ORIGINAL ARTICLE

Nano Incorporation of iron oxides into carrageenan gels and magnetometric and morphological characterizations of the composite products

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Carrageenan-based magnetic composites were prepared via *in situ* synthesis of iron oxides in a gelatinous network of the polysaccharide. The repeatable synthesis process involved three steps: immersion into ferrous salt (FeCl_2) solution, alkali treatment in sodium hydroxide solution and oxidation with hydrogen peroxide, successively performed with τ - or κ -carrageenan hydrogels as the starting material. Field emission scanning electron microscope observations, X-ray diffractometry and superconducting quantum interference device (SQUID) magnetometry were carried out for the freeze-dried composites. Ferroxylite and magnetite and/or maghemite particles were produced after one cycle and multicycles of the *in situ* process, respectively, with a size less than several tens of nanometers, and were distributed throughout the inside as well as on the surface of numerous fibrillar entities constituting the carrageenan matrix. Nearly all the composite products explored displayed a superparamagnetic (SPM) property at 298 K; the estimated saturation magnetization (M_s) increased with increasing concentrations of FeCl_2 in the gel immersion step and with repetition of the standardized process of iron oxide synthesis. By repeating the synthesis cycle 3–4 times, a composite of practically high M_s reaching $\sim 25 \text{ emu (g sample)}^{-1}$ was easily obtained without impairing the SPM character. Insight was provided into the evolution mechanism of the oxidation state and dimensional distribution of the cyclically loaded iron oxide nanoparticles through comparison with another composite series obtained by a co-precipitation method with a 1:2 mixture of ferrous/ferric salts.

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INTRODUCTION

Polymer/inorganic nanocomposites are usually defined as polymer materials containing a small amount of inorganic particles structured at an average scale (in diameter or thickness) of less than several tens of nanometers. These nanocomposites are expected to be indispensable in future engineering technologies, including biomaterial design. As a functional development of carbohydrate polymers towards advanced materials, the design of magnetic nanocomposites based on cellulose^{1–8} and related polysaccharides^{6,9–15} has attracted much attention since the early 1990's owing to the potential applications of these materials, including information transfer and storage media, electromagnetic shielding fabrics, new filtration and separation systems, magnetic drug-delivery systems and more.

In situ synthesis of iron oxide particles in fibrillar suspensions or gels of polysaccharides has been a useful chemical technique for the generation of these nanocomposites. As initially proposed by Ziolo *et al.*¹⁶ and Marchessault *et al.*,¹ a typical route for preparing the composite samples consists of the following steps: (1) ferrous ion-absorption of the original polymer materials following their swelling or gelation in a ferrous salt solution (for example, aqueous FeCl_2 or

FeSO_4); (2) *in situ* precipitation of ferrous hydroxide by treatment of the swollen polymers with aqueous hydroxides of alkali or alkali-earth metals; and (3) oxidation of the ferrous hydroxide with an oxidizing agent (for example, H_2O_2) or O_2 -bubbling.

It is noteworthy that the composites obtained by such an *in situ* synthesis method can exhibit superparamagnetism (SPM) at ambient temperature. That is, there appears to be no remanent magnetization (M_r) or coercive force (H_c) in measurements of magnetization (M) vs applied magnetic field (H), in contrast to common ferro(i)magnetism (FM), which shows a definite hysteresis loop. This unique magnetic character can be observed when the magnetic particles are dispersed in a matrix on a scale of less than a few tens of nanometers, such a product being defined as a nanocomposite.

The above standardized process should be optimized for reaction conditions and chemicals used based on the target system's composition or the polymer subject employed. The author has previously constructed interpenetrating network-type alginate/poly(vinyl alcohol) gels containing iron oxide nanoparticles through modification of the *in situ* ferrite synthesis technique, where the gelation and alkali treatment were carried out with the aid of a metallic borate.¹⁴ The

interpenetrating network gels were designed to acquire a variable viscoelastic property in addition to the SPM susceptibility to an external magnetic stimulus. Recently, we also succeeded in the fabrication of a see-through woody magnetic sheet exhibiting SPM via a sequence of procedures including chemical modification of wood flour, nanoincorporation of iron oxides into the wood flour matrix and hot-molding of the wood flour/iron oxide composite.⁷

The standard process of (1)–(3) described above may be repeated several times for the purpose of elevating the iron content and enhancing the oxidation or alteration of the iron compounds precipitated.^{2,3} Ordinarily, this repetition will heighten the value of saturation magnetization (M_s) of the resulting composite, resulting in a target that again displays an SPM character but with quite a high M_s (for example, $>25 \text{ emu (g sample)}^{-1}$).² Thereby, although the material is sharply and largely magnetized by a modest H , it never retains the magnetization if the external field is removed. This property would be particularly desirable for use as a core material of actuators responsive to magnetic stimuli.

Carrageenan, a sulfated galactan derived from red seaweeds, is a polymer matrix used in the present work.¹⁷ Conventionally available carrageenans are of the τ , κ and λ types; τ - and κ -carrageenan polymers (see the structural formula in Figure 1) possess a hydrogel-forming ability, whereas λ -carrageenan only has a limited hydrogel-forming ability.^{17–19} The gelation and solution behavior of the τ - and κ -carrageenans in water is thermo-reversible, and the gel networks formed at lower temperatures (typically $<70^\circ\text{C}$) are more stabilized in the presence of alkaline or alkali-earth metallic cations.^{18,19} In such gels, the cations seem to promote a side-by-side association of carrageenan chains, partly assuming a double-helical structure.¹⁹ As was suggested in a previous study,¹¹ multivalent cations of the iron-group elements (Fe, Co and Ni) may also act as effective stabilizers of carrageenan gels.

