Synthesis of starch-carrageenan bio-thermoplastic composites on the type and concentration of thermoplastic forming materials as packaging materials

A Hartiati¹,²,³, B A Harsojuwono¹, H Suryanto², and I W Arnata¹

¹ Department of Agroindustrial Technology, Faculty of Agricultural Technology, Udayana University, Badung, 80361 Bali, Indonesia.
² Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Badung, 80361, Indonesia.
³ e-mail: amnahartiati@unud.ac.id

Abstract. Plastic waste is one of the primary environmental pollutants; in addition to being very large in number, it is also complicated to be degraded by microbes. One of the efforts to overcome plastic pollution is to develop biodegradable thermoplastic (bio-thermoplastic), namely plastic that is easy to form and melts at high temperatures and is easily degraded. This study aims to determine the effect of the type and concentration of thermoplastic forming materials (glycerol and castor oil) on bioplastic composites made from cassava starch with carrageenan. Another goal is to get the best characteristics of the treatment. This study used a randomized block design with 12 treatments derived from 2 types (glycerol and castor oil) and six concentrations (1, 2, 3, 4, 5, 6%) of thermoplastic forming materials. The treatments were grouped into two based on the time of the research. The data obtained were analyzed for diversity, and if it had a significant effect, it was continued with Duncan's multiple comparison test. The observed variables included mechanical properties, swelling, WVTR, and biodegradation. The results showed that the type and concentration of the thermoplastic forming material had a significant effect on tensile strength, elongation, elasticity, WVTR and had no effect on swelling and biodegradation. The bio-thermoplastic composite with the best characteristics was made from starch and carrageenan in a ratio of 25:75 using 1% glycerol with a tensile strength of 33.98 MPa and 1% castor oil with a tensile strength of 35.71 MPa.

1. Introduction
Plastic waste is one of the environmental pollutants in large quantities and is very difficult to decompose by microbes. Decomposition of plastic by microbes takes tens to hundreds of years [1]. Efforts to solve this plastic pollution include the development of biodegradable bio-thermoplastic. This plastic is easy to form and melts at high temperatures, and is easily decomposed in the soil by microbes [2].

Several studies have reported manufacturing bioplastic composites [3] and [4]. The research still does not meet the stipulated SNI requirements, so other alternatives are sought, such as varying the composite raw materials derived from polysaccharides, types, and concentrations of thermoplastic forming materials, fillers, and others. Several studies on composite raw materials, including [5], reported that composites with 1% glycerol could cause glucomannan-modified cassava starch composites to be bio-thermoplastic.[6] informed that the best formula for thermoplastic elastomer was natural rubber/polypropylene at a ratio of 60:40 using 5% castor oil. The study results [7] showed that 1.5% w/w diphenylmethane diisocyanate and 2% w/w castor oil resulted in cross-linking above 90%. Recent research [8] stated that the best bioplastic composite of polysaccharides is tapioca starch:carrageenan=25:75.
This research still does not meet the requirements of the Indonesian National Standard on biothermoplastic products [9], so it is necessary to research the types and concentrations of thermoplastic forming materials in composites of starch and carrageenan [5]. In this regard, the study aims to determine the effect of the type and concentration of thermoplastic forming materials (glycerol and castor oil) on bioplastic composites made from cassava starch with carrageenan. Another goal is to get the best characteristics of the treatment.

2. Materials and methods

2.1. Materials
Research materials include the primary raw materials: cassava starch (tapioca) and carrageenan, which were purchased at CV. Chemical Planet. Other ingredients are glycerol and castor oil purchased through Tokopedia. The tools used include a 20 cm diameter Teflon, a Shimadzu-Prestige-21 FTIR spectroscopy functional group characterization tool.

2.2. Experimental design and data analysis
This study used a randomized block design with 12 treatments derived from 2 types (glycerol and castor oil) and six concentrations (1, 2, 3, 4, 5, and 6%) of biothermoplastic constituents. The treatments were grouped into two based on the research time so that 24 experimental units were obtained. The data obtained were analyzed for diversity, and if it had a significant effect, it was continued with Duncan's multiple comparison test.

