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Bioplastics synthesis based on sorghum–*Eucheuma spinosum* modified with sorghum stalk powder

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Abstract. In this study, a bioplastic was produced by addition of filler and plasticizer. Sorghum stalk powder was selected as a filler and glycerol as plasticizer. The effects of filler and plasticizer concentration on physical and mechanical characteristics of the bioplastics were observed. In the bioplastic production, the amount of sorghum stalk powder varied from 0.25 to 1 g, and glycerol concentration was varied from 5 to 20%. On the other hand, the amount of *Eucheuma spinosum*, as a fiber, and sorghum starch as a matrix remained constant. The bioplastic production has conducted by stirring the starch, fiber, filler, and glycerol for 35 minutes at 95°C and 375 rpm. The mixture was dried at 50°C for 8 hours. The best physical and mechanical characteristics of the product were obtained from the formulation consisting 0.5 g of filler and 10% of plasticizer concentration. The bioplastic itself had 21.265 MPa of tensile strength, 4.467% of elongation, 498.463 MPa of Young's Modulus, 0.95 g/cm³ of density, and 21.265% of water uptake which are in the range of commercial HDPE plastic characteristics.

1. Introduction

Plastic has become an integral part of human life due to their versatility and a wide range of application. It is a synthetic polymer with high molecular weight obtained from petroleum. Approximately, there is 4% of total petroleum production has been used as plastic production feedstock [1]. However, production of plastics has led to a severe environmental crisis because of non-biodegradable properties. Hence, finding an alternative for a diversified and sustainable raw material is one of the grand challenges in reducing petroleum consumption and environmental pollution. In recent years, bioplastics production has shown great attention to replace synthetic plastic due to biodegradability, environmentally friendly and biocompatibility [2].

Bioplastics are produced from biomass with or without modification, such as starch, polysaccharides, protein, and lipid [3]. Sorghum starch could be an alternative source of a matrix, having starch content up to 80.42% [4, 5]. Sorghum has kafirin that is high hydrophobicity and rich of sulfur amino acid. Sulfur amino acids are responsible for the disulfide cross-linking and aggregating capacity of kafirin during thermal processes [6]. The sorghum plants were tolerant to drought and standing water and relatively resistant to nuisance pests. In Indonesia, sorghum has currently used as an animal feedstock because of its high tannin concentration, between 0.40 to 3.60%.



In bioplastic production, some additives are commonly added to enhance its properties such as filler and plasticizer. A filler is used to improve hydrophilicity and durability that allows the plastic to be biodegradable naturally [7]. Sorghum stalk is one of a filler having amylose ranging from 209 to 1764 ppm [8]. Besides sorghum stalk, natural fibers are also be used as filler. Fibers are a robust organic material and very abundance in volume on the biosphere [9].

Seaweed (*Eucheuma spinosum*) contain fibers, consisting of cellulose and hemicelluloses. According to JECFA, *E. spinosum* contains cellulose in the form of lignocelluloses [10]. Lignocellulose is separated through solvent extraction. Sodium hydroxide is the most common solvent used for this purpose and modifying the surface of the fiber to increase interface adhesion between the natural fibers and matrix [11].

The plasticizer is another additive in sending down stiffness of a polymer, as well as increase flexibility of polymer. Glycerol is a commonly-used plasticizer. The flexibility of polymer is the critical bioplastics characteristics. However, the optimum concentration of plasticizer in bioplastic production is still in research.

In this study, a bioplastic was produced by sorghum starch in line with the previous experiment [12]. As additives, *E. spinosum* was chosen as a fiber combined with sorghum stalk as a filler. Meanwhile, glycerol was selected as a plasticizer, another additive needed in plastic production. Before the study, Darni et al. had modified filler with a combination of chitosan and sorghum stalk [13]. This research conducted to observe the effect of sorghum stalk as a filler and glycerol concentration on the physical and mechanical properties of bioplastics.

