

RESEARCH ARTICLE

Initial Properties Identification of Refined- and Semi Refined-Carrageenans as Raw Materials for Biodegradable Plastic Production

Bakti Berlyanto Sedayu^{1*}, Putri Wullandari¹, Arif Rahman Hakim¹, and Dina Fransiska²

¹ Indonesian Research Institute for Fisheries Postharvest Mechanization, Ministry of Marine Affairs and Fisheries, Jl. Imogiri Barat Km. 11,5, Bantul, Yogyakarta, Indonesia 55781

² Research Center for Marine and Fisheries Product Processing and Biotechnology, Jl. Petamburan VI, Jakarta, Indonesia 10260

* Corresponding Author:
baktibsedayu@gmail.com,
bakti.sedayu@kkp.go.id

Received: 17 March 2021

Accepted: 04 July 2021

Published: 9 August 2021

©Squalen Bulletin of Marine and Fisheries Postharvest and Biotechnology, 2021. Accreditation Number: 148/M/KPT/2020. ISSN: 2089-5690, e-ISSN: 2406-9272. doi: 10.15578/squalen.533

Abstract

Powdered refined- and semi-refined carrageenans (RC and SRC) have been characterized as alternative raw materials for industrial bioplastic production. Several basic parameters, i.e., the melting temperature, crystallinity, chemical structure (FTIR), and tensile properties, were observed. The melting temperature of RC was slightly higher than that of SRC, i.e., 176 °C and 172 °C, respectively. These temperatures were corresponded to their crystallinity degree (performed by X-ray diffraction). Nonetheless, the SRC demonstrated an overall higher thermal stability during heating. RC produced a clear transparent film. Meanwhile, SRC was yellowish and less transparent. The overall mechanical properties showed that RC produced more flexible film than SRC. However, both materials showed relatively equal tensile strength. In general, RC and SRC could be potentially used for biodegradable film production with different applications. RC was suitable for a flexible and clear plastic film, whereas SRC was suitable for rigid plastic film applications.

Keywords: refined-carrageenan, semi-refined carrageenan, thermal, mechanical, properties

Introduction

Plastic waste pollution has raised global concerns, particularly when a ubiquitous presence of microplastic in nature evidently threaten wildlife and human beings (Germanov et al., 2019). Microplastic occurrence is a critical issue since Indonesia has been listed as the world's second-largest plastic waste emitter to the ocean (Jambeck et al., 2015). These tiny plastic fragments also have been identified in some Indonesian fish digestive tracts and in consumer's food (Germanov et al., 2019; Kim, Lee, Kim, & Kim, 2018).

The Indonesian government has implemented plastic banning to reduce plastic pollution. However, explorations on alternative materials for plastic production are pivotal to suppress the environmental damage caused by synthetic plastic usage. Various biomass, such as corn, cassava, sugarcane, celluloses, etc., has been studied for biodegradable plastic production (Cerqueira, Souza, Teixeira, & Vicente, 2012; Perez, Felix, Romero, & Guerrero, 2016; Prachayawarakorn & Pomdage, 2014) and resulted in positive outcomes. For example, polylactic-acid (PLA),

starch, polyhydroxyalkanoates (PHAs), and biopolypropylene are now easily found in the market. These biomaterials have been produced commercially with significant annual growth rates (European Bioplastics, 2020). However, to meet the rising demand for bioplastic in the future, we may need more sustainable raw materials. These materials should be abundant in nature and their utilization should not compete with human consumption, such as farmed seaweeds (Rajendran, Puppala, Sneha Raj, Ruth Angeeleena, & Rajam, 2012).

Red seaweed (*Rhodophyceae*) is the source of carrageenan, a hydrogel polysaccharide that can be well transformed into a plastic film (Blanco-Pascual, Montero, & Gómez-Guillén, 2014; Paula et al., 2015). Carrageenan consists of a linear backbone of D-galactose residues linked by alternating α -1,3 and β -1,4 linkages (Barbeyron, Michel, Potin, Henrissat, & Kloareg, 2000).

Indonesia is the biggest producer of red seaweed globally, i.e., *Kappaphycus alvarezii* (previously *Eucheuma cottonii*).

Therefore, carrageenan-based bioplastic would be potentially developed in the country (Sedayu, Cran, & Bigger, 2019). Refined and semi-refined carrageenans (RC and SRC) from *K. alvarezii* have been widely used for applications in food, pharmaceutical, and cosmetic industries (Dewi, Darmanto, & Ambariyanto, 2012; Tye, 1989). The production methods of RC and SRC are primarily similar. During RC production, the carrageenan is solubilized to remove solids materials. Meanwhile, the SRC production retains the carrageenan within the algal cellulosic structural matrix. Hence, the SRC still contains up to 15% of seaweed's residual cellulose (Younes et al., 2018). The short extraction process of carrageenan is beneficial in reducing the production costs for commercial purposes.

