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Magnetic nanostructured composites using alginates of different M/G ratios as polymeric matrix

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Abstract

Alginate extracted from *Sargassum fluitans* and *Macrocystis pyrifera* with different molecular weights and mannuronic/guluronic ratios, M/G, were used as gel matrixes in order to obtain magnetic nanostructured composites. Magnetic nanocrystalline particles of iron oxides were formed inside the alginate matrix by in situ alkaline oxidation of ferrous ions. The magnetic materials obtained were subjected to several oxidative cycles and the increment in iron content was determined after each cycle. X-ray diffraction, magnetometry and Mössbauer spectroscopy were used to examine the materials. The high magnetic response, the absence of hysteresis, and the centered paramagnetic doublet in the Mössbauer spectra indicate the presence of nanocrystalline particles with a superparamagnetic behavior. X-ray diffractograms show peaks that correspond to maghemite. After the first cycle, *Sargassum* had four times the magnetic response of *Macrocystis*, which had more than twice the M/G ratio. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alginate; Maghemite; Magnetic nanocomposites

1. Introduction

Nanostructured magnetic materials with superparamagnetic behavior, i.e. they display little or no remanence and coercivity while keeping a very high saturation magnetization, have potential applications in medical diagnostic technologies, magnetic drug delivery and cell-sorting systems [1,2]. Cross-linked synthetic polymers and different polysaccharides like cellulose and alginate were used as polymeric matrix for synthesizing magnetic composites with interesting results [3–7].

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 (Fig. 1).

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]. Also, for a given species the polysaccharide composition and yield vary considerably depending upon the season, age, and the part of the plant used for extraction [12–15].

G sequences of alginate have a buckled minimum energy conformation and the crystalline packing forms an array of cavities simulating the 'egg box' [16]. G sequences organize by selectively binding Ca^{2+} and other divalent ions such as Fe^{2+}, to form ordered domains (Fig. 2), which are responsible for gelation. monovalent cations and Mg^{2+} ions do not induce gelation [17].

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 that are subject to syneresis, while alginates with high content of M form more elastic gels [18].

The molecular weight and the M/G ratio are important structural factors in the complexing with divalent ions [19]. In the preparation of iron oxides nanocom-

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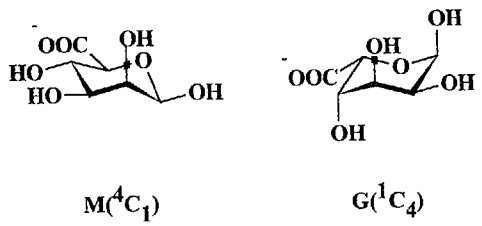

Fig. 1. β-D-Mannopyranuronate (M) and α-L-Gulopyranuronate (G) in their preferential conformation [19].

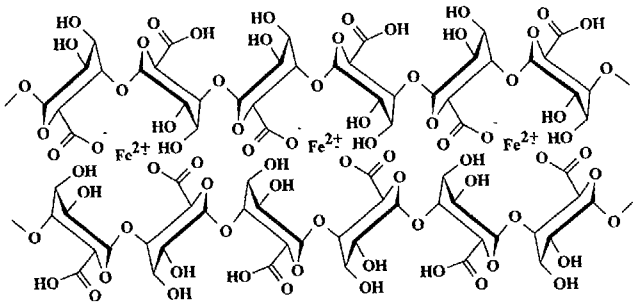

Fig. 2. Representation of two G-blocks forming an 'egg box' with ferrous ions.

posites we assumed that the M/G ratio also plays a role. In this paper we report the multicycle synthesis and properties of magnetic composites using two very different alginates as polymeric matrix. The products were examined by X-ray diffraction, magnetometry and Mössbauer spectroscopy.

2. Experimental

2.1. Materials

Alginate extracted from *Sargassum fluitans* with a viscosity average molecular weight of 34 000 g/mol [20] and a M/G ratio of 0.6 [21] was obtained from the Biomaterials Center of Havana University, Cuba and samples of alginate from *Macrocystis pyrifera* with a viscosity average molecular weight of 140 000 g/mol [20] and a M/G ratio of 1.6 [21] was purchased from Sigma Chemical Company.

