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Fabrication of κ -Carrageenan Fibers by Wet Spinning: Addition of ι -Carrageenan

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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 study on artificial spinning will be necessary for investigating their spinnability. So far a number of polysaccharides have been successfully spun into fibers, including cellulose, chitosan, hyaluronic acid, dextran, pullulan, and starch (Kong & Ziegler, 2012; 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 β -D-galactopyranose (A residue) linked through positions 1 and 3, and α -D-galactopyranose (B residue) linked through positions 1 and 4. κ -Carrageenan is one of the three dominant carrageenan species, i.e. κ , ι , and λ -carrageenan, which differ in their disaccharide structures. κ -Carrageenan is mainly used in food applications as a texturizing agent, but other applications including cosmetics, pharmaceuticals, and paints are also of importance. Recently, people are also interested in fabricating κ -carrageenan-

based hydrogel and films that are potential for many new applications mainly in the biomedical field, such as drug delivery, wound dressing, cell encapsulation, and enzyme immobilization (Lindblad Margaretha, Sjöberg, Albertsson, & Hartman, 2007).

Fibers are promising delivery matrix given their high surface area, porous structure, and orientation-induced mechanical strength. We have, for the first time, shown that κ -carrageenan can be spun into fibers by wet-spinning method (Kong & Ziegler, 2011). A few spinning parameters involved, i.e. spinning rate, coagulation bath composition, and post-spinning drawing, have been discussed. 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 can be adjusted on the carrageenan chain. However, this is not practical since desulfation reaction will also depolymerize the carrageenan significantly (Kolender & Matulewicz, 2004; Navarro, Flores, & Stortz, 2007). Another approach will be using κ - ι - hybrid carrageenan, which is also referred to as kappa-2 carrageenan (van de Velde, 2008). But these carrageenan samples are not commercially available. The κ - ι - ratio and their sequence distribution on the chain cannot be artificially controlled. Even though we can have a series of κ - ι - hybrids with varying κ - ι - ratio, their alternating sequence may also bring confounding effects. Therefore, we add ι -carrageenan into κ -carrageenan as an estimation of the variation in charge density.

The wet-spinning method was based on the ability of κ -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, 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 et al. (Morris, Rees, & Robinson, 1980) as modified by Rochas and Rinaudo (Rochas & 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. ι -Carrageenan is believed to adopt the first mechanism, while κ -carrageenan proceeds to form aggregated “domains”.

In this communication, we report our study on the rheological and thermal properties of κ - and ι -carrageenan bicomponent gel. Fibers were spun from the bicomponent gel by wet-spinning method and their diameters and tensile properties are discussed.

2. Experimental

2.1. Materials

κ -Carrageenan (Gelcarin® GP911 NF) and ι -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 (Rochas & 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 its cation composition by a Perkin-Elmer Optima 5300 inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer, Waltham, MA). Before measurement, samples were dissolved in hot distilled water and acidified. Synthetic standards from High Purity Standards were used to calibrate the results. Fourier transform infrared spectroscopy (FTIR) spectra of the purified carrageenan samples were recorded using the Bruker IFS 66/S FT-IR Spectrometer (Bruker Optics Inc., Billerica, MA) equipped with attenuated total reflectance (ATR) accessory containing diamond crystal. The spectra were scanned at room temperature over the wave number range of 4000 to 400 cm^{-1} , with an accumulation of 400 scans and a resolution of 6 cm^{-1} .

2.4. Wet-Spinning

Spinning dope was prepared by dissolving purified carrageenan samples of different κ/ι ratios in deionized water at 80 °C for at least 1 hour. 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 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 CaCl₂ in 50% (v/v) ethanol. The as-spun fiber was kept in the bath for at least 2 hours 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 κ - ι -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 μ L hermetic stainless steel pans (Perkin-Elmer

Instruments, Bridgeville, PA). At least 50 mg of the κ - ι -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.

2.8. Tensile Test

Fiber tensile tests were performed on a texture analyzer (TAXT2i, Stable Microsystems, Godalming, UK) with film/fiber clamps. The clamp sawteeth were covered with a piece of foam and a piece of paper to avoid slip and fracture of fibers at the clamp sawteeth. Initial fiber length was 20 mm. Crosshead speed was set at 0.2 mm/s for tensile test. The ultimate tensile stress (g) is the maximum stress applied to break a single fiber. The break elongation (%) is defined as the ratio of the elongated length at break to the initial fiber length (20 mm).

