ARPN Journal of Engineering and Applied Sciences

UTILIZATION OF JACKFRUIT SEEDS (*Artocarpus heterophyllus*) IN THE PREPARING OF BIOPLASTICS BY PLASTICIZER ETHYLENE GLYCOL AND CHITOSAN FILLER

Maulida[1], Mara Bangun Harahap[2], Alfarodo[1], Anita Manullang[1] and M. Hendra S. Ginting[1]
[1]Departement of Chemical Engineering, Faculty of Engineering, University of Sumatera Utara, Medan, Indonesia
[2]Department of Physics, Faculty of Mathematics and Natural Science, State University of Medan, Medan, Indonesia
E-Mail: maulida@usu.ac.id

ABSTRACT

Bioplastic is the plastic that is naturally decomposed with the help of microorganisms. The use of starch as the main ingredient for the plastic manufacture has a great potential, because in Indonesia, there are varieties of starch crops and one of them is jackfruit. This study was aimed to determine the effect of chitosan and ethylene glycol in the physicochemical properties of bioplastic which was made by utilizing jackfruit seeds. In the manufacture of bioplastic, the ratio of jackfruit seeds: chitosan was 7: 3, 8: 2 and 9: 1 (w/w), while the concentrations of ethylene glycol were varied as 20 mL/ g, 25 mL/ g, 30 mL/ g, 35 mL/ g, and 40 mL/ g (v/w). The product was physically and chemically analyzed by using RVA (Rapid Visco Analyzer), FTIR (Fourier Transform Infra Red), tensile strength measurement, and SEM (scanning electron microscopy). From the RVA analysis of jackfruit seeds starch, the gelatinization temperature was obtained as 88.82 °C with the peak of viscosity of 3276.5 cP. Characterization of FT-IR spectra of the bioplastics with chitosan and ethylene glycol indicated O-H and N-H groups. The best conditions for bioplastics tensile strength was in the ratio of jackfruit seed starch and chitosan (w/w) with 7: 3 and a plasticizer of 0.35 mL/ g at 28.271 MPa. The results of mechanical test was supported by scanning electron microscopy (SEM) analysis that showing bioplastics with chitosan filler and plasticizer ethylene glycol has a smooth and soft surface and also was slightly void.

Keywords: jackfruit seeds, bioplastics, chitosan, gelatinization, ethylene glycol.

INTRODUCTION

The production of plastic is in its mainstream phase over the past two decades. Its lightness and strong characteristic make people tend to use plastics for their daily actvities. However, it raises a new problem for the environment, mainly because of the plastic is difficult to be degraded. If the plastic waste is dumped in final landfills and incineration process of plastic is performed to reduce the piles of garbage, it will cause massive air pollution [1].

The answer to tackle this issue is by replacing the polymer materials with bioplastics, as it will be easily degraded by nature [2]. Bioplastics can also be recycled because of its constituent compounds are derived from plants such as starch, cellulose, and lignin as well as animals such as casein, proteins and lipids [3]. One of the isolatable starch is jackfruit seeds. Jackfruit seed weight is about 8-15% of the total weight of the fruit [4]. Jackfruit seeds have a carbohydrate content of 36.7 grams per 100 grams and for every 36.7 grams of carbohydrates; the starch content is amounted to 94.5% [5]. Chitosan is used as bioplastics filler. The selection of chitosan as an alternative to modify the plastic into environmentally friendly plastic is due to an excellent biodegradation properties which is possesed by chitosan [6]. The elasticity of chitosan is very weak, but it can be enhanced with the addition of a liquid/ solid substance in order to improve the properties of plasticity [4] [6]. The process of this addition is known as a plasticizer, while the added substance is called as plasticizers [4].

MATERIALS AND METHODS

Materials

ackfruit seed were purchased from the fruits seller at traditional market in Padang Bulan, North Sumatera, while ethylene glycol, shrimp chitosan, aquadest, and acetic acid glacial were purchased from Merck.

