Mechanical, SEM and FTIR characteristics of bioplastics from mango seed starch with nanoparticle zinc oxide as filler and ethylene glycol as plasticizers

Maulida Lubis¹, Mara B Harahap², Muhammad H S Ginting¹, Alissha T Sebayang¹, Toni Chandra¹, Yoeselyn Wangi¹ and Jose¹

¹Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan, 20155, Indonesia
²Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Medan, 20371, Indonesia

Email: maulida@usu.ac.id

Abstract. Plastic products are difficult to be degraded and cause environmental problem. To overcome this, plastic material is made from biodegradable natural resource which is called bioplastics. The aim of this research is to know the potency of mango seed starch, nanoparticle zinc oxide as filler and ethylene glycol as plasticizer. The mango seed starch size of 5 grams, with variation of zinc oxide filler mass of 0; 3; 6 and 9% (wt) and ethylene glycol 0; 20; 25; 30 and 35% (wt). The bioplastics films was analyzed the mechanical properties include tensile strength, elongation at break, SEM and FTIR. The optimum result obtained at nanoparticle ZnO concentration 6% and ethylene glycol 25% with tensile strength 3.78 MPa and elongation at break 2.23%. The SEM and FTIR result prove that addition of filler and plasticizer gives better surface morphology and dispersion in the bioplastics.

1. Introduction

For a number of products, like food packaging, beverage pads, office, automotive, and other sectors, plastics are commonly used. It is because plastics have many benefits, such as versatile, clear, cost efficient and strong characteristics [1]. Yet plastics do have a downside that is difficult to degrade and causes environmental harm. If the plastic waste is deposited in landfill and the incineration process is carried out to the garbage piles, significant air pollution would result [2]. In order to produce biodegradable plastics, starch is one of the most studied and encouraging raw materials.

Mango (Mangifera indica) is a common tropical fruit, widely grown and cultivated in many of the world's tropical regions [3]. Mango seeds have been reported to contain 44.0% moisture, 6.0% protein, 12.8% calories, 32.8% carbohydrates, and 2.0% ash [4]. Mango seeds have 70.76% starch content that has the potential in bioplastics as raw material [5]. Adding filler as reinforcement is required to improve the mechanical properties and characteristics.

Several researchers have studied the addition of fillers to enhance the mechanical properties of bioplastics. Nanofillers are one of the most promising fillers and have aroused great interest among researchers. Studies have shown that the wide surface area of nanofillers contributes to stronger polymer matrix interactions [6]. Due to its biocompatibility, low cost and the ability to make surface
modifications with different functional groups, ZnO has been of significant research interest. It is an environmentally friendly, non-toxic material and exhibits an antimicrobial [7].

The processing of starch and filler bioplastic films is stiff when heated, but difficult when cooled, so plasticizers must be used before the bioplastics are dried. The purpose of adding plasticizers is to improve elasticity, elongation at break, and enhance the fluidity and flexibility of bioplastic film properties. Plasticizers are usually added to polyol categories including glycerol and sorbitol [8][9]. Plasticizer is ethylene glycol which is used in this study.

The goal of this research is to understand the effect of nanoparticles ZnO as filler and ethylene glycol as plasticizers on mango seed bioplastics like tensile strength, elongation at break, Scanning Electron Microscope (SEM) and FTIR.

2. Materials and methods

2.1. Materials

Starch generated from mango seeds was acquired in Medan from juice sellers. Nanoparticle ZnO as filler with the average size of 30 nm was purchased from Zhejiang Huqian Gaofei New Materials Co. Ltd, China. Ethylene glycol (C$_2$H$_6$O$_2$) as plasticizer was obtained from juice traders in Medan.

2.2. Preparation of starch from mango seeds

Wash the mango seeds (100 grams) from the waste of the local juice seller with water and cut into small pieces. Then peel the chopped mango seeds and add 100 ml of water to the blender. After the mixing process, the solution was filtered and settled for about 30 minutes. Separate the starch deposits from the slurry and wash again with pure water. After the second precipitation, the starch precipitate is dried in an oven at a temperature of ±60°C to eliminate moisture. Sieve the starch to a 100 mesh/inch filter.

