Comparison of Two Different Preparation Methods of Wet-Spun Carrageenan Fibers Directly from Chondrus Extractions

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ABSTRACT: In order to improve the characters of carrageenan fibers, two different process methods were presented in this study. Dopes prepared directly from Chondrus extraction by Route A—adding NaOH after Chondrus extraction—or Route B—using NaOH solution to extract Chondrus and carrageenan fibers (Fibers A and Fibers B)—were obtained using the wet spinning process using barium chloride as the coagulant at room temperature. The properties of dopes were studied by dynamic light scattering and gel permeation chromatography. The properties of Fibers A and Fibers B were comprehensively studied by Fourier transform infrared, thermal analysis, scanning electron microscopy, and tensile testing. The results showed that carrageenan with a larger molecule weight in Dope A and Fibers A showed higher intensity, better morphology, and stable thermal properties.

1. INTRODUCTION

Chondrus is a species of red algae which is found along the shores of the Bohai Sea, Yellow Sea, and East China Sea and is usually used to extract carrageenans.1-3 Chondrus has triphasic biological cycles: gametophytic phase, tetrasporophytic phase, and carposoprohytic phase,4,5 and at each phase of their life cycle, different kinds of carrageenans are produced.6 Our research group has reported that the Chondrus we used was at the gametophytic phase, and the Chondrus contained mainly iota-carrageenan.7 i-Carrageenan is characterized by an alternating disaccharide unit of (1→3)-linked α-D-galactose-4-sulphate and (1→4)-linked 3,6-anhydro-β-D-galactose-2-sulphate.8-10

In our previous research, we obtained carrageenan fibers directly from extraction of Chondrus without the steps of precipitation and drying to form the powder.11 The process of preparing carrageenan fibers from extraction directly would play a crucial role in energy saving and emission reduction. We found the use of alkali solution as a solvent to dissolve carrageenan, and the resultant solution can be spun at room temperature.12 In addition, the mechanism of the NaOH-induced complete dissolution process of carrageenan has been studied thoroughly.13 Therefore, the addition of alkali is essential in the preparation of dopes. However, the optimal addition time of the alkali during the process of extraction and the effect of the alkali on the spinning solution and the carrageenan fibers have not been studied.

In the present research, extractions and carrageenan fibers were prepared using two different extract processes shown as Route A and Route B in Figure 1. In Route A, Chondrus was extracted using distilled water, and NaOH was added to the extraction to obtain Dope A and Fibers A. In Route B, Chondrus was extracted with NaOH solution to obtain Dope B and Fibers B. The properties of these two kinds of dopes and fibers were characterized by dynamic light scattering (DLS), gel permeation chromatography (GPC), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), thermogravimetry (TG)—derivative TG (DTG), and tensile properties.

2. RESULTS AND DISCUSSION

2.1. Properties of Dopes. The particle dispersion index (PDI) value of Dope A was 0.224 in DLS experiments (Figure 2A). There are two peaks with the volume of diameter distributions (d(H)). Peak 1 occupied almost all the volumes at 89.7%. Moreover, the PDI value of Dope B was 0.466. Dope B showed three peaks, whose volumes were about 66.1, 31.0, and 2.8%, respectively. Peak 1 represents the diameter distribution of a single molecular chain, and peak 2 and peak 3 represent different degrees of aggregation between carrageenan molecular chains. The value of peak 1 for Dope A was 89.92 nm and spinning solution B was 39.46 nm, which indicates that the carrageenan molecular chains in Dope B had been degraded and molecular chain association was serious. At room temperature (25 °C), NaOH solution was used as the solvent for carrageenan, and NaOH and carrageenan molecular...
chains formed a hydrogen bond protection structure, contributing to reduce the association between carrageenan molecular chains,
15,16 but in a high-temperature environment (95 °C), this protective structure could be destroyed to a certain extent, resulting in the association between carrageenan molecules, and after processing for 2 h, the carrageenan molecular chains could be degraded.

In addition, M_w of carrageenan in Dope A was compared with that in Dope B (Figure 2B). The average molecular weight of Dope A was 1.05 × 10^6 g/mol and that of Dope B was 7.64 × 10^5 g/mol and the M_w/M_n of Dope A was 1.55 and that of Dope B was 1.56. Dope A prepared by Route A—adding NaOH after Chondrus extraction—had a narrower molecular weight distribution than Dope B prepared by Route B—using NaOH solution to extract Chondrus. d(H) distribution and GPC results show that Dope A had larger carrageenan molecular chains with good solution properties, and the carrageenan molecular chains of Dope B were easily degraded and associated under the action of NaOH at a high temperature.