2.9. Statistical Evaluation

For the measurements of fiber diameters, at least 30 spots on the fiber were randomly measured and averaged. For tensile tests, 3 fiber samples were examined. Quantitative data were presented as mean \pm standard deviation (SD). One-way ANOVA was conducted. $p < 0.05$ indicated significant difference.

3. Results and discussion

After purification, the κ -carrageenan sample was shown to be much lower in the specific cation (K^+) as compared with the commercial sample (Table 1). The Ca^{2+} content remained about the same, whereas the Na^+ concentration increased. The purified ι -

carrageenan sample has lower K^+ and Ca^{2+} contents than the raw sample. The FTIR-ATR spectra of purified κ - and ι -carrageenan samples are shown in Fig. 1. The spectra show two bands at around $840\text{--}845\text{ cm}^{-1}$ and 930 cm^{-1} , which were assigned to C-O-SO₄ on the C4 of the β -D-galactopyranose unit and C-O of the anhydride group on the α -D-galactopyranose unit, respectively [8]. The spectrum of ι -carrageenan also shows a characteristic band at 805 cm^{-1} , which is assigned to C-O-SO₄ on the C2 of α -D-galactopyranose residue. This sulfate group is absent in κ -carrageenan backbone. The absence of this band at 805 cm^{-1} suggested that the ι -carrageenan content in the κ -carrageenan sample was negligible.

Table 1. Cation contents of the commercial and purified κ - and ι -carrageenan samples, expressed in g/100g.

Cation	κ -carrageenan		ι -carrageenan	
	Raw sample	Purified	Raw sample	Purified
K^+	4.80	1.23	3.67	0.68
Ca^{2+}	2.40	1.07	3.75	2.14
Na^+	0.72	2.30	1.23	3.18

Heat scans of concentrated blend gels of different κ -/ ι - ratios were recorded in Fig. 2. The gel-sol transition of pure κ -carrageenan appears at about $55\text{ }^\circ\text{C}$. When ι -carrageenan was added, a new endotherm at around $70\text{ to }75\text{ }^\circ\text{C}$ becomes apparent, which is attributed to the ι -carrageenan dissociation. The onset and peak temperatures of both κ -carrageenan and ι -carrageenan dissolutions decreased with ι -carrageenan addition. At a fixed ionic strength, the thermal transition temperature of carrageenan gels should be independent of the polymer concentration. However, the K^+ content is lower in ι -carrageenan raw powder and κ -carrageenan sample has less Ca^{2+} (Table 1). The κ -carrageenan gelling is

specific to K^+ , whereas ι -carrageenan requires Ca^{2+} to efficiently mediate the gel network. Therefore when more ι -carrageenan is added, the blended system should have lower K^+ and Ca^{2+} concentration than pure κ -carrageenan and ι -carrageenan gel, respectively.

Thermograms of pure components and their simple addition were compared with that of the κ -/ ι -carrageenan blend gel (κ -/ ι - ratio of 70/30) in Fig. 3. Thermal response of the real blend cannot be reproduced by simple summation of those from pure components. Endotherms of both κ - and ι -carrageenan gel-sol transition shift to higher temperatures. This indicates that phase separation took place in the blend. The phase separation increased the effective concentrations of both polymers and thus their thermal transition temperatures (Cairns, Miles, Morris, & Brownsey, 1987). Even though, the possibility of forming an interpenetrating network, though not complete, could not be ruled out.

Small deformation rheological measurements during the cooling of blend carrageenan dispersions agree well with thermal analysis with respect to the decrease of dissolution temperature upon ι -carrageenan addition and the possibility of phase separation in the blend gel. When more ι -carrageenan was mixed, the temperature range responsible for κ -carrageenan gelation broadened and shifted to lower values (Fig. 4). Due to syneresis, the gelling temperature of κ -carrageenan was lower than its dissolution temperature. As expected, ι -carrageenan experienced no syneresis since the two temperatures coincide. The rheological response of the real mixture (κ -/ ι - ratio of 80/20) could not be reproduced by simple summation of individual curves (Fig. 5). Similar to thermal responses, the gelling temperature of ι -carrageenan shifted from around 60 °C to a higher temperature around 75 °C in the blend. This phenomenon was also observed by using optical rotation experiments (Rochas, Rinaudo, & Landry, 1989), and these authors

suggested the cause was molecular interactions between κ - and ι -carrageenans. However, we otherwise consider this as a confirmation of phase separation that took place in the blend system. The storage modulus responsible for κ -carrageenan gelation shifted very little but broadened. This broadening may result from the overlap of the gelling event of both κ - and ι -carrageenan, which suggested that interpenetrating network might also partially exist, at least at the interface.