2.3. Bioplastics preparation

Bioplastic film development started with the dispersion of 100 ml of distilled water with filler (zinc oxide) 0, 3, 6 and 9% wt/wt and plasticizer (ethylene glycol) with variations 0, 20, 25, 30 and 35% wt/v. The solution was put into KUDOS tank with ultrasonic homogenizer and processed for around 50 minutes. The solution was discarded from the tank after ultrasonic. Starch (5 grams) was applied to the solution and heated until gelatinized (80.53°C) using a hot plate while stirring. Following mixing, the solution was flattened to 12 x 12 cm and dried for 24 hours at a temperature of 60°C. When set, bioplastics were cooled to ambient temperature before removing off the flat.

2.4. Tensile strength and elongation at break

GoTech universal testing machine uses ASTM D882-91 standard to measure tensile strength. From the observed data, the tensile strength value was obtained and is expressed in MPa. Break elongation is an indicator of flexibility in bioplastics, and is expressed in percentage.

2.5. Scanning electron microscopy (SEM) and fourier transform infrared (FTIR)

The surface morphology of the bioplastic film was checked by using a scanning electron microscope. By using IR Prestife-21 Shimadzu, the functional groups of bioplastics were analyzed. Use FTIR to describe the spectral data in the figure and the wave number of each data given by the bioplastic functional group in the analysis.
3. Results

3.1. Extraction of starch from mango seed
In this study, starch is extracted from mango seeds, the raw materials for bioplastics. Mango seeds from juice sellers in Medan. The resulting form of the starch powder has a particle size of ± 100 mesh. Starch extraction results from mango seeds’ yield is 43.2% starch, which produced as much as 43.2g of 100g of dried starch mango seeds and then obtained additional starch analysis.

![Mango seeds and Starch from mango seeds](image)

**Figure 1.** (a) Mango seeds and (b) Starch from mango seeds

3.2. Tensile strength
Figure 2 shows the effect of various filler and plasticizer concentrations on the tensile strength of bioplastics film. The highest tensile strength value with nanoparticle ZnO filler 6% and plasticizer 25% is 3.78 MPa. While the lowest value is 0.38 MPa, that is obtained at 0% filler nanoparticle ZnO and plasticizer 35%. After 6% of filler, the tensile strength decreases for all plasticizer variations.

![Tensile strength of starch based bioplastics with zinc oxide as filler and ethylene glycol as plasticizer](image)

**Figure 2.** Tensile strength of starch based bioplastics with zinc oxide as filler and ethylene glycol as plasticizer.

The tensile strength value increases due to the interface adhesion between matrix and the filler which enables the increase in hydrogen bonding between the matrix and the composite filler [10] [11]. However, there is a decrease in tensile strength value after 6% of fillers. This is triggered by the broad filler material that inhibits the interaction of molecules, which accelerates the formation of aggregates and the film’s heterogeneous structure [12]. Throughout the manufacture of bioplastics, plasticisers need to be applied to boost durability and usage [13]. As the plasticizer concentration increases, the hydrogen bonds in the film will decrease, increasing flexibility and decreasing the tensile strength value [1].

3.3. Elongation at break
Figure 3 shows the effect of different concentrations of fillers and plasticizers on the elongation of bioplastic films. At 0% nano-ZnO and 35% ethylene glycol (5.68%), the elongation at break is the highest. The increase of nano-ZnO filler will reduce the elongation at break, 9% nano-ZnO and 0% plasticizer reach the lowest.
Elongation at break is the extensibility of the length of the film from initial length to break point. Moraes et al. [14] described Elongation at Break (E%) as film's ability to deform until finally breaking. The flexibility and stretching potential of films can be determined by this parameter (E%).

