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Effect of concentration of kappa-carrageenan on the physico-chemical properties of rice starch film

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Abstract

This study aimed to enhance the properties of rice starch (RS) and kappa-carrageenan (KC) edible film. The properties were observed at various RS/KC ratios (0.5 to 2.5 w/v) and glycerol (1% w/v). The highest tensile strength was at the ratio of RC/KC (1:1) of 1.7502 MPa, further addition of RC resulted in a decrease in tensile strength. The best elongation at break was also found in the variable with a RS/KC (1:1) of 39.7%. The highest solubility in RS/KC ratio was 0.5:1 which is 52.727%. The solubility of edible film in water decreased with the addition of rice starch concentration. The fourier transform infrared (FTIR) show the new peak in 3305 cm^{-1} indicate O-H groups, 2935 cm^{-1} (asymmetric stretching vibration peak of C-H), 1023 cm^{-1} (interaction between the film structure and hydroxyl group of plasticizers) and 850 cm^{-1} (ester sulphate group).

1. Introduction

It has been investigated whether edible films made of polysaccharides could replace synthetic materials that are not biodegradable (Cerqueira *et al.*, 2012). Despite not being meant to replace synthetic packaging films, edible films can potentially decrease the use of petroleum-based packaging. There are three materials from plants that are most commonly used in the development of edible films: cellulose, starch and lignin (Vianna *et al.,* 2021). Starch is one of the most promising candidates for edible film production (Liu *et al*., 2016). A biopolymer made of complex polysaccharides called starch is the material of choice for creating edible films. Many studies have been reported about the edible film were made by starch (González and Villanueva, 2011; Żołek-Tryznowska and Kałuża, 2021). The use of starch as raw material for making edible films is based on the abundance of raw materials, good thermoplastic properties and relatively low cost compared to other materials such as proteins and lipids (Żołek-Tryznowska and Kałuża, 2021).

Branched and amorphous amylopectin (poly-α-1,4-D -glucopyranoside), linear and crystalline amylose (poly-α -1,4-D-glucopyranoside), and α-1,6-D-glucopyranoside are among the polysaccharides that make up the hydrophilic granules that makeup starch. Starch-based films are typically combined with other biopolymers to create robust films with improved features since they share properties with synthetic polymers, such as high transparency, odorlessness and tastelessness. Due to its structure and hydrogen bond-induced crystallinity, rice starch is considered a suitable material for biopolymer films (Thakur *et al*., 2016). On the other hand, combining polysaccharides with substances with a high molecular weight has produced great miscibility and interactions with better mechanical properties.

Kappa-Carrageenan is a sulfated polysaccharide extracted from several species of red seaweed (Rhodophyceae) (Aga *et al*., 2021). A linear chain of sulfated galactan hydrocolloid found in carrageenan is water-soluble (Prasetyaningrum *et al*., 2021). Kappa-carrageenan has the chemical structure of 3-linked-β-D-galactose-4-sulfate and 4-linked-6-anhydro-α-galactopyranose. Kappa-Carrageenan is a good material to combine with starch to get better film characteristics. Carrageenan has been employed as a foundation for edible films in several earlier research, such as the one by Thakur *et al*. (2016) and Thakur *et al*. (2017), in which edible films made from a combination of rice starch and iota-carrageenan displayed superior mechanical properties and had better solubility. Lipids like glycerol can be added to increase these qualities

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(Zakaria *et al*., 2018). This study aimed to investigate how interactions at various RS/KC ratios affected the characteristics of the developed film. In order to evaluate the mechanical and physical qualities, this study looked at tensile strength and water solubility. Characterization of the chemical structural behaviors of the composite films was also carried out.

2. Materials and methods

2.1 Materials

The rice starch was purchased from Sigma Aldrich in Darmstadt, Germany (CAS: 9005-25-8). CV. Karaindo, Semarang, Indonesia, offered semi-refined-carrageenan. Furthermore, 98% glycerol under the brand name LOBA chemie Pvt. Ltd., Ajax finechem.

