

## Short communication

Fabrication of  $\kappa$ -carrageenan fibers by wet spinning: Addition of  $\iota$ -carrageenan

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## ABSTRACT

Taking advantage of the gelation process of  $\kappa$ -carrageenan, we have developed a wet-spinning process to fabricate micro-scale fibers from  $\kappa$ -carrageenan. Effects of three important spinning parameters, i.e. coagulation bath composition, spinning rate and post-spinning mechanical drawing, on fiber morphological and tensile properties have been discussed. In the present report, we studied the addition of  $\iota$ -carrageenan on thermal and rheological properties of the bicomponent gels and the fibers spun from them. It was found that  $\kappa$ - and  $\iota$ -carrageenan underwent phase separation in the bicomponent gel. Upon addition of  $\iota$ -carrageenan, the diameter and compliance of the blend fiber was increased.

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## 1. Introduction

Better utilization of natural fibers and synthetic bio-based fibers has attracted much attention from academia and industry (Kong, Ziegler, & Bhosale, 2010). Carbohydrate polymers, also known as polysaccharides, are the most abundant bio-based, renewable and inherently biodegradable polymeric materials, making up around 75% of all the organic mass on the earth. Hence, carbohydrate polymers have the potential to replace their synthetic counterparts in various applications. Because of their diversity and availability, polysaccharides provide countless choices and sustainable supply of starting materials for fiber production. Some polysaccharides, e.g. cellulose and chitosan, exist in fibrous form in nature. They can be either used in their original form with some modifications or as starting materials for artificial spinning. Other polysaccharides do not take fibrous form in nature and thus artificial spinning will be necessary for their use. To date a number of polysaccharides have been successfully spun into fibers, including cellulose, chitosan, hyaluronic acid, dextran, pullulan, and starch (Kong & Ziegler, submitted for publication; Kong et al., 2010).

The carrageenans are linear, sulfated polysaccharides extracted from various species of red seaweed. The “ideal” carrageenan backbone is based on a repeating disaccharide unit of  $\beta$ -D-galactopyranose (A residue) linked through positions 1 and 3, and  $\alpha$ -D-galactopyranose (B residue) linked through positions 1 and 4.  $\kappa$ -Carrageenan is one of the three dominant carrageenan species, i.e.  $\kappa$ ,  $\iota$ , and  $\lambda$ -carrageenan, which differ in their disaccharide structures.  $\kappa$ -Carrageenan is mainly used in food applications as a texturizing agent, but other applications including cosmetics,

pharmaceuticals, and paints are also of importance. Recent interest in fabricating  $\kappa$ -carrageenan-based hydrogels and films is motivated by their potential for new applications mainly in the biomedical field, e.g. drug delivery, wound dressing, cell encapsulation, and enzyme immobilization (Lindblad Margaretha, Sjöberg, Albertsson, & Hartman, 2007).

Fibers are promising delivery matrices given their high surface area, porous structure, and orientation-induced mechanical strength. We have shown that  $\kappa$ -carrageenan can be spun into fibers by a wet-spinning method (Kong & Ziegler, 2011). We previously investigated the impact of a few spinning parameters, i.e. spinning rate, coagulation bath composition, and post-spinning drawing, on fiber formation. In the current study, we consider the impact of a molecular parameter, i.e. charge density (sulfate) on carrageenan chain, on the bicomponent spinning dope and resultant fiber properties.

Optimally, the sulfate content and placement could be altered on the carrageenan chain to modify spinnability and fiber properties. However, this may not be practical, since for example desulfation reactions will also depolymerize the carrageenan significantly (Kolender & Matulewicz, 2004; Navarro, Flores, & Stortz, 2007). Another approach would be to use  $\kappa$ -/ $\iota$ -hybrid carrageenan, which is also referred to as kappa-2 carrageenan (van de Velde, 2008), but these carrageenan samples are not commercially available. The  $\kappa$ -/ $\iota$ -ratio and their sequence distribution on the chain cannot easily be artificially controlled. Therefore, the approach we have taken here is to add  $\iota$ -carrageenan to  $\kappa$ -carrageenan to vary the average charge density.

The wet-spinning method was based on the ability of  $\kappa$ -carrageenan to form cold- and salt-setting reversible gels. The gelation process of carrageenans has been extensively studied with respect to the conformational transition of carrageenan molecules (Piculell,

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1995). Although the conformational nature, i.e., single or double helices, and their further association during gelation are still under debate, most evidence tends to support a “two-step model” (Kong & Ziegler, 2011) of coil–helix–gel mechanism proposed by Morris, Rees, and Robinson (1980) as modified by Rochas and Rinaudo (1984). Gel network formation from helical polymers proceeds on either a helical or superhelical level. In the first mechanism, each chain joins in double helices with more than one other chain, whereas in the second phenomenon, multiple helices aggregate to form one junction zone of the network.  $\iota$ -Carrageenan is believed to adopt the first mechanism, while  $\kappa$ -carrageenan proceeds to form aggregated “domains”.

In this communication, we report our study on the rheological and thermal properties of  $\kappa$ - and  $\iota$ -carrageenan bicomponent gels. Fibers were spun from these bicomponent gels by a wet-spinning method and their diameters and tensile properties were evaluated.

## 2. Experimental

### 2.1. Materials

$\kappa$ -Carrageenan (Gelcarin® GP911 NF) and  $\iota$ -carrageenan (Gelcarin® GP379) were kindly provided by FMC Biopolymers (Philadelphia, PA). Ethanol (200 proof) was obtained from the Penn State Chemistry Stockroom. All other reagents were purchased from VWR International (Radnor, PA) and used as received.