2. Experimental

2.1. Materials and tools

The bioplastic was produced from sorghum starch as a matrix and combined with filler (sorghum stalk), fiber (*E. spinosum*), and plasticizer (glycerol). Sorghum grain as a raw material of starch was obtained from a traditional market in Yogyakarta, Indonesia. Meanwhile, sorghum stalk was provided by BPPT Natar, Lampung Selatan, Indonesia. *E. spinosum* was retrieved from municipal agriculture in Madura, Indonesia. Glycerol used in the experiment was anhydrous glycerol for analysis (MERCK).

The bioplastic preparation was conducted in beaker glasses. The heat was supplied by a hot plate stirrer (Corning DC-620D 155614044052). The size of the materials was measured by sieve 63 microns. The acidity was measured by a digital pH-meter (Luckystone pH Tester PH-009 with two pack of calibration solution/11654465).

2.2. Materials preparation

About 30 g of *E. spinosum* and 240 mL of 40% NaOH solution was placed in a 1000 mL beaker glass. The extraction proceeded on 100°C for 3 hours and 375 rpm. The filtered material removed and washed with water until value of 11 of pH attained. The H₂O₂ solution with 6% of concentration was added to the residue by 1:8 (w/v) ratio. The mixture was kept for three hours on ambient temperature (about 27°C) while stirring on every 15 minutes. This solution was then filtered and washed with distilled water until the value of 7 of pH achieved. The residue obtained was dried in an oven on 105°C until its weight was constant. The dried *E. spinosum*, sorghum grain and sorghum stalks were milled in a disk mill and sieved to give 63 microns of size.

2.3. Synthesis of bioplastics

The bioplastic was produced according to Weiping Band procedures with some modifications [14]. The hotplate turned on and kept on 200°C. Starch and fiber weighed to about 7.5 g and 2.5 g respectively. About 0.25 g of filler (sorghum stalk powder), and 5% of a plasticizer (glycerol) and distilled water with some variations mixed to give 225 mL volume of the mixture. Starch and fiber added to the mixture and located in a 500 mL beaker glass while it agitated homogeneously. This solution then mixed for 35 minutes and 375 rpm on the hotplate stirrer.

After cooking was complete, the mixture was poured into a mold corresponding predetermined height limit (30 mL). The mold was left in surrounding to release smoke while the oven was prepared on 50°C. The mold was then inserted into the oven and kept for 8 hours. The bioplastic was withdrawn from the oven and put in a desiccator for 24 hours. Then it was pulled out from the mold and stored in a zip-lock bag and given a labeled. The procedures were repeated by entirely random design and the filler varied to be 0.5 and 1 g respectively likewise the glycerol varied to be 10, 15, and 20% respectively.

2.4. Analysis and characterization

2.4.1. Mechanical properties

The bioplastics were analyzed of its mechanical properties, namely: tensile strength, percent of elongation, and Young's modulus using Universal Testing Machine Autograph AGS-500 Shimadzu.

2.4.2. Physical properties

The physical properties measurement for the products were density and water uptake. Density of bioplastics was determined by dividing its mass to volume. On the other hand, analysis of water uptake was done according to ASTM D 570. A slice of 1 cm x 1 cm of the sample was scaled its initial weight and put in oven to dry for 24 hours and stored in a desiccator for 24 hours. The sample was immersed in 10 mL of water for 22 hours. The sample took away and removed its water surface and weighted.

2.4.3. FTIR analysis

The samples cut and crushed together with potassium bromide to give a pellet form and then placed into the FTIR (Shimadzu Prestigrade 21) and then the functional groups in the bioplastics were identified from the absorbance profile results.

2.4.4. Morphological characterization

The morphology of bioplastics structure was determined by scanning electron microscopy (ZEISS EVO MA 10). A sample, 1 cm x 1 cm was prepared and patched to the holder, and then inserted in the vacuum chamber for flaming electrons.