This study seeks to demonstrate that SPM carrageenan composites loaded with iron oxide nanoparticles can be easily prepared to exhibit an M_s value as high as $25 \text{ emu (g sample)}^{-1}$. Insight is provided into an effect of the repetition of the previously described synthesis cycle on the evolution, in oxidation state, of the magnetic particles, as well as into some differences in magnetometric profiles between the two cases using either τ - or κ -carrageenan as the matrix polymer. Additionally, a comparative characterization is made for carrageenan-based composites prepared by a stoichiometric co-precipitation method²⁰ with a 1:2 mixture of ferrous/ferric salts, a technique that has also been applied to iron oxide nanocompositions with diverse polysaccharides.^{4,5,8,11–13,15}

EXPERIMENTAL PROCEDURE

Original materials

The polymer samples used were commercially available τ -carrageenan (Copenhagen Pectin Ltd (Copenhagen, Denmark), GENUGEL CJ, lot no. 016822; $M_w = 8.52 \times 10^5$, $M_w/M_n = 2.49$ and $S = 7.65 \text{ wt\%}$) and κ -carrageenan (Copenhagen Pectin Ltd, GENUGEL WR-78-J, lot no. 035400;

Figure 1 Idealized repeating disaccharide structure of τ -carrageenan ($R = \text{SO}_3^-$) and κ -carrageenan ($R = \text{H}$), composed of 1,3-linked β -D-galactopyranose and 1,4-linked 3,6-anhydro- α -D-galactopyranose.

$M_w = 8.28 \times 10^5$, $M_w/M_n = 2.21$ and $S = 5.97 \text{ wt\%}$). The sulfur (S) content data were obtained through elemental analysis, and the values of weight-averaged molecular mass (M_w) and polydispersity (M_w/M_n) were determined by GPC chromatography (mobile phase, 75 mM sodium nitrate aqueous solution at 40°C) in comparison with poly(ethylene oxide) standards.

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and H_2O_2 aqueous solutions were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and all the other chemicals and solvents used were guaranteed reagent grade and employed without further purification.

Preparation of iron oxide-containing carrageenan composites

The following procedures for *in situ* synthesis of iron oxides in the gelatinous carrageenan matrix were carried out in an atmosphere of nitrogen, except for an oxidizing step. The distilled water and ethanol used were degassed with N_2 -bubbling. The volume ratio of ethanol/water used as a mixed solvent was always 1:1.

The original powder of τ - or κ - type carrageenan was dissolved in distilled water at $\sim 95^\circ\text{C}$. A portion of the aqueous solution (polymer concentration, 3–8 wt%) was put into a syringe and cooled. Subsequently, the solution, already gelatinous but transparent and colorless, was injected in a long cylindrical form ($\phi = \sim 2.5 \text{ mm}$) into an excess amount of ethanol/water (20°C) containing FeCl_2 at a concentration of 0.01–0.50 M. After immersion in the salt solution for 2 h, the ferrous carrageenan gel, imparting a slightly yellowish hue, was lightly washed with ethanol/water and steeped in 1.0 M NaOH /ethanol/water ($\text{pH} \approx 13$) for 2 h. The alkaline solution bath ($\sim 150 \text{ ml}$) was heated to $\sim 65^\circ\text{C}$, and 2 wt% H_2O_2 solution ($\sim 15 \text{ ml}$) was added dropwise over a period of 1 h. The oxidized gel, colored dark reddish brown, was washed with ethanol/water and lyophilized (for magnetometry and FE-SEM observations) or vacuum dried.

Selected gel samples oxidized once in the above-mentioned way were further oxidized in additional cycles involving the ferrous ion-absorption, alkali treatment and oxidation with hydrogen peroxide. In what follows, the code ' $x\%$ τ - y - n ' denotes a product sample obtained after n cycles of the reaction scheme by using a starting $x \text{ wt\%}$ τ -carrageenan aqueous solution gelled in $y \text{ M}$ ferrous chloride/ethanol/water. For κ -carrageenan-based products, a similar code ' $x\%$ κ - y - n ' is defined.

A co-precipitation method with a stoichiometric mixture of $\text{Fe}^{2+}/\text{Fe}^{3+} = 1:2$ (mol/mol) was applied to obtain κ -carrageenan-based composites for comparison. An aqueous solution of the polymer was prepared at 5 wt% in the same way as that described above. A portion of the cooled solution (gelatinous) was immersed in a 1:2 ferrous/ferric chloride solution in ethanol/water (20°C) over a time period of 2 h. The salt solution was prepared at 0.10 M with respect to the total iron ions, by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the solvent to yield the adequate $\text{Fe}^{2+}/\text{Fe}^{3+}$ proportion specified above. Subsequently, the κ -carrageenan gel was immersed in 1.0 M NaOH /ethanol/water at $\sim 68^\circ\text{C}$ without agitation for 24 h and then thoroughly washed with ethanol/water under ordinary atmospheric conditions. Selected samples of the dark-brown composite gels thus prepared were subjected to additional cycles of the same procedure. A solid product freeze-dried after n cycles is designated as ' $5\% \kappa$ -0.10(cop)- n ' hereafter.

Measurements

The iron content in the respective composites described above was determined by a redox titration method. Iron ions were extracted from a weighed fragment of each dried composite with a warmed HCl solution; the ions were then reduced to Fe^{2+} with the aid of tin(II) chloride. The ferrous ionic solution was titrated with potassium dichromate by using diphenylamine-4-sulfate as an indicator.

Fourier transform infrared spectra of carrageenan samples were obtained at each stage of the *in situ* synthesis of iron oxides by using a Shimadzu FTIR-8000 spectrometer (Shimadzu, Kyoto, Japan) purged with N_2 gas in advance. An ordinary KBr pellet method was adopted for the measurements. After the ferrous ion-absorption step and the alkali treatment step, the samples were ground and mixed with KBr under a nitrogen atmosphere.