The development of RC and SRC for biodegradable plastic materials is still currently in the early stage. They have been mainly manufactured at a laboratory/small production scale using the solvent casting method (Aji, Praseptianga, Rochima, Joni, & Panatarani, 2018; Ramu Ganesan, Shanmugam, & Bhat, 2018; Sedayu, Cran, & Bigger, 2020). Meanwhile, to meet industrial needs, carrageenan-based plastic should undergo a continuous production system such as the extrusion method (Kannadhasan & Muthukumarappan, 2010; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Standau, Castellón, Delavoie, Bonten, & Altstädt, 2019). Using extrusion techniques for carrageenan-based bioplastics production can leverage their production and create opportunities for commercial purposes. Previous studies of the extrusion method for carrageenan substances are very limited. Most of the investigations were related to functional food development and pharmaceutical (Thommes, Blaschek, & Kleinebudde, 2007; Oliveira et al., 2019). Nonetheless, to the best of our knowledge, the extrusion has not been applied in carrageenan-based bioplastic production.

Parameters such as thermal behavior, plasticizer incorporation, and machine setting must be considered when using an extrusion method to obtain an optimum process (Sudhakar, Magesh Peter, & Dharani, 2020). Thus, exploration of the raw material's basic characteristics such as melting point, thermal degradation temperature, and chemical properties is necessary. These data are required to find the optimum condition for the carrageenan-based bioplastic production using a polymer extrusion machine. In this investigation, powdered RC and SRC as biodegradable plastic raw materials were observed for their thermal properties, crystallinity, and chemical structures. The specific properties of SC and SRC may be fundamental to evaluate further applications, including processing method in a commercial production system.

Materials and Methods

RC and SRC powders form were purchased respectively from Sigma Aldrich (Australia) and W-Hydrocolloids Inc. (Philippines). Detailed specifications of these materials have been described in detail in the previous study (Sedayu et al., 2020).

Thermal Properties

The glass transition (T_g) and/or melting temperature (T_m) of the sample powders were observed by differential scanning calorimetry (DSC) analysis using a Mettler Toledo DSC-1 thermal analyzer. Meanwhile, their thermal decompositions were observed by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC-1 thermal analyzer (Mettler-Toledo, Switzerland). Both analyses were performed under a nitrogen atmosphere. For the DSC testing, 4 mg of the powder sample was mounted and hermetically sealed in an aluminum pan with lid. The sample was then tested at heating temperatures from 40 to 280 °C ramping up at a 10 °C/min. In the TGA analysis, 8 mg sample was placed into a silica pan and tested at 30 to 400 °C with 10 °C/min interval.

Degree of Crystallinity

The crystalline molecular formation from each powder specimen was observed using a Rigaku Miniflex 600 diffractometer over the range of $2\theta = 5^\circ$ to 60° ramping at 0.05 °/s. The relative crystallinity degree was calculated using the equation below (Köksel et al., 1993)

$$X_c = \frac{A_c}{A_t} = \frac{A_c}{A_c + A_a} \dots\dots\dots (\text{Eq. 1})$$

whereas A_c is the crystalline peak area, A_a is the amorphous area, and A_t is the total area.

Structural Properties

Infrared spectra of the specimen powders were recorded using an FT-IR spectrometer (PerkinElmer, Inc., USA) equipped with a horizontal attenuated total reflectance (ATR). An average of the 16-scan spectral transmittance at 4 cm^{-1} resolution was measured over the range of 4000 - 600 cm^{-1} . A Perkin-Elmer Spectrum 10™ Software was used for the spectra data processing.

Appearance and Mechanical Properties

Prior to analysis, the RC and SRC powders were transformed into thin films through a solvent casting method (Sedayu, Cran, and Bigger, 2018).

Approximately 40% glycerol (w/w of SRC) was added into formulation as plasticizer. The films were cut into a rectangular shape of 45 mm x 12.5 mm for opacity measurement and were prepared in triplicate. Each sample was mounted directly into the test cell of the spectrophotometer and assessed at 550 nm using a Biochrom Libra S12 spectrophotometer (Gómez-Estaca et al., 2009). For the mechanical properties testing, at least five film strips (120 x 20 mm) with a thickness range of 0.05 – 0.07 mm were tested using an Instron Testing Machine Model 4301. A 5 kN load-cell was used for measurement at an initial grid separation of 2.5 cm following the ASTM Method D 882-12 (ASTM, 2012). Before testing, the film strips were equilibrated in a desiccator with 58% RH condition using $Mg(NO_3)_2$ saturated solution (Sigma-Aldrich, Australia). The equilibration was conducted at RT for 24 h.

The tensile strength (TS) represents a peak/maximum load against the cross-sectional area of the film. The elongation at break (EAB) was calculated as a percentage of change in filmstrip's length during stretching until torn apart. Young's Modulus (E-modulus) represents the stiffness of the film samples, and it is calculated as the ratio of stress to strain.

Data Analysis

All sample analyses were performed in triplicate and the collected data were presented as mean.

Results and Discussion

X-Ray Diffraction

X-ray diffraction (XRD) was performed to observe the crystalline nature of both carrageenans samples. This technique was also used to investigate the impurities elements in SRC powder in correlation with the SRC crystalline structure. The X-ray diffractograms of the RC and SRC powders are shown in Figure 1. A broad XRD band of SRC at $2\theta = 10^\circ - 28^\circ$ was

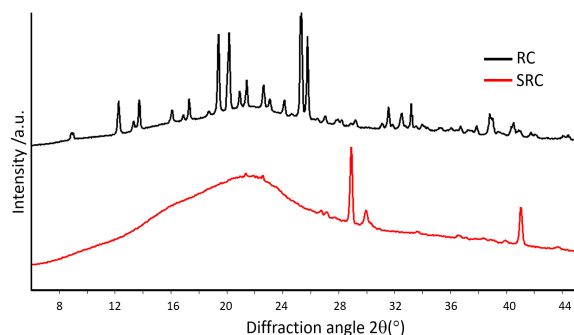


Figure 1. X-ray diffractograms of refined-carrageenan and semi-refined carrageenan powders.

attributed to the inherent SRC semicrystalline molecular structure (Liew, Loh, Ahmad, Lim, & Wan Daud, 2017). The similar peak was also observed in RC particles, however it was not as prominent as shown in the SRC. Compared to that of SRC, the RC diffractogram presented more dominant sharp diffraction peaks along the curve contributed by its higher crystalline molecular structure. A calculation based on the diffraction peaks areas (see Eq.1) showed that the crystallinity degree of RC was about four times higher than that of the SRC's.