2.4.5. Thermal analysis

The response of the bioplastics on heating were observed using differential scanning calorimetry (DSC) (Seiko Inc.) according to ASTM D 3418 method. The melting temperature, T_m , glass transition temperature, T_g , and enthalpy change of the sample were measured. About 5 mg of sample incorporated into a crucible 40 μ L. The analysis was done by heating the samples from room temperature to 250°C on 10°C.min⁻¹ of heating rate. Liquid nitrogen was used for cooling with a flow rate of 50 mL.min⁻¹.

3. Results and discussion

3.1. Mechanical properties of the bioplastics

Tensile strength, percent of elongation, and Young's modulus were three mechanical properties measured to the bioplastics. Figure 1 to 3 show the results of these properties.

From Figure 1 it is shown that the tensile strength of bioplastics tended to reduce as the rise of plasticizer. Meanwhile, the properties did not show a regular pattern for the increase of filler addition. However, the addition of filler in the bioplastic, in general, gave a tendency to enhance its value. Another study showed that the increase of filler in composite materials can make it stronger and harder [15]. In contrast, the tensile strength weakness due to the higher of plasticizer within. This results as a consequent of glycerol ability to improve the elasticity of bioplastics, due to decreasing the intermolecular force along the polymer chain [16]. Fiber is another additive that might promote its tensile strength [9].

Nevertheless, as its composition remained steady in this study, the tensile strength changed because of the amount of filler and plasticizer. HDPE as commercial plastic has tensile strength from 20.67 to 51.675 Mpa [17]. Therefore, three bioplastics with addition plasticizer and filler: 5% and 0.5 g, 5% and 10 g, and 10% and 0.5 g were selected as products with better tensile strength properties.

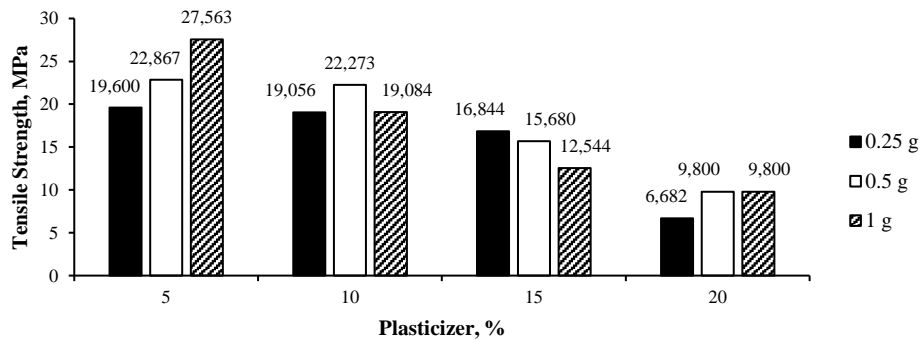


Figure 1. The effect of addition of filler and plasticizer on tensile strength of the bioplastics.

Elongation is a change from initial length to the maximum extent possible as the plastics stretch. The result of elongation from different ingredients is shown in Figure 2. It can be seen that elongation is strongly affected by plasticizer concentration. The addition of glycerol as plasticizer leads to reduce intermolecular force along the polymer molecules contributes to elasticity and so gives greater elongation. Widyaningsih et al. [18] found that plasticizer was able to reduce brittleness.

On the other hand, the addition of filler can improve this property if the presence was not too high. The addition of filler decreased the percent of elongation for plasticizer concentration was 20%. Therefore, it is more convenient to use a lower amount of filler and a higher concentration of plasticizer. Utilization of starch as the main substance in bioplastic preparation gave a disadvantage to brittle bioplastic structure. Whereas the addition of natural fibers in composites can improve bioplastic flexibility [19]. The bioplastics using concentration of filler 15 to 20% satisfied the elongation of commercial HDPE plastic (10 to 500%) [17].