Wide-angle X-ray diffraction (WAXD) measurements were carried out with a Rigaku RINT2200V diffractometer at room temperature (20°C) in a

reflection mode. Nickel-filtered CuK α radiation was used at 40 kV and 30 mA. Diffraction intensity profiles mainly in a range of $2\theta = 25\text{--}65^\circ$ were collected to identify the iron oxide particles synthesized in the carrageenan matrix.

Fracture-surface morphologies of carrageenan/iron oxide composites were observed using a field emission scanning electron microscope (FE-SEM), Hitachi S-4500 (Hitachi, Tokyo, Japan); the fractured samples were sputter-coated with platinum before the observation. Transmission electron microscopy (TEM) using a JEOL JEM-1220 microscope (JEOL, Tokyo, Japan) was also conducted to inspect the dimensions of the iron oxide particles present in the composites. The sample for this observation was prepared on a microscope grid from an aqueous micro-suspension of iron oxide residues. The suspension was made through dissolution into distilled water of the desired carrageenan constituting the composite.

Magnetometry measurements were carried out on 5–7 mg samples (freeze-dried) with a superconducting quantum interference device (SQUID), MPMS-5 of Quantum Design Inc (San Diego, CA, USA). The magnetic field (H) applied was varied through the cycle of $0\text{ T} \rightarrow 5\text{ T} \rightarrow -0.1\text{ T} \rightarrow 0\text{ T}$ at a constant temperature. For a given sample, the magnetization (M) vs H data were collected at 298, 200 and 100 K. The temperature dependence of magnetization was examined in the so-called zero-field-cooled (ZFC) and field-cooled (FC) conditions for a few selected series of carrageenan composites. First, for the ZFC magnetization, the sample was cooled to 5 K with the magnetic field set at zero. After stabilization at 5 K for 20 min, a magnetic field of 0.01 T was applied to the regulated sample and the magnetization, M , was evaluated. The measurement was performed consecutively while the temperature was increased from 5 to 300 K in 20 K increments. Following this ZFC experiment, the same sample was then cooled from 300 to 5 K under a constant field of 0.01 T, and concomitantly, the FC magnetization data were recorded every 20 K.

RESULTS AND DISCUSSION

Magnetization (M) vs applied field (H) behavior

All the composite products prepared via the three chemical steps (see above) were attracted to a conventional bar magnet but all were visually inert to steel materials at ambient temperature.

Figure 2a illustrates the magnetization behavior of a series of 5% τ -0.10- n at 298 K as a function of the applied magnetic field. All of the $n = 1\text{--}3$ samples exhibit a characteristic M vs H profile in which a steep magnetization occurs and there appears no remanent magnetization (see an inset of the figure), meaning that the magnetism can be regarded as SPM. For estimation of the M_s , the respective data in a range of 0–5 T were regressed in terms of the following classical Langevin function,²¹

$$M = M_s [\coth(\alpha) - \alpha^{-1}] \quad (1)$$

with $\alpha = \mu H/k_B T$, where μ is a magnetic moment per particle, k_B is the Boltzmann constant and T denotes absolute temperature. Values of $M_s = 2.9$ ($n = 1$), 14.3 ($n = 2$) and 21.9 ($n = 3$) in $\text{emu (g sample)}^{-1}$ were thus estimated, demonstrating that the cyclic repetition of the *in situ* synthesis resulted in a marked elevation in M_s .

In Figure 2b, M vs H data for the sample 5% τ -0.10-3 at 100 K is compared with that obtained at 298 K. As shown on an enlarged scale in the figure inset, the sample imparted a hysteresis in the range of -0.05 to 0.05 T at 100 K. That is, the magnetism is judged to be FM at this low temperature, which is in contrast to the situation at 298 K.

Magnetic properties of iron oxide-containing carrageenan composites prepared under different conditions are summarized in Table 1. In this tabulation, three or four samples on family terms are grouped in a series to generally recognize the diversity of data that arises from altering one of the preparation conditions.

As observed from the comparison between the two series 5% τ - γ -1 and 5% κ - γ -1, the dependence of the Fe amount loaded into a polymer matrix on the ferrous ion concentration (γ) in gel immersion is stronger in the κ -carrageenan series. A similar observation refers to

Figure 2 Plots of magnetization vs applied magnetic field. (a) Data obtained at 298 K for 5% τ -0.10- n ; Δ , $n = 1$; $\square$, $n = 2$; $\circ$, $n = 3$. (b) Data for 5% τ -0.10-3 measured at different temperatures: $\bullet$, 100 K; $\circ$, 298 K. Insets provide the data on an enlarged scale.

the concentration dependence of M_s (per gram sample) at 298 K, compared between the same two series. Plots of M_s vs Fe^{2+} concentration are presented in Figure 3a, where data are compiled for all the τ - and κ -carrageenan composites of $n = 1$. Irrespective of the starting polymer concentration (x), the τ -carrageenan series showed a relatively gradual slope while the κ type-based series shows a steeper slope. As is well known,^{17–19} τ -carrageenan gels significantly strengthen in the presence of divalent cations, such as Ca^{2+} , a behavior that differs from the modest hardening of κ -carrageenan gels. In contrast, however, many of the monovalent cations promote the gelation of κ -carrageenan more strongly than that of τ -carrageenan. Ferrous cations worked on τ -carrageenan in the same way as Ca^{2+} to tighten the gel structure, an observation that was actually discernible by manipulation. As a result, comparatively smaller particles of iron oxide could be produced in the tighter network system of ferrous τ -carrageenan but with a wide distribution over the whole polymer matrix. The results show a tendency for the τ -carrageenan composite series to retain the SPM character at lower temperatures compared with the tendency shown by the κ -carrageenan series (Table 1).