A low crystalline region in SRC particles can be explained by low hydrogen bonding in the inter-molecular structure of the material. Moreover, this internal structure may be disrupted by the impurity elements. This result is supported by the low intensity of the hydroxyl groups observed in the SRC FTIR spectra, as shown in Figure 4 (Doh, Dunno, & Whiteside, 2020). Furthermore, the low intensity of the 3,6-anhydrogalactose groups in SRC was also contributed to its low crystalline structural formation. This finding is in agreement with those of other studies on the crystallinity of seaweed-based composite reported by Doh et al. (2020). This result is also consistent with the previous study on RC dan SRC films produced through a solvent casting (Sedayu et al., 2020). In contrast, the inherent impurities in SRC such as cellulose and minerals can be present in amorphous and crystalline regions. This crystalline formation interfere with the inter and extra molecular hydrogen bonding in carrageenan structure. Also, the height of crystalline peaks for SRC at $2\theta = 29^\circ$ and $2\theta = 41^\circ$ representing KCl (Jumaidin, Sapuan, Jawaid, Ishak, & Sahari, 2017) were disappeared/reduced. This explained certain minerals that remained in SRC were removed during the processing to neat carrageenan. Certain minerals attached in seaweed thallus were removed throughout the carrageenan processing during alkaline extraction, water extraction, and filtration.

Thermal Behaviour

The DSC thermograms of (a) SRC and (b) RC powders are presented in Figure 2. The remarkable endothermic peaks occurred at a range of 160 - 180 °C, representing a glass transition (T_g) of the sample powders. This data indicated a changing of the molecular crystalline structures of SRC and RC from brittle to rubbery state (Ili Balqis, Nor Khaizura, Russly, & Nur Hanani, 2017). The glass transition of RC occurred at a higher temperature at ca. 178 °C compared to SRC at ca. 167 °C. In the case of RC and SRC, their glass transition temperature is also associated with the melting temperature (T_m) of the particles. The T_g of a material is correlated to the crystalline formation within its chemical structure. The

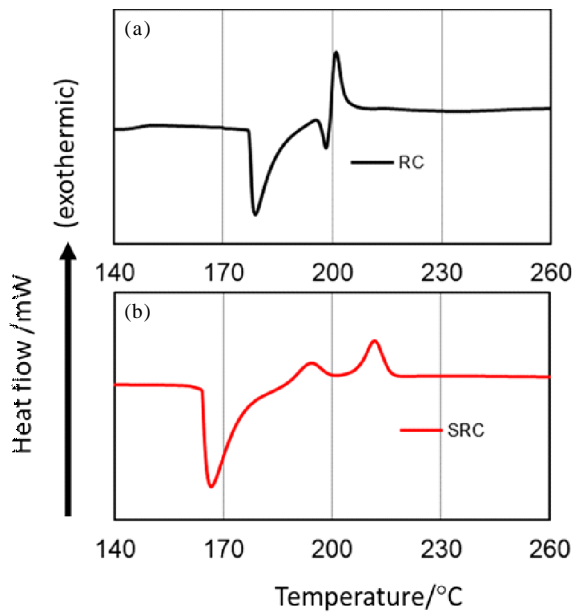


Figure 2. Differential scanning calorimetry traces of (a) refined-carrageenan and (b) semi-refined carrageenan powders.

DSC thermograms showed that the glass transition phases for those two samples correspond with their level of crystallinity. To sum up, the higher the crystallinity of the particles, the higher its glass transition. This result is similar to other findings on chitosan (Prateepchanachai, Thakhiew, Devahastin, & Soponronnarit, 2017) and SRC films (Ganesan, Munisamy, & Bhat, 2018). Meanwhile, synthetic polymers, i.e., polyethylene terephthalate (PET), polystyrene (PS), nylon, and polyvinyl chloride (PVC)

have glass transitions at 190 - 500 °C (Ghanbarzadeh, Almasi, & Entezami, 2010). RC and SRC particles exhibited generally lower T_g than the synthetic polymers. These results indicated that RC and SRC have less rigidity and higher mobility of intermolecular chains during heating than their counterparts.

In biodegradable plastic production using a continuous extrusion process, the glass transition and melting temperatures of the polymer are critical parameters. These variables are required to obtain an optimum setting condition of the extruder, as well as an optimum processing condition. Those parameters are also crucial in polymer blending applications to find the right filler candidate to be mixed with the main polymer. Some polymers showing relatively similar melting temperatures with those of RC and SRC. For example, PLA (165 °C), PHA (100-175 °C), polypropylene (PP) (176 °C), and poly-3-hydroxybutyrate (PHB) (180 °C) (Alaerts, Augustinus, & Van Acker, 2018; Maraveas, 2020).