2.2. Structure Properties of Carrageenan Fibers. The chemical structures of Fibers A and Fibers B are analyzed by FTIR. It is easy to observe that these two fibers exhibit similar IR spectra (Figure 3). For them, two broad peaks were located at 3710–3000 cm⁻¹ (centered at 3400 cm⁻¹), belonging to the stretching vibration of hydroxyl groups (υO–H),
13,14 while Fibers B displayed a peak at 3400 cm⁻¹ that was broader than that of Fibers A, which was because the carrageenan molecular chains aggregated in Dope B so that hydrogen bonds of Fibers B formed between the carrageenan molecular chains, meaning the stretching vibration frequency of the hydroxyl group increased and the absorption band widened. However, because of the low degree of aggregation between carrageenan molecular chains in Dope A, the hydrogen bonds of Fibers A between the molecular chains were smaller, and the stretching vibration peaks of the hydroxyl groups were narrower. This result is consistent with the DLS test result. In addition, the structure of the two carrageenan fibers did not change greatly, including the asymmetric stretching vibration band of CH₃ (at 2960 cm⁻¹) and asymmetric and symmetric stretching vibration bands of CH₂ (at 2900 cm⁻¹),
17 a strong band of C–O–SO₄ on C₄ of 4-sulfate (4S) (at approximately 845 cm⁻¹), C–O bonds of 3,6-anhydro-D-galactose (DA) (at approximately 930 cm⁻¹), and the presence of sulfate ester in the 2-position of the anhydro-D-galactose residues (DA2S) (around 805 cm⁻¹).

Figure 1. Comparison of preparation processes of carrageenan fibers [(A) adding NaOH after extraction. (B) Adding NaOH during extraction].

Figure 2. d(H) distribution (A) and GPC curves (B) of Dope A and Dope B.

Figure 3. FTIR spectra of Fibers A and Fibers B.
2.3. Morphology Properties of Carrageenan Fibers. The digital photographs in Figure 4A,B show that Fibers A and Fibers B had good fiber morphology. Figure 4A,B shows white precipitates on the surface of Fibers A and Fibers B, indicating that the carrageenan molecules contained sulfate groups and the barium ions combined with the sulfate groups in the carrageenan molecule formed barium sulfate precipitates. In addition, from Figure 4A,B, the average diameter of Fibers A was smaller than that of Fibers B: they were about 40 and 45 μm, respectively. Comparing the cross-sections of the two fibers, the internal structure of Fibers B was more loose than that of Fibers A.

2.4. Mechanical Properties of Carrageenan Fibers. The parameters and the strength data are shown in Table 1.

| samples     | breaking force (cN) | linear density (dtx) | linear intensity (cN/dtx) | breaking elongation (%) | breakdown time (s) |
|-------------|---------------------|----------------------|---------------------------|-------------------------|-------------------|
| Fibers A    | 21.38               | 29.28                | 0.73                      | 9.59                    | 6.90              |
| Fibers B    | 25.72               | 46.76                | 0.55                      | 10.46                   | 6.97              |

Because of the different diameters of Fibers A and Fibers B, linear intensity was the only reliable indicator of the intensity properties of fibers. The relationship between linear intensity, breaking force, and linear density is as follows:

\[
\text{Linear intensity} = \frac{\text{breaking force}}{\text{linear density}}
\]

As the linear density of Fibers B was much higher than that of Fibers A, the linear intensity of Fibers A was higher than Fibers B: the values of Fibers A and Fibers B were 0.73 and 0.55 cN/dtx, respectively. The elongation at break and breaking time of Fibers A and Fibers B showed similar values; therefore, the tensile property of Fibers A was better than that of Fibers B.

2.5. Thermal Properties of Carrageenan Fibers. The TG and DTG curves showing the thermal properties of carrageenan fibers are illustrated in Figure 5. The first stage of the thermal decomposition of Fibers A and Fibers B were 39–181 and 39–169 °C respectively, related to fiber dehydration. The second stage was the primary stage of thermal decomposition for fibers. The mass loss of Fibers A residue decreased sharply in the temperature range of 181–184 °C (Figure 5A), corresponding to the sharp mass loss rate peak in Figure 5D. The massive rupture of the polysaccharide bonds started at this stage; at the same time, macromolecular pyrolysis produced a variety of medium molecules, small molecules, and some gases. The pyrolysis process of Fibers B (from 169 to 173 °C) was similar to that of Fibers A. However, the initial decomposition temperature (165 °C) of Fibers B was significantly lower than that of Fibers B (181 °C) (Figure 5B,C). As a result, the structure of Fibers A is more stable than that of Fibers B, indicating that Fibers A have higher tensile strength. The third stage of Fibers A and Fibers B was located in the range of 184–1000 and 173–1000 °C, with the quality of residues being 34.8 and 36.4%. Notably, the amount of the residual layer formed in the final stage was similar. These results strongly suggest that Fibers A has a more stable structure, which can also explain why the tensile strength of the Fibers A was higher than Fibers B.

3. CONCLUSIONS

Two kinds of carrageenan fibers—Fibers A and Fibers B have been prepared with two different ways—Route A and Route B via wet spinning processes directly from Chondrus extractions in this paper. The DLS showed that Dope A had a larger hydrodynamic diameter, and GPC showed that the average molecular weight of Dope A was larger than that of Dope B, indicating that there was degradation of carrageenan molecules in the process of extraction of Route B. In addition, the mechanical properties, morphology, and pyrolysis of Fibers A are better than those of the Fibers B. Therefore, Route A is a better process for preparing carrageenan fibers directly from Chondrus extraction.