In Figure 3b, the dependence of M_s at 298 K on the cycle number n of the *in situ* synthesis of iron oxides is shown for the τ - and κ -carrageenan composite series prepared at a starting polymer

Table 1 Magnetic properties of iron oxide-containing carrageenan composites prepared under different conditions

Sample code	Fe content (wt%)	Magnetism			Saturation magnetization at 298 K	
		100 K	200 K	298 K	$M_s/\text{emu (g sample)}^{-1}$	$M_s(\text{Fe})/\text{emu (g Fe)}^{-1}$
5% τ -0.01-1	6.7	FM	SPM	SPM	2.3	33.5
5% τ -0.10-1	8.1	FM	SPM	SPM	2.9	36.0
5% τ -0.50-1	14.4	FM	FM	SPM	4.7	32.7
5% κ -0.01-1	5.1	FM	FM	SPM	1.5	28.6
5% κ -0.10-1	8.7	FM	FM	SPM	3.2	37.1
5% κ -0.50-1	22.3	FM	FM	SPM	8.6	38.4
3% τ -0.10-1	8.2	FM	FM	SPM	2.6	31.4
3% κ -0.10-1	10.4	FM	FM	SPM	3.9	37.3
8% τ -0.10-1	8.2	FM	SPM	SPM	3.0	36.4
5% τ -0.10-2	16.3	FM	SPM	SPM	14.3	87.8
5% τ -0.10-3	21.6	FM	FM	SPM	21.9	101.3
5% τ -0.10-4	25.8	FM	FM	SPM	27.1	105.0
5% τ -0.10-5	31.5	FM	FM	FM	31.4	99.6

Abbreviations: FM, ferromagnetic; SPM, superparamagnetic.

concentration of 3 or 5 wt% and with a 0.10-M ferrous salt solution in the gel immersion step. It is evident that irrespective of the type of carrageenan, M_s increases drastically with the cycle number. M_s exceeds 20 emu (g sample)^{−1} in the $n=3$ treatment and is well over 25 and 30 emu (g sample)^{−1} for τ -carrageenan-based examples of $n=4$ and 5, respectively. The magnetism at 298 K of the sample encoded as 5% τ -0.10-5 is marked FM in Table 1, but the hysteresis loop observed in a range of $H = -0.01$ to 0.01 T was quite narrow ($H_c < 10^{-3}$ T, $M_r < 1$ emu (g sample)^{−1}). Thus, repetition of the reaction cycle is found to be much more effective than adjusting the starting polymer concentration, or even the ferrous ion concentration, in rapidly elevating M_s .

M_s data were also assembled in a specific value ($M_s(\text{Fe})$) that was normalized by the Fe content for each composite sample. As seen in Table 1, most of the $n=1$ composites gave a specific $M_s(\text{Fe})$ of 34 ± 4 emu (g Fe)^{−1} without displaying any dependence on the polymer and Fe²⁺ concentrations in the initial gel treatment. In Figure 3c, plots of $M_s(\text{Fe})$ vs the cycle number are constructed for the same series of samples as those used in Figure 3b. A major observation is that as the reaction cycle is repeated, the specific value of $M_s(\text{Fe})$ increases, but the rate of increment slows, resulting in a convergence of $M_s(\text{Fe})$. This result suggests that the iron oxides incorporated into any of the $n=1$ composites are mainly of a lesser magnetic character (for example, ferric oxyhydroxide), and repetition ($n \geq 2$) increases the proportion of more familiar magnetic particles, such as ferric oxide (for example, $\gamma\text{-Fe}_2\text{O}_3$) and ferrous ferric oxides (for example, Fe_3O_4).

Morphology of iron oxide-containing carrageenan composites

Figure 4 shows Fourier transform infrared spectra for τ -carrageenan samples obtained at each stage of the *in situ* synthesis of iron oxides, the final product corresponding to 5% τ -0.10-1. In this figure, the spectrum (i) was measured for a purified τ -carrageenan powder prepared by re-precipitation in ethanol from aqueous solution. An important absorption band warranting attention is the ester sulfate signal, appearing as dual peaks in a wavenumber range of 1200–1300 cm^{−1}. With respect to the sample of ferrous ion-intercalated τ -carrageenan (see (ii) in Figure 4), the S-O asymmetric stretching peak shifted to 1210 cm^{−1} from the original position of 1230 cm^{−1}, accompanied by broadening of the sulfate signal as a whole. This

observation implies an electrostatic interaction between the sulfate group and Fe²⁺, which also supports the stabilization of the gel structure by the divalent cation. Following alkali treatment, the sulfate band was restored to its original shape (see (iii) in Figure 4), indicating that the intercalated Fe²⁺ ions were liberated from the sulfate groups and consumed to produce ferrous hydroxide in the polymer network. Even after the subsequent oxidation step, the absorption band was unchanged (see (iv) in Figure 4). An additional measurement was made for a sample of 5% τ -0.10-3 subjected to three cycles of the sequential reactions, but the spectrum was essentially the same as (iv).

IR investigation was also performed on a κ -carrageenan-based series, and a similar result to the τ -carrageenan-based series (above) was acquired for the observations on the ester sulfate band in the 1200–1300 cm^{−1} region; however, the spectral feature of κ -carrageenan was different from that of τ -carrageenan for lower wavenumbers (600–1100 cm^{−1}). It was difficult to find a clear difference in gel structure or interaction strength with Fe²⁺ between the two types of carrageenan from the present IR measurements.

Fracture-surface morphologies of carrageenan/iron oxide composites were examined by FE-SEM. Figure 5 shows micrographs obtained for lyophilized τ - and κ -carrageenan gels containing iron oxides (photos c, e and g) for comparison with their respective reference samples without Fe content (photos a, b, d and f). The reference samples were prepared without immersing the gels into ferrous chloride solution (resulting in the parameter $\gamma=0$) in the cycle of *in situ* synthesis; however, an exceptional sample encoded as 5% τ -0.10(Ca)-1 underwent the gel immersion step, but with CaCl₂ instead of FeCl₂ at 0.10 M.