Preparation of starch

As much as 100 grams of shelled parts of the outer sheath and the epidermis of Jackfruit seeds was cleaned with water. Seeds were cutted with the size of 1 cm^2 approximately and then crushed by using a blender with the addition of water. The soft material was removed from the blender and filtered through a plastic sieve to obtain a pulp and liquid filtrate (starch suspension). The resulting suspension was then deposited for 24-48 hours until the starch settled perfectly. The liquid in a bottom side which contains big amount of starch was filtered using Whatman filter paper no.1 to obtain a wet starch. Then, the precipitate was dried in the oven with a temperature of 70 °C for 30 minutes. Retrieved dry starch powder and sieved with 100 mesh sieve [7].

General procedures

As many as 10 grams of starch was provided. Starch solution was made with a ratio of starch: distilled water as 1: 20 as much as 100 grams in 500 ml glass beaker. Then, the mixture of starch and chitosan was created with the volume that has been calculated on a glass beaker. 500 ml glass beaker containing mixed starch was placed on a magnetic stirrer with a regulated temperature of 88.82 °C for 25 minutes and stirred constantly with rotation speed of 400 rpm. After 25 minutes, ethylene glycol with a variation of 20%, 25%, 30%, 35% and 40% starch solution was added, and then stirred for 15 minutes. After that, the magnetic stirrer was turned off and 50 ml solution was poured into the 20x20 cm mould flexi glass, then dried in an oven at T = 60 °C for 24 hours. Once it had drained, it was putted in desiccators for 24 hours. Then, the bioplastic was removed from the mould and ready to be analyzed [8].

RESULTS AND DISCUSSIONS

Pasting behaviour and gelatinization temperature

In this study, the method used to determine the starch gelatinization behaviour was determined by using the Rapid Visco Analyzer (RVA). RVA is a method which is widely used to determine the nature and viscosity of starch paste from the nature itself. The amylograph of jackfruit seed starch which was measured by RVA can be seen in Table-1. The gelatinization temperature is the critical temperature at which the starch granules losing its refractive properties (birefringence) and its crystallinity during the heating process [9]. The value of jackfruit seed starch gelatinization temperature can be seen in table 1. The gelatinization temperature was high due to the big amount of amylose content [10].

Table-1. The amylograph of jackfruit seed starch.

Parameter	Jackfruit seeds starch
Gelatinization temperature	88,82 °C
Peak Viscosity	3.276,5 cP
Hold Viscosity	2.453,5 cP
Final Viscosity	5.366 cP
Breakdown	823 cP
Setback 1	2,912,5 cP

There are several steps in the process of gelatinization. The first step is, the starch in cold water will absorb water for about 5-30%, and this process is reversible. The second step, due to the heating supplied hydrogen bonding between amylose and amylopectin in the starch granules, it begins to break up, so that water can get into the starch granules and granule begins to swell. The process of water absorption into the starch granule is irreversible [11]. In the second step of gelatinization process, the starch granules swelling is causing a rapid increase in viscosity and produce maximum viscosity namely as Peak Viscosity (PV) [12]. The maximum temperature at which the final viscosity reached is called as gelatinization. At this temperature, the starch granules have lost its birefringence properties and grainy already and do not have a crystal in its form [13]. The greater the swelling ability of the starch granules, the higher its viscosity paste [10]. RVA measurement resulted PV jackfruit seed starch as 3276.5 cP. The third step of gelatinization showed the greater swelling granules. The amylose which came out from the starch granules was dispersed in the mixed liquid until the starch granules ruptured [11]. The outbreak of the structure of the starch granules lead to a decrease in viscosity paste. The viscosity peak decreased to hit 2453.5 cP. This viscosity is called as hold viscosity (HV). HV is the ability to hold the starch granules and press the heating strain. The difference between PV and HV can be seen by their viscosity value difference as 823 cP. Low viscosity breakdown showed that granules possesed higher stability towards heating [14]. In the cooling phase, the viscosity of starch paste increased due to the formation of amylose and amylopectin molecules through the hydrogen bonds [12]. RVA viscosity measurement result increased to 5366 cP. This viscosity is called as cold viscosity or Final Viscosity (FV). Setback is the difference between the HV with FV. It demonstrates the ability of starch pastes to undergo a retro-gradation. It is the process of reshaping the starch matrix which has already been gelatinized. The higher the value of the viscosity setback means that the higher the ability of starch to have a retro-gradation properties [15]. Based on the results of the RVA, the setback of viscosity value of the jackfruit seed starch was 2912.5 cP. The high value of setback was obtained due to the increasing of brittleness in starch granules diametres during the gelatinization and disintegration process which facilitates the releasing of amylose chains and recombining amylose. Starch with high setback value indicates that the number of amylose is rebounded via hydrogen bonds so that the formed starch structure becomes stronger. To sum up, the higher the number of amylose starch, the higher the value of the final viscosity [10, 22].

