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Effect of epichlorohydrin on the wet spinning of carrageenan fibers under optimal parameter conditions

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ABSTRACT

Motivated by the extensive application of carrageenans, this work prepared carrageenan fibers via wet spinning. The optimum spinning parameters were explored by means of an orthogonal test. According to the results of tensile test, dope concentration, draw ratio, coagulation bath temperature, and coagulation bath concentration set to 9%, 1.2, 15 °C and 5%, respectively, were the optimum spinning conditions. These parameters were then applied to fabricate fibers treated with epichlorohydrin in a stretch bath. The result of tensile testing demonstrated a positive improvement in the intensity, and SEM showed obvious necking phenomenon of the crosslinked carrageenan fibers. The structures and special groups were characterized with X-ray diffraction and FTIR, and the results indicated the regularity of the net structure and the increase in ether bond and methylene. In some, crosslinking reactions in optimum parameter conditions yield excellent fibers and thus present promising applications.

1. Introduction

The inner tissues of seaweeds, such as Chondrus, Eucheuma, Gigartina, and Hypnea, comprise extensive carrageenans called algal polysaccharides. These carrageenans are wildly used as gelling, thickening, and stabilizing agents in industrial applications, as well as in food, personal care, and pharmaceutical products (Abad, Aranilla, Relleve, & Dela Rosa, 2014; Azevedo, Torres, Sousa-Pinto, & Hilliou, 2015). The modification of carrageenan fibers has attracted significant attention from academia and the industry. Carrageenans, the raw material of these fibers, are sulfated galactans that are widely used as anionic polysaccharides (Azevedo et al., 2015). The linear polymer comprises alternating disaccharide repeating units of 3-linked β-D-galactopyranose (G units) and 4-linked α-D-galactopyranose (D units) or 4-linked 3, 6-anhydro-α-D-galactopyranose (DA units) (Das, Sharma, Mondal, & Prasad, 2016; Perez Recalde et al., 2016). Three main types of carrageenan have been identified according to the number and position of sulfate groups: kappa (κ), iota (ι), and lambda (λ) carrageenans (Van De Velde, Peppelman, Rollema, & Hans Tromp, 2001). Meanwhile, these types of carrageen comprise abundant hydroxide radicals, which are capable of inducting crosslinking reactions with some crosslinking reagents.

The physical or chemical characteristics of carrageenans are relevant to their structures and functional groups. A particular feature is a sequential layout with hexatomic rings, sulfate groups, and hydroxide radicals included in every repeat unit. They have an important effect on molecular weight, appearance, solubility, viscosity, and gelation of carrageenans (Farahnaky, Azizi, Majzoobi, Mesbahi, & Maftoonazad, 2013). Chemically, sulfate groups and hydroxide radicals play dominant roles in reactivity and mechanisms, such as strong anionic properties and crosslinking reactions. These characteristics are considered to produce additional agents to improve the quality of food, cosmetic, and pharmaceutical products (Liu, Zhan, Wan, Wang, & Wang, 2015; Selvakumaran & Muhamad, 2015; Selvakumaran, Muhamad, & Abd Razak, 2016; Wang, Chen, Huynh, & Chang, 2015).

The crosslinking method is widely used because the crosslinking agent and matrix can form a three-dimensional reticular structure, which plays an important role in the change of the performance of a crosslinked product (Rodrigues, da Costa, & Grenha, 2012). For example, the crosslinking reaction significantly affects the rheological and viscoelastic behavior of products, as well as their swelling and kinetic properties are also changed along with the structure (El-Aassar, El Fawal, Kamoun, & Fouda, 2015; Keppeler, Ellis, & Jacquier, 2009). A feasible approach has been adopted to reduce the degradation of molecular mass through the interaction between