The exothermic peaks at high temperatures following the glass transition or melting phase of the samples were attributed to their thermal decompositions. The decompositions were corroborated by the mass losses from each powder specimen at similar heating temperatures ranges, as shown in Figure 3. Interestingly, RC's curve showed only a prominent exothermic peak at c.a. 202 °C. Whereas, the SRC's showed two exothermic peaks at 195 °C and 215 °C. The broad range of the SRC thermal decompositions might be contributed by the impurities. These contaminations might have interfered the thermal decompositions of the carrageenan molecules. Some impurity elements were degraded earlier or close to the carrageenan decomposition temperature, such as glucose (Kang & Zhang, 2020; Quan, Gao, & Song, 2016). Meanwhile, others were decomposed at a higher temperature such as xylose, cellulose, and inorganic materials (ICF, 2011; Quan et al., 2016). These results were also confirmed by the TGA and dTGA analyses depicted in Figure 3.

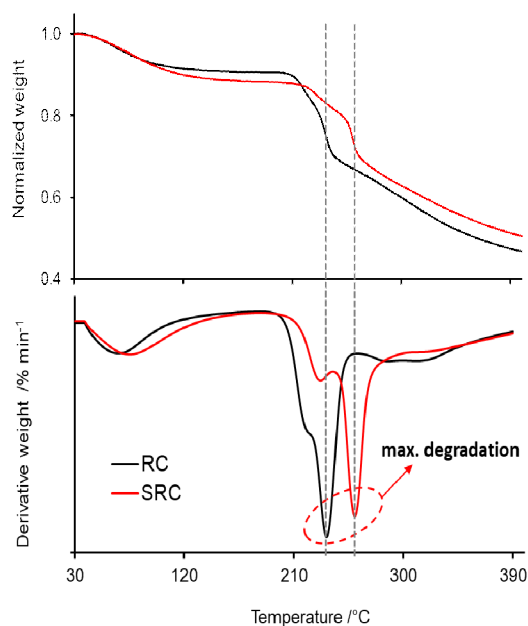


Figure 3. Thermogravimetric analysis (TGA) and dTGA of refined-carrageenan and semi-refined carrageenan powders.

According to the TGA thermograms presented in Figure 3, both RC and SRC powders exhibited a relatively similar pattern. These patterns are also typical with thermal decompositions observed in marine algae *Gigartina skottsbergii*, *Myriogramme manginii*, and *Plocamium cartilagineum* (Kebelmann, Hornung, Karsten, & Griffiths, 2013). These algae demonstrated three major stages of thermal decompositions. At the first stage of decomposition below 210 °C, dehydration took place and light volatile compounds were released from the particles (Yadav & Chiu, 2019). It was followed later by the second decomposition stage at ca. 210 - 270 °C. At this temperature, degradation of heavy volatile compounds, hemicellulose, carrageenan

and cellulose (at initial phase) mainly occur (Yadav & Chiu, 2019). Furthermore, at ca. 270 - 400 °C heating temperature, degradation of lignin and cellulose had taken place in this last stage (Jumaidin et al., 2017).

At the initial stage of decomposition, the degradation rate of SRC was found higher than that of RC's. The mass loss after a 200 °C heating for RC and SRC were respectively 10.18% and 12.99%. This might be caused by the higher contents of water and residual volatile materials, i.e. organohalogens in SRC than those in RC (Mtolera et al., 1996). Such compounds were more susceptible to evaporate during the first stage of decomposition. At the second stage, SRC interestingly showed higher thermal stability with a lower mass loss than RC. After heating to 275 °C, the mass losses of RC and SRC were 35.23% and 32.41%, respectively. At a 400 °C heating temperature, the mass losses were 50.65% and 46.89%. The higher thermal stability of SRC than that of RC was also indicated from the maximum degradation peaks in the dTGA curves (see Figure 3). The maximum degradation temperature during the second stage of decomposition of SRC (261 °C) was higher than the RC's (237 °C). Higher thermal stability of the SRC might be contributed by some residual celluloses and other inorganic materials. The latter may act as a heat retardant delaying thermal degradation of the particles (Zhang et al., 2014).

From the TGA and DSC thermographs, the optimum conditions for thermal processing of RC and SRC by extrusion were between 160-180 °C. In accordance to their melting point, the thermal processing may not be processed over 200 °C as the carrageenan will be degraded. However, during the extrusion of bioplastic in a continuous production system, incorporating additives or any other blends is not unusual. The formulation used in bioplastic production will interfere with the melting and decomposition temperatures of the RC/SRC formulations.

Structural Properties

The ATR-FTIR spectra were observed to identify any distinguish functional groups between the two carrageenan samples. As presented in Figure 4, the spectra for RC and SRC powders look identical. Nonetheless, there were still few differences identified, particularly on the intensity of certain peaks of their functional groups.