Bicomponent fibers were obtained from the κ -/ ι -carrageenan blend dispersions by wet-spinning method. Both as-spun and dried fiber diameter increased with addition of ι -carrageenan (Fig. 6). The increase may be attributed to the relaxation of ι -carrageenan and insufficient κ -carrageenan gel network interrupted by ι -carrageenan. Ultimate tensile stress the bicomponent fibers decreased upon of ι -carrageenan addition, whereas the break elongation increases (Fig. 7). These trends in mechanical properties of bicomponent fibers were quite similar to those of blend gels (Villanueva, Mendoza, Rodriguez, Romero, & Montaña, 2004). The gel strength was gradually weakened with addition of ι -carrageenan, while the deformation showed a slight increase followed by a reduction for high potassium content.

4. Conclusion

In conclusion, κ - and ι -carrageenan interaction in blend gels may involve incomplete phase separation and partial interpenetrating network. Addition of ι -carrageenan gradually increased the as-spun and dried fiber diameter. Addition of ι -carrageenan increased compliance but overall the blend fibers are still hard and brittle.

Acknowledgement

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References

- Cairns, P., Miles, M. J., Morris, V. J., & Brownsey, G. J. (1987). X-Ray fibre-diffraction studies of synergistic, binary polysaccharide gels. *Carbohydrate Research*, *160*, 411-423.
- Kolender, A. A., & Matulewicz, M. a. C. (2004). Desulfation of sulfated galactans with chlorotrimethylsilane. Characterization of β -carrageenan by ^1H NMR spectroscopy. *Carbohydrate Research*, *339*(9), 1619-1629.
- Kong, L., & Ziegler, G. R. (2011). Fabrication of κ -carrageenan fibers by wet spinning: discussion of spinning parameters. *Materials*, *4*, 1805-1817.
- Kong, L., & Ziegler, G. R. (2012). Fabrication of pure starch fibers by electrospinning. *Biomacromolecules*, *Submitted*.
- Kong, L., Ziegler, G. R., & Bhosale, R. (2010). Fibers spun from polysaccharides. In R. Ito & Y. Matsuo (Eds.), *Handbook of carbohydrate polymers: development, properties and applications* (pp. 1-43). New York: Nova Science Pub Inc.
- Lindblad Margaretha, S., Sjöberg, J., Albertsson, A.-C., & Hartman, J. (2007). Hydrogels from Polysaccharides for Biomedical Applications *Materials, Chemicals, and Energy from Forest Biomass* (Vol. 954, pp. 153-167): American Chemical Society.
- Morris, E. R., Rees, D. A., & Robinson, G. (1980). Cation-specific aggregation of carrageenan helices: Domain model of polymer gel structure. *Journal of Molecular Biology*, *138*(2), 349-362.
- Navarro, D. A., Flores, M. L., & Stortz, C. A. (2007). Microwave-assisted desulfation of sulfated polysaccharides. *Carbohydrate Polymers*, *69*(4), 742-747.
- Piculell, L. (1995). Gelling Carrageenans. In A. M. Stephen (Ed.), *Food polysaccharides and their applications* (pp. 205-244). New York: Marcel Dekker.
- Rochas, C., & Rinaudo, M. (1980). Activity coefficients of counterions and conformation in kappa-carrageenan systems. *Biopolymers*, *19*(9), 1675-1687.
- Rochas, C., & Rinaudo, M. (1984). Mechanism of gel formation in κ -carrageenan. *Biopolymers*, *23*(4), 735-745.
- Rochas, C., Rinaudo, M., & Landry, S. (1989). Relation between the molecular structure and mechanical properties of carrageenan gels. *Carbohydrate Polymers*, *10*(2), 115-127.
- van de Velde, F. (2008). Structure and function of hybrid carrageenans. *Food Hydrocolloids*, *22*(5), 727-734.
- Villanueva, R. D., Mendoza, W. G., Rodriguez, M. R. C., Romero, J. B., & Montaña, M. N. E. (2004). Structure and functional performance of gigartinacean kappa-iota

hybrid carrageenan and solieriacean kappa-iota carrageenan blends. *Food Hydrocolloids*, 18(2), 283-292.