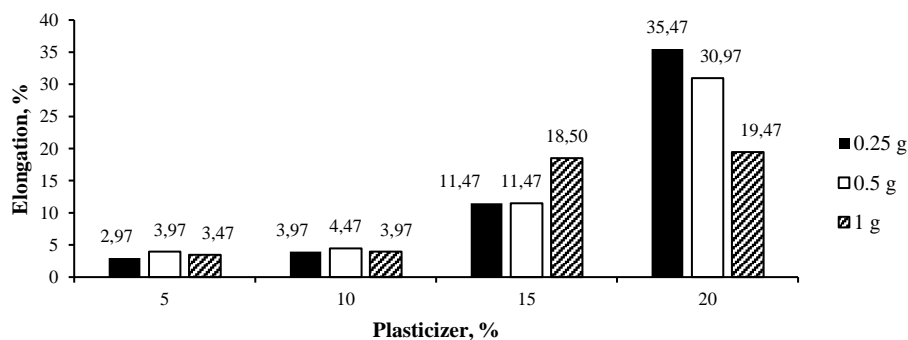


Figure 2. The effect of addition of filler and plasticizer on elongation of the bioplastics.

Young’s modulus is another mechanical property to measure the stiffness of a material. This property results from tensile strength to elongation ratio. Figure 3 shows Young’s modulus from variations of filler and plasticizer addition in this study. The Young’s modulus declined sharply as the increase of plasticizer concentration.

Addition of plasticizers can increase the flexibility of the polymer film by interfering hydrogen bonds between adjacent polymer molecules that reduce the strength of intermolecular attraction polymer chains [18]. The pattern of the bar charts is somewhat similar to the tensile strength. Addition of sorghum stalk powder, fiber powder to the composites will give bioplastics to be more rigid and dense [20].

Moreover, the addition of natural fibers in composites can improve the toughness [19]. Cellulose gives strength and stability to cell walls plant, and so it also played a role in enhancing the matter of the biopolymer [8]. The addition of plasticizer 5 to 10% satisfied Young's modulus of commercial HDPE plastics (227.89 to 455.8 MPa) [17].

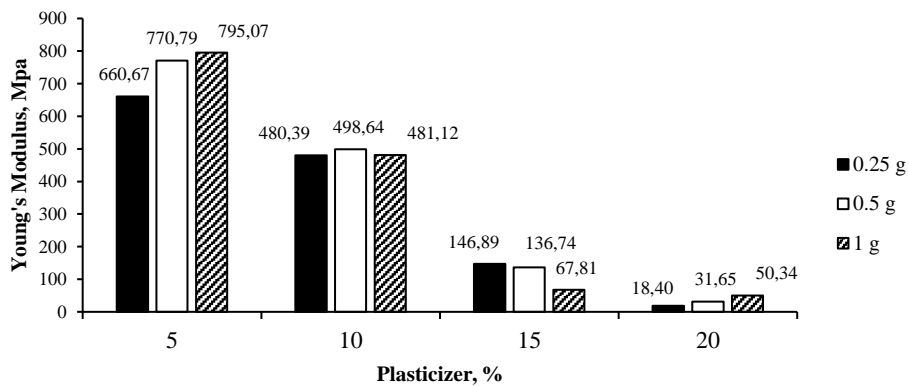


Figure 3. The effect of addition of filler and plasticizer on Young's Modulus of the bioplastics.

3.2. Physical properties of the bioplastics

Figure 4 shows the density of bioplastics with a variation of filler and plasticizer added. In general, the density is getting higher as the increase of plasticizer concentration and filler, although the difference is not significant. However, a further amount of filler additive tends to reduce its property. It can be seen for 1 g of filler addition values which are lower than the value with 0.5 g filler addition. Commercial HDPE plastics have a density of 0.94 to 0.97 g/cm³ [17]. Therefore, products that are relevant to this interval made from combination of filler and plasticizer additive exactly 1 g : 5% (0.95 g/cm³), 0.5 g : 10% (0.95 g/cm³) and 1 g : 15% (0.94 g/cm³) respectively.