The broad stretching band of the hydroxyl groups was found higher in RC than in SRC between 3020 - 3650 cm^{-1} . This may explain the higher crystallinity of the RC sample described previously in Figure 1. A high amount of hydroxyl groups in the RC intermolecular structure imparts its strong molecular packing and crystallinity through the hydrogen bonds (Liu et al.,

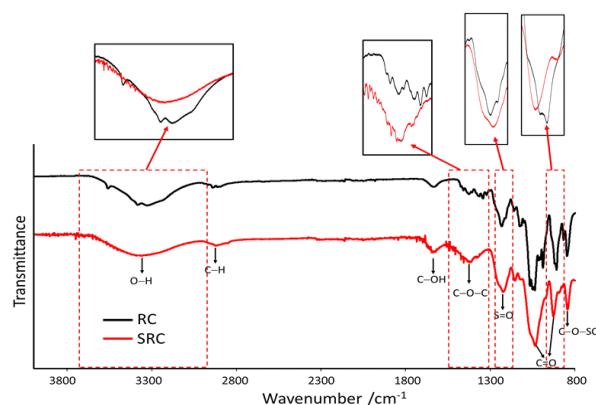


Figure 4. FTIR spectra of refined-carrageenan and semi-refined carrageenan powders.

2020). On the other hand, intensity for the stretching band peaked at 1424 cm^{-1} ascribed to the C-O-C asymmetric bonding of cellulose. This stretching was found higher in SRC than the RC's, and this may depict the residual cellulose presence in SRC powder.

Furthermore, SRC showed higher intensity of the S=O groups of sulfate ester peaked at 1220 cm^{-1} stretching vibration than RC. On the other hand, it oppositely showed a low stretching band of C-O-C of 3,6-anhydrous-D-galactose peaked at 927 cm^{-1} . These results may be caused by the desulfation degree that is found to be high during the RC production (Ganesan et al., 2018). The alkaline treatment during the carrageenan production increases the amounts of 3,6-anhydrogalactose while reduces the sulfate contents of the material. This change in carrageenan's molecular structure is imparting an increase of carrageenan's gel strength (Anisuzzaman, Bono, Samiran, Ariffin, & Farm, 2013). This desulfation may also contribute to the increasing crystallinity degree in the polymer chains of carrageenan (Doh et al., 2020). A similar result was also observed during the purification of ι-carrageenan whereby the purified carrageenan showed a higher 3,6-anhydrogalactose than crude carrageenan before purification (Ghani, Othaman, Ahmad, Anuar, & Hassan (2019).

Optical and Mechanical Properties

Optical and mechanical properties are considered as fundamental parameters for common packaging materials. They are required to preserve the quality of the products inside the packaging and to protect the products during transportation and storage. Additionally, they must also be able to meet the consumer's preferences.

Due to residual elements such as celluloses, uronic acids, and cations (Aldalbahi, 2012), the SRC film was translucent with moderately opaque and yellowish color.

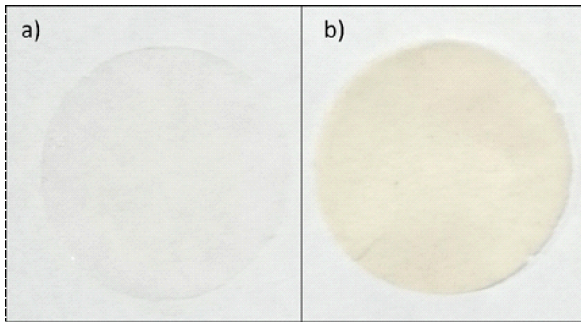


Figure 5. The visual appearance of (a) refined carrageenan and (b) semi-refined carrageenan films.

On the other hand, the RC produced a clear and transparent film (Figure 5). These results corresponded to the opacities of RC (1.12) and SRC films (12.45) as indicated by spectrophotometer testing at 550 nm. The appearance of the films is an important factor for determining a suitable application of their production. In the case of food packaging application, the clear transparent film is more favorable than its counterpart in regards to consumer preferences. However, there are many commercial applications using an opaque or colored film to protect the products inside the packaging from UV light.

Compared to the RC film, the SRC's showed an overall stiffer texture or less stretchability. This was indicated by the lower elongation at break (EAB) and higher E-Modulus values of SRC film than those of RC's. The EAB and E-Modulus of RC film were 17.74% and 305 MPa, while those of SRC were 12.23% and 634 MPa (Figure 6). Elongation or stretchability is most of the time an essential characteristic in film selection. The film must be able to dissipate and absorb external force or mechanical shock, in particular for packaging applications.

The stiff texture of SRC can be attributed to the presence of impurities elements in the film. These elements filled and interrupted the hydrogen bonding

within the carrageenan molecular structure or between carrageenan and plasticizer within the matrix. This results also suggested that SRC contained fewer moieties of the polymer chains than RC. A similar phenomenon was observed in other biopolymers, i.e., PLA, starch, or agar containing solid particulates like minerals, cellulose, metals, or clays (George, Sabapathi, & Siddaramaiah, 2015; Oun & Rhim, 2017; Rhim, 2011). These results were also supported by the low intensity of hydroxyl groups in SRC's spectra shown in Figure 4. However, the tensile strength of SRC film almost similar to the RC's of around 21 - 23 MPa. Regarding these results, the RC film may be suitable for clear and flexible products, i.e., food wrap, plastic bag, or lid cover. While the SRC is appropriate for rigid plastic applications like food containers, cups or bowls, and the like.

The tensile properties of the RC and SRC films are comparable with those of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyvinylidene chloride (PVDV). These plastics exhibited TS values of 8.2 - 31.4 MPa, 22-31 MPa, and 19.3 - 34.5 MPa, respectively (Farhan and Hani, 2017). These results indicated the potential applications of SRC/RC to replace synthetic plastic materials, particularly for food packaging and other applications.