2.2 Edible film preparation

The film was made by mixing rice starch (RS) and kappa-carrageenan (KC) into 100 mL of distilled water with the following ratio of RS/KC: 0.5:1; 1:1, 1.5:1, 2:1; 2.5:1 w/v. Glycerol were each added to the solution as much as 1% w/v, then the solution was heated with a heater with stirring at 200 rpm for 25 mins at a temperature of 70°C. The solution was then poured into the center of a spotless glass plate and allowed to dry for 30 hrs at room temperature. The dried films were taken from the casting surfaces and kept in desiccators at 25°C and relative humidity of 87%. Before the characterization processes, all films were removed from the casting plates and held in the same conditions for 12 hrs.

2.3 Tensile strength and elongation at break analysis

Using a universal testing machine (UTM) (Shimadzu EZ-SX, Kyoto, Japan) and the American Standard Testing and Material (ASTM) D-882-02 technique, tensile strength (TS) and elongation at break (EAB) were assessed. Strips of BEF samples (7×25 mm) were cut, and measurements were taken at a crosshead speed of 2 mm/s with a grip separation of 50 mm.

2.4 Water solubility analysis

Water solubility (WS) was measured according to previously reported method (Prasetyaningrum *et al*., 2021). The films were divided into equal pieces (5 x 5 cm) and were then agitated continuously for 24 hrs at 25°C in 50 mL of distilled water. After filtering, the insoluble films were dried at 110°C. The insoluble dry films were weighed to constant weight is reached. The

$$WS(\%) = ((W0 - Wf)/W0) \times 100 \quad (1)$$

water solubility (WS) of the edible film under test was calculated in this equation:

Where W0 is the film's initial dry matter weight, and Wf is the film's dry weight upon immersion.

2.5 Fourier transform infrared spectroscopy analysis

The structure and operation of RS/KC films were analyzed using Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer PC 1600, Houston, USA). In the 4000-400 cm^{-1} band, the FTIR spectrum was captured. Before the examination, the sample pieces were pulverized in a 1:10 ratio with KBr salt. Afterward, the sample was placed inside the FTIR, where IR absorption was measured for functional group analysis (Prasetyaningrum *et al*., 2021).

3. Results and discussion

3.1 Effect of rice starch and kappa carrageenan ratio on mechanical and water solubility

3.1.1 Mechanical properties

Table 1 and Figure 1 show the link between the ratio of RS/KC and the mechanical characteristics of the resulting edible film. The highest tensile strength is in the variable with a 1:1 RS/KC ratio of 1.7502 MPa, further additions result in a decrease in tensile strength. The best elongation at break was also found in the variable with a 1:1 RS/KC ratio of 39.7%.

Theoretically, a pure kappa-carrageenan film will have a higher tensile strength than a pure starch film. The combination of polysaccharides has an affinity for each other between their functional groups to form intermolecular bonds so as to produce good mechanical properties. Rice starch and kappa-carrageenan when combined in appropriate proportions produce strong intermolecular bonds via -OH or -COOH groups

Table 1. Effect of RS/KC ratio on film mechanical properties.

RS:KC Ratio	Tensile Strength (MPa)	Elongation at break (%)
0.5:1.0	1.268	34.00
1.0:1.0	1.705	39.70
1.5:1.0	1.337	35.30
2.0:1.0	0.746	26.33
2.5:1.0	0.740	13.33

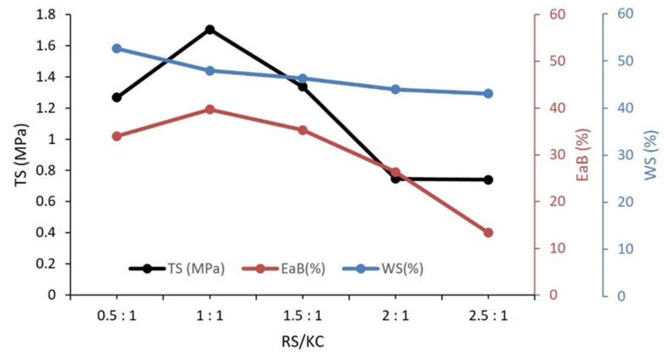

Figure 1. Graph of the effect of the ratio of RS/KC versus tensile strength, elongation at break and water solubility for selecting the best ratio.