FTIR

The information of the appearance of several peaks is shown in Figure-1. It also shows that for both bioplastics with chitosan and without chitosan have a similar spectrum. Bioplastics with chitosan indicating the O-H group stretching at 3649.32 cm-1 while for bioplastic without chitosan is at 3676.32 cm-1. The C-H group stretching on bioplastics with chitosan and without chitosan are recorded at 2993.52 to 2877.79 and 2993.52 to 2877.79 cm^{-1} respectively. Also, C-O band appeared for bioplastics with chitosan and without chitosan at 1172.72 to 1118.71 and 1176.58 to 1114.86 cm^{-1} respectively [16]. The amide carboxyl group spectra is clearly visible at 1647.21 cm^{-1}. And there is also a hydroxyl groups O-H absorption band in the area of 3433.29 cm^{-1} [17].

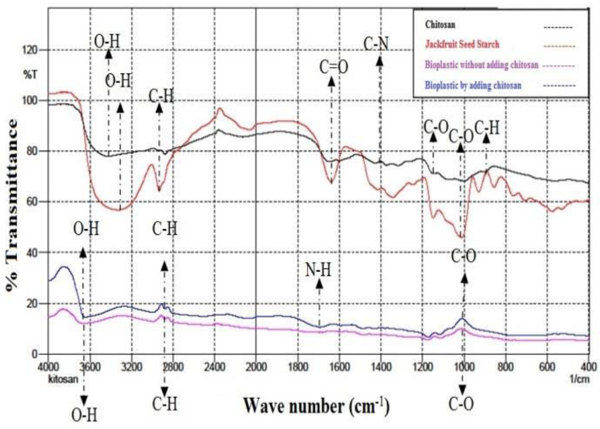


Figure-1. The FTIR result among jackfruit seed starch, chitosan, bioplastic without/by adding chitosan filler and ethylene glycol plasticizer.

According to Darni and Herti (2010), the bioplastics which contain the C=O functional groups and ester carbonyl (C-O) indicate that the bioplastics are biodegradable. These functional groups are owned by starch and chitosan. This is due to the C=O and ester carbonyl (C-O) which are hydrophilic. The ability of both groups to bind water molecules derived from microorganisms that can lead to enter the plastic matrix and make them easily to be degraded [16].

Tensile strength

Figure-2 shows the relationship of the addition of ethylene glycol to chitosan and to the tensile strength of bioplastics. From the figure below, it can be seen that the highest tensile strength value of bioplastic is resulted by the addition of 3 grams chitosan and ethylene glycol of 0.35 mL/ g with the amount of 28.271 MPa, while the lowest tensile strength is resulted by the addition of 1 gram of chitosan and ethylene glycol of 0.20 mL/ g with the amount of 14.881 MPa.