4. EXPERIMENTAL SECTION

4.1. Materials. Chondrus was collected in Bohai Sea (Dalian Bay, China) during May and dried for later use. Ethanol, barium chloride, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., LTD. (Shanghai, China), and those reagents were of analytical grade, commercially available, and used as received.

4.2. Methods. The processes of preparing carrageenan fibers from Chondrus are shown in Figure 1.

4.3. Preparation of Dopes. The dried Chondrus was first pretreated with 8% NaOH solution, and the pretreatment steps have been reported in our previous essay, after which the extractions were prepared from Route A and Route B. In Route A, pretreated Chondrus was added to distilled water with the weight ratio of 1/1, and the mixture was extracted at 95 °C for 2 h. Then, the extraction containing impurities was filtered with a 200-meshgauze of two layers, and the extraction A was collected. Then, Dope A was prepared by adding NaOH to extraction A and Dope A was carrageenan solutions containing 8 wt % NaOH. In Route B, Chondrus was added to 8 wt % NaOH solution with the weight ratio of 1/1, and the mixture was also extracted at 95 °C for 2 h. The method of collecting the extraction B was similar as that in Route A, and Dope B is exactly extraction B.

4.4. Preparation of Carrageenan Fibers. The processes of wet-spun Fibers A and Fibers B were similar, as explained in our previous report. Carrageenan fibers were spun at room temperature using a wet-spinning device. First, the spinning solution was loaded into a 1 L dope storage cylinder and...
extruded under a pressure of 0.2 MPa. The speed of the metering pump was 40 rpm through a spinneret (60 holes, diameter = 0.08 mm) into the first coagulation bath containing 10% barium chloride solution and the stretch bath containing 7% barium chloride solution. The fibers were drawn at a stretching ratio of 1.25 between two sets of rollers. Finally, the fibers were collected in the second rollers. The as-spun fibers were immersed and washed using alcohol (50%, v/v), and alcohol (95%, v/v) for 12 h, and finally dried at ambient temperature.

4.5. Characterizations of Dopes. DLS was utilized to characterize the chain conformation of carrageenan in the dilute solution at a constant temperature (25 °C). A laser particle size analyzer (Mastersizer 3000) was used at scattering angles θ of 173°. Dope A and Dope B each of 0.5 mL were added to 50 mL of distilled water and stirred for 24 h at room temperature to form a uniform solution. The resultant solution was filtered through 0.22 μm Millipore filters (NYL, 13 mm syringe filter). In the DLS measurements, the CONTIN program was used for the analysis of the dynamic light-scattering data. The hydrodynamic diameter \(d(H)\) of carrageenan in dilute solution was calculated using the following Stokes–Einstein relation as

\[
d(H) = \frac{kT}{3\pi\eta D}
\]

where \(k\) is the Boltzmann constant, \(T\) is the temperature in units of K, \(\eta\) is the solvent viscosity, and \(D\) represents the translational diffusion coefficient.

The average molecular weights \(\langle M_a \rangle\) of carrageenan were measured by GPC on a Viscotek GPCmax (Malvern Instruments Ltd, UK) using A 6000 M GPC column. Poly(ethylene oxide) was used as the standard for GPC calibration. NaNO₃/H₂O (0.1 M) solution was used as the solvent for carrageenan and eluent for GPC measurement.¹²

4.6. Characterizations of Carrageenan Fibers. FTIR spectroscopy of Fibers A and Fibers B were obtained via a FTIR spectrometer (Thermo Scientific Nicolet iS50, America). The range of wave numbers was set from 4000 to 500 cm⁻¹ at the resolution of 4 cm⁻¹.

The cross-section and surface of Fibers A and the Fibers B were examined using a scanning electron microscope (Jietech TM-3000, Japan) at 15 kV after gold coating. The shape and appearance of fibers was also measured using digital camera technology.

Fiber samples were kept in the state of constant temperature and humidity (20 ± 5 °C; 65 ± 5%) for 24 h before measurement. Mechanical properties of fibers were tested using a strength tester (LLY-06, Laizhou Electron Instrument Co. Ltd.) at a gauge length of 10 mm and an extension speed of 10 mm/min and at constant temperature and humidity. Thirty fiber samples were examined for tensile measurements, and the averaged results were calculated.

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**Figure 5.** (A) Thermogravimetric profiles of carrageenan fibers and (B) enlarged one with the temperature region of 165–195 °C. (C) Initial decomposition temperature of carrageenan fibers. (D) DTG thermograms of Fibers A and Fibers B.

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https://dx.doi.org/10.1021/acsomega.9b04435  
ACS Omega 2020, 5, 6661−6665
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the National High Technology Research and Development Program of China (2010AA093701), the National Natural Science Foundation of China (grant 50803030), the Program for Changjiang Scholars and Innovative Research Team in University (IRT0970), the Postdoctoral Science Special Foundation of Shandong Province, China (ZR2016EMB21). Particularly, I want to thank my husband—Shunqing Yang for his tremendous help in my experiments.

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