate, (b) starch, (c) chitosan, and (d) maghemite.

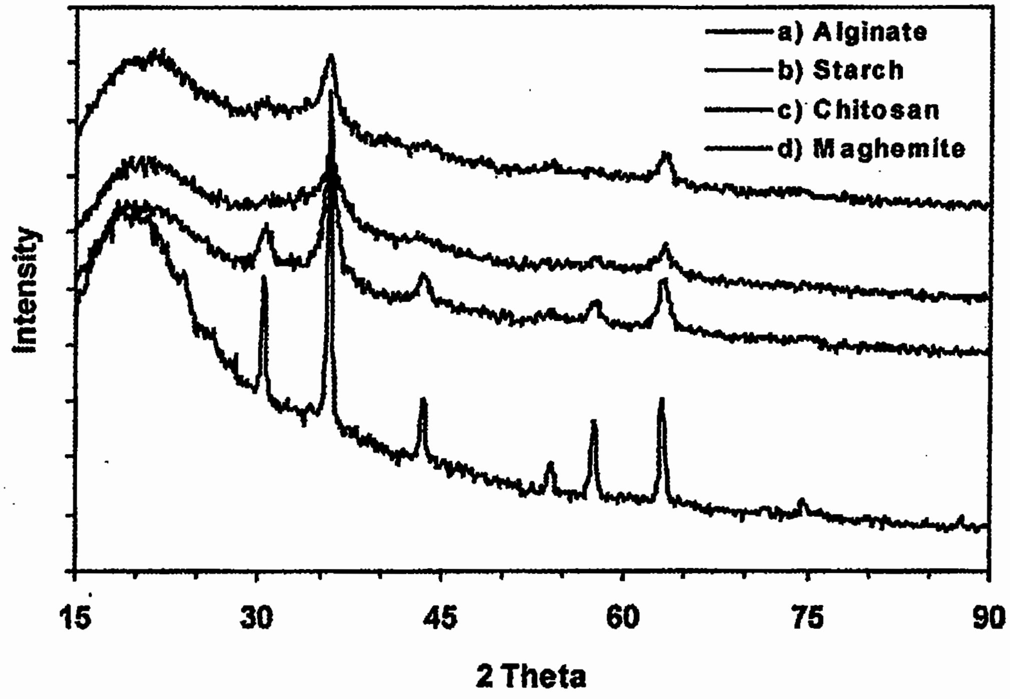

FIGURE 2 Room temperature magnetization curves of magnetic composites from (a) starch, (b) alginate, and (c) chitosan.

