Effects of Water on Hydrophobization and Mechanical Properties of Thermoplastic Agar

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Abstract. Thermoplastic agar (TPA) was prepared by a melt extrusion process and the effects of water contents on the material properties of these foams were investigated. Bioplastics were produced by mixing agar, glycerol, and water at ratio agar:glycerol:water was 5:3:2; 5:3:3; and 5:3:4 through the melting process at 120 °C and 18 rpm. The addition of water affected the extrusion process more easily, so the pellet could move easily from the extruder, but the moisture content of TPA increased with water addition. Then, TGA analysis showed no difference in decreasing mass in the sample with water addition. Permeability, elongation, contact angle, density, moisture content, and WVTR of bioplastics increased with water addition. The FTIR curves indicated that the interaction between water and agar may form much more hydrogen bonds. The best treatment was bioplastics with agar:glycerol:water=5:3:2, which have characteristics: tensile strength 16.19 MPa, elongation at break 102.56%, moisture content 3.09%, transparency value 0.067, and WVTR 1334.59 g/m².24 h.

1. Introduction
Plastic is a polymer compound with a rigid structure formed from the polymerization reaction of hydrocarbon monomers to form long chains [1]. As a polymer, plastic has many benefits. Starting from materials for making straws to materials for making vehicle bodies made of plastic. The abundant benefits result in an increasing need for plastic. According to Adhyasta Dirgantara [2], plastic production in Indonesia in 2019 as of November 2019 reached 7.23 million tons. The high level of production results in an increase in the waste produced and causes environmental problems. Research by Lau et al. [3] even predicts that there will be 710 million metric tons of plastic waste that will pollute the environment. Some efforts that can be done to minimize this problem are by recycling unused plastic, developing bacteria that can degrade plastics, and making plastics that can be degraded by living things (biodegradable).
Raw materials commonly used as bioplastic materials are starch [4], chitosan [5], lignin and pectin [6], and seaweed [4]. In this research, the raw material to be used is agar flour from seaweed *gracillaria* sp. The choice of seaweed as a raw material for making bioplastics is due to the abundance of laud grass in Indonesia. Indonesia's potential in seaweed cultivation is inseparable from the vastness of Indonesia's oceans which reaches 6.4 million km² with a total area of seaweed cultivation reaching 1,110,900 ha [7]. One of the most cultivated seaweed commodities in Indonesia is the *gracillaria* sp. Gracillaria sp. is a seaweed that produces agar. This type of seaweed has been widely cultivated by seaweed farmers in Indonesia. The harvest period, which only takes 40 days, is also the reason for using seaweed as a bioplastic raw material. So far, agar only uses an emulsifier, stabilizer, gel former, suspension agent, coating, and inhibitor [8].

Agar extracted from Gracilaria is mixed with glycerol to be made bioplastic which is classified as a thermoplastic. Thermoplastic is a group of synthetic polymers that can soften when heated above their glass transition temperature (Tg) and returning to their original chemical state upon cooling [9]. Thermoplastic can be softened or fully melted and reshaped upon heating. Besides, the chemical properties of this compound tend to stabilize over a wide range of operating temperature and pressure.

Development of agar for bioplastic is still in early-stage development and has been mainly manufactured through an extrusion method. For the best extrusion, knowledge of the melting point, thermal degradation, and chemical properties are required. In this research, water addition in extrusion for making agar-based bioplastic was observed, especially for their material properties. The properties of this material (agar-based bioplastic) might be fundamental for further applications.

2. Method
2.1. Material
In this work, it was employed by CV Sari Mutiara Agar (Malang, Indonesia), Technical grade glycerol (Indonesia) was used as plasticizers. Agar has a gel strength of 793.12 g/cm².

2.2. Formulation and processing of thermoplastic agar
Mixtures of agar (A), glycerol (G), and distilled water (W) were prepared with a ratio of A: G: W= 5:3:2; 5:3:3; and 5:3:4. Formulations were named as follows: AGW2; AGW3 and AGW4, in which numbers referred to the ratio employed for the water. Thermoplastic agar was prepared by the extrusion and hot-pressing method. The mixture was extruded through a co rotating twin-screw extruder. The screw speed was adjusted to 18 rpm and the feeder-to-nozzle temperature ware set to 120 °C. Subsequently, the obtained linear materials were air-cooled and granulated with a nominal 2-mm internal diameter. Finally, the plasticized starch granules were equilibrated at RH 50 and then thermopressed at 135 °C under a load of 40 kg/cm² to produce AGW films with the approximate thickness