2.3. Procedure for making bioplastic composites
Tapioca starch composite raw material: carrageenan=25:75 [8], weighing a total of 6 g. Then weigh the thermoplastic forming material according to the type and concentration according to the treatment. Then followed by weighing 0.6 g of ZnO and 1% acetic acid solution as needed until the total material is 100 g. Composite raw materials were added with 1% acetic acid solution weighing 6 g and thermoplastic forming materials according to treatment (glycerol in concentrations of 1, 2, 3, 4, 5, and 6% and castor oil in concentrations of 1, 2, 3, 4, 5, and 6%). Meanwhile, ZnO 0.6 g was added with the remaining 1% acetic acid solution which had been prepared. Both mixtures were stirred for 10 minutes, each with a spatula in a beaker glass. Then the two mixtures were mixed and stirred for 10 minutes so that the mixture was homogeneous.

The mixture was then heated and stirred in a water bath at 70°C to form a gel. Bioplastic composites were made using the casting method, where the gel formed was printed on Teflon with a diameter of 20 cm. After that, it was dried in a drying oven with a hot airspeed of 5 ± 0.1 m²/min at a temperature of 50°C for 5 hours. After that, the Teflon containing the bioplastic composite sheet was removed and cooled at room temperature for 24 hours. Furthermore, the bioplastic composite sheet is removed from the Teflon and ready to be tested for its characteristics.

2.4. Sample Analysis
The observed variables included tensile strength, elongation at break, Young's modulus (ASTM), swelling, biodegradation, WVTR (Water Vapor Transmission Rate) for all treatments

3. Results and Discussion

3.1. Tensile strength
The analysis showed that the type and concentration of the thermoplastic forming material had a very significant effect on the tensile strength of the resulting biothermoplastic, which can be seen in Table 1.
Table 1. Average tensile strength of starch: carrageenan bio-thermoplastic composites = 25:75 in various types and concentrations of thermoplastic forming materials.

| Materials     | Concentration (%) | 1     | 2     | 3     | 4     | 5     | 6     |
|---------------|-------------------|-------|-------|-------|-------|-------|-------|
| Glicerol      |                   | 33.98 | 20.22 | 19.77 | 26.49 | 24.81 | 18.02 |
| Castor oil    |                   | 35.71 | 30.00 | 24.71 | 23.39 | 12.64 | 10.78 |

Note: the same letter behind the average value shows no significant difference at the 5% error level (p<0.05).

Table 1 shows that the range of tensile strength of bio-thermoplastic composites is 10.78 – 35.71 MPa. The bio-thermoplastic composite starch obtained the highest tensile strength: carrageenan=25:75 with 1% castor oil which was not significantly different from the treatment of 1% glycerol thermoplastic forming material. The low tensile strength of the bio-thermoplastic composite treated with starch: carrageenan = 25:75 with 6% castor oil which was not significantly different from the use of 5% castor oil.

This study also indicates that the higher the concentration of the thermoplastic-forming material, the lower the tensile strength of the bio-thermoplastic composite. This is because the higher the concentration of the thermoplastic-forming material, the lower the cohesive force of the composite components. According to Sanyang et al. [11], the reduction in tensile strength is due to the weakening of hydrogen bonds between the molecular chains of the composite materials. According to [12], stable and homogeneous compatibility will be disrupted by unstable conditions, such as the concentration of the thermoplastic material or the process temperature, which causes the thermoplastic material to bloom or come out again as a result of disrupted dispersion of thermoplastic molecules into polysaccharides. The thermoplastic forming material must be soluble in each polysaccharide monomer to facilitate the polysaccharide's activity and reduce the temperature, crystallization temperature, or polysaccharide melting temperature [13]. The tensile strength of the starch-carrageenan bio-thermoplastic composite = 25:75 has a much higher value than the research results of [14], which made the modified starch bio-thermoplastic composite:husk:PLA = 70: (15:15) which resulted in tensile strength of 8.55 MPa.

3.2. Elongation at break

The analysis showed that the type and concentration of the thermoplastic forming material had a very significant effect on the elongation at break of the resulting bio-thermoplastic, which can be seen in Table 2.