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(Sucheta *et al*., 2019). According to Larotonda *et al.* (2016) the tensile strength of edible film starch/kappa-carrageenan will increase with the increase in the ratio of rice starch/kappa-carrageenan. This phenomenon occurs because starch crystals will strengthen the kappa-carrageenan matrix by forming intermolecular bonds through the -OH and -COOH groups. The intermolecular distance between starch and kappa-carrageenan is reduced by this network, which also preserves a comparatively stable form. It increases the density of the network structure and the tensile strength qualities of the film (González and Villanueva, 2011; Żołek-Tryznowska and Kałuża, 2021). However, if the addition of more starch concentration will decrease the tensile strength. The addition of rice starch/kappa-carrageenan with a ratio of more than 1:1, the nature of rice starch will become more dominant in regulating the mechanical properties of the film. This is because the intermolecular bonds of rice starch are more dominant than the intermolecular bonds of rice starch/kappa-carrageenan (Larotonda *et al*., 2016). This will have an effect on lowering the manufactured edible film's tensile strength.

On the other hand, increasing the rice starch/kappa-carrageenan ratio will increase the elongation at break film value. This is because the interaction between starch -kappa carrageenan molecules has a stronger and more elastic bond than the bond between starches (Dick *et al*., 2015). Therefore, the rice starch/kappa-carrageenan ratio up to a ratio of 1:1 will increase the elongation at break value. However, the use of a rice starch/kappa-carrageenan ratio above 1:1 will reduce the elongation at break value.

The results obtained in this study have similar results to previous studies. According to Larotonda *et al*. (2016) that the tensile strength and elongation at break film will increase with the addition of kappa-carrageenan, but will decrease with the addition of starch. Previous studies by Abdillah and Charles (2021) and Thakur *et al*. (2016) also demonstrated that the addition of carrageenan to the starch-based film increased the mechanical properties of the film.

3.1.2 Water solubility

The film sample's resistance to water can be determined by how soluble it is in water. The film will be more quickly damaged when exposed to water the higher the water solubility value. The relationship between the addition of the ratio of rice starch to kappa-carrageenan with the value of water solubility is shown in the Table 2.

Table 2 shows that the solubility of edible film in water reduced when rice starch concentration was added. The RS/KC ratio of 0.5:1 has the highest solubility, which is 52.727%. While the ratio of RS/KC 2.5:1 has the lowest solubility, which is 43.077%.

Table 2. Effect of RS/KC ratio on water solubility film.

RS:KC Ratio	Water Solubility (%)
0.5:1.0	52.727
1.0:1.0	48.000
1.5:1.0	46.364
2.0:1.0	44.000
2.5:1.0	43.077

Solubility is strongly influenced by the presence of amylose content. Amylose which is linearly arranged has strong intermolecular bonds in starch granules. This results in reduced -OH bonds that can interact with water. This causes a decrease in the solubility of the formed films (Thakur *et al*., 2016). According to Larotonda *et al.* (2016), the addition of rice starch in the kappa-carrageenan film formulation resulted in a decrease in the hydrophilic properties of the film. The increase in the amount of rice starch certainly results in an increase in amylose content as the amount of starch used increases. Therefore, there will be a decrease in the water solubility of the edible film along with the addition of rice starch.

Similar results were also obtained by Thakur *et al*. (2016) which stated that the addition of carrageenan to edible films made from rice starch would reduce the solubility of the edible films produced. In the study of Abdillah and Charles (2021) the addition of i-carrageenan to arrowroot starch films also reduced the solubility of the edible film produced.

