Influence of Carrageenan on the Mechanical Strength of Starch Bioplastic Formed by Extrusion Process

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Abstract. The waste of synthetic plastic was the critical environmental problems so the biodegradable plastic is a viable remedy to solve this problem. Addition of biopolymer into bioplastic as the blend could provide a synergistic effect that influences their properties. This study aim was to show the influence of carrageenan on the mechanical properties of bioplastic cassava starch obtained through the extrusion process. This experimental research involved varies concentrations of carrageenan i.e. 0%, 2.5%, 5%, 7.5%, and 10%. The extrusion process was conducted in a single screw extrusion at 120°C. The extruded bioplastic was characterized by a tensile test and observed using the Scanning Electron Microscope (SEM). The bioplastic starch/carrageenan blend had the tensile strength of 1.1 MPa, 1.62 MPa, 4.87 MPa, 2.137 MPa, and 2.876 MPa and elongation of 28.69%, 20.22%, 19.48%, 17.27%, and 14.78% at carrageenan addition of 0%, 2.5%, 5%, 7.5%, and 10%, respectively.
Keywords: Bioplastic, carrageenan, extrusion, mechanical strength, starch

1. Introduction
Petroleum-based plastics are material that is difficult to decompose within a short time; they take about 50 years to degrade completely in the landfills [1]. In worldwide, the synthetic plastic usage reaches 297.5 million tons by 2015 [2]. In Indonesia, plastic usage increase with the waste reached 14% of total waste or 5.4 million tons by 2015 [3]. A common application of plastics are for packaging materials because of lightweight, inexpensive, and chemically resistant [4]. Many efforts were conducted to solve the problem by developing bioplastics that are easily degraded.

Biopolymers are made from renewable sources material such as polysaccharides, lipids, and proteins, that has a great benefit to the environment and health. Biopolymer has been used in the biomaterial products and food or as packaging films because of its degradable and properties preservative capabilities, [5]. Starch is a biopolymer material extracted from tubers such as cassava, which is abundant, inexpensive, renewable, biodegradable and biocompatible, [6]. Cassava starch contains of 72.61% to 87.71% amylpectin and 12.28% to 27.38% amylose. The amylose content affects the mechanical properties of bioplastics, while the amylpectin content gives optimum stickiness [7].
Carrageenan is a family of polysaccharides extracted from a specific red seaweeds species in the Rhodophyceae family [8] formed by alternate units of D-galactose and 3,6-anhydro-galactose (3,6-AG) joined by \(\rightarrow\)1,3 and \(\beta\)-1,4-glycosidic linkage [9]. \(\kappa\)-carrageenan have the ability to form the gels and membranes with better mechanical properties [10]. New bio-based materials have been developed to improve the quality of bioplastic and to reduce the plastic waste. The main advantages of bioplastic compared to the synthetic packaging are use of renewable sources, potential and edibility biodegradability. However, biopolymer materials present sensitive to humidity and poor in mechanical properties [11].

Blending starch with polycaprolactone, polylactic acid, and also gelatin has been reported [12] [13] [14]. Polymer blend could provide a synergistic effect to their physicochemical properties [11]. However, the wide application of starch-based bioplastic has been restricted because of their moisture sensitivity, brittleness, poor mechanical properties [14] and poor processability in common industrial equipment [15]. Therefore, this study investigated the characteristics of bioplastic starch/carrageenan blend produced through a single screw extrusion process.

2. Method

2.1 Materials
The materials used in this research were both cassava starch and kappa carrageenan in technical grade, glycerol, and distilled water.

2.2 Extrusion Process
The bioplastics were made from cassava starch, glycerol, and distilled water with a fraction of 40%, 30%, and 30 wt%, respectively. The distilled water and glycerol were mixed in magnetic stirrer for 5 min the starch added into the solution then stirred for 15 min at 90°C and increasing the temperature up to 135 °C with stirring for 15 min. Carrageenan was added into solution with each concentration of 2.5%; 5%; 7.5%; 10% (w/w). The solution was then heated over a hot plate at 165°C until it changed into gel then the mixture was fed into a hopper at 120°C and held for 10 minutes or 600 seconds before extrusion [16]. The extrusion process was operated at screw rotation of 5 rpm. The extruded bioplastic was put in the oven at 80°C for 4 hours for the drying process then stored in a dry box for further analysis.