Table 2. Average elongation at break of starch:carrageenan composite = 25:75 in various types and concentrations of thermoplastic forming.

| Materials     | Concentration (%) | 1     | 2     | 3     | 4     | 5     | 6     |
|---------------|-------------------|-------|-------|-------|-------|-------|-------|
| Glicerol      |                   | 42.857| 41.429| 44.286| 52.857| 68.571| 68.794|
| Castor oil    |                   | 45.714| 50.000| 41.844| 45.714| 47.143| 48.936|

Note: the same letter behind the average value shows no significant difference at the 5% error level (p<0.05).

Table 2 shows that the range of elongation at break of bio-thermoplastic composites is 41,429 – 68,794%. The highest elongation at break (68.794%) was obtained from the bio-thermoplastic composite starch:carrageenan = 25:75 with 6% glycerol which was not different from the elongation at break of the bio-thermoplastic composite with all treatments except the use of 1, 2, 3% glycerol. Meanwhile, the low elongation at break was found in the bio-thermoplastic composite starch:carrageenan = 25:75 with 1, 2, 3% glycerol which was not significantly different from all treatments except those using 5 and 6% glycerol.

This value is in accordance with the results of research [14], which showed an elongation at break of 49.17% of the modified starch bio-thermoplastic composite:husk:PLA = 70: (15:15) which met the
criteria of SNI 7818: 2014. Similar results were also shown in the bio-thermoplastic composite of seed starch. Mango research results [15] have an elongation at break of 58.148%. Basically, elongation at break is influenced by differences in macrostructure and microstructure of bioplastic composites [16]. According to Ioelovich [17], the macrostructure and microstructure are influenced by the degree of crystallinity, the degree of cross-linking, the value of the glass transition point and melting point, molecular mass, and polydispersity or Young’s modulus.

3.3. Elasticity

The analysis showed that the type and concentration of thermoplastic forming materials had a very significant effect on the elasticity of the resulting bio-thermoplastic composites, which can be seen in Table 3.

Table 3. Average elasticity of starch:carrageenan bio-thermoplastic composites = 25:75 in variations of types and concentrations of thermoplastic forming materials.

| Materials    | Concentration (%) |
|--------------|-------------------|
|              | 1     | 2     | 3     | 4     | 5     | 6     |
| Glicerol     | 78.86  | 47.94 | 50.37 | 49.46 | 40.04 | 28.60 |
| Castor oil   | 79.25  | 62.25 | 53.96 | 47.81 | 25.10 | 20.48 |

Note: the same letter behind the average value shows no significant difference at the 5% error level (p<0.05).

Table 3. shows that the range of elasticity of the bio-thermoplastic composites is 20.48 – 79.25 MPa. The bio-thermoplastic composite starch had the highest elasticity:carrageenan=25:75 with 1% castor oil which was not significantly different from 1% glycerol and 2% castor oil. Low elasticity in bio-thermoplastic composites treated with starch:carrageenan=25:75 with 6% castor oil which was not significantly different from 5% castor oil and 5 and 6% glycerol.

This value is much higher than the study results [18], which showed that the bio-thermoplastic composite glucomannan:starch=30:70 with 25% glycerol had an elasticity of 21.14 MPa. [17] explained that the material’s elasticity is strongly influenced by the intermolecular forces between the polymer chains of the composite material [19]. Elasticity is the ratio between tensile strength and elongation at break. Therefore, elasticity and tensile strength are directly proportional. Both elasticity and tensile strength are strongly influenced by the macrostructure and microstructure of the polymer [16], such as the degree of crystallinity, the degree of cross-linking, the value of the glass transition point, and melting point, molecular mass, and polydispersity or molecular mass distribution [17].

3.4. Swelling

The analysis results showed that the type and concentration of the thermoplastic forming material did not significantly affect the swelling of the resulting bio-thermoplastic composite, which can be seen in Table 4.