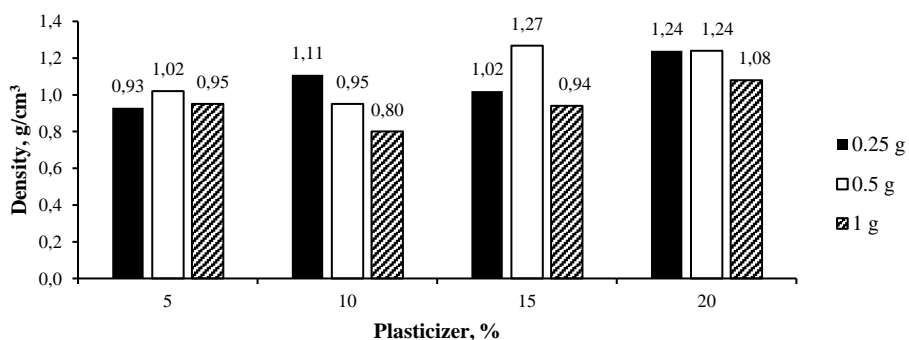


Figure 4. The effect of addition of filler and plasticizer on density of the bioplastics.

Water up use analysis is performed to measure absorptivity of bioplastics to water. Figure 5 shows the results of this test. Water absorption tends to increase with higher plasticizer concentration. In contrast, the water uptake generally decreases as expanding filler used. Comparing to values commercial HDPE plastics (0.3 to 0.65%) [17] these results were too much lower. The higher levels of water from products indicated its hydrophilic properties of starch. Also, the hydrophilicity was strengthened by the addition of plasticizer (glycerol) because of its hydroxyl group.

On the other hand, the use of filler (sorghum stalk powder) increases the plastic hydrophobicity which succeeded in reducing water absorption. As it is observed from its chemical structure, fiber is predicted to possess a strong affinity for water due to the hydroxyl groups present in the molecule that can form hydrogen bonds with water. However, the reality is not so, because fiber is not only insoluble in water but also in other solvents. This phenomenon was distinct because of its chain stiffness and high inter-chain forces due to hydrogen bonds between adjacent hydroxyl groups. This factor is considered to be a cause of high crystallinity of fiber [21].

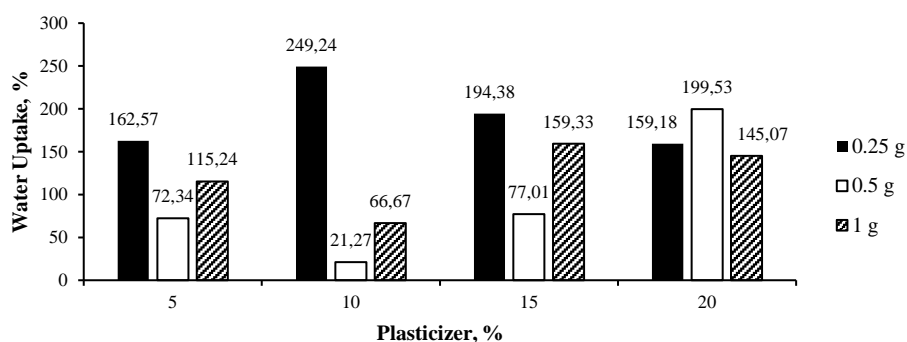


Figure 5. The effect of addition of filler and plasticizer on water uptake of the bioplastics.

Based on the mechanical and physical properties result, the best bioplastics provided by addition 0.5 g of filler combined with 10% of the plasticizer. These results are summarized as in Table 1.

Table 1. Properties of the selected bioplastic and commercial HDPE as its comparison.

| Property | Commercial HDPE [17] | Bioplastics |
|-----------------------------|----------------------|-------------|
| Tensile strength, MPa | 20.67 – 51.68 | 22.27 |
| Elongation, % | 10 – 500 | 4.47 |
| Young's modulus, MPa | 227.89 – 4558 | 498.64 |
| Density, g.cm ⁻³ | 0.941 – 0.965 | 0.95 |
| Water uptake, % | 0.3 – 0.65 | 21.27 |

3.3. Functional group analysis

Fourier Transform Infrared (FTIR) analysis based on the specific peaks indicate the type of functional groups distinct in the compounds. Both raw materials and product were examined its spectrum and shown in Figure 7. It shows that the spectrum of sorghum stalk (a) is quite similar to sorghum grains (b). Even though these patterns look different to *E. spinosum* has (c), all of them have the same characteristic of functional groups, namely –OH, C=O, and C-O.