Conclusion

The basic properties of refined- and semi-refined-carrageenan powders were analyzed to obtain fundamental information for the production process towards commercial applications. The particulate impurities in SRC imparted little differences in the thermal properties and chemical structure compared to those of RC. However, some prominent differences were observed in the mechanical and optical properties. SRC produced a more rigid, brittle texture and more opaque film than RC. These results suggested that the SRC is favorable to be implemented for a rigid and

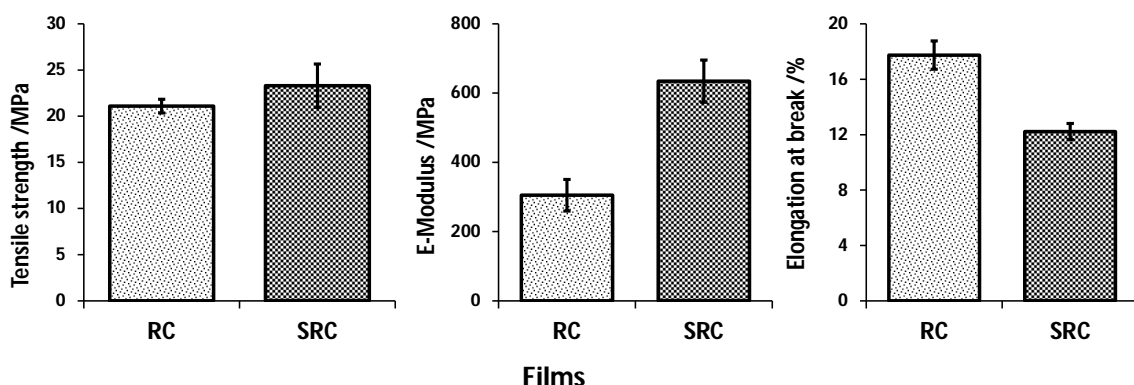


Figure 6. Mechanical properties of refined-carrageenan and semi-refined carrageenan films.

non-transparent bioplastic application. Whereas, the RC can be used for flexible and transparent plastic products. For further investigation, formulation of additives or fillers, and the scale-up production of carrageenan-based bioplastic using extrusion processing should be performed.

Acknowledgments

This project was supported by The Australian Awards Scholarships (AAS), Victoria University of Melbourne, and The Ministry of Marine Affairs and Fisheries - Republic Indonesia.