Table 4. Average swelling of starch:carrageenan bio-thermoplastic composites = 25:75 in variations of types and concentrations of thermoplastic forming materials.

| Materials    | Concentration (%) |
|--------------|-------------------|
|              | 1     | 2     | 3     | 4     | 5     | 6     |
| Glicerol     | 70.77  | 81.58 | 66.64 | 61.11 | 65.50 | 57.74 |
| Castor oil   | 80.07  | 56.84 | 53.37 | 58.15 | 56.44 | 43.71 |

Note: the same letter behind the average value shows no significant difference at the 5% error level (p<0.05).

Table 4. shows that the swelling value of the bio-thermoplastic composites ranged from 43.71 to 80.07%, and all of them were not significantly different between treatments. This is because there is no significant difference in the molecular weight of the bio-thermoplastic composites and the content of functional groups in terms of number and type. According to [20], the swelling value is closely related to the molecular weight of the building blocks of bio-thermoplastic composites.
3.5. Water Vapor Transmission Rate (WVTR)

The analysis showed that the type and concentration of thermoplastic-forming materials significantly affected the WVTR of the produced bio-thermoplastics, which can be seen in Table 5.

Table 5. Average WVTR of bio-thermoplastic composite starch-carrageenan ratio 25:75 in various types and concentrations of thermoplastic forming materials.

| Materials  | Concentration (%) |
|------------|-------------------|
|            | 1     | 2     | 3     | 4     | 5     | 6     |
| Glicerol   | 251.66 a | 193.42 b | 264.14 a | 264.14 a | 232.94 ab | 247.50 ab |
| Castor oil | 207.98 ab | 262.06 a | 272.46 a | 232.94 ab | 257.90 a | 268.30 a |

Table 5 shows that the WVTR values of the bio-thermoplastic composites ranged from 193.42 – 272.46 g/m²/day. The smallest WVTR of bio-thermoplastic starch:carrageenan = 25:75 with 2% glycerol was not significantly different from the WVTR of bio-thermoplastic with 1, 5, 6% glycerol, and 4% castor oil, but significantly different from the others. Meanwhile, the high WVTR of bio-thermoplastic composites with 3 and 4% glycerol and 2, 3, 5, 6% castor oil were not significantly different from the WVTR of bio-thermoplastic composites with 1.5, 6% glycerol, and 1.4% castor oil. The results also showed that using glycerol, bio-thermoplastic composites with thermoplastic castor oil had a higher WVTR value than the WVTR of bio-thermoplastic composites. This is because the molecular weight of castor oil is more significant than glycerol. It has the opportunity to absorb more water due to the presence of hydrogen bonds. The molecular weight of glycerol is 92.09 g/mol, while castor oil is 130.23 g/mol.

3.6. Biodegradation time

The analysis showed that the type and concentration of the thermoplastic forming material had no significant effect on the biodegradation time of the resulting bio-thermoplastic composite, which can be seen in Table 6.

Table 6. Average biodegradation time of starch:carrageenan bio-thermoplastic composites = 25:75 in various types and concentrations of thermoplastic forming materials.

| Materials  | Concentration (%) |
|------------|-------------------|
|            | 1     | 2     | 3     | 4     | 5     | 6     |
| Glicerol   | 8.5 a  | 8.5 a  | 8.5 a  | 9.5 a  | 9.0 a  | 9.0 a  |
| Castor oil | 8.0 a  | 7.5 a  | 8.5 a  | 8.5 a  | 8.0 a  | 8.0 a  |

Table 6 also shows that the biodegradation time of the starch:carrageenan bio-thermoplastic composite = 25:75 ranged from 7.5 to 9.5 days and all of them were not significantly different between treatments. According to [3] and [21], the process of biodegradation of bioplastics in the natural environment begins with chemical degradation, namely the process of molecular oxidation to produce polymers with low molecular weights followed by an attack by microorganisms such as fungi and bacteria. According to [22], biopolymer degradation will produce simple compounds such as CO2 and H2O.

4. Conclusion

The type and concentration of thermoplastic forming materials (glycerol and castor oil) significantly affected tensile strength, elongation at break, elasticity, swelling but had no significant effect on WVTR biodegradation. The best cassava starch-carrageenan bio-thermoplastic composite that meets the SNI requirements is the one made from starch-carrageenan=25:75 with the type of thermoplastic glycerol and castor oil at a concentration of 1% and has complied with the SNI requirements.
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