2.3. Film Characterization
2.3.1. Tensile test
Samples were pre-conditioned at room temperature and relative humidity of 53 ± 2%. The mechanical properties of films were determined from sample cuts. Film samples were investigated using a TA XT Analyzer (Stablemycrosystem, UK) at room temperature, recording tensile strength (TS) and percentage elongation at break (E). The crosshead speed was set at 50.0 mm/min and the width and thickness of each sample were measured before testing. The measurement was repeated three times for each sample, and the results were averaged.

2.3.2. Water contact angle
The hydrophilic/hydrophobic of the film was evaluated by the ASTM D5946-04 method. The experiments were conducted depositing the water on the surface of sample films (1 x 1 cm) using an automatic microsyringe (5 μL). For all samples, the average was calculated on three measurements and the standard deviation was determined.

2.3.3. Density
The density test was carried out as follows: The mass / m (gram) of the sample to be tested was weighed using a digital scale. Then the 10 mL measuring cup is filled with water up to 5 mL and the plastic sample was put in a measuring cup filled with water. After 15 minutes, the new volume of water (v) was recorded to calculate the actual volume of plastic by calculating the difference between the final volume of water and the initial volume of water. Then we get plastic ρ with the following equation: \( \rho = \frac{m}{v} \)

2.3.4. Water Resistance
The water resistance test was carried out to determine the occurrence of bonds and bond regularity in the polymer, which was determined by the weight gain percentage of the polymer after experiencing swelling. The process of diffusing the solvent molecules into the polymer would produce a swollen gel. The nature of bioplastic resistance to water was determined by a swelling test, namely the percentage of film swelling in the presence of water [10]. Water absorption was tested according to ASTM: D-570. The samples were dried at 105 ° C for 3 hours and then immersed in distilled water. The amount of water absorbed by the sample was counted every day for 30 days. The water absorption percentage was calculated as follows:

A (%) = \( \frac{W - W_0}{W_0} \times 100\% \)

Note:
A = water absorption (%)
W_0 = initial sample weight (g)
W = weight of the sample after immersion

2.3.5. DSC
The DSC thermograms were acquired by a DSC-4000 (Perkin Elmer Pyris 1 equipped with intercooler) equipment to determine the glass transition temperature (Tg) of the samples by DSC measurements. Before an examination, an empty aluminum pan was taken as a reference test. Film samples weighing about 5 mg were placed individually in other aluminum pans and hermetically sealed. All the samples were scanned at a rate of 10 °C/min from 20 °C to 400 °C under a nitrogen atmosphere (40 ml/minute).

2.3.6. TGA
A thermogravimetric analyzer (TGA 4000 Perkin Elmer) was employed to test samples under the protection of N2. The temperature ranges from 25~750 °C and the heating rate at 10°C/min

2.3.7. FTIR
Fourier Transform-Infrared Spectroscopy (FTIR) spectrum of all thermoplastic starch films was obtained using Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Nicolet iS 5 ATR iD5, Thermo Scientific, USA). The transmission sampling approach was implemented. The measurement was recorded between 4000-500 cm\(^{-1}\).
2.3.8. WVTR
The water vapor transmission rate was carried out according to the ASTM standard E96 method. In this method, the water vapor transmission rate (WVTR) was determined gravimetrically, using a WVTR tool from Labthink, China.

3. Result and Discussion
3.1. Mechanical properties
The mechanical properties of thermoplastic agar involved tensile strength and elongation at break were shown in Figure 1. Modification of water ratio in blend significantly influenced these properties. A higher ratio of water content to lower the tensile strength. The increasing water content in the blends led to reducing other components (agar and glycerol). The agar consisted of agarose and agaropectin which are responsible for gelling and thickening a solution, therefore the higher Agar ratio caused the tensile strength of the thermoplastics to improve. Contrarily, as the ratio of Agar with water content declined, the tensile strength decreased. Junaid et al. [11] stated that the increasing content of agar tended to cause higher strength and Young’s modulus of thermoplastic.