2.2. In situ synthesis

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

2.3. Ferrous 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 mol/l) to form ferrous alginate beads. The solution was gently stirred during the whole addition and remained stirred for 30–45 min. 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 mol/l) was added stirring for 30 min. At last, the suspension was placed in a 65 ± 5°C water bath and a solution of hydrogen peroxide (10 ml, 10 wt.%) was added dropwise. The suspension was stirred at 65 ± 5°C for 60 min. Nitrogen was 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 with a high magnetic response when submitted to the effect of a small magnet.

2.4. Multicycle magnetic composite

The dry reddish-brown magnetic composite obtained (1 g) was suspended in a ferrous chloride tetrahydrated solution (250 ml, 0.5 mol/l) and stirred for 2 h. The treated material was then separated and washed several times with methanol/water 1:1 by centrifugation, and the ferrous ions were oxidized by the same process described above (second and third cycles).

2.5. Total iron content

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

2.6. 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.

2.7. Magnetometry

Magnetization and susceptibility measurements were made on a Quantum Design PPMS equipped with a 9 T superconducting magnet and operating between 5 and 300 K. Susceptibility measurements, χ_{ac}, were carried out over a frequency range of 10 Hz–10 kHz. 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 [22] (cf. below).

Table 1
Total iron content of alginate magnetic composites

Composite	Alginate M/G	Iron content (%)	
		One cycle	Three cycles
Sargassum alginate	0.6	31.15	47.09
Macrocystis alginate	1.6	14.01	48.29

2.8. Mössbauer spectroscopy

Room temperature ^{57}Fe Mössbauer spectra were obtained on a constant-acceleration spectrometer using a 1 GBq ^{57}Co**Rh** 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.

3. Results and discussion

3.1. Total iron content

The total iron content of the samples (Table 1) indicates that in a first cycle the nanocomposite product from *Sargassum* alginate retains much more oxide particles than that from *Macrocystis*, however, after three cycles, the total iron content is almost the same for both.

Sargassum alginate has an M/G ratio of 0.6 indicating a higher content of G sequences. In one cycle it retains twice as much magnetic particles as *Macrocystis* alginate. This is atributed to the superior complexing ability of G sequences with iron compared to M. Presumably, the complexing is possible with both G and M sequences since after three cycles the iron contents are similar.

3.2. X-ray diffraction

The presence of maghemite was detected in the samples by its characteristic diffraction peaks at 2θ: 30.4, 35.8 (100%), 43.6, 54.2, 57.5 and 63.1 (Fig. 3). A difference in the line broadening is also observed, indicating the presence of smaller particles (broad peaks) in the one cycle magnetic composite from *Macrocystis* compared to one cycle from *Sargassum*.

3.3. Magnetic properties

Room temperature magnetization curves (Fig. 4) show a substantial magnetization in all cases for *Sargassum* and *Macrocystis* alginates, however no remanence or coercitivy is observed ($B_c < 1$ mT). The *Macrocystis* sample shows a greater increase after three deposition cycles, consistent with the change in iron content shown in Table 1. After three cycles the two loaded alginates have similar magnetization curves. Cooling the 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