As demonstrated by the micrographic data in photos (d) and (f), the blank samples of κ -carrageenan gels are well endowed with fibrous and porous structures in the interior; we can see numerous fibrillar entities of a few tens of nanometers in width percolate through the matrix space, interspersed with lateral coalescences and thick junctions. The percolation morphology of fibrils was also prevalent in iron oxide-incorporated κ -carrageenan gels; this was confirmed by FE-SEM observations at relatively low magnifications. However, the fibrillar entities were full of humps after one cycle treatment of the *in situ* reactions, and after three repetitions of the cycle, the apparent aspect ratio of fibrils was considerably reduced as

Figure 3 Plots of M_s data for various series of iron oxide-incorporated carrageenan composites: (a) M_s vs Fe^{2+} concentration in gel immersion; (b) M_s vs number of reaction cycle; (c) $M_s(Fe)$ vs number of reaction cycle. Plots in (a) are constructed for $x\%$ τ - y -1 ($x=3, 5, 8$) and $x\%$ κ - y -1 ($x=3, 5$), and data in both (b) and (c) are shown for $x\%$ τ -0.10- n ($x=3, 5$) and $x\%$ κ -0.10- n ($x=3, 5$). Starting polymer concentrations ($x\%$): circle, $x=3$; square, $x=5$; triangle, $x=8$. Open and solid symbols refer to the τ -carrageenan and κ -carrageenan series, respectively.

evidenced by the enlarged micrographs (e) (for 3% κ -0.10-1) and (g) (for 3% κ -0.10-3) in Figure 5. As represented schematically in the insets to the photos (e) and (g), it is supposed that the inorganic nanoparticles were dispersed throughout the inside as well as on the surface area of fibrillar entities constituting the polymer matrix, and the fibrils were partly sectioned as a result of this inorganic incorporation.

With respect to the τ -carrageenan series, the blank samples prepared without a supply of ferrous ions but exposed to sodium monovalent cations in the alkali treatment formed a weak gel. The interiors of these samples were generally poor in ramified fine fibrils

Figure 4 Fourier transform infrared (FT-IR) spectra of τ -carrageenan in a cycle of the *in situ* synthesis of iron oxides, measured at stages: (i) pristine state (after purification); (ii) after intercalation of ferrous ions; (iii) after alkali treatment; and (iv) after oxidation.

and made up of more thickset entities 100–150 nm in width, as exemplified by photo (a) in Figure 5 taken for 5% τ -0-1. In contrast, another reference sample that underwent gel immersion with divalent calcium cations, such as 5% τ -0.10(Ca)-1, showed a well-developed fibrous structure (see photo (b) in Figure 5). It is likely that a similar fibrous architecture would develop in the τ -carrageenan gels treated with ferrous ions, eventually causing iron oxide particles to be produced in the interior and on the fibrils in the subsequent oxidation step in the same manner as that observed for the κ -carrageenan-based composite gels. This effect is demonstrated by a morphology observed in 5% τ -0.10-1 (photo (c) in Figure 5), although the exemplified fibrillar structure is somewhat rugged compared with that seen in photo (e) for 3% κ -0.10-1.

Figure 6 illustrates WAXD intensity profiles for 5% τ -0.10- n ($n=1-3$). The 2θ values of the observed diffraction peaks are listed in Table 2 and are compared with the corresponding data of JCPDS (Joint Committee on Powder Diffraction Standards) for Fe_3O_4 (JCPDS card no. 19-629), γ - Fe_2O_3 (JCPDS card no. 39-1346) and δ - $FeOOH$ (JCPDS card no. 13-87). Based on this comparison, the iron oxides incorporated into the $n=1$ composite are mainly ferroxite (δ - $FeOOH$), showing a weaker magnetism and lower crystallinity, while more definitively crystalline ferrites of magnetite (Fe_3O_4) and/or maghemite (γ - Fe_2O_3) are dispersed in the $n \geq 2$ samples with additional treatments, as suggested in the preceding section. WAXD observations were essentially unchanged for the other test series, namely 3% τ -0.10- n , 5% τ -0.50- n and 5% κ -0.10- n ($n=1-3$). As discussed below, the ferroxite first produced would serve as a precursor, yielding the more familiar ferrites in repeated cycles of the *in situ* synthesis process.

Figure 7 shows TEM photographs of iron oxides extracted from two composites, 5% τ -0.10-1 and 5% τ -0.10-3. Photos (a) and (b) were obtained for the 5% τ -0.10-1 sample of $n=1$, and photo (c) refers to the 5% τ -0.10-3 sample of $n=3$. As demonstrated by photo (a), iron oxide nanoparticles of ~ 15 nm in diameter were dotted throughout the inside of the 5% τ -0.10-1 sample. Some agglomerates composed of needle-like particles of ~ 5 nm width and 30–60 nm length were also observed in various locations on the grid specimen as

Figure 5 Field emission scanning electron microscope (FE-SEM) photographs of fracture surfaces for τ - and κ -carrageenan composites containing iron oxides (right side: **c**, **e**, **g**), compared with data for their respective reference samples of naught Fe content (left side: **a**, **b**, **d**, **f**). A sample 5% τ -0.10(Ca)-1 (**b**) was prepared with CaCl_2 instead of FeCl_2 at the stage of gel immersion in the scheme of iron oxide synthesis. The other blank samples (**a**, **d**, **f**) were obtained by skipping the gel immersion into FeCl_2 solution, that is, via only two steps including alkali treatment with NaOH and oxidation with H_2O_2 . Scale bars denote 200 nm. Drawings inserted into photos (**e**) and (**g**) schematically show the precipitation of iron oxide nanoparticles in the interior and on the surface area of carrageenan fibrils.

illustrated in photo (b). This type of morphology, that is, a crystalline growth habit in an acicular shape, might be characteristic of the magnetic iron compound ferroxhyte, as has been noted in an earlier study³ on cellulose/iron oxide compositions.