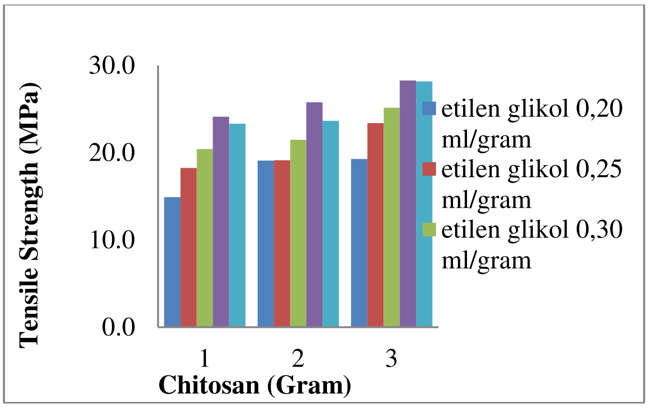


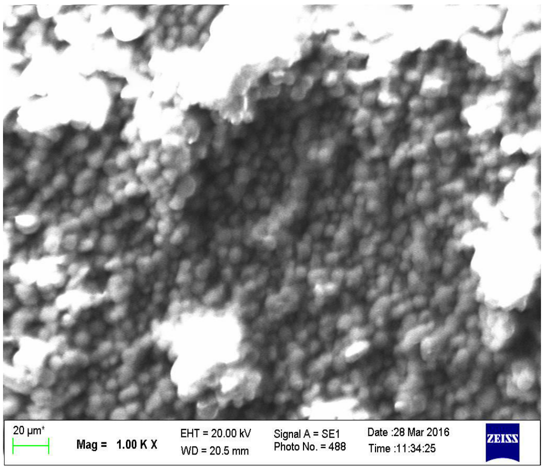
Figure-2. Effect of chitosan and ethylene glycol on tensile strength of bioplastic.

Based on Figure-2, the addition of chitosan fillers and plasticizers ethylene glycol has given an effect to the tensile strength of bioplastics. With the increasing number of chitosan may cause the tensile strength value of bioplastics is increased. This is caused by the addition of chitosan as filler may increase the density and resulting a bioplastics with a dense structure so that the tensile strength of bioplastics is increased [18]. The addition of plasticizer varies inversely with the addition of fillers and decrease the value of the tensile strength. This is caused by the addition of a plasticizer lowers the density of the structure of the polymer chains which causes a decrease in tensile strength [17]. In the figure above, it shows a decline in tensile strength on the addition of 1, 2, and 3 grams of chitosan with ethylene glycol of 0.35 mL/ g. According to Chrismaya (2012), a decrease in tensile strength of bioplastic conditions is caused by the presence of plasticizer in the mixture. This leads to a state of saturation plasticizer resulted as a plasticizer effect which lowers the value of the tensile strength [19].

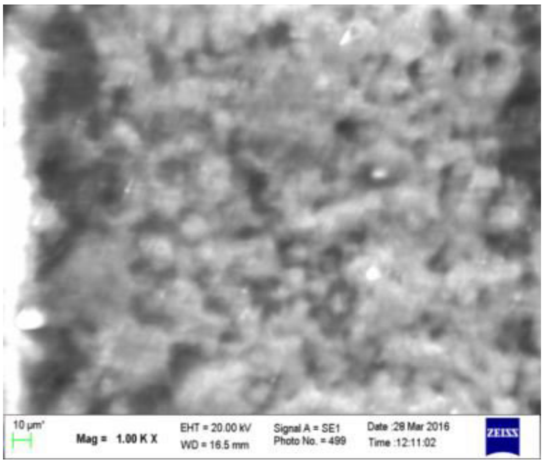
SEM

Figure-3 shows the results of SEM characterization of jackfruit seed and bioplastics products with and without the addition of fillers and plasticizersn with a 1,000 times magnification. In Figure-3(a), the result of SEM analysis showed that the morphology of jackfruit seed starch has a particle size which is not uniform. SEM is a method to produce the image of the microscopic surface area of the sample [20]. SEM analysis result of jackfruit seed starch shows a starch granule size of 7.6 µm.