The different spectra of product from its raw material may be as the result of the change of intermolecular force. As the same functional groups still exist within its molecules and regarding its spectrum pattern, it indicates that the bioplastic formed due to mixing its raw materials physically.

3.4. Morphological structure

The morphology of the resulting bioplastic was observed through SEM at various magnifications and commercial HDPE as a comparison as shown in Figure 7. Ununiform surfaces can be caused by less homogeneous mixing as a result of the insoluble nature of fibers in organic solvents. The ratio of amylose to amylopectin in raw materials can also affect the plastic film produced. Sorghum starch has a ratio of amylose to amylopectin of 28 to 72. High amylose content will create a homogeneous plastic film, and conversely, a higher amylopectin content will increase phase separation [16]. Therefore amylopectin forms a lump which causes the resulting bioplastics to be less homogeneous. The morphology of bioplastics with 0.5% glycerol concentration of 10% is quite tight and resembles that of HDPE. This appearance is due to the effect of the addition of filler which can fill space in bioplastic films.

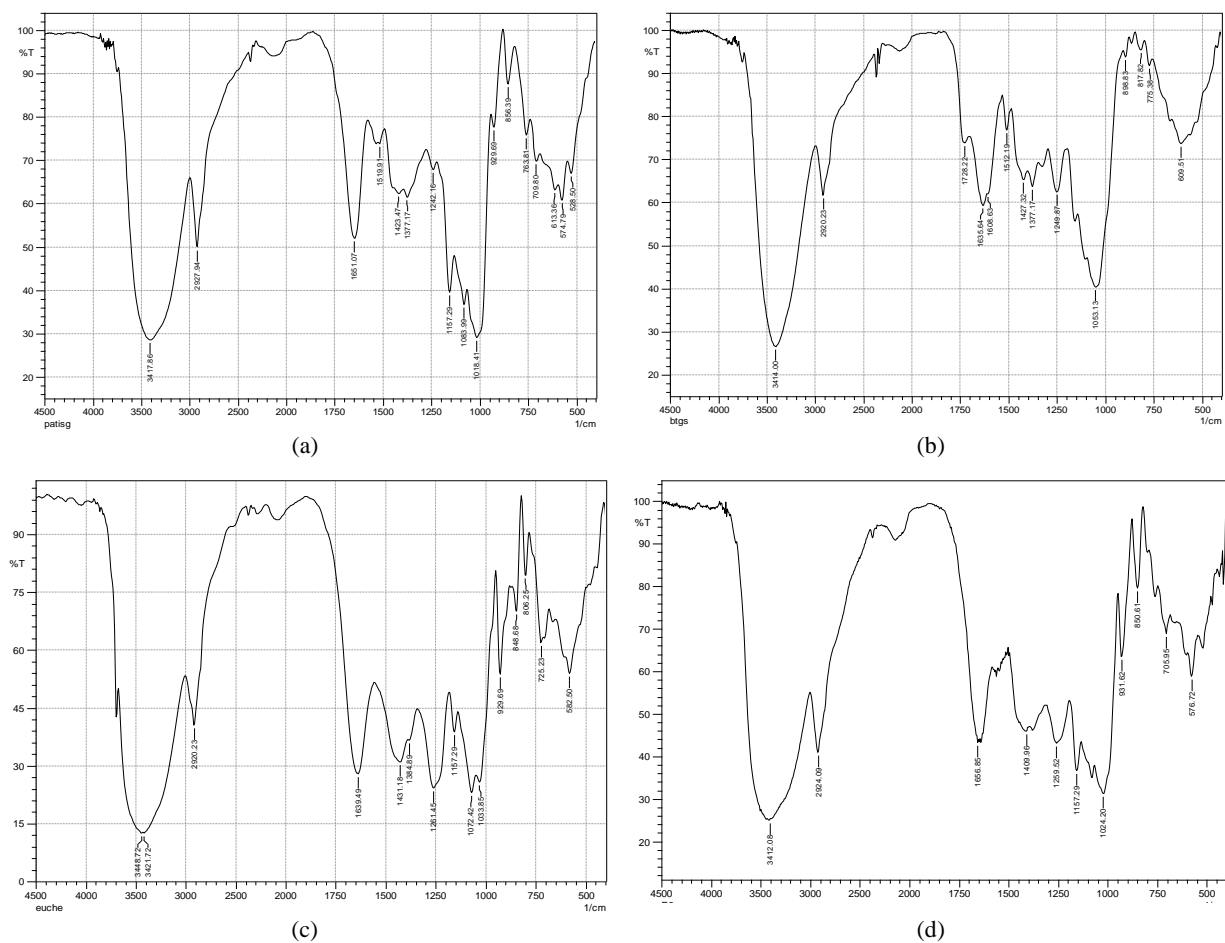


Figure 6. FTIR spectrum from raw materials and the bioplastic: (a) sorghum stalk, (b) sorghum starch, (c) *E. spinosum* and (d) bioplastic.

3.5. Thermal analysis results

The response of bioplastic on heating was observed by differential scanning calorimetry (DSC) analysis of which its result is shown in Figure 8. The lowest and highest peak on a curve indicated the effects of the magnitude of thermal properties. It can be seen the bioplastic has melting temperature, T_m 169.65°C as it is shown as the highest peak.

On the other hand, the bioplastic has transition glass temperature, T_g 72.67°C corresponding to the lowest peak. Crystallization can come at a given temperature on T_g and under the melting point (T_m). The peaks in Figure 8 indicates the bioplastic crystallinity, means the sharper it, the higher crystallinity of bioplastic. The addition of plasticizer contributes to the increase of amorphous fraction in polymer and so, will decrease the melting point of the polymer [22]. Therefore, the presence of plasticizer is needed to enhance bioplastic properties but its concentration must be optimized to avoid the high of amorphous content.