Elongation at break and reducing it with increasing filler loading suggests the filler's inability to sustain the transfer of tension from the filler to the polymer matrix [10]. Adding a plasticizer should be inversely related to the application of fillers. Plasticizer increases the elongation at breakage and decreases the tensile strength of the film, which weakens the gelatin structure and bond in the bioplastic film [15].

![Elongation at Break](image)

**Figure 3.** Elongation at break of starch based bioplastics with zinc oxide as filler and ethylene glycol as plasticizer.

3.4. **Scanning electron microscope (SEM)**

The outcome of the SEM characterization of bioplastics with and without fillers and plasticizers with a magnification of 1000 x is shown in Figure 4. In figure 4(a), morphology shown as a result of SEM analysis is less smooth and there is insoluble starch that is poorly soluble, defined by the star in the matrix. In figure 4(b), SEM result analysis of bioplastics with filler and plasticizer showed that a uniform dispersion of nanoparticle ZnO filler in the mango seed starch matrix. The surface is smoother than without addition of plasticizer.

The difference between two images is caused by the absence of fillers in bioplastic so that becomes more fragile and the surface is not tight [2]. The application of starch fillers allows the starch granules to swell. Increasing starch swelling makes starch softer [16]. The ultrasonic method of ZnO nanoparticles is designed to prevent agglomeration and achieve a homogeneous dispersion filler into the matrix and increase the miscibility of the polymer phase [17].

![SEM Images](image)

**Figure 4.** SEM of starch based bioplastics (a) without filler and plasticizer and (b) with filler and plasticizer with magnification 1000 x.
3.5. *Fourier transform infra red (FTIR)*

Figure 5 presents the characteristics of bioplastic Fourier Transform Infra Red (FTIR) without and with filler zinc oxide and ethylene glycol plasticizer to classify functional groups.

Wavenumber 3599.17 cm\(^{-1}\) and 2989.66 cm\(^{-1}\) bioplastics without filler indicating the presence of the O-H group, 1693.50 cm\(^{-1}\) indicates the C = O group, 2873.94 cm\(^{-1}\) and 2758.21 cm\(^{-1}\) represent the C-H alkanes, 1172.72 cm\(^{-1}\) and 1114.86 cm\(^{-1}\) due to the presence of alcohols, ethers, C-O esters. It also showed the peak bioplastic at 3645.46 cm\(^{-1}\) is O-H group with zinc oxide filler and plasticizer. Absorption at wavenumber 2993.52 cm\(^{-1}\) and 2877.79 cm\(^{-1}\) are C-H alkanes. The wavenumber 1697.36 cm\(^{-1}\) represent C=O aldehyde group. Peak at wavenumber 1176.58 cm\(^{-1}\) and 1126.43 cm\(^{-1}\) show the presence of C-O esters group.

![Figure 5](image)

*Figure 5. Fourier transform infra red of bioplastic without and with filler zinc oxide and ethylene glycol plasticizer*

Increasing concentrations of ZnO nanoparticles in bioplastics, according to Harunsyah et al[6], involve a greater alkane bond, C-C bond, C = C bond, and C-C bond which will affect better structural strength as shown in the material characteristics of films. The bioplastics containing the C = O group and the carbonyl ester group imply that the bioplastics are biodegradable [2].

4. **Conclusion**

According to the research results, it can be concluded that mango seed starch can be used as a raw material for bioplastics. The amount of starch in 100 grams of mango seed is 43.2%. The optimum result is obtained with nanoparticle ZnO filler concentration of 6% and ethylene glycol as plasticizer of 25% with tensile strength of 3.78 MPa and elongation of 2.23%. The Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR) result prove that addition of filler and plasticizer gives better surface morphology and dispersion in the bioplastics.

**Acknowledgments**

The authors acknowledge gratefully that the current research is funded by Indonesia's Ministry of Research and Technology and Higher Education for the year 2020.