Furthermore, the elongation at break of thermoplastics Agar (Figure 1) tends to increase by increasing the ratio of water content in the blend. The enhancement elongation of the thermoplastic agar can be attributed to the formation of a more hydrogen bonded. According to Ramirez et al. [12], thermoplastic agar consists of agarose and agaropectin which is hydrophilic due to the formation of a bond between the hydroxyl groups and oxygen bonds with water.

![Figure 1. Tensile strength and elongation of bioplastic agar](image)

Note:
AGW2: Agar: Glycerol: Water=5:3:2
AGW3: Agar: Glycerol: Water=5:3:3
AGW4: Agar: Glycerol: Water=5:3:4

3.2. Contact angle
The hydrophilic properties of the thermoplastic agar were evaluated by measuring their water contact angle data on the surface of the films. The measurement of the water contact angle was carried out by dropping a drop of water on the upper surface of the films as Figure 2 shown. It has been observed that the water contact angle of the films increased with the addition of water in the thermoplastic agar. AGW2 film has the lowest water contact angle (70°) due to the number of hydroxyl groups. All thermoplastic agar contact angles increased from 70° to 80°, respectively, indicating water can increase the properties of the hydrophilic thermoplastic agar.
3.3. Density

The density of bioplastics with variations in the addition of water can be seen in Figure 3. One of the physical parameters of bioplastics is density or density. The density of bioplastics with variations in the addition of water ranges from 1.37-1.40 g/mL. The density value obtained is higher than the density standard for commercial HDPE plastics, namely 0.94-0.96 g/mL [13]. Based on Figure 3, it can be seen that the higher the volume of water used, the higher the density obtained. High density indicates that the spaces between molecules are close to each other so that fewer air cavities are formed [14]. This results in a decrease in elasticity and tensile strength along with an increase in density.

![Figure 3. Density of bioplastic](image)

**Figure 3.** Density of bioplastic
3.4. Water resistance

The resulting bioplastic has low water resistance because the main ingredient of agar flour has more hydroxyl groups so it easily absorbs water. With the addition of a certain amount of water and heating it at high temperatures, the agar granules would absorb water and swell.

Note:
AGW2: Agar: Glycerol: Water = 5:3:2
AGW3: Agar: Glycerol: Water = 5:3:3
AGW4: Agar: Glycerol: Water = 5:3:4

Figure 4. Water resistance of bioplastic

The tendency of bioplastics to absorb water may result in plastic with lower elasticity because moisture content may alter the elastic modulus of the resulting plastic [15].

3.5. DSC

The DSC graph of the agar bioplastic sample is presented in Figure 4. The blunt peaks and width of the sample are considered to be the evaporation of water and glycerol. This is also evidenced by the TGA measurement in the sample which shows a greater loss of mass in the first stage. Besides, the presence of an endothermic peak in the sample indicates that the presence of agar causes the transformation of the molecular state from the amorphous phase to the crystal phase. It was assumed that this phase transformation was triggered by changes in intermolecular interactions that affect the mobility of the polymer chains [16]. The possible interactions were hydrogen bonds. The extraordinary endothermic peak occurring in the range of 70 °C represents the glass transition (Tg) of the sample which shows a change in the crystal structure of the molecule from a brittle state to a spongy state [17]. The Tg of material correlates with the formation of crystals in its chemical structure, and the DSC thermogram shows that the glass transition phase for the three samples corresponds to the degree of crystallinity (Figure 5). In short, the higher the crystallinity of a particle, the higher its Tg. These results were similar to other findings on chitosan [18] and SRC films [19]. Compared with synthetic polymers showing Tg at 190-500 °C [20] agar bioplastics show a generally lower Tg which may be due to lower stiffness and higher mobility of the intermolecular chains during heating.

3.6. TGA

The thermal degradation properties of bioplastics are shown in Figure 6. The starting point of degradation varies between bioplastic samples. Bioplastic experiences a mass loss of about 5%. This
mass loss is calculated as the process of hydrate or solvate evaporation of the OH groups of polymer and plasticizer followed by the second stage of mass degradation in the range of 150-250 °C.

The maximum degradation for agar bioplastic starts at around 300 °C. The addition of water affects the degradation pattern of the bioplastic mass. The addition of water to the bioplastic sample during the extruder process increased the percentage of degradation of the bioplastic sample.