Figure captions

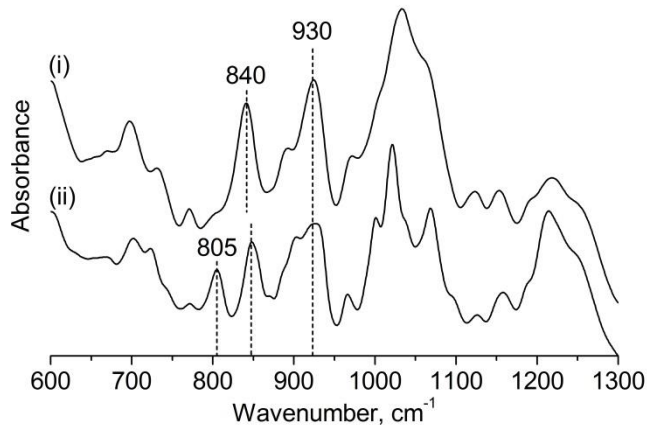


Fig. 1. FTIR spectra of (i) κ -carrageenan and (ii) ι -carrageenan samples.

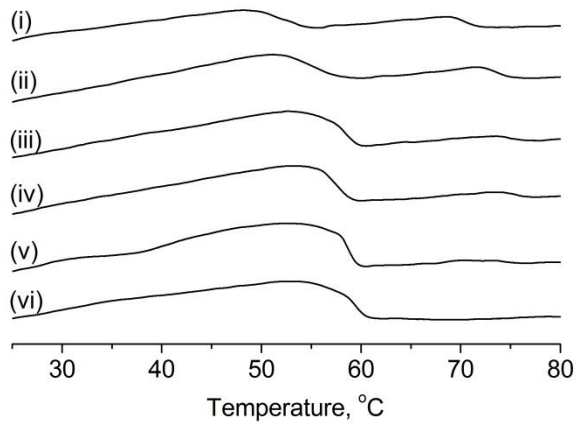


Fig. 2. Thermograms of heating blend gels with different κ -/ ι - ratios (i) 50/50, (ii) 60/40, (iii) 70/30, (iv) 80/20, (v) 90/10, and (vi) 100/0.

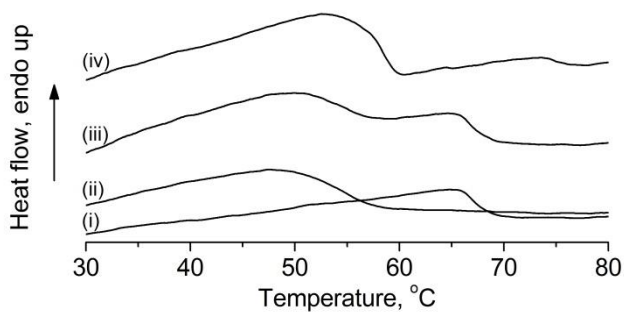


Fig. 3. Thermograms of heating (i) 1.8% (w/v) ι -carrageenan, (ii) 4.2% (w/v) κ -carrageenan, (iii) simple addition of (i) and (ii), and (iv) real blend gels of 1.8% (w/v) ι -carrageenan and 4.2% (w/v) κ -carrageenan.

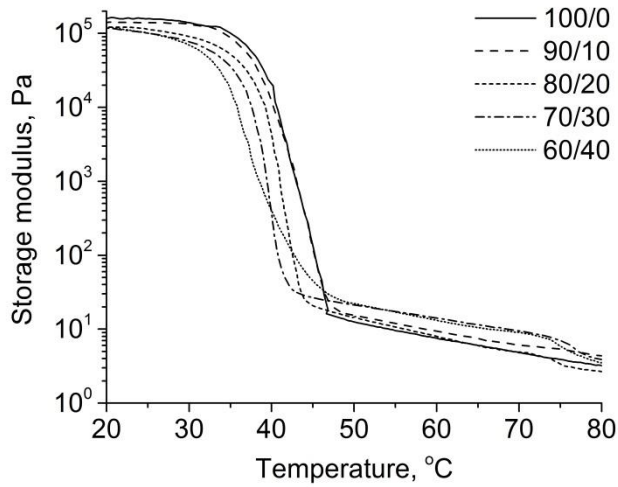


Fig. 4. Small deformation rheological response (storage modulus) during cooling of blend dispersions with different κ - ι - ratios.