References

- Aji, A. I., Praseptianga, D., Rochima, E., Joni, I. M., & Panatarani, C. (2018). Optical transparency and mechanical properties of semi-refined iota carrageenan film reinforced with SiO₂ as food packaging material. *AIP Conference Proceedings*, 1927(1), 030039. doi: 10.1063/1.5021232
- Alaerts, L., Augustinus, M., & Van Acker, K. (2018). Impact of bio-based plastics on current recycling of plastics. *Sustainability*, 10(5), 1487.
- Aldabahi, A. (2012). Nano-composite materials from carrageenan, conducting polymers and carbon nanotubes. Doctor of Philosophy thesis, School of Chemistry, University of Wollongong, 2012. <https://ro.uow.edu.au/theses/3753>
- Anisuzzaman, S. M., Bono, A., Samiran, S., Ariffin, B., & Farm, Y. Y. (2013). Influence of potassium hydroxide concentration on the carrageenan functional group composition. In R. Pogaku, A. Bono, & C. Chu (Eds.), *Developments in Sustainable Chemical and Bioprocess Technology* (pp. 355-363). Boston, MA: Springer US.
- ASTM. (2012). Standard test method for tensile properties of thin plastic sheeting (Vol. D882-12). West Conshohocken, PA: ASTM International.
- Barbeyron, T., Michel, G., Potin, P., Henrissat, B., & Kloreg, B. (2000). ι -Carrageenases constitute a novel family of glycoside hydrolases, unrelated to that of κ -Carrageenases. *Journal of Biological Chemistry*, 275(45), 35499-35505. doi: 10.1074/jbc.M003404200
- Blanco-Pascual, N., Montero, M. P., & Gómez-Guillén, M. C. (2014). Antioxidant film development from unrefined extracts of brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum*. *Food Hydrocolloids*, 37, 100-110. doi: 10.1016/j.foodhyd.2013.10.021
- Cerqueira, M. A., Souza, B. W. S., Teixeira, J. A., & Vicente, A. A. (2012). Effect of glycerol and corn oil on physicochemical properties of polysaccharide films – A comparative study. *Food Hydrocolloids*, 27(1), 175-184. doi: 10.1016/j.foodhyd.2011.07.007
- Dewi, E. N., Darmanto, Y. S., & Ambariyanto. (2012). Characterization and quality of semi refined carrageenan (SRC) products from different coastal waters based on fourier transform infrared technique. *Journal of Coastal Development*, 16(1), 25-31.
- Doh, H., Dunno, K. D., & Whiteside, W. S. (2020). Preparation of novel seaweed nanocomposite film from brown seaweeds *Laminaria japonica* and *Sargassum natans*. *Food Hydrocolloids*, 105, 105744. doi: 10.1016/j.foodhyd.2020.105744
- European Bioplastics (2020). Bioplastics market data. <https://www.european-bioplastics.org/market/Cited on 13/03/2021>.
- Farhan, A., & Hani, N. M. (2017). Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol. *Food Hydrocolloids*, 64, 48-58. doi:10.1016/j.foodhyd.2016.10.034
- Ganesan, A. R., Munisamy, S., & Bhat, R. (2018). Effect of potassium hydroxide on rheological and thermo-mechanical properties of semi-refined carrageenan (SRC) films. *Food Bioscience*, 26, 104-112. doi: 10.1016/j.fbio.2018.10.003
- Germanov, E. S., Marshall, A. D., Hendrawan, I. G., Admiraal, R., Rohner, C. A., Argeswara, J., Loneragan, N. R. (2019). Microplastics on the menu: Plastics pollute Indonesian manta ray and whale shark feeding grounds. *Frontiers in Marine Science*, 6(679). doi: 10.3389/fmars.2019.00679
- Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. (2010). Physical properties of edible modified starch/carboxymethyl cellulose films. *Innovative Food Science & Emerging Technologies*, 11(4), 697-702. doi: 10.1016/j.ifset.2010.06.001
- Ghani, N. A. A., Othaman, R., Ahmad, A., Anuar, F. H., & Hassan, N. H. (2019). Impact of purification on iota carrageenan as solid polymer electrolyte. *Arabian Journal of Chemistry*, 12(3), 370-376. doi: 10.1016/j.arabj.2018.06.008
- Gómez-Estaca, J., Giménez, B., Montero, P., & Gómez-Guillén, M. C. (2009). Incorporation of antioxidant borage extract into edible films based on sole skin gelatin or a commercial fish gelatin. *Journal of Food Engineering*, 92(1), 78-85. doi: 10.1016/j.jfoodeng.2008.10.024
- ICF. (2011). *Carrageenan: Handling/Processing*. Retrieved from <https://www.ams.usda.gov/sites/default/files/media/Carrageenan%20TR%202011.pdf>
- Ili Balqis, A. M., Nor Khaizura, M. A. R., Russly, A. R., & Nur Hanani, Z. A. (2017). Effects of plasticizers on the physicochemical properties of kappa-carrageenan films extracted from *Eucheuma cottonii*. *International Journal of Biological Macromolecules*, 103, 721-732. doi: 10.1016/j.ijbiomac.2017.05.105
- Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., . . . Law, K. L. (2015). Plastic waste inputs from land into the ocean. *Science*, 347(6223), 768. doi: 10.1126/science.1260352
- Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M. R., & Sahari, J. (2017). Characteristics of *Eucheuma cottonii* waste from East Malaysia: physical, thermal and chemical composition. *European Journal of Phycology*, 52(2), 200-207. doi: 10.1080/09670262.2016.1248498
- Kannadhasan, S., & Muthukumarappan, K. (2010). Effect of starch sources on properties of extrudates containing DDGS. *International Journal of Food Properties*, 13(5), 1012-1034. doi: 10.1080/10942910902937416
- Kang, W., & Zhang, Z. (2020). Selective production of acetic acid via catalytic fast pyrolysis of hexoses over potassium salts. *Catalysts*, 10(5), 502.
- Kebelmann, K., Hornung, A., Karsten, U., & Griffiths, G. (2013). Thermo-chemical behaviour and chemical product formation from Polar seaweeds during intermediate pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 104, 131-138. doi: 10.1016/j.jaap.2013.08.012