However, as seen from photo (c) in Figure 7, the composite sample 5% τ -0.10-3 accommodated more iron oxide particles in a clear-cut granulated form of $\phi = 15\text{--}40\text{ nm}$. An assemblage of the granular particles, observed to be a size of $>100\text{ nm}$, can be understood to be formed in the process of the preparation of the grid specimen for TEM. The diameter size of $15\text{--}40\text{ nm}$ for the dispersed magnetic particles is consistent with the condition providing a composite

material with SPM character. From major diffraction peaks ($2\theta = 30.1^\circ$, 35.5° and 57.1°) appearing in the WAXD curve of the 5% τ -0.10-3 sample (Figure 6c), a crystallite size L of the produced ferrites was approximated using a conventional Scherrer equation:

$$L = 0.9\lambda/B \cos\theta \quad (2)$$

where λ is the wavelength (0.1542 nm) of $\text{CuK}\alpha$ radiation and B is a half-height width of the diffraction peak considered. This equation results in calculated values of $L = 10\text{--}15\text{ nm}$, consistent with the TEM and magnetometric observations described above.

From the results of the analysis of morphological features and magnetic properties for a series of composite products, it can be said that as originally expected, the hydrogels of the anionic sulfate-containing polysaccharide carrageenan made a suitable matrix, providing cavity sites suitable for the *in situ* synthesis of iron oxide nanoparticles and accommodating the magnetic assemblage of SPM character to a considerable degree.

Figure 6 Wide-angle X-ray diffraction (WAXD) intensity profiles for 5% τ -0.10- n : (a) $n=1$; (b) $n=2$; (c) $n=3$. The marking of diffraction peaks indicates that they are derived from δ -FeOOH (Δ) or from Fe_3O_4 and/or γ - Fe_2O_3 ($\bullet$).

Table 2 2θ values of the diffraction peaks observed for 5% τ -0.10- n ($n=1-3$) (Figure 6), and comparable JCPDS data for Fe_3O_4 , γ - Fe_2O_3 and δ -FeOOH

Values observed for 5% τ -0.10- n			Data of standards		
$n=1$	$n=2$	$n=3$	Fe_3O_4^a	γ - Fe_2O_3^b	δ -FeOOH ^c
35.18	30.10	30.12	30.14	30.26	35.28
40.40	35.46	35.48	35.52	35.64	40.00
54.22	43.22	43.12	43.06	43.31	54.52
63.16	53.60	53.60	53.49	53.74	63.20
	57.12	57.12	56.98	57.37	
	62.78	62.76	62.53	62.93	

Abbreviation: JCPDS, Joint Committee on Powder Diffraction Standards.

^aJCPDS card 19-629.

^bJCPDS card 39-1346.

^cJCPDS card 13-87.

Further insight into evolution of magnetic nanoparticles

SQUID magnetometry was also conducted for κ -carrageenan/iron oxide composites (5% κ -0.10(cop)- n ($n=1-3$)) prepared by the co-precipitation method with a 1:2 mixture of ferrous/ferric ions. This characterization included magnetization measurements of M vs T as well as M vs H . The major analytical results are summarized in Table 3 together with corresponding data for the comparable 5% κ -0.10- n samples obtained by the standardized *in situ* method via $\text{Fe}(\text{OH})_2$ production using only Fe^{2+} . In the co-precipitation process under the alkaline condition adopted here, Fe_3O_4 is expected to be primarily produced according to the following reaction:

However, the magnetite precipitate may be further oxidized into γ - $\text{Fe}_2\text{O}_3/\text{Fe}(\text{OH})_3$ depending on the operative conditions of oxygen, temperature and aging time.^{13,15,20} WAXD measurements supported the particle formation of Fe_3O_4 (and possibly of maghemite γ - Fe_2O_3) in the composites 5% κ -0.10(cop)- n , irrespective of the cycle number n .

In the M vs H measurements for 5% κ -0.10(cop)- n at 298 and 100 K, all samples of $n=1-3$ demonstrated a non-hysteretic loop lacking either coercivity or remanence. Therefore, the composites were all SPM, even at 100 K. As listed in Table 3, values of the M_s at 298 K were estimated to be $M_s=2.9$ ($n=1$), 5.6 ($n=2$) and 9.0 ($n=3$) in emu (g sample)⁻¹. Interestingly, these were generally lower than the respective corresponding M_s values obtained for 5% κ -0.10- n , even though each comparable pair of the two composite series showed a similar degree of Fe uptake. The difference in M_s was particularly noticeable when the two series were treated in the multicycles of $n=2$ and 3. From these observations, it can be inferred that the ferrite particles embedded in the matrix of 5% κ -0.10(cop)- n are of definitively smaller sizes than those in the other series of 5% κ -0.10- n . This effect is more pronounced in M vs T measurements in the ZFC and FC modes shown below.

Figure 8 illustrates ZFC and FC curves obtained for two samples, 5% κ -0.10-2 (Figure 8a) and 5% κ -0.10(cop)-2 (Figure 8b), in an applied field of 0.01 T. For both samples, the convergence of the ZFC and FC plots at higher temperatures (≥ 200 K for 5% κ -0.10-2 and ≥ 100 K for 5% κ -0.10(cop)-2) and a divergence of the two plots at lower temperatures can be seen. This behavior is typical of SPM materials. In this case, the FC curve continues to increase with decreasing temperature, while the ZFC curve assumes a peak maximum at T_{max} and decreases below T_{max} . T_{max} is related to a

Figure 7 Transmission electron microscopy (TEM) photographs of iron oxides extracted from 5% τ -0.10- n ($n=1$ and 3): photo (a) and (b), data for 5% τ -0.10-1; photo (c), data for 5% τ -0.10-3.