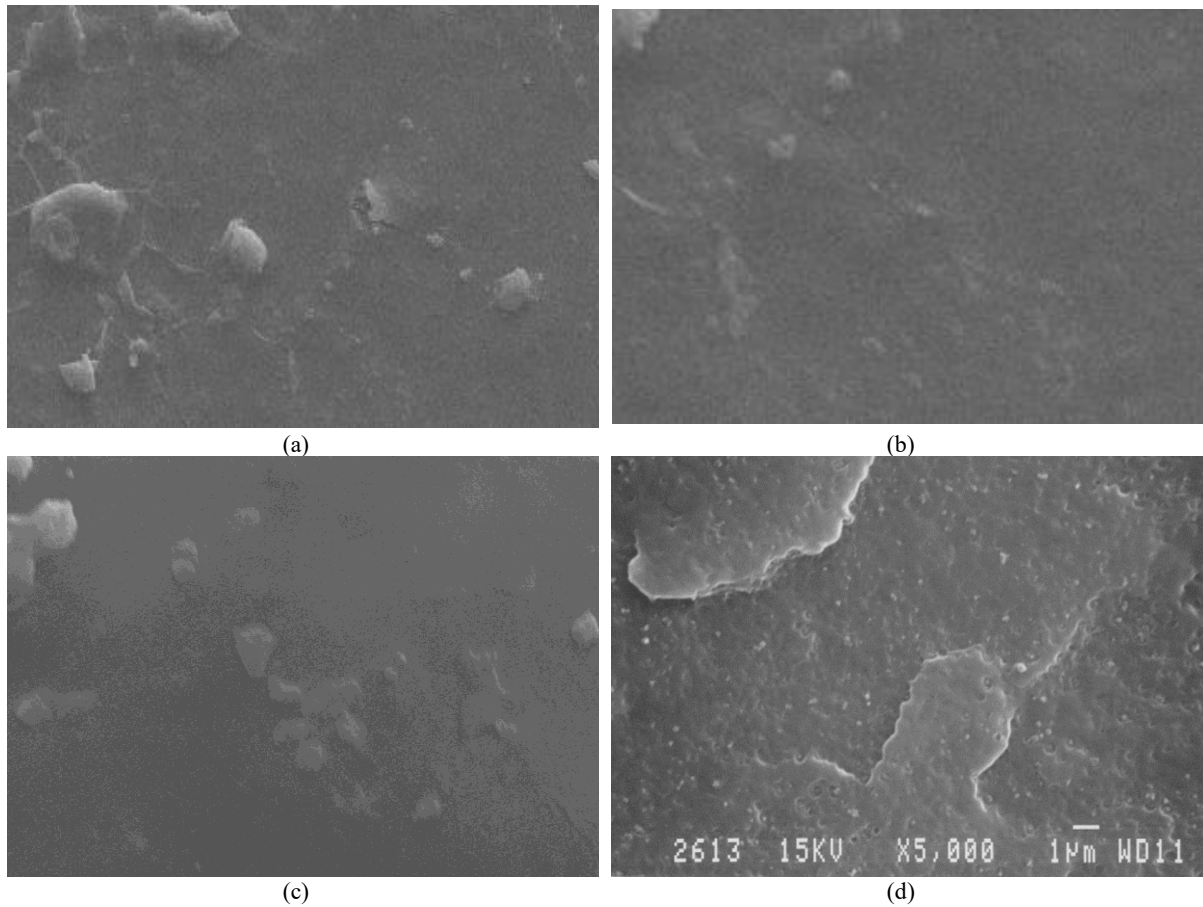


Figure 7. Morphology of the bioplastic (addition 0.5 g filler and 10% plasticizer) from SEM on 500x magnification (a), 1000x magnification (b), 5000x magnification (c) and commercial HDPE as its comparison (d).

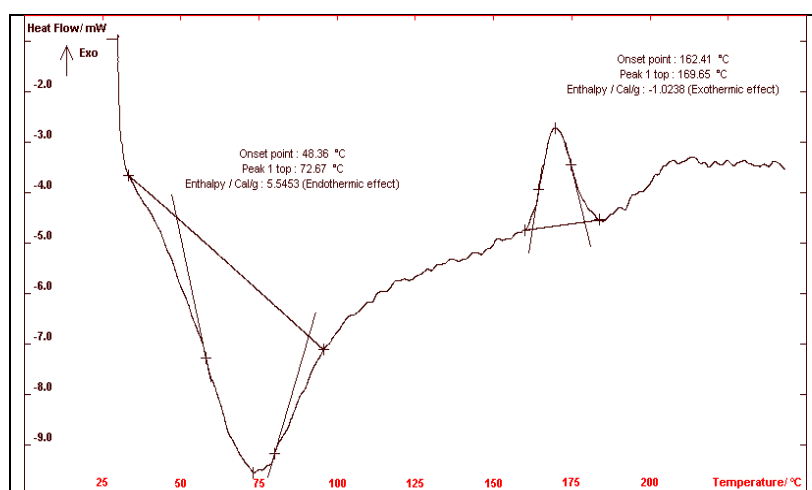


Figure 8. Thermal characteristic of the bioplastic.

4. Conclusion

The addition of filler and plasticizer in a bioplastic synthesis is proven to enhance its physical and mechanical properties and also its morphological characteristics. However, the presence of these substances must be optimized as it is added more it can no longer to support these properties. Apart from it water uptake that is still too much higher than commercial HDPE has, the other bioplastic properties fulfill standard properties of commercial HDPE. Therefore, this could be an alternative to plastic packaging in the future.

5. Acknowledgments

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