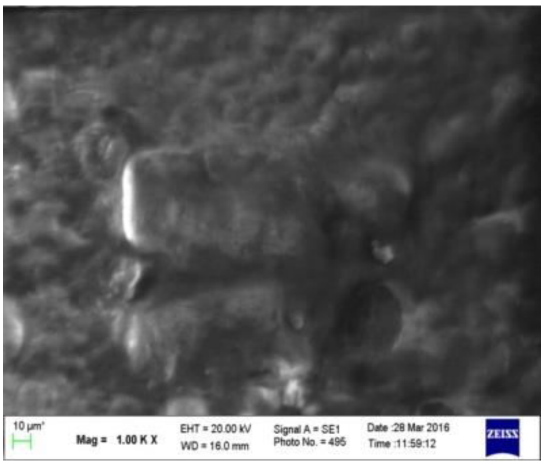
In Figure-3(b), the bioplastics without filler are indicated to partly undergo the gelatinization process. Figure-3(b) also shows that bioplastics without filler has a structure that is less dense and the surface is less smooth. This is caused by the absence of fillers in bioplastic so that it becomes fragile and its surface morphology is not tight. In contrast, Figure-3(c) shows the bioplastics, which its surface looks denser and smoother compared to the Figure-3(b). In Figure-3(c), the starch granules were not detected which means that the starch has been gelatinized perfectly. In addition, bubble (void) is identified in Figure-3(c). It is caused by hydrogen bonding chains of starch which started to break down when reaching the gelatinization temperature and the water molecules began to infiltrate into hydroxyl groups in the starch molecule [21, 22].



(a)



(b)



(c)

Figure-3. Morphology analysis of bioplastic surface (a) SEM characterization of jackfruit seeds with 1000 times magnification, (b) bioplastics without filler and plasticizer ethylene glycol chitosan with 1000 times magnifications, and (c) bioplastics with addition of chitosan and plasticizer ethylene glycol with 1000 times magnification.

CONCLUSIONS

Based on the results of the research, it can be concluded that the jackfruit seed starch reached the gelatinization temperature of 88.82 °C with the viscosity peak of 3276.5 cP. Characterization of FT-IR spectra of the bioplastics with chitosan and ethylene glycol indicated the O-H and N-H groups. The best conditions of starch bioplastics tensile strength in comparison with jackfruit seed starch: chitosan (w/w) was 7: 3 with a plasticizer of 0.35 mL/ g at 28.271 MPa. The elongation break with the ratio of starch: chitosan (w/w) of 9 : 1 with a plasticizer of 0.40 mL/ gram at 1.999% and the young modulus ratio of starch: chitosan (w/w) was 7: 3 with a plasticizer of 0.30 mL/ gram at 42.581 MPa.

REFERENCES

[1] F.L. Sahwan dkk. 2005. Sistem Pengelolaan Limbah Plastik di Indonesia. Jurnal Teknologi Lingkungan. 6(1): 311-318.

[2] A. Buzarovska *et al*. 2009. Eco-challenges of bio-based polymer composites. Material. 2, 911-925.

[3] Ave´rous, L. 2004. Biodegradable Multiphase Systems Based on Plasticized Starch: a review. Journal of Macromolecular Science - Part C Polymer Reviews, C4(3): 231-274.

[4] Erfan Ahmad. 2012. Sintesis Bioplastik Dari Pati Ubi Jalar Menggunakan Penguat Logam ZnO Dan Penguat Alami Kitosan. Skripsi. Program StudiTeknik Kimia. Fakultas Teknik. Universitas Indonesia.

[5] Chayatinufus Chairunisa. 2014. Pembuatan Maltodekstrin dari Pati Biji Nangka (Artocarpus Heterophyllus) dan Aplikasinya sebagai Enkapsulan Asap Cair. Skripsi, Jurusan Teknologi Pangan dan Hasil Pertanian, Universitas Gadjah Mada.

[6] Prashanth K.V., Harish K. L, Shamalab T.R., dan Tharanathan R.N. 2005. Biodegradation of Chitosan-Graft-Polymethylmethacrylate Films. Journal of International Biodeterioration & Biodegradation. 56: 115-120.

[7] Fairus dkk. 2010. Pengaruh Konsentrasi HCl dan waktu hidrolisis terhadap Perolehan Glukosa yang Dihasilkan dari Pati Nangka. Prosiding Seminar Nasional Teknik Kimia “kejuangan.

[8] Darni Yuli, Sri Ismiyati D, Tigor Marbun. 2010. Influence Concentration of Plasticizer and Formulation of Banana Starch - Chitosan to

Mechanical Property and Water Uptake of Bioplastic. International Journal of Engineering and Science. 1(4). Teknik Kimia. Fakultas Teknik. Universitas Malahayati Press.