Table 3 Comparison of magnetic properties between the two series of composites, 5% κ -0.10- n and 5% κ -0.10(cop)- n ($n = 1-3$), the former prepared by the standardized *in situ* method via producing $\text{Fe}(\text{OH})_2$ with only Fe^{2+} and the latter by the co-precipitation method with a 1:2 mixture of $\text{Fe}^{2+}/\text{Fe}^{3+}$

Sample code	Fe content (wt%)	Magnetism ^a		Saturation magnetization at 298 K		Temperatures referring to blocking phenomenon ^a	
		100 K	298 K	$M_s/\text{emu (g sample)}^{-1}$	$M_s(\text{Fe})/\text{emu (g Fe)}^{-1}$	T_{max}/K	T_B/K
5% κ -0.10-1	8.7	FM	SPM	3.2	37.1	130	65–87
5% κ -0.10-2	15.4	FM	SPM	13.1	85.5	160	80–107
5% κ -0.10-3	25.9	FM	SPM	23.3	90.0	230	115–153
5% κ -0.10(cop)-1	6.3	SPM	SPM	2.9	45.1	60	30–40
5% κ -0.10(cop)-2	13.6	SPM	SPM	5.6	41.2	60	30–40
5% κ -0.10(cop)-3	20.8	SPM	SPM	9.0	43.3	70	35–47

Abbreviations: FM, ferromagnetic; SPM, superparamagnetic.

^a T_{max} , temperature giving a ZFC peak maximum in M vs T measurements; T_B , blocking temperature approximated from $T_{\text{max}} = \beta T_B$ ($\beta = 1.5-2.0$). **Figure 8** Temperature dependence of magnetization in a field of 0.01 T, measured for (a) 5% κ -0.10-2 and (b) 5% κ -0.10(cop)-2. Field-cooled (FC) and zero-field-cooled (ZFC) curves were obtained for each sample with and without the field before the measurement, respectively.so-called blocking temperature T_B by the following equation:^{22,23}

$$T_{\text{max}} = \beta T_B \quad (4)$$

where β is a parameter associated with the size distribution of the magnetic particles concerned, typically situated in the range of 1.5–2.0. At temperatures lower than T_B the magnetic moment of the particles is frozen along their respective anisotropy axes so that a FM character is manifested instead of the high-temperature SPM.²¹

In Figure 8b the ZFC data for 5% κ -0.10(cop)-2 has a maximum at $T_{\text{max}} = 60$ K, which leads to $T_B = 30-40$ K. Therefore, the SPM observation in the M vs H measurement at 100 K for the same sample is quite reasonable. In contrast, in Figure 8a, the 5% κ -0.10-2 sample imparts a broader ZFC peak with a maximum at a higher temperature

of $T_{\text{max}} = 160$ K. The peak broadening is interpreted to be a result of a wider particle size distribution. The value of $T_{\text{max}} = 160$ K leads to $T_B = 80-107$ K; thus, a hysteretic FM behavior in M vs H observed at 100 K may also be reasonable (Table 3).

Comparing three samples ($n = 1-3$) of the co-precipitation series, while the magnetization at each temperature increased with an increase in the cycle number n , the three sets of ZFC and FC data were almost identical in shape, irrespective of n . With respect to the other series of 5% κ -0.10- n , it was observed that the ZFC peak became broader while T_{max} and T_B increased as the *in situ* synthesis process was repeated. For the $n = 1$ sample, $T_B = 65-87$ K was estimated; nevertheless, the M vs H data at 100 K provided a hysteresis loop with nonzero values of remanent magnetization and coercive force. The presence of magnetic particles of comparatively larger sizes (for example, ≥ 35 nm) should be responsible for the FM behavior at 100 K, reflecting the distribution of particle dimension that is wider than that in the co-precipitation series.

As tabulated in Table 3, the specific M_s , $M_s(\text{Fe})$, for the 5% κ -0.10(cop)- n samples was evaluated as $\sim 42-45$ emu (g Fe)⁻¹. Obviously, these values are much smaller than those of bulk ferrites, $M_s(\text{Fe}) = 110-131$ (for Fe_3O_4) and $100-109$ (for $\gamma\text{-Fe}_2\text{O}_3$) in emu (g Fe)⁻¹ which are converted from $M_s = 80-95$ (for Fe_3O_4)²⁴⁻²⁶ and $70-76$ (for $\gamma\text{-Fe}_2\text{O}_3$)^{25,27} in emu per gram of the respective iron oxides. The significant reduction in the specific magnetization may be attributed principally to the quantum-size effect in ultrafine nanoparticles ($\phi < 10$ nm) inviting a lack of magnetic saturation.^{24,26,27} In the M vs H measurements for the 5% κ -0.10(cop)- n series, the magnetization never completely saturated at 5 T but tended to continually rise with additional magnetic field application.

In view of the comparisons described above, it is possible to conclude that the stoichiometric co-precipitation method results in carrageenan composites containing very minute magnetic nanoparticles (for example, 5–15 nm) of a narrower size distribution, whereas, the method of producing $\text{Fe}(\text{OH})_2$ from only a ferrous salt produces somewhat larger magnetic nanoparticles (15–40 nm) of a wider size distribution embedded in the carrageenan composites. With equal iron uptake, the former series of composites show the SPM to FM transition at a lower blocking temperature (< 50 K) as the latter series of composites displays a relatively high value of M_s while retaining SPM character at temperatures of > 150 K. It should be noted that these comparisons were made between two composite series prepared in nearly identical alkaline conditions at 65–70 °C where the carrageenan matrices remained in a clear gel form without collapsing. Therefore, the observed difference in nanoparticle dimensions may be

ascribed simply to the difference in kinetics of whether the oxidation of irons (ions) into magnetic iron oxides went through an immediate pathway (referring to the co-precipitation method) or a step-by-step one (referring to the method via $\text{Fe}(\text{OH})_2$ production).