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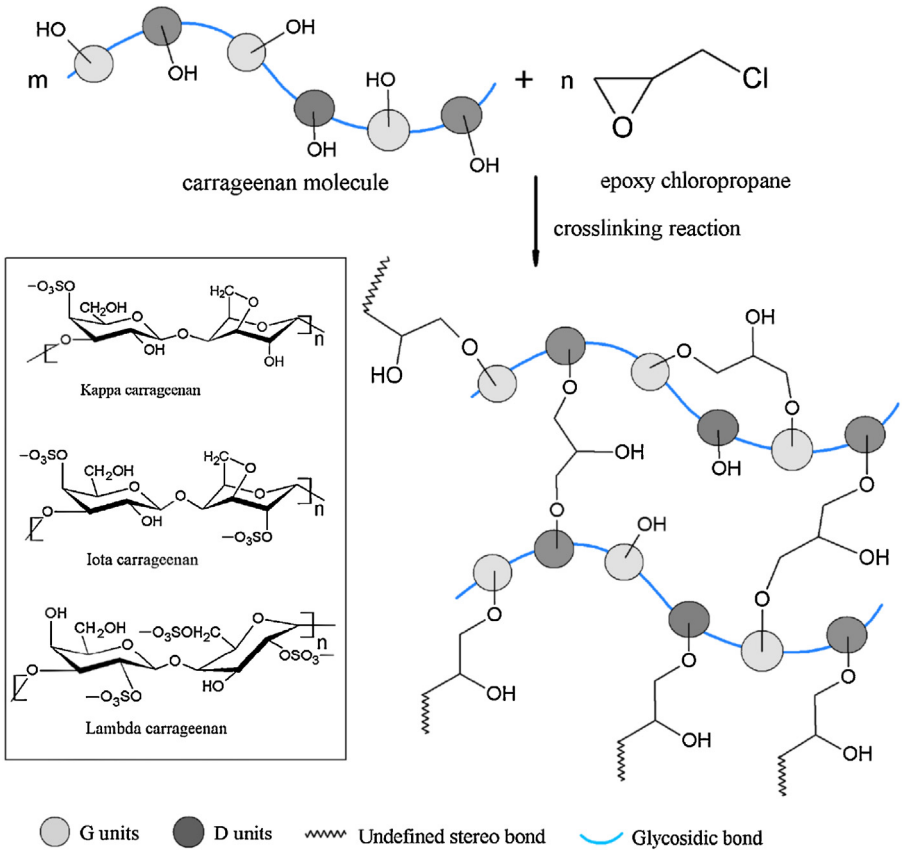

Fig. 1. Principle diagram of the crosslinking reaction. The inset shows three main carrageenan molecular structures.

crosslinking agents and matrixes (Aminlashgari et al., 2015). Moreover, the control of release delivery systems by preparing them as beads is an innovative application of the crosslinking approach (Keppeler et al., 2009). Hence, crosslinked polymers are expected to become hot research topics in the near future.

The emerging applications of radiation-modified carrageenans, whose molecular structure backbones are changed by radiation, show immense potential in the areas of healthcare and environment. These materials are used as antioxidants, radiation dose indicators, wound dressings, superwater absorbent materials, and plant growth promoters (Abad et al., 2014). Owing to carrageenans bear sulfate group, they can be mixed with chitosan according to different proportions taking part in anti-thrombogenic and anti-calcification mechanisms. Thus they show great promise as stent coating (Campelo et al., 2016). The anionic groups of carrageenans demonstrate strong interactions with cation groups, similar to negatively charged sulfate groups and positively charged groups (such as amino groups in gelatin). This condition leads to significant transformations in coagulation kinetics and gelation abilities (Derkach, Ilyin, Maklakova, Kulichikhin, & Malkin, 2015). Recent studies have attempted to replace the gelatin with dually modified sogo starch through the addition of an appropriate amount of carrageenan. Moreover, carrageenan mechanism in rheology has been widely described in several studies (Fakharian, Tamimi, Abbaspour, Mohammadi Nafchi, & Karim, 2015). As another advanced exploration, carboxymethyl κ-carrageenan collagen peptides can generate new epithelium when smeared on wounded skin (Fan et al., 2015). Therefore, the biological activities of carrageenan macromolecules will continue to serve as an important research area.

These peculiarities are closely related to the spinnability of carrageenan solutions when prepared in the appropriate concentrations. The spinning of carrageenan fiber involves at least two prerequisites: (i) a carrageenan spinning dope with a high concentration to achieve enough viscosity for spinning and (ii) an effective spinning process which is capable of commercializing and yielding lustrous carrageenan fibers with a uniform diameter, circular profile, and tensile properties that are similar to or better than those of natural fibers. The wet spinning process is successfully applied to natural extracts (Kong & Ziegler, 2013), organic composite materials (Lai, Wei, Zou, Xu, & Lu, 2015), and blended materials (He et al., 2012).

In many reports, ethanol has been used as coagulant for the wet spinning of carrageenan fibers (Kong & Ziegler, 2013). However, the coagulant does not produce usable fibers, probably because ethanol induces excessively rapid conformation transition from a random coil/helix structure to a double helix structure that prevents adequate molecular chain adjustment. Calciumions (Ca^{2+}) favor the gelation of ι-carrageenans, whereas potassium ions (K^{+}) favor the gelation of κ-carrageenans (Morris & Chilvers, 1983; Tako & Nakamura, 1986; Tako, Nakamura, & Kohda, 1987). Therefore, we can use these inorganic salt solutions as coagulation bath. After the traditional extrusion of synthetic polymers or cellulosics, post-drawing to improve molecular orientation and packing is important to the mechanical properties of fibers (Hufenus, Reifler, Fernández-Ronco, & Heuberger, 2015). In this paper, we use barium chloride solution ($BaCl_2$) as coagulation bath to further explore the fiber state under crosslinking conditions. A custom-made simplified industrial wet spinning device is also applied for continuous mechanical post-drawing. In this work, we detailedly describe the combined effects of spinning dope concentration, coagulant concentration, coagulant temperature, and draw ratio on the morphology and tensile properties of the resultant carrageenan fibers.