2.3 Mechanical Properties of Bioplastic
The strength of extruded bioplastic was evaluated using the “Techno” fiber tensile tester (Techno Lab., Indonesia). The bioplastic was cut into 30 mm long, placed into the clamp with a length of 10 mm, and stretched with a velocity of 0.025 mm.s\(^{-1}\). The average of the cross-sectional area of five samples was measured using the software of ImageJ 1.51K after taken its photograph.

2.4 Morphology observation by SEM
The morphology of the bioplastic specimens surface was observed by the FEI, Inspect-S50 type of Scanning Electron Microscope (SEM) at 10.00 kV after gold coating on the surface sample with a thickness of 10 nm (sputter coater, SC7-620 Emitech) [17].

3. Results and Discussion

3.1 The product of bioplastic extrusion
The image of the biocomposite product obtained by an extrusion process was shown in Figure 1. The process of extrusion of bioplastic was shown in Fig. 1A. The bioplastic made of starch show a transparent clear (Fig. 1B). In SEM observations, after the extrusion process, bioplastic show void (Fig. 1C) that meaning need to vacuum during the extrusion process.
3.2 Mechanical Properties

As shown in Figure 2 and Figure 3, the addition of carrageenan effects on mechanical properties of bioplastic. After addition of carrageenan by 0%, 2.5%, 5%, 7.5%, and 10%(w/w), the bioplastic show elasticity of 28.69%, 20.22%, 19.48%, 17.27%, and 14.78%, tensile strength of 0.22 MPa, 0.77 MPa, 1.07 MPa, and 1.43 MPa, and elastic modulus of 0.77 MPa, 4.38 MPa, 5.47 MPa, 6.20, and 9.65 MPa, respectively.
Figure 2. Influence of carrageenan concentration on the elongation of starch/carrageenan bioplastic

Figure 3. Influence of carrageenan concentration on the tensile strength and elastic modulus of starch/carrageenan bioplastic
A determining factor in the improvement of mechanical properties is the blending carrageenan with the starch matrix [18]. Increasing in the elastic modulus due to properties of kappa carrageenan that tend to form rigid an brittle structure through aggregate gel mechanism [5] and due to good compatibility, high robustness, and persistent viscoelasticity [9]. Starch contain branched chains of amylpectin and linear chains of amylose. High flexibility of polymer chains and small molecular weight are the primary factors supporting the interaction between starch and carrageenan chains [19]. In the starch/carrageenan blend system, the higher quantity of the amylpectin was released from the starch when starch swelling increases. Before or after swelling of starch, carrageenan always adsorbs on starch after interacts. The level of adsorption depends on the charges and molecular weight of the carrageenan. The lower of the charge and molecular weight the higher the adsorption level [9].

3.3 Surface Morphology
Surface morphology of bioplastic starch/carrageenan blend obtained from extrusion process was shown in Fig. 4.

![Image](image_url)

Figure 4. Surface of starch bioplastic product through extrusion process with addition of carrageenan of (A) 0%; (B) 2.5%; (C) 5.0%; (D) 7.5%, and (E) 10%
The bioplastic surface made of starch without carrageenan show a rough surface (Fig. 4a). After addition of carrageenan, bioplastic surface was smoother (Fig. 4b, Fig. 4c, Fig 4d). Addition of carrageenan by 10% (w/w), the bioplastic surface was smooth that indicate a better interaction between starch and carrageenan (Fig. 4e). The addition of carrageenan in the starch gel phase cause swelling of starch granules. When swelling starch increases, starch becomes softer the less resistance to mechanical treatment [9]. This condition makes bioplastic easier to be formed with the extrusion process.

4. Conclusion
The blending of carrageenan in starch bioplastic could increase the elastic modulus and tensile strength of the extruded bioplastics. The higher concentration of carrageenan, the higher the mechanical strength of starch bioplastic result.

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