[9] Doutch, James. *et al*. 2012. Structural Changes during Starch Pasting Using Simultaneous Rapid Visco Analysis ana Small-Angle Neutron Scattering. Carbohydrate Polymers. 88: 1061-1071. Elsevier.

[10] Kategunya Rengsutthi dan Sanguansri Charoenrein. 2011. Physico-Chemical Properties of Jackfruit Seed Starch (Artocarpus Heterophyllus) and its Application as a Thickener and Stabilizer in Chilli Sauce. Journal Food Science and Technology. 44: 1309-1313. Elsevier.

[11] Dimas Damar Adi Krisna. 2011. Pengaruh Regelatinisasi dan Modifikasi Hidrotermal terhadap Sifat Fisik pada Pembuatan Edible Film dari Pati Kacang Merah (Vigna angularis sp). Tesis, Program Studi Magister Teknik Kimia Universitas Diponegoro. hal. 17-18.

[12] Didah Nur Faridah, Dedi Fardiaz, Nuri Andarwulan, dan Titi Candra Sunarti. 2014. Karakteristik Sifat Fisikokimia Pati Garut (Maranta arundinaceae). Agritech. 34(1).

[13] Jin-song. Bao. 2008. Accurate Measurement of Pasting Temperature by the Rapid Visco Analyzer: a Case Study Using Rice Flour. Rice Science. 15(1): 69-72. Elsevier

[14] Sondeep Sing *et al*. 2010. Effect of sowing time on protein quality and starch pasting characteristics in wheat (Triticum aestivum L.) genotypes grown under irrigated and rain-fed conditions. Food Chemistry 122, 559-565. Elsevier

[15] Nur Richana dan Titi Chandra Sunarti. 2004. Karakterisasi Sifat Fisikokimia Tepung Umbi dan Tepung Pati dari Umbi Ganyong, Suweg, Ubikelapa dan Gembili. J.Pascapanen 1(1): 29-37

[16] Darni, Yuli dan Herti Utami. 2010. Studi Pembuatan dan Karakteristik Sifat Sorgum dan Hidrofobisitas Bioplastik dari Pati Sorgum. Jurnal Rekayasa Kimia dan Lingkungan. 7(4): 88-93, ISSN 1412-5064.

[17] Fitria Yenda Elpita, Yuli Darni. 2015. Peningkatan Karakteristik Mekanik Dan Fisik Bioplastik Berbahan Dasar Pati Sorgum Dan Serbuk Batang Sorgum. Seminar Nasional Sains & Teknologi VI Lembaga Penelitian dan Pengabdian Universitas Lampung.

[18] Kumar A.P., Singh R.P. 2008. Biocomposites of cellulose reinforced starch: improvement of properties by photo-induced crosslinking. Bioresour. Technology. 99, 8803-8809.

[19] Chrismaya B., F. Selvy D. S. Retnowati. 2012. Biofilm dari Pati Nangka dengan Additif Karanginan. Jurnal Teknologi Kimia dan Industri. 2(3): 138-142.

[20] M. Hendra S. Ginting, M. Fauzy Ramadhan Tarigan, Annisa Maharani Singgih. 2015. Effect of Gelatinization Temperature and Chitosan on Mechanical Properties of Bioplastics from Avocado Seed Starch (Persea Americana mill) with Plasticizer Glycerol. The International Journal Of Engineering And Science (IJES). 4(12): 36-43. ISSN (e): 2319-1813 ISSN (p): 2319-1805.

[21] Ganda Merisiyanto dan Lizda Johar Mawarani. 2013. Pengembangan Plastik Photobiodegradable Berbahan Dasar Umbi Ubi Jalar. Jurnal Teknik POMITS. 2(1), ISSN: 2337-3539.

[22] Maulida Lubis *et al.* 2016. Utilization starch of jackfruit seed (Artocarpus heterophyllus) as raw material for bioplastics manufacturing using sorbitol as plasticizer and chitosan as filleUtilization starch of jackfruