



Macromolecular Nanotechnology

Thermoreversible gelation and scaling laws for graphene oxide-filled κ -carrageenan hydrogelsSijun Liu^a, Hongqian Bao^b, Lin Li^{a,*}^a School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore^b Corporate Research Laboratory, 3M Singapore R&D Centre, 100 Woodlands Avenue, Singapore 738205, Singapore

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ABSTRACT

The effects of graphene oxide (GO) and ammonia functionalized graphene oxide (AGO) on microstructure, thermoreversible and critical gelation properties of κ -carrageenan in aqueous solution were studied by micro-differential scanning calorimetry (micro-DSC), field emission scanning electron microscopy (FESEM) and rheology. The presence of GO or AGO was able to decrease the gel formation and melting temperatures and reduce gel strength. The effect of AGO was more evident than that of GO. It was observed by FESEM that κ -carrageenan gel was induced by the formation of a fibrillar network, and fibrillar size and density decreased with increasing GO or AGO content. The viscoelastic properties at the gel point were examined using the Winter-Chambon criterion to obtain the critical relaxation exponent n and the critical gel strength S_g . n increased but S_g decreased with increasing GO or AGO content. The more obvious increase in n and decrease in S_g were observed in the AGO/ κ -carrageenan solution, which further demonstrated the stronger weakening effect of AGO. A schematic diagram has been proposed to explain the effect of AGO on the gelation of κ -carrageenan, where AGO sheets attracted a number of κ -carrageenan chains through hydrogen bonding and electrostatic interaction between sulfate groups of κ -carrageenan and amine groups of AGO. As a result, the number of free κ -carrageenan chains in solution decreased and the coil-helix transition and aggregation of helices of κ -carrageenan were affected negatively.

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1. Introduction

Carrageenans belong to the family of hydrophilic linear sulphated galactans extracted from various species of marine red algae. κ -Carrageenan, distinguished by its primary structure, is one of carrageenans and is composed of alternating $\alpha(1-3)$ -D-galactose-4-sulfated and $\beta(1-4)$ -3,6-anhydro-D-galactose. The gelation of κ -carrageenan in water is complex even though the gelation of κ -carrageenan has been known for more than 30 years. The ${}_4C^1$ conformation of 3,6-anhydro-D-galactose unit allows a helicoidal secondary structure, which is essential for the gelation of κ -carrageenan [1,2]. It is generally accepted that the gelation of κ -carrageenan takes two steps: the coil-helix transition followed by aggregation of helices [3,4]. Cardoso and Sabadini investigated the gelation of κ -carrageenan in water and found that the formation and melting of κ -carrageenan hydrogel were thermoreversible [5]. Ueda et al. further indicated that the formation and dissociation of double helical aggregates resulted in a hysteresis between the cooling and heating curves, which was not observed for carrageenan hydrogels

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induced by single helical aggregates [6]. The similar experimental results have also been reported in the past two decades [7,8].

On the other hand, κ -carrageenan is a polyion and very sensitive to the presence of salts. Many studies have demonstrated that monovalent cations can bind to the helices, which will promote the aggregation of helices. For example, Michel et al. confirmed the interaction between potassium ions and κ -carrageenan as that potassium ions bind to κ -carrageenan helices to reduce considerably the charge density of helices [9]. The studies by Watase et al. further showed that potassium, rubidium and cesium ions are more effective in inducing gelation than lithium and sodium ions because the shielding effect, which induces the decrease of the charge density of helices, increases with increasing the radius of alkali metal ions [10]. Recently, MacArtain et al. found that the addition of divalent calcium ions at low concentrations can also promote the aggregation of helices where storage modulus G' increases with increasing calcium ion concentration. But, a high concentration of calcium ions leads to the decrease of G' significantly [11]. Morris et al. thought that the decrease of G' in the presence of excessive cations should be attributed to the formation of an inhomogeneous network structure [12]. During adding a mixture of potassium ions and calcium ions into a κ -carrageenan aqueous solution, a synergistic effect was observed [13]. From the previous results, it can be concluded here that the presence of monovalent or divalent cations generally facilitates the coil-helix transition and the aggregation of helices, leading to that the sol-gel transition temperature and gel strength increase with increasing cation content.

A number of studies have also been performed to understand the effect of inorganic fillers on κ -carrageenan hydrogels. Daniel-da-Silva et al. found that the addition of nanosilica impairs the gelation of κ -carrageenan and leads to the decrease of gel formation and melting temperatures as well as reduction of gel strength [14]. Subsequently, Daniel-da-Silva et al. further studied the effect of magnetite nanoparticles, Fe_3O_4 , on the gelation of κ -carrageenan, and found that the presence of Fe_3O_4 promoted the gelation of κ -carrageenan, which is an opposite effect in contrast to nanosilica [15]. They thought that the increase in the sol-gel transition temperature should be attributed to adsorption of potassium ions on the surface of Fe_3O_4 nanoparticles, which led to an increase of the potassium ion concentration within the “ κ -carrageenan cages”. In contrast to Fe_3O_4 , nanosilica just acts as steric barriers to hinder the aggregation of κ -carrageenan helices. Salgueiro et al. investigated the effect of different shapes of Au nanoparticles (spherical and rod-shaped) on κ -carrageenan hydrogel and found that the κ -carrageenan hydrogel incorporated with both shapes of Au nanoparticles shows an enhanced storage modulus as compared to pure κ -carrageenan hydrogel, while the anisotropy of the rod-shaped Au affected the aggregation of κ -carrageenan helices leading to the formation of a less homogeneous microstructure with a low strength in contrast to the spherical Au [16]. All of these works indicated that there is a complicated process for the formation and melting of κ -carrageenan hydrogels filled with inorganic particles especially when inorganic fillers have various shapes and contain functionalized groups that can produce different interactions with κ -carrageenan.

Graphene, a single-atom-thick sheet of sp^2 -hybridized carbon atoms, has been attracted tremendous attentions in the past decade [17–23]. However, it is difficult to obtain a good dispersion if graphene is added into water directly. In order to improve the dispersion of graphene in aqueous solution, an oxidization method was used to produce a derivative graphene, graphene oxide (GO), with oxygen-containing groups on its basal planes and edges, such as hydroxyl, carboxyl and epoxide groups. These oxygen-containing groups make graphene completely exfoliated and ready to be prepared into an aqueous suspension of GO by sonication. Furthermore, the epoxide groups on GO sheets can react with special reagents to produce a functionalized GO to further improve the interaction between GO and a polymer matrix. For example, Nie et al. prepared alginate composite films by adding tetraethylenepentamine functionalized GO where the amine groups can be protonated and readily form electrostatic interaction with negatively charged COO^- groups on alginate chains, which can greatly enhance the thermal stability and mechanical property of the resulting alginate composite films [24]. Liu et al. found that the GO-carrageenan composite, where GO was functionalized by carrageenan, can be used as a substrate for biomimetic and cell-mediated mineralization of hydroxyapatite to facilitate the nucleation of hydroxyapatite on the surface of GO-carrageenan [25].

However, despite the numerous studies devoted to GO/biopolymer composites, it has not been found that there are any reports dealing with the interaction between κ -carrageenan and GO (or functionalized GO) in aqueous solution and their influence on κ -carrageenan composite hydrogels. Therefore, in the present work, we have systematically studied the effects of GO and ammonia functionalized GO (AGO) on the thermoreversible gelation properties of κ -carrageenan, gel network microstructures, and viscoelastic properties at the gel point using micro-differential scanning calorimetry (micro-DSC), field emission scanning electron microscopy (FESEM) and rheology. The rheological gelation properties of the GO or AGO-filled κ -carrageenan hydrogels have been analyzed and discussed for the validity of the scaling laws and for understanding of the gelation mechanism. A schematic diagram has been proposed for the effects of GO and AGO on the gelation of κ -carrageenan in aqueous solution.

2. Experimental

2.1. Materials and solution preparation

κ -Carrageenan in the powder form was purchased from Sigma-Aldrich (Singapore). According to the supplier, the molecular weight of κ -carrageenan is about 3.0×10^5 g/mol. Before use, the κ -carrageenan powder was dried and kept in

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