3.2 Functional group analysis

FT-IR was applied to measure the interaction between components characterized by a shift in the absorption band. Changes in the stretch absorption band indicate structural interactions between components in the film matrix. Absorption bands of OH group were observed at 3298–3305 cm^{-1}, C–H group at 2888–2935 cm^{-1}, and sulfate ester group at 843-850 cm^{-1}, which were interpreted in all samples (Thakur *et al*., 2016; Abdillah and Charles, 2021; Hazrati *et al*., 2021). In this study, the infrared spectrum of the RS/KC-based edible film is shown in Figure 2B. The visible absorption bands at 3298 cm^{-1} were due to the formed hydrogen bonds by O–H groups' interaction. The peak at 2935-2828 cm^{-1} was ascribed to the asymmetric stretching vibration peak of C–H. The peaks at 1023 cm^{-1} indicate the interaction between the film structure and the hydroxyl group of plasticizers. Peak at 850 cm^{-1} was ascribed the ester sulfate group. The presence of the sulfate ester group which functions as an antioxidant and antimicrobial. Its presence in the film matrix results increase the water

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solubility of the film (Prasetyaningrum *et al*., 2021). The assignment of these bands is in line with previously reported results with *Dioscorea hispida* starch film (Hazrati *et al*., 2021).

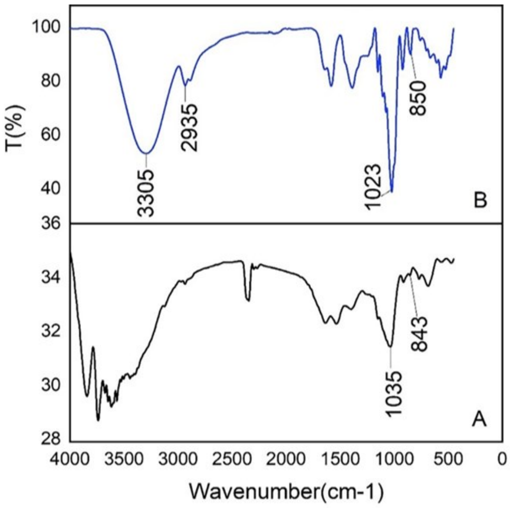

Figure 2. FTIR spectrum of native (A) KC and (B) RS/KC film (B).

4. Conclusion

The tensile strength value decreased, and the water solubility value increased when the rice starch/kappa-carrageenan ratio increased. The optimal circumstances were attained when the ratio of kappa-carrageenan to rice starch was 1:1. The value of tensile strength decreased, and the value of water solubility increased because of the addition of glycerol plasticizer. The optimal condition was achieved when the glycerol concentration was 1% (w/v) with TS value of 1.705 MPa, EaB 39.7%, and WS 47%. FTIR spectrum showed that the changes in the stretch absorption band at 1023 cm^{-1} indicate structural interactions between components in the film matrix.

Conflict of interest

The authors declare no conflict of interest.

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References

Abdillah, A.A. and Charles, A.L. (2021). Characterization of a natural biodegradable edible film obtained from arrowroot starch and iota-carrageenan and application in food packaging. *International Journal of Biological Macromolecules*, 191, 618–626. https://doi.org/10.1016/j.ijbiomac.2021.09.141

Aga, M.B., Dar, A.H., Nayik, G.A., Panesar, P.S., Allai, F., Khan, S.A., Shams, R., Kennedy, J.F. and Altaf, A. (2021). Recent insights into carrageenan-based bio-nanocomposite polymers in food applications: A review. *International Journal of Biological Macromolecules*, 192, 197–209. https://doi.org/10.1016/j.ijbiomac.2021.09.212

Cerqueira, M.A., Souza, B.W.S., Teixeira, J.A. and 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. https://doi.org/10.1016/j.foodhyd.2011.07.007