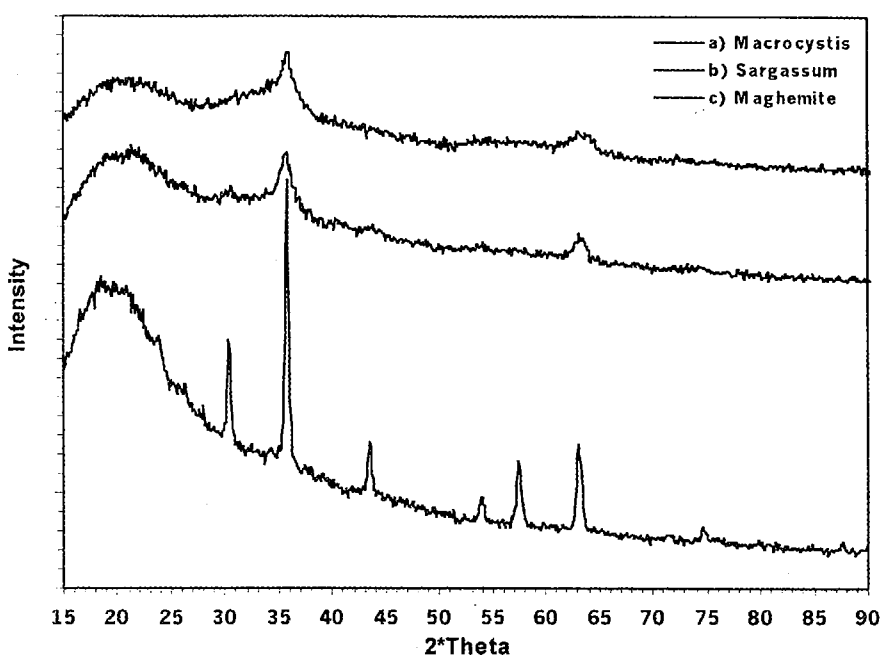

Fig. 3. XRD powder pattern of one cycle (a) *Macrocystis* alginate magnetic composite (b) *Sargassrum* alginate magnetic composite and (c) Maghemite.

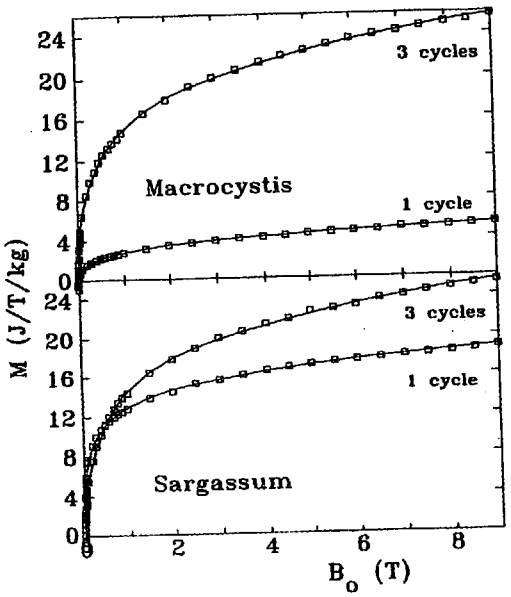

Fig. 4. Magnetization curves of the first and third cycle of *Macrocystis* and *Sargassum* alginate magnetic composites.

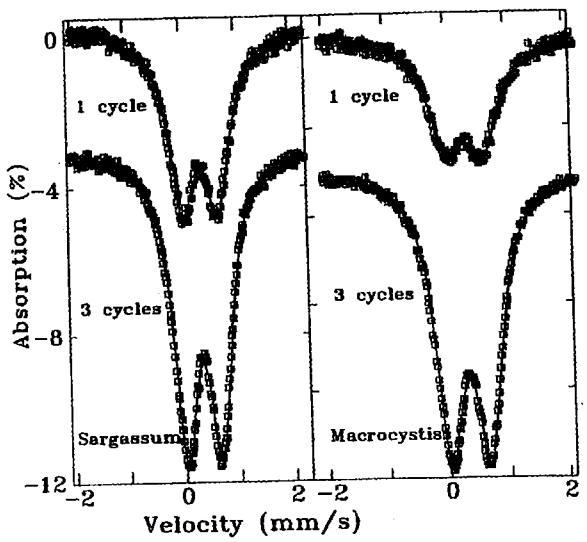

Fig. 5. RT Mössbauer spectra of the first and third cycle of *Macrocystis* and *Sargassum* alginate magnetic composites.

in the alginate are small enough to be superparamagnetic at room temperature.

Mössbauer spectra, at room temperature (Fig. 5) show slightly broadened quadrupole doublets, with no evidence of magnetic order (absence of magnetic sextet pattern). The fitted parameters of the spectra are, within error, the same for all samples, being: $+0.33 \pm 0.01$ mm s^{-1} (isomer shift) and 0.65 ± 0.01 mm s^{-1} (quadrupole splitting). These values are consistent with fine-particle maghemite, and there is a tendency toward sharper lines after three cycles. The high magnetization coupled with the paramagnetic Mössbauer spectra is only consistent with the iron oxide being in the form of superparamagnetic fine particles.