With respect to the case where the carrageenan matrix is treated in multicycles of the standardized synthesis process, the mechanism of iron oxide nanoparticle growth within the matrix can be explained in terms of the following reaction scheme: in the first cycle ($n=1$), alkali (NaOH) treatment of ferrous ion-intercalated carrageenan ($\text{Car-SO}_3^- - \cdots - \text{Fe}^{2+} - \cdots - \text{SO}_3^- - \text{Car}$) causes $\text{Fe}(\text{OH})_2$ to precipitate inside the polymer network (Equation (5)). In the subsequent step of oxidation with H_2O_2 , the ferrous hydroxide is transformed into $\delta\text{-FeOOH}$, according to Equation (6).

In the next cycle ($n=2$), besides repetition of the above chemical reactions, freshly supplied Fe^{2+} actively adsorbs onto the feroxyhite seed to form an intermediate to Fe_3O_4 in alkaline surroundings, as indicated by Equation (7). Finally, the intermediate ($\delta\text{-FeOOH}$) $_2\text{FeOH}^+$ may smoothly oxidize into Fe_3O_4 (Equation (8)).

This route has also been adopted by Sourty *et al.*,³ but it was originally based on a mechanism of dissolution and recrystallization of $\gamma\text{-FeOOH}$ (lepidocrocite) into magnetite reported by Tamura *et al.*²⁸ A similar transformation from the precursor $\delta\text{-FeOOH}$ into MnZn ferrite has been studied by Hao *et al.*²⁹

In the repeated cycles ($n \geq 2$), a certain quantity of Fe^{2+} ions should be oxidized into Fe^{3+} by trace amounts of oxygen that inevitably remains in the aqueous solvent after the first oxidation step. Therefore, the formation of Fe_3O_4 nanoparticles in smaller sizes throughout the co-precipitation process according to Equation (3) may also be admitted as a concurrent route during the present *in situ* method.

The present oxidizing conditions at $<70^\circ\text{C}$ seem to be insufficient, at least in a single cycle, for the successful oxidation of Fe_3O_4 to its counterpart $\gamma\text{-Fe}_2\text{O}_3$, that is, $\text{Fe}_3\text{O}_4 + (1/4)\text{O}_2 \rightarrow (3/2)\gamma\text{-Fe}_2\text{O}_3$, which has been shown in more rigorous hydrothermal conditions.^{13,25,27} However, when the magnetite-containing composite is further treated in the $n \geq 3$ multicycles, the conversion may partially occur with longer times because of an aging effect.^{15,25}

CONCLUSIONS

Carrageenan-based magnetic composites were successfully prepared by the repeatable *in situ* synthesis of iron oxides in a ferrous ion-intercalated polysaccharide gel network. The magnetic properties and morphology of the composite products were well-characterized by SQUID magnetometry, X-ray diffractometry and electron microscopy. The evolution mechanism of the oxidation state and the dimensional distribution of the cyclically loaded iron oxide particles were also examined through comparison with another composite series obtained by the co-precipitation method with a 1:2 mixture of ferrous/ferric ions.

All the composites prepared via only one cycle of the standardized *in situ* process showed a SPM property at 298 K, and the respective values of M_s were situated in a range of 2–9 emu (g sample)⁻¹ with a positive dependence on the ferrous salt concentration used for gel

immersion. The dependence on ferrous salt concentration was steeper when using κ -carrageenan rather than τ -carrageenan as the gel matrix. The ferrous ion-intercalated network of τ -carrageenan may be slightly tighter than that of the κ type. In support of this idea, the τ -carrageenan composites were generally superior to the κ -carrageenan composites in SPM retention at ≤ 200 K. The standard synthesis route with 3–4 cycles resulted in both the κ and τ types of carrageenan composites imparting $M_s \geq \sim 25$ emu (g sample)⁻¹ while the property of room temperature SPM was maintained.

The iron oxide particles loaded in the first cycle were predominantly feroxyhite ($\delta\text{-FeOOH}$), whereas the particles present in the composites treated in the multicycles were assumed to be mainly magnetite (Fe_3O_4). Presumably, the majority of the magnetite particles were derived from the feroxyhite seeds formed in advance, and also smaller magnetite particles produced by co-precipitation from a secondary mixture of $\text{Fe}^{2+}/\text{Fe}^{3+}$ were interspersed with the acquired majority. Further oxidation of Fe_3O_4 into maghemite ($\gamma\text{-Fe}_2\text{O}_3$) might have been restricted to a small contribution of the aging effect possible in the course of preparation and storage of the composite samples.

As a morphological feature common to the composite products, it was observed that the pertinent iron oxides were produced in a particle size less than several tens of nanometers ($\phi = 15\text{--}40$ nm) and dispersed in the interior as well as on the surface area of fibrillar entities constituting the carrageenan gel matrix. The observed dimensional scale was consistent with the SPM property that arose in the composites. The particle size distribution was regarded as somewhat wider relative to that ($\phi = 5\text{--}15$ nm) attainable in the comparable composite series created using co-precipitation. However, the latter series showed considerably lower values of magnetization against an applied magnetic field of practical magnitudes.

The carrageenan/iron oxide nanocomposites investigated in this study were virtually all magnetically isotropic. The results obtained in this work will serve as a cornerstone in a subsequent study focusing on fabricating polysaccharide-based smart materials that can show an anisotropic magnetization response favorable for a diversity of dynamic functionalities.

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