- Kim, J.-S., Lee, H.-J., Kim, S.-K., & Kim, H.-J. (2018). Global pattern of microplastics (MPs) in commercial food-grade salts: Sea salt as an indicator of seawater MP pollution. *Environmental Science & Technology*, 52(21), 12819-12828. doi: 10.1021/acs.est.8b04180
- Köksel, H., Sahbaz, F., Özboy, O. (1993). Influence of wheat-drying temperatures on the birefringence and X-ray diffraction patterns of wet-harvested wheat starch. *Cereal Chemistry*, 70, 481-483.
- Liew, J. W. Y., Loh, K. S., Ahmad, A., Lim, K. L., & Wan Daud, W. R. (2017). Synthesis and characterization of modified κ -carrageenan for enhanced proton conductivity as polymer electrolyte membrane. *PLoS One*, 12(9), e0185313. doi: 10.1371/journal.pone.0185313
- Liu, X., Wang, X., Xiao, Y., Yang, Q., Guo, X., & Li, C. (2020). H-bonds-assisted molecular order manipulation of nonfullerene acceptors for efficient nonannealed organic solar cells. *Advanced Energy Materials*, 10(8), 1903650. doi: 10.1002/aenm.201903650
- Maraveas, C. (2020). Production of sustainable and biodegradable polymers from agricultural waste. *Polymers*, 12(5), 1127.
- Matzinos, P., Tserki, V., Kontoyiannis, A., & Panayiotou, C. (2002). Processing and characterization of starch/polycaprolactone products. *Polymer Degradation and Stability*, 77(1), 17-24. doi: 10.1016/S0141-3910(02)00072-1
- Mtolera, M. S. P., Collén, J., Pedersén, M., Ekdahl, A., Abrahamsson, K., & Semesí, A. K. (1996). Stress-induced production of volatile halogenated organic compounds in *Eucheuma denticulatum* (Rhodophyta) caused by elevated pH and high light intensities. *European Journal of Phycology*, 31(1), 89-95. doi: 10.1080/09670269600651241
- Oliveira, M.E.A.S, Carvalho, C.W.P, da Silva do Nascimento, M., von Hertwig, A.M., Mellinger Silva, C., Takeiti, C.Y. (2019). Extrusion of λ carrageenan gum: Physical properties and in vitro bifidogenic effect. *Journal of Food Processing Preservation*. 43:e14027. doi: 10.1111/jfpp.14027
- Paula, G. A., Benevides, N. M. B., Cunha, A. P., de Oliveira, A. V., Pinto, A. M. B., Morais, J. P. S., & Azeredo, H. M. C. (2015). Development and characterization of edible films from mixtures of κ -carrageenan, ι -carrageenan, and alginate. *Food Hydrocolloids*, 47, 140-145. doi: 10.1016/j.foodhyd.2015.01.004
- Perez, V., Felix, M., Romero, A., & Guerrero, A. (2016). Characterization of pea protein-based bioplastics processed by injection moulding. *Food and Bioprocess Processing*, 97, 100-108. doi: 10.1016/j.fbp.2015.12.004
- Prachayawarakorn, J., & Pomdage, W. (2014). Effect of carrageenan on properties of biodegradable thermoplastic cassava starch/low-density polyethylene composites reinforced by cotton fibers. *Materials & Design*, 61, 264-269. doi: 10.1016/j.matdes.2014.04.051
- Prateepchanachai, S., Thakhiew, W., Devahastin, S., & Soponronnarit, S. (2017). Mechanical properties improvement of chitosan films via the use of plasticizer, charge modifying agent and film solution homogenization. *Carbohydrate Polymers*, 174, 253-261. doi: 10.1016/j.carbpol.2017.06.069
- Quan, C., Gao, N., & Song, Q. (2016). Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization. *Journal of Analytical and Applied Pyrolysis*, 121, 84-92. doi: 10.1016/j.jaap.2016.07.005
- Rajendran, N., Puppala, S., Sneha Raj, M., Ruth Angeeleena, B., & Rajam, C. (2012). Seaweeds can be a new source for bioplastics. *Journal of Pharmacy Research*, 5(3), 1476-1479.
- Ramu Ganesan, A., Shanmugam, M., & Bhat, R. (2018). Producing novel edible films from semi-refined carrageenan (SRC) and ulvan polysaccharides for potential food applications. *International Journal of Biological Macromolecules*, 112, 1164-1170. doi: 10.1016/j.ijbiomac.2018.02.089
- Sedayu, B. B., Cran, M. J., & Bigger, S. W. (2018). Characterization of semi-refined carrageenan-based film for primary food packaging purposes. *Journal of Polymers and the Environment*, 26(9), 3754-3761. doi: 10.1007/s10924-018-1255-y
- Sedayu, B. B., Cran, M. J., & Bigger, S. W. (2019). A review of property enhancement techniques for carrageenan-based films and coatings. *Carbohydrate Polymers*, 216, 287-302. doi: 10.1016/j.carbpol.2019.04.021
- Sedayu, B. B., Cran, M. J., & Bigger, S. W. (2020). Improving the moisture barrier and mechanical properties of semi refined carrageenan films. *Journal of Applied Polymer Science*, 137(41), 49238. doi: 10.1002/app.49238
- Standau, T., Castellón, S. M., Delavoie, A., Bonten, C., & Altstädt, V. (2019). Effects of chemical modifications on the rheological and the expansion behavior of polylactide (PLA) in foam extrusion. *e-Polymers*, 19(1), 297-304. doi:10.1515/epoly-2019-0030
- Sudhakar, M. P., Magesh Peter, D., & Dharani, G. (2020). Studies on the development and characterization of bioplastic film from the red seaweed (*Kappaphycus alvarezii*). *Environmental Science and Pollution Research*. doi:10.1007/s11356-020-10010-z
- Thommes, M., Blaschek, W., & Kleinebudde, P. (2007). Effect of drying on extruded pellets based on kappa-carrageenan. *European Journal of Pharmaceutical Sciences: Official Journal of the European Federation for Pharmaceutical Sciences*, 31(2), 112-118. doi: 10.1016/j.ejps.2007.02.010
- Tye, R. J. (1989). Industrial and non-food uses for carrageenan. *Carbohydrate Polymers*, 10(4), 259-280. doi: 10.1016/0144-8617(89)90066-0
- Yadav, M., & Chiu, F.-C. (2019). Cellulose nanocrystals reinforced κ -carrageenan based UV resistant transparent bionanocomposite films for sustainable packaging applications. *Carbohydrate Polymers*, 211, 181-194. doi: 10.1016/j.carbpol.2019.01.114
- Younes, M., Aggett, P., Aguilar, F., Crebelli, R., Filipiè, M., Frutos, M. J., . . . Dusemund, B. (2018). Re-evaluation of carrageenan (E 407) and processed *Eucheuma* seaweed (E 407a) as food additives. *EFSA Journal*, 16(4). doi: 10.2903/j.efsa.2018.5238
- Zhang, J., Yue, L., Kong, Q., Liu, Z., Zhou, X., Zhang, C., ... Chen, L. (2014). Sustainable, heat-resistant and flame-retardant cellulose-based composite separator for high-performance lithium ion battery. *Scientific Reports*, 4(1), 3935. doi: 10.1038/srep03935