



## Research Paper

# Superparamagnetic IPN gels of carrageenan/PHEMA excelling in shape retention



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## ABSTRACT

Iron oxide nanoparticles-incorporated carrageenan (CAR)/PHEMA composites of interpenetrating network (IPN) type were successfully prepared by *in situ* ferrite synthesis in the polymer network. The IPN structure was constructed at CAR/PHEMA compositions of 15/85 and 40/60 (wt/wt) by polymerization and cross-linking of 2-hydroxyethylmethacrylate as an impregnating solvent of CAR gels. As a result of this IPN construction, the composites were firm and showed a good shape-retentivity in their gelatinous state. SQUID magnetometry and X-ray diffractometry were conducted for evaluation of the magnetic property of the inorganic-hybridized IPN composites. Magnetite particles with 10–30 nm sizes were distributed inside the IPNs treated with the repeatable ferrite synthesis; thereby, the hybrids displayed a superparamagnetic character at ambient temperature. Specifically, the 40/60 CAR/PHEMA IPN imparted a practically passable value (10–15 emu (g sample)<sup>-1</sup>) of saturation magnetization. The present IPN system offers a potential for application as a biocompatible magnetic material used in hydro-surroundings.

## 1. Introduction

Electrolytic polysaccharides derived from natural algae, such as alginate and carrageenan, constitute an important part of healthy foodstuff and are used as viscosifiers or coating and binding agents in commodities involving food, excipient, textile, and paper (Draget, Smidsrød, & Skjåk-Bræk, 2002; Van de Velde & De Ruiter, 2002). Besides the traditional utility, the algal polysaccharides may be further developed in high technical and biomedical fields in combination with other polymeric and/or inorganic ingredients.

The substantially anionic polysaccharides are interactive with alkali-earth and other metallic cations when gelatinized (Clark & Ross-Murphy, 1987; Morris, Rees, & Robinson, 1980), and thus they should offer a relevant network accommodation to realize specific mineralization therein. For example, nano-structuring of magnetic iron oxides in such gel matrices as absorber of ferrous/ferric ions can be a research subject along the advanced lines mentioned above. Actually, not a few efforts have been made to fabricate magnetic nanocomposites based on gelatinous alginate (Kroll, Winnik, & Ziolo, 1996; Laurent et al., 2008; Li et al., 2010; Llanes, Ryan, & Marchessault, 2000; Nishio, 2006; Nishio et al., 2004; Shen et al., 2003) and carrageenan (Daniel-da-Silva et al., 2007; Jones, Cölfen, & Antonietti, 2000; Nishio, 2006; Oya, Tsuru, Teramoto, & Nishio, 2013; Yoshitake, Sugimura, Teramoto, & Nishio, 2016) for application to the biomedical and pharmaceutical fields (e.g.,

as a magnetic drug-delivery system) and/or for other possible uses as components of electromagnetic shielding fabrics, novel filtration and separation systems, etc. The major technique for those compositions was an *in situ* synthesis of iron oxide nanoparticles in the gel networks, the process involving the oxidation of ferrous hydroxide produced after Fe<sup>2+</sup> intercalation (Marchessault, Ricard, & Rioux, 1992; Nishio, 2006; Ziolo et al., 1992) or the coprecipitation from a stoichiometric 2:1 mixture of Fe<sup>3+</sup> and Fe<sup>2+</sup> (or M<sup>2+</sup> of other metals) (Laurent et al., 2008; Tartaj, Morales, González-Carreño, Veintemillas-Vedaguer, & Serna, 2005). The magnetic nanocomposites obtained by such a chemical incorporation method can exhibit superparamagnetism (SPM) at ambient temperature. That is, they show no definite hysteresis loop in measurements of magnetization (*M*) versus applied magnetic field (*H*) and may be a material that responds to an external magnetic stimulus on demand and without energy loss (i.e., remanent magnetization *M<sub>r</sub>* ≈ 0). This unique SPM character is usually observed when the magnetic particles are dispersed in a matrix on a scale of less than several tens of nanometers (Cullity & Graham, 2009; Tartaj et al., 2005).

In the preparation of iron oxides by the *in situ* process stated above, the gel matrices are usually subjected to a hydrothermal treatment in caustic alkaline atmosphere. The relatively fragile nature of alginate and carrageenan hydrogels is at a disadvantage in fabrication of magnetic composites in film form or three-dimensional figure, compared

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with the easier processing into spherical beads or short filaments. The stability in shape of the produced magnetic composites may also be important for the uses in warmish hydro-surroundings. A possible way to remedy the fragility of the algal gels is blending the constituent polysaccharide compatibly with an appropriate vinyl polymer. To take a successful example, the authors' group has formerly constructed interpenetrating network (IPN)-type alginate/poly(vinyl alcohol) (PVA) 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 (e.g.,  $\text{CaB}_4\text{O}_7$ ) (Nishio et al., 2004). The IPN gels were designed to acquire a variable viscoelastic property in addition to the SPM susceptibility to an external magnetic field, but they were generally viscous and deformable.

In the present paper, we would like to show another preparation of iron oxide-incorporated IPNs using carrageenan (CAR) and poly(2-hydroxyethylmethacrylate) (PHEMA) as the network-constituting polymers. Then, the target is directed toward realizing a magnetic composite of SPM character that excels in shape-retentivity and filling-storage ability in the warmed gelatinous state. It has been reported that CAR gels have an excellent capacity for iron oxide loading to produce a SPM material of high saturation magnetization ( $M_s$ ) (e.g.,  $M_s > 20 \text{ emu (g sample)}^{-1}$ ) (Daniel-da-Silva et al., 2007; Oya et al., 2013). The other component PHEMA is a biocompatible polymer and used as an essential material for the fabrications of contact and intraocular lenses, catheters, and embedding media to immobilize enzymes, drugs, and other bio-related substances (Klee & Höcker, 1999; Montheard, Chatzopoulos, & Chappard, 1992). Therefore the magnetic CAR/PHEMA IPNs designed herein might be a promising new element of biomedical materials, e.g., for specific catheters with a sensor and actuator function usable in diagnosis and inward treatment.

## 2. Experimental

### 2.1. Materials

The CAR sample used was a commercially available  $\kappa$ -carrageenan, GENUCEL WR-78-J (Copenhagen Pectin Ltd., lot no. 035400), and the molecular weight and the sulfur (S) content have been determined in a previous study (Oya et al., 2013);  $M_w = 8.28 \times 10^5$ ,  $M_w/M_n = 2.21$ , and S = 5.97 wt%. Aqueous solutions of this CAR (3–5 wt%) showed a sol-gel transition in a range of ca. 70–80 °C on standing. HEMA monomer (Wako Pure Chemical Ind., Ltd.) was purified before use by distillation at 60 °C under reduced pressure. A radical initiator, 2,2'-azobisisobutyronitrile (AIBN; Tokyo Kasei Kogyo Co., Ltd.), and a cross-linking agent, ethylene glycol dimethacrylate (EDMA; Tokyo Kasei Kogyo Co., Ltd.), were used as received. Ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and  $\text{H}_2\text{O}_2$  aqueous solution, purchased from Wako Pure Chemical Industries, Ltd., and other chemicals and solvents were all guaranteed reagent-grade and employed without further purification. However, water (usually distilled one) and ethanol involved in the synthesis of iron oxides in polymer gels were degassed with  $\text{N}_2$ -bubbling in advance of the use. The volume ratio of ethanol/water used as a mixed solvent was 1:1.

### 2.2. Preparation of CAR/PHEMA IPNs

A 5.0 wt% CAR solution in distilled water was prepared by dissolving the original powder material at 95 °C. A portion of the solution was poured into a Teflon tray and transformed into a hydrogel by cooling to room temperature (20 °C). The hydrogel (~19 g) was immersed for 1 h in HEMA (50 g) containing EDMA (2.5 wt%) and AIBN (0.5 wt%). Following this, the solvent-exchanged gel was solidified by polymerization of the monomer solvent with irradiation of UV light centering 350 nm. A 15 W UV lamp (Panasonic FL15BL-B) was used for the purpose. The gel was irradiated for 1.5 h at a distance of 30 mm from the light source in an atmosphere of  $\text{N}_2$  gas. The polymer composite

thus synthesized was washed with ethanol and then stored in a gelatinous state for 24 h while immersing in a 1:1 mixture of ethanol/water. The CAR content was estimated at 40.3 wt% in a dried state of the composite, and this sample was nominated as an IPN of CAR/PHEMA = 40/60.

In the solvent-exchanging step of the above procedure, the HEMA monomer as impregnant was also diluted to 50% with addition of water; thereby, shrinkage of the CAR gel was restrained, and, consequently, a more PHEMA-rich composite was successfully obtained. This sample was nominated as another IPN of CAR/PHEMA = 15/85 (CAR content, 14.7 wt%).

Additionally remarking, a similar attempt was made to prepare CAR gels impregnated with HEMA by employing  $\iota$ -type carrageenan (Copenhagen Pectin Ltd., GENUCEL CJ, lot no. 016822;  $M_w = 8.52 \times 10^5$ ,  $M_w/M_n = 2.49$ , and S = 7.65 wt% (Oya et al., 2013)); however, the polymer agglomerated into a solid without taking on a gel form due to less compatibility with the monomer. In  $\iota$ -carrageenan, a constituent saccharide, 3,6-anhydro- $\alpha$ -D-galactopyranose unit, has a sulfate group at C2 position, instead of the hydroxyl one in  $\kappa$ -type carrageenan. This structural difference would be responsible for such a difference in gelation property between the two types.

### 2.3. Iron oxide incorporation into CAR/PHEMA IPNs

The incorporation of iron oxide nanoparticles into CAR/PHEMA IPNs was carried out in a sequence of procedures formerly standardized for the *in situ* ferrite synthesis in carrageenan gel matrices (Oya et al., 2013). In brief, each of the IPN gels obtained above was immersed in an excess amount of ethanol/water mixture (20 °C) containing  $\text{FeCl}_2$  at a concentration of 0.01–0.50 M. The  $\text{Fe}^{2+}$ -intercalated gel was then steeped in 1.0 M NaOH/ethanol/water (pH  $\approx$  13) for more than 2 h to precipitate ferrous hydroxide in the polymer network. After that, the alkaline solution (~150 ml) was heated to 65 °C, and 2 wt%  $\text{H}_2\text{O}_2$  solution in ethanol/water (~15 ml) was added thereto dropwise over a period of 1 h. Selected gel samples thus once oxidized were further oxidized in additional cycles involving the ferrous ion-absorption, alkali treatment, and oxidation with  $\text{H}_2\text{O}_2$ , and finally washed with ethanol/water. Reference samples of iron oxide-incorporated CAR gels (CAR/PHEMA = 100/0) were also prepared in a similar way. In what follows, the sample code " $x/y$ - $m$ - $n$ " denotes a gel product obtained after  $n$  cycles of the standardized synthesis scheme by using  $m$  M  $\text{FeCl}_2$  solution for  $\text{Fe}^{2+}$ -intercalation to a polymer composition of CAR/PHEMA =  $x/y$  (= 15/85, 40/60, or 100/0).

### 2.4. Measurements

The iron content in each magnetic composite of  $x/y$ - $m$ - $n$  was determined according to a redox titration method described previously (Oya et al., 2013; Yoshitake et al., 2016). It is denoted as a weight percentage to the dried sample.

Magnetometry measurements were performed on 5–7 mg samples (dried gels) using a superconducting quantum interference device (SQUID), MPMS-5 of Quantum Design Inc. The magnetic field ( $H$ ) applied was usually varied through the cycle of 0 T  $\rightarrow$  5 T  $\rightarrow$  -0.1 T  $\rightarrow$  0 T at a constant temperature. For a given sample, the magnetization ( $M$ ) vs.  $H$  data were collected at 298 and 100 K. The temperature dependence of magnetization (i.e.,  $M$  vs.  $T$ ) was also examined for selected samples in the so-called zero-field-cooled (ZFC) and field-cooled (FC) conditions. The field strength applied was 0.01 T, and the experimental procedure has been described in the preceding paper (Oya et al., 2013).

Wide-angle X-ray diffraction (WAXD) measurements were made using a Rigaku RINT2200 V diffractometer. The apparatus was operated at 40 kV and 30 mA, and Ni-filtered  $\text{CuK}\alpha$  radiation (0.154 nm) was utilized. Diffraction intensity profiles in a range of  $2\theta = 20$ – $70^\circ$  were collected.

Dynamic viscoelastic measurements were conducted by using a

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