![DSC of bioplastic](image1)

Note:
AGW2: Agar: Glycerol: Water=5:3:2
AGW3: Agar: Glycerol: Water=5:3:3
AGW4: Agar: Glycerol: Water=5:3:4

Figure 5. DSC of bioplastic

![Thermogram TGA bioplastic](image2)

Note:
AGW2: Agar: Glycerol: Water=5:3:2
AGW3: Agar: Glycerol: Water=5:3:3
AGW4: Agar: Glycerol: Water=5:3:4

Figure 6. Thermogram TGA bioplastic

3.7. Moisture content

The moisture content of bioplastics increased with the addition of water (Figure 7). However, the water contained in the bioplastic has decreased compared to when it was added. This is because during the mixing process in the extruder there was an evaporation process because the heating of the extruder
exceeds the boiling point of water. The conditioning process in the extruder is at 120°C, and 18 rpm speed.

Figure 7. The moisture content of bioplastic

Moisture impacts the production of almost all plastics, especially hygroscopic equivalents like nylon (polyamide) and polybutylene adipate terephthalate (PBAT). Certain polymers tend to degrade when molded wet, leading to decreased material characteristics [21]. Besides that, the moisture content may alter the elastic modulus of the resulting plastic. The higher the moisture content, the lower the tensile strength of bioplastic [15].

3.8. FTIR

ATR-FTIR spectra curves show absorbance peaks attributed to the different functional group structure. The obtained spectra curve of neat TPS film and MCC/TPS composite films are shown in Figure 8. As shown in the figure, the characteristic peak in 3500-3000 cm\(^{-1}\) corresponds to the O-H stretch band attributed to vibrations of the hydrogen-bonded hydroxyl (O-H) [22].

Figure 8. Spectra IR of bioplastic
The peaks at 2900 cm\(^{-1}\) are due to the aliphatic saturated C-H stretching vibration of CH2 of agar. The peak at 1750 cm\(^{-1}\) and 1370 cm\(^{-1}\) is due to the C=O. The peak at 930 cm\(^{-1}\) is attributed to 3,6-anhydro-L-galactose. The peak at 890 cm\(^{-1}\) represents 1,3 beta-D-galactose. The peak at 740 cm\(^{-1}\) is due to galactose bonding.

3.9. Light Transmittance

Table 1 shows the transmission of UV and visible light at a wavelength range of 280–800nm of agar bioplastic. As shown in Table 1, bioplastic light transmittance values ranged from 0.067 to 0.071. The results of the analysis show that there is no effect of adding water on the light transmittance value. Significantly, an edible film could protect food from the effects of light, particularly UV radiation [23].

| Sample | Light transmittance (%) at a different wavelength (nm) | Transparency value |
|--------|------------------------------------------------------|--------------------|
|        | 280  | 350  | 400  | 500  | 600  | 700  | 800  |                |
| AGW2   | 27.743 | 45.994 | 66.416 | 79.485 | 83.587 | 85.781 | 86.980 | 0.067±0.013    |
| AGW3   | 17.524 | 32.127 | 57.825 | 77.229 | 83.692 | 86.485 | 88.014 | 0.066±0.012    |
| AGW4   | 33.638 | 51.175 | 67.475 | 77.699 | 81.147 | 82.556 | 83.505 | 0.071±0.025    |

Note:
AGW2: Agar: Glycerol: Water=5:3:2
AGW3: Agar: Glycerol: Water=5:3:3
AGW4: Agar: Glycerol: Water=5:3:4

Figure 9. WVTR value of bioplastic

3.10. WVTR

Bioplastic water vapor transmission rates ranged from 1334.59-1914.53 g/m\(^2\).24 h. The addition of water has a significant effect on the WVTR value. WVTR revealing water vapor barrier properties of the bioplastic as influenced by the addition of water are shown in Figure 9. WVTR of the bioplastics
increased with an increasing amount of water. The results demonstrated that the WVTR values of the bioplasticity depend on the hydrophilic/hydrophobic ratio of the film component.

4. Conclusion
The prepared thermoplastic agar was characterized by various test instruments. The FTIR curves indicated that the interaction between water and agar might form much more hydrogen bonds. Permeability, elongation, contact angle, density, moisture content, and WVTR of bioplastics increased with water addition. The best treatment was bioplastics with agar:glycerol:water=5:3:2, which have characteristics: tensile strength 16.19 MPa, elongation at break 102.56%, moisture content %, contact angle 72.81°, density 1.38 g/ml, moisture content 3.09%, transparency value 0.067, and WVTR 1334.59 g/m2.24 jam.

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