### 2.2. Carrageenan purification

The carrageenan samples were purified from excess salts and low molecular weight carbohydrates by a method modified from Rochas and Rinaudo (1980). In detail, 1.0% (w/v) of carrageenan sample was completely dissolved in deionized water heated to 80 °C with stirring. The carrageenan was precipitated with absolute ethanol (4 times the volume of the dispersion). The precipitate was collected using vacuum filtration (Whatman #4, Whatman, Piscataway, NJ). The precipitate was washed in ethanol/water mixture (80/20, v/v) and again filtered. This re-suspension and filtration was repeated 4 times. Finally the precipitate was dried in a forced air oven at 40 °C overnight.

### 2.3. Carrageenan characterization

The purified carrageenans were characterized for cation composition by inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Optima 5300, Perkin–Elmer, Waltham, MA). Fourier transform infrared spectroscopy (FTIR) spectra of the purified carrageenan samples were recorded using a Bruker IFS 66/S FT-IR Spectrometer (Bruker Optics Inc., Billerica, MA) equipped with an attenuated total reflectance (ATR) accessory containing a diamond crystal. The spectra were scanned at room temperature over the wave number range of 4000–400  $\text{cm}^{-1}$ , with an accumulation of 400 scans and a resolution of 6  $\text{cm}^{-1}$ .

### 2.4. Wet spinning

Spinning dope was prepared by dissolving purified carrageenan samples of different  $\kappa$ -/ $\iota$ -ratios in deionized water at 80 °C for at least 1 h. The dispersion was homogeneous by visual observation before spinning. A total solid concentration of 6% (w/v) was used throughout the study. Wet spinning was carried out using a bench-top device. A jacket-type circulating device (Penn State Glass Shop) was used to maintain the spinning dope temperature in a 3 ml syringe (Becton, Dickinson and Company, Franklin Lakes, NJ). The dope was extruded by a syringe pump (Cole-Parmer 74900, Vernon

**Table 1**

Cation contents of the commercial and purified  $\kappa$ - and  $\iota$ -carrageenan samples, expressed in g/100 g.

Cation	$\kappa$ -Carrageenan		$\iota$ -Carrageenan	
	Raw <sup>a</sup>	Purified <sup>b</sup>	Raw	Purified
K <sup>+</sup>	6.45	1.23	3.67	0.68
Ca <sup>2+</sup>	1.55	1.07	3.75	2.14
Na <sup>+</sup>	0.86	2.30	1.23	3.18

<sup>a</sup> Compositions according to datasheets from commercial providers.

<sup>b</sup> Compositions according to ICP-AES results.

Hills, IL) through a blunt stainless steel needle (20 G, 0.51 mm) into a coagulation bath containing 0.5 M KCl and 0.5 M CaCl<sub>2</sub> in 50% (v/v) ethanol. The as-spun fiber was kept in the bath for at least 2 h to ensure complete ion diffusion into the fiber.

### 2.5. Small deformation rheology

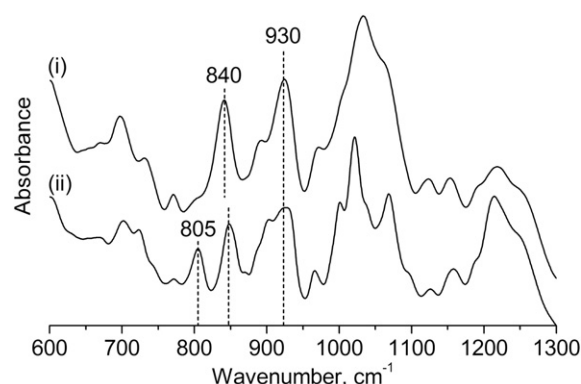
The carrageenan dispersions were subject to small deformation oscillatory measurements using a cone and plate geometry on a strain-controlled rheometer (ARES, TA Instrument, New Castle, DE). The probe diameter was 25 mm and the cone angle was 5.73°. Sample was loaded between the plates when hot and sealed by mineral oil on the periphery to avoid solvent evaporation. Spectra were recorded on cooling of the  $\kappa$ -/ $\iota$ -carrageenan spinning dope from 90 °C to 10 °C at a frequency of 1 Hz and strain of 1%.

### 2.6. Morphological characterization

Observation of fibers was performed using an Olympus BX41 optical microscope (Hitech Instruments, Edgemont, PA) equipped with cross polarizers and a SPOT Insight QE camera (SPOT Diagnostic Instruments, Sterling Heights, MI). Analysis was completed using SPOT analytical and controlling software.

### 2.7. Thermal characterization

Thermograms were recorded using a differential scanning calorimeter (DSC Q100, TA Instrument, New Castle, DE) and 60  $\mu\text{L}$  hermetic stainless steel pans (Perkin–Elmer Instruments, Bridgeville, PA). At least 50 mg of the  $\kappa$ -/ $\iota$ -carrageenan spinning dope was filled into the pan. Samples were equilibrated at 10 °C, and then heated to 170 °C at a scanning rate of 2 °C/min. The DSC was calibrated with indium, and an empty sample pan was used as a reference.



**Fig. 1.** FTIR spectra of (i)  $\kappa$ -carrageenan and (ii)  $\iota$ -carrageenan samples.

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