**References**

[1] Sofiah Y, Martha A and Melianti 2019 Mechanical Properties of Bioplastics Product from Musa Paradisica Formatypica Concentrate with Plasticizer Variables *Journal of Physics*
1167 012048

[2] Maulida, Mara B H, Alfarodo, Anita M and M H S Ginting 2018 Utilization of Jackfruit Seeds (Artocarpus heterophyllus) in the Preparing of Bioplastics by Plasticizer Ethylen Glycol and Chitosan Filler *APRN Journal of Engineering and Applied Sciences* 13 1 ISSN: 1819-6608

[3] Shahrim N A, N Srifuddin and H Ismail 2018 Extraction and Characterization of Starch From Mango Seeds *Journal of Physics* 1082 012019

[4] Eleogbede J A, Achoba I I and Richard H 1995 Nutrient composition of mango characteristics of seed kernel from Nigeria *Journal of Food Biochemistry* 19 391–398

[5] Septiosari A, Latifah and Ella K 2014 Pembuatan dan Karaterisasi Bioplastik Limbah Biji Mangga dengan Penambahan Selulosa dan Gliserol *Indonesian Journal of Chemical Engineering* 3 2 ISSN: 2252-6951

[6] Harunsyah, M Yuus and Reza F 2017 Mechanical properties of bioplastics cassava starch film with Zinc Oxide nanofiller as reinforcement *IOP Conf. Series: Materials Science and Engineering* 210 012015

[7] Sapei J, Padmawijaya K S and Wardhana P J 2016 Study of the influence of ZnO addition on the properties of chitosan-banana starch bioplastics *IOP Conf. Series: Materials Science and Engineering* 223 012044

[8] Ginting M H S, R Hasibuan, M Lubis, F Alaniani, F A Winoto and R C Siregar 2018 Utilization of Avocado Seeds as Bioplastics Films Filler Chitosan and Ethylene Glycol Plasticizer *Asian Journal of Chemistry* 30 7 1569-1573

[9] Pivsa-Art W, Kazunori F, Keiichiro N, Yuji A, Hitomi O and Hideki Y 2015 The effect of poly(ethylene glycol) as plasticizer in blends of poly(lactic acid) and poly(butylenes succinate) *Journal of Applied Polymer Science*

[10] Chris-Okafor P U, Nwakaye J N, Oyom P O and Ilodigwe C B 2018 Effect of snail powder on the mechanical properties of low density polyethylene (LDPE) *London Journal of Research in Science: Natural and Formal* 18 4 7-12

[11] Syafri E, Anwar K, Hairul A, and Alfi A 2017 Effect of precipated calcium carbonate on physical, mechanical and thermal properties of cassava starch bioplastics composites *International Journal on Advanced Science Engineering Information Technology* 7 5 1950-1956

[12] Lubis M, Mara B H, Ginting M H S, Mora S and Hidayatul A 2018 Production of bioplastics from avocado seed starch reinforced with microcrystalline cellulose from sugar palm fibers *Journal of Engineering Science and Technology* 13 2 381-393

[13] Maulida, Siagian M and Tarigan P 2016 Production of starch based bioplastics from cassava peel reinforced with microcrystalline cellulose avicel PH101 using sorbitol as plasticizer *Journal of Physics* 710 012012

[14] De Moraes J O 2009 *Propriedades de filmes de amidoincorporados de nanoargilas e fibras de cellulose* Universidade Federal de Santa Cantaria Brazil

[15] Rezaei, Mahsa and Ali Motamedzadegan 2015 The effect of plasticizers on mechanical properties and water vapor permeability of gelatin-based edible films containing clay nanoparticles *World Journal of Nano Science and Engineering* 5 178-193

[16] Suryanto H, A W Rahmawan, Solichin, R T Sahana, M Muhajir and U Yanuhar 2019 Influence of Carrageenan on the Mechanical Strength of Starch Bioplastic Formed by Extrusion Process *IOP Conf. Series: Materials Science and Engineering* 494 012075

[17] Pilla S 2011 *Handbook of Bioplastics and Biocomposites Engineering Applications* (USA: Wisconsin Institute For Discovery, University of Wisconsin-Madison)