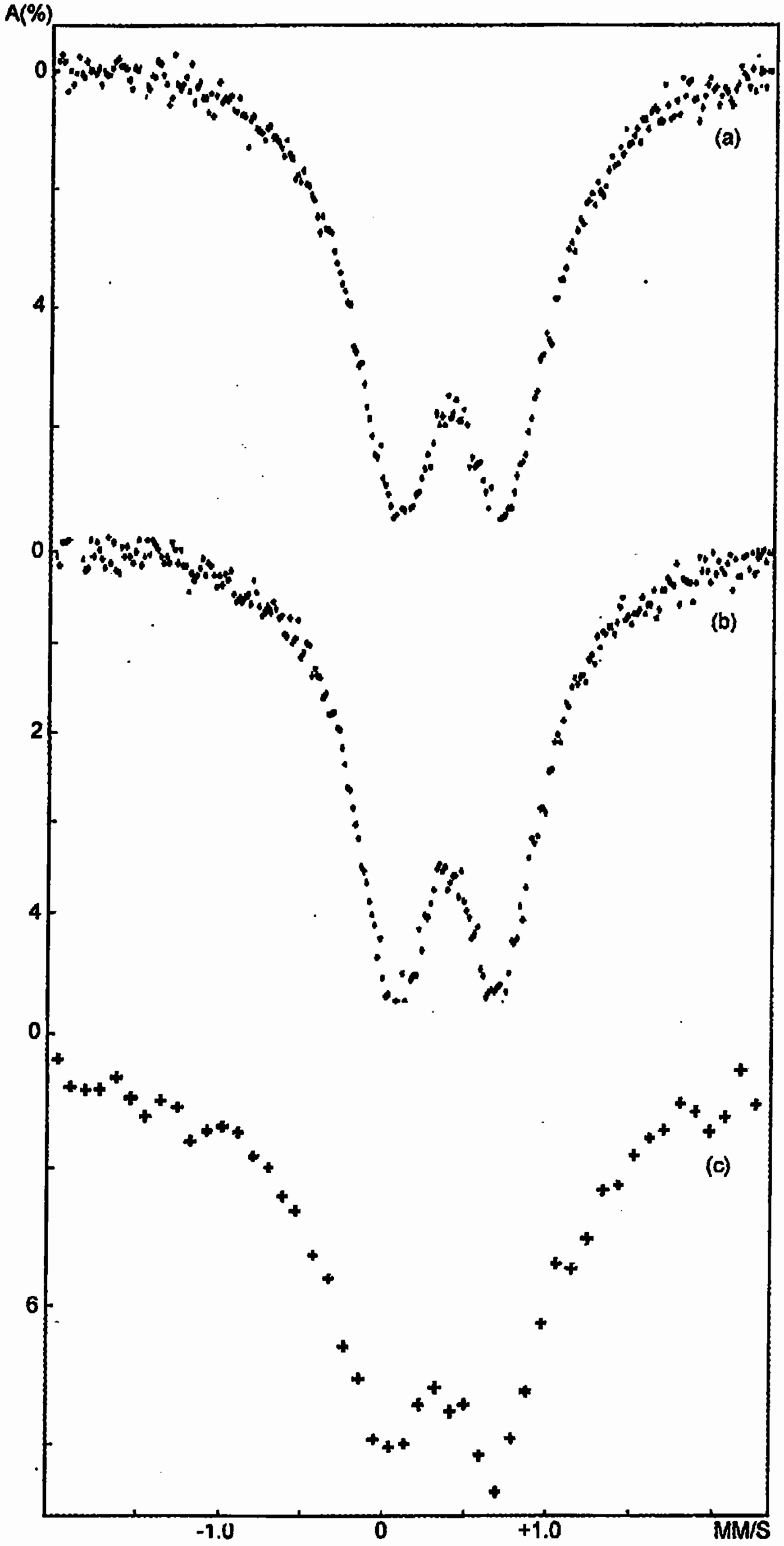

FIGURE 3 Room temperature Mössbauer spectra of (a) alginate magnetic composite, (b) starch magnetic composite, and (c) chitosan magnetic composite.

chemical gel, alginate is a linear copolymer with different proportions of mannuronic and guluronic acid residues (M/G ratio) and chitosan is a linear homopolysaccharide. Crosslinked starch have a high swelling capacity and absorbs the iron (II) solution retaining a large quantity of iron. Alginates forms a physical gel with iron (II) ions and also retains a large quantity of iron. Chitosan forms a complex with a limited quantity of iron (II) ions, less than crosslinked starch and alginate.

X-ray Diffraction

The presence of maghemite was detected in the samples by its characteristic diffraction peaks at $2\theta = 30.4, 35.8$ (100%), 43.6, 54.2, 57.5 and 63.1 (Fig. 1). A difference in the line broadening is also observed, indicating the presence of small particles.

Magnetic Properties

Room temperature magnetization curves (Fig. 2) shows higher magnetization in the crosslinked starch and alginate composites than in chitosan. However no remanence or coercitivy is observed ($B_c < 1\,\mathrm{mT}$) in all the samples. Cooling samples to 5 K leads to an increase in magnetization and also to the appearance of coercivity. These results suggest that the magnetic particles grown in the composites are small enough to be superparamagnetic at room temperature.

Mössbauer spectra, at room temperature (Fig. 3) show slightly broadened quadrupole doublets, with no evidence of magnetic order (absence of magnetic sextet pattern). The values for the isomer shift and the quadrupole splitting are consistent with fine-particle maghemite. The high magnetization coupled with the paramagnetic Mössbauer spectra is only consistent with the iron oxide being in the form of superparamagnetic fine particles. As a magnetic particle is reduced in size it eventually becomes too small to accommodate domains (the energy associated with forming a domain wall becomes too great) and the particle becomes a single-domain particle. Often, when the particle is very small, the barrier can be comparable to thermal energies kT so that the magnetization direction fluctuates rapidly and the particle is superparamagnetic, exhibiting a large magnetization in an applied field, but no remanence.

CONCLUSIONS

Crosslinked starch, alginate and chitosan can be used as polymeric matrixes in the synthesis of nanostructured magnetic composites with superparamagnetic properties. A large amount of magnetic oxide is incorporated in the matrix by this method. Crosslinked starch and guluronic-rich alginate

(M/G < 1) retain large amounts of iron and thus, more magnetic oxide is formed and retained inside the matrix compared to chitosan in a single oxidative reaction.

By a well controlled oxidative reaction using alkaline hydrogen peroxide at 60–65°C, the ferrous ions are converted to nanometric maghemite particles.

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