Dick, M., Costa, T.M.H., Gomaa, A., Subirade, M., Rios, A.D.O. and Flôres, S.H. (2015). Edible film production from chia seed mucilage: Effect of glycerol concentration on its physicochemical and mechanical properties. *Carbohydrate Polymers,* 130, 198–205. https://doi.org/10.1016/j.carbpol.2015.05.040

González, R.M. and Villanueva, M.P. (2011). Starch-based polymers for food packaging. Multifunctional and Nanoreinforced Polymers for Food Packaging, p. 527–570. United Kingdom: Woodhead Publishing Limited. https://doi.org/10.1533/9780857092786.4.527

Hazrati, K.Z., Sapuan, S.M., Zuhri, M.Y.M. and Jumaidin, R. (2021). Effect of plasticizers on physical, thermal, and tensile properties of thermoplastic films based on *Dioscorea hispida* starch. International *Journal of Biological Macromolecules,* 185, 219–228. https://doi.org/10.1016/j.ijbiomac.2021.06.099

Larotonda, F.D.S., Torres, M.D., Gonçalves, M.P., Sereno, A.M. and Hilliou, L. (2016). Hybrid carrageenan-based formulations for edible film preparation: Benchmarking with kappa carrageenan. *Journal of Applied Polymer Science*, 133(2), 42263. https://doi.org/10.1002/app.42263

Liu, P., Sun, S., Hou, H. and Dong, H. (2016). Effects of fatty acids with different degree of unsaturation on properties of sweet potato starch-based films. *Food Hydrocolloids,* 61, 351–357. https://doi.org/10.1016/j.foodhyd.2016.05.033

Prasetyaningrum, A., Utomo, D.P., Raemas, A.F.A., Kusworo, T.D., Jos, B. and Djaeni, M. (2021). Alginate/κ-carrageenan-based edible films incorporated with clove essential oil: Physico-chemical characterization and antioxidant-antimicrobial activity. *Polymers*, 13(3), 354. https://doi.org/10.3390/polym13030354

Sucheta, Rai, S.K., Chaturvedi, K. and Yadav, S.K.

(2019). Evaluation of structural integrity and functionality of commercial pectin based edible films incorporated with corn flour, beetroot, orange peel, muesli and rice flour. *Food Hydrocolloids*, 91, 127–135. https://doi.org/10.1016/j.foodhyd.2019.01.022

Thakur, R., Pristijono, P., Golding, J.B., Stathopoulos, C.E., Scarlett, C.J., Bowyer, M., Singh, S.P. and Vuong, Q.V. (2017). Amylose-lipid complex as a measure of variations in physical, mechanical and barrier attributes of rice starch- ι -carrageenan biodegradable edible film. *Food Packaging and Shelf Life*, 14(Part B), 108–115. https://doi.org/10.1016/j.fpsl.2017.10.002

Thakur, R., Saberi, B., Pristijono, P., Golding, J., Stathopoulos, C., Scarlett, C., Bowyer, M. and Vuong, Q. (2016). Characterization of rice starch-ι-carrageenan biodegradable edible film. Effect of stearic acid on the film properties. *International Journal of Biological Macromolecules*, 93(Part A), 952–960. https://doi.org/10.1016/j.ijbiomac.2016.09.053

Vianna, T.C., Marinho, C.O., Marangoni Júnior, L., Ibrahim, S.A. and Vieira, R.P. (2021). Essential oils as additives in active starch-based food packaging films: A review. *International Journal of Biological Macromolecules,* 182, 1803–1819. https://doi.org/10.1016/j.ijbiomac.2021.05.170

Zakaria, N.H., Muhammad, N. and Abdullah, M.M.A.B. (2018). Effect of glycerol content on mechanical, microstructure and physical properties of thermoplastic potato starch film. *AIP Conference Proceedings*, 9, 020230. https://doi.org/10.1063/1.5066871

Żołek-Tryznowska, Z. and Kałuża, A. (2021). The influence of starch origin on the properties of starch films: Packaging performance. *Materials*, 14(5), 1146. https://doi.org/10.3390/ma14051146