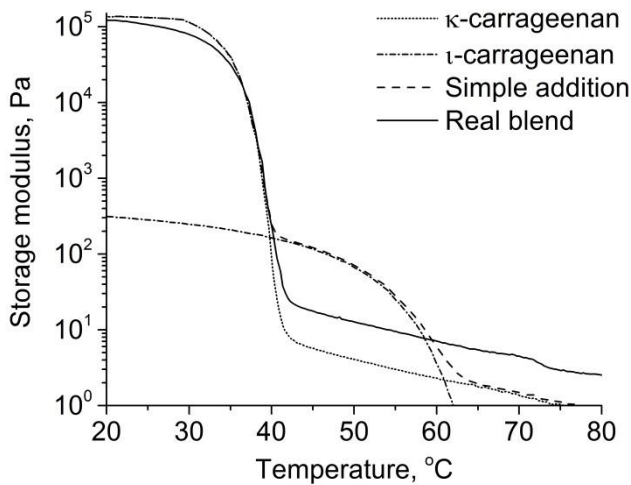


Fig. 5. Small deformation rheological response (storage modulus) of 1.2% (w/v) ι -carrageenan, 4.8% (w/v) κ -carrageenan, simple addition of pure components, and real blend dispersion of 1.2% (w/v) ι -carrageenan and 4.8% (w/v) κ -carrageenan.

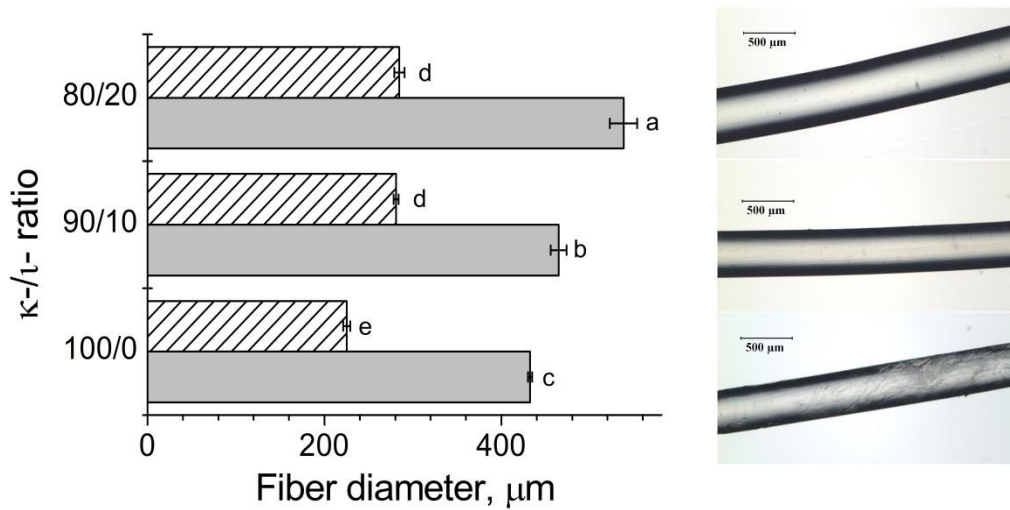


Fig. 6. As-spun (filled column) and dried (patterned column) fiber diameter and optical micrographs as a function of κ - ι ratios ($a > b > c > d > e$, $p < 0.05$).

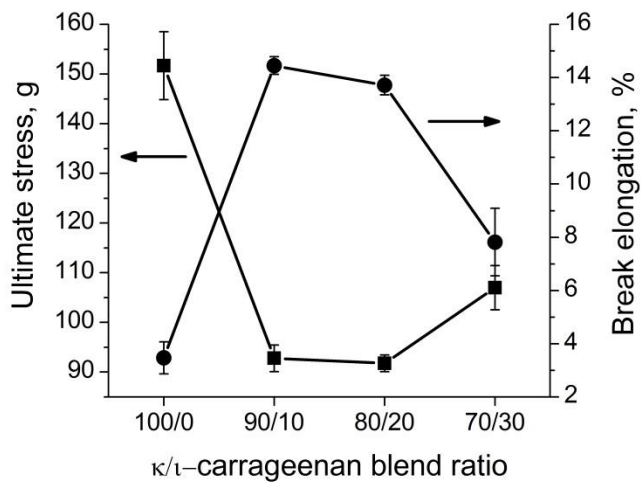


Fig. 7. Ultimate tensile stress (filled square) and break elongation (filled circle) of the dry fibers as a function of κ - ι ratios.