Susceptibility measurements, χ_{ac}, provide more detailed information on the superparamagnetic particles (Fig. 6). 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. At this point, intrinsic anisotropy and the shape of the particle control the energy barrier for magnetization reversal. 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. As the temperature is reduced the fluctuations slow, and eventually stop and the particle is then said to be blocked. The temperature at which blocking occurs depends on the frequency at which the magnetization (or susceptibility) is measured. In χ_{ac} (Fig. 6), a peak is observed when the measuring frequency matches the fluctuation rate. Since the fluctuations are thermally activated, the rate follows $f = f_0 \exp(-E_b/kT)$, with f_0 being a characteristic fluctuation rate (typically 10^{12}–10^{15} Hz) and E_b being the energy barrier. Fitting the position of the peak vs. measuring frequency for the one cycle *Macrocystis* alginate (inset to Fig. 6) yields an energy barrier of 4800 ± 150 K. The fit predicts a fluctuation rate of 300 MHz at room temperature, too fast for the particles to appear blocked by Mössbauer spectroscopy, and consistent with the paramagnetic spectra shown in Fig. 4. The behavior of all the alginate superparamagnetic samples in this study was qualitatively the same as shown in Fig. 6.

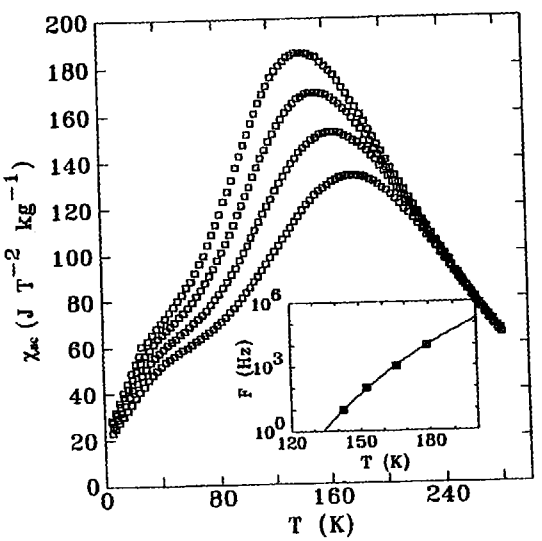

Fig. 6. χ_{ac} data for the first cycle *Macrocystis* alginate magnetic composite at (from top to bottom): 10, 100 Hz, 1 and 10 kHz, showing a peak at the temperature and frequency characteristic of superparamagnetic blocking. The inset shows the position of the peak vs. frequency and temperature fitted with an activated fluctuation model.

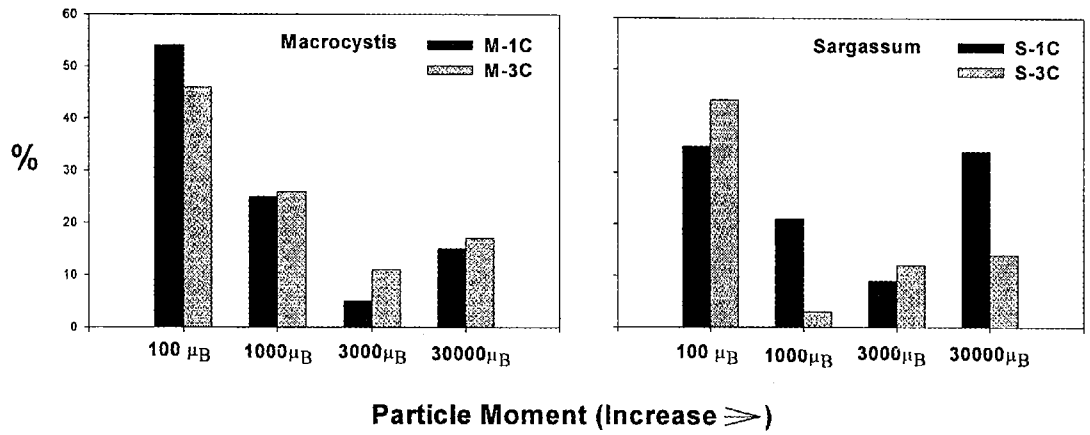

Fig. 7. Particle moment distribution for the first and third cycle of *Macrocystis* and *Sargassum* alginate magnetic composites. To be noted that *Sargassum* has larger particles initially but the amount of small particles increases with the number of cycles.

The rather broad thermal response apparent in the χ_{ac} data coupled with the form of the magnetization curves indicates that there is a significant range of particle sizes present in the alginates. Closer examination of the magnetization data, shows that the majority of the increase in magnetization is apparent at high fields (above 2 T) in the form of a high field slope (the effect is less obvious for the *Macrocystis* alginate as the changes in shape are swamped by the very large increase in total iron content). Such a high-field slope is characteristic of much smaller particles that require a larger field to orient them. Furthermore, χ_{ac} data for both samples show a clear shift in peak position to lower temperatures as measuring frequency decreases, again indicating the presence of more small particles after three cycles. Since the original beads are prepared by mixing the alginate directly with the ferrous chloride solution, and subsequent cycles rely on diffusion, it is likely that ferrous ion loading is less efficient in the later cycles and that this leads to the formation of smaller maghemite particles.

In order to quantify this idea, the room temperature magnetization curves were fitted assuming a discrete distribution of superparamagnetic particles, where for each component of the distribution, the magnetization is assumed to follow the relation:

$$M/M_s = \coth(\mu B_0/kT) - kT/\mu B_0$$

where B_0 is the applied field, M_s is the saturation magnetization in infinite field for maghemite, k is Boltzmann's constant and μ is the particle moment. A distribution containing four particle moments between $100\mu_B$ and $30\,000\mu_B$ was found to be sufficient to fit the data without causing instability due to too many parameters. These fits are shown as the solid lines in Fig. 4.

It is immediately clear from the derived particle moment distributions shown in Fig. 7 and from the relative breadth of the peaks in the X-ray diffraction patterns (Fig. 3), that the *Sargassum* alginate yields larger particles in the first cycle than the *Macrocystis* alginate, and this accounts for the much greater magnetization of the *Sargassum* samples. Subsequent cycles tend to add more fine particles, which lead to an increase in magnetization at high fields, without affecting the low-field response, as the smaller particles are harder to align in a given field. The increase in the fine particle component is most easily seen in the magnetization data for the *Sargassum* sample (Fig. 4) where the change between the first and third cycles is confined to an increase in the high field (i.e. above 2 T) slope and the initial magnetization, which is dominated by contributions from the largest particles is unchanged.

4. Conclusions

Both types of alginates can be used as polymeric matrices in the synthesis of nano-structured magnetic composites with superparamagnetic properties. A large amount of magnetic oxide is incorporated in the matrix by this method. A multicycle procedure increases the fine particles in the matrix. Guluronic-rich alginate (M/G < 1) like that from *Sargassum* species retain large amounts of iron in the gel and thus, more magnetic oxide is formed and retained inside the matrix compared to other alginate gels [6] in a single oxidative reaction.

By a well-controlled oxidative reaction using alkaline hydrogen peroxide the ferrous ions are converted to nanometer maghemite particles. The process for preparation of these nanocomposites is adapted to the physical characteristics of the alginate gels and the *Sargassum* species appears to be a more desirable material because of its heavier loading in the first cycle.

Beads of alginate are a convenient way to package superparamagnetic ferrites. The instability of the calcium alginate beads in alkaline pH, as used in this study, can be overcome by 'hardening'. This well-known treatment using an aqueous chitosan solution maintains the bead integrity. The M/G ratio is a measure of the ease of iron complexing with a given alginate. Thus the *Sargassum* alginate complexed to the greater extent on the first cycle treatment. However, other factors are important in gel structure, e.g. molecular weight that influences mechanical properties of the gel. Other things being equal it is the fine structure of the gel that controls the size distribution of the ferrites and ensures formation of a superparamagnetic system.

In many respects, the alginate gel is similar to that of a regenerated cellulose gel cellophane or never-dried *Acetobacter xylinum* cellulose. However, the latter are neutral gels but nevertheless suitable to act as matrix for synthesis of superparamagnetic ferrites. The effectiveness of the neutral cellulose matrix [7] shows that ion-exchange is not an essential feature of the gel substrate to complex the ferrous iron [3]. The stereochemistry and conformational properties of carbohydrates and carbohydrate polymers favor complexing with ferrous and ferric iron.

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