European Polymer Journal 76 (2016) 147–155

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Nanocomposite hydrogels based on iota-carrageenan and maghemite: Morphological, thermal and magnetic properties

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ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form 15 January 2016
Accepted 27 January 2016
Available online 28 January 2016

Keywords:
Magnetic hydrogels
Iota-carrageenan
Maghemite
Morphological properties
Magnetic properties
Thermal properties

ABSTRACT

The objective of this work was to prepare and characterize magnetic hydrogels based on iota-carrageenan, a polysaccharide obtained from biomass (*Rodophyceae* algae), containing maghemite (γ-Fe_2O_3) nanoparticles. The morphological, thermal and magnetic properties of the hydrogels were evaluated, as well as the influence of the crosslinking agent ($CaCl_2$) at different concentrations (0.3 mol L^{-1} and 0.5 mol L^{-1}) on the hydrogels' properties. The samples were characterized by scanning and transmission electron microscopy, vibrating sample magnetometry, thermogravimetry, Fourier-transform infrared spectroscopy and Mössbauer spectroscopy. The swelling degree of the hydrogels was also determined. The results showed that the synthesized magnetic material was mostly composed of γ-Fe_2O_3 and presented ferrimagnetic behavior. The hydrogels had spherical morphology and particle size in the range of 710 µm. The TEM images proved the magnetic particles had nanometric size. The hydrogels had good thermal stability and swelling degree in water of around 55%. Both the magnetic nanoparticles and crosslinking agent (Ca^{2+}) were well distributed on the surface of the hydrogels. The samples responded to the stimulus of a magnet.

1. Introduction

Hydrogels based on polysaccharides (biopolymers that are biorenewable resource, environmentally friendly) have been used in many fields because of their characteristics, such as biodegradability, biocompatibility, stimuli-responsive characteristics and biological functions making them a material of choice for many applications (including biomedical, toxic ion removal and water purification) [1–5]. Compared to their synthetic counterparts, renewable polymer-based materials offer a number of advantages especially regarding their environmental friendliness and low cost [6].

Among the polysaccharides, carrageenan stands out for its high capacity to absorb water, non-toxicity and abundance, since it is extracted from red algae [7,8].

The carrageenans are a group of linear sulfated polysaccharides, present in the cell structure of *Rodophyceae* algae. Besides this source, *Gigartinaceae* produce Kappa (κ) and Lambda (λ) carrageenans, while *Solieriaceae* produce Kappa and Iota (ι) car-

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http://dx.doi.org/10.1016/j.eurpolymj.2016.01.043
0014-3057/

rageenans. All carrageenans have high molecular mass and are formed of alternating units of D-galactose and 3,6-anhydro-D-galactose (3,6-AG) joined by α-1,3 and β-1,4-glycosidic bonds [7–12].

The main differences between the types of carrageenan are the position and number of ester sulfate groups (3,6-anhydro-D-galactose-n-sulfate). The content of 3,6-anhydro-D-galactose (3,6-AG) determines the characteristics among the carrageenan types and higher levels of ester sulfate imply smaller gelling force and lower solidification temperature [7,10,13].

Iota-carrageenan contains from 28% to 35% ester sulfate and 25% to 30% 3,6-AG units. It has the particular feature of forming colloids and gels in aqueous media at very low concentrations. These gels are transparent and thermoreversible, and can have a wide range of textures, from highly elastic and cohesive to firm and brittle, depending on the combination of fractions utilized. In particular, ι-carrageenan (Fig. 1) is insoluble in cold water but is soluble in hot water ($\geqslant$60 °C) [8,13].

The characteristics of a nanocomposite are determined by the synergism between the intrinsic properties of the polymer and the properties of the inorganic particles that are added to the system. In this work, we prepared a polymeric nanocomposite with superparamagnetic properties composed of a polysaccharide (iota-carrageenan) and magnetic nanoparticles of iron oxide.

Superparamagnetism occurs when a material is composed of sufficiently small crystals with spins oriented in monodomains that can be considered as being thermodynamically independent particles. The magnetic moments of these monodomains affect the interaction of the unpaired electrons. The resulting magnetic moment becomes greater than that of a paramagnetic substance, and the specific magnetic sensitivity of these particles can substantially exceed the value of the corresponding soluble paramagnetic species due to this magnetic ordering [15,16].

Superparamagnetic substances need remanent magnetization near zero when the magnetic field is removed, because the orientations of the monodomains return to being random. This means that the superparamagnetic iron oxide contrast agents will not aggregate due to the magnetic attraction [16].

The superparamagnetic property of a material is directly related to the size of its magnetic nanoparticles. Only particles with diameter smaller than 30 nm are superparamagnetic [15,17,18].

Nanoparticles of an iron oxide, such as maghemite (γ-Fe_2O_3), are nontoxic, making them attractive for the preparation of polymeric materials with magnetic properties for use in many areas [16].

Therefore, this paper describes the preparation and characterization of nanocomposite hydrogels based on ι-carrageenan and nanoparticles of γ-Fe_2O_3, crosslinked with Ca^{2+} ions. For this purpose, the morphological, thermal and magnetic properties of the hydrogels formed were evaluated. This research paper is of great importance; since it describes the preparation of a new hybrid polymeric material, eco-friendly, based on polysaccharide and iron oxide, which combines the characteristics of organic and inorganic compounds. Until now, were not found in the literature, works that deal with a systematic study on the preparation of magnetic hydrogels based on iota-carrageenan with spherical morphology. This type of carrageenan may provide a hydrogel with improved properties, because it contains a larger number of sulfate groups along its chain, which may lead to a more cross-linked polymeric network.

2. Materials and methods

The reagents used in this study were analytical grade (PA) and were used as received: ethanol (C_2H_6O) (Sumatex Produtos Químicos Ltda.), iron (III) chloride ($FeCl_3$), 1% sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), iron (II) sulfate ($FeSO_4$), 1% chlorhydric acid (HCl), 1% nitric acid (HNO_3) (Vetec Química Fina Ltda.), oleic acid ($C_{18}H_{34}O_2$) (B. Herzog Comércio e Indústria S.A.), iota-carrageenan (Iota-90 – Agargel Ltda.) and anhydrous calcium chloride ($CaCl_2{\cdot}2H_2O$) (Farmos).

2.1. Synthesis of the magnetic material

The magnetic material was synthesized by mixing the iron II and III salts using NH_4OH as a base in a system composed of a three-neck round bottom flask, thermostatically controlled bath and mechanical stirrer. First, 14 g of iron sulfate was dissolved in a beaker containing 50 mL of distilled water, under magnetic stirring. In another beaker, 27 g of iron chloride was dissolved in 50 mL of distilled water, under magnetic stirring. These two solutions were then mixed in a three-neck round bottom flask with capacity of 500 mL, under magnetic stirring, after which 130 mL of a solution of NH_4OH (PA grade) was added slowly, followed by 10 mL of oleic acid. The flask was placed in a thermostatically controlled silicon oil bath at 80 °C, under mechanical stirring for 30 min and the pH was measured. After this period, the mixture with the precipitate was left to cool slowly to room temperature and was washed with water and ethanol to remove the excess oleic acid.

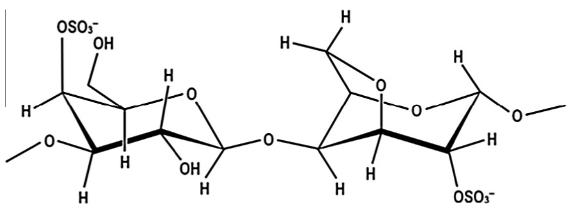

Fig. 1. Chemical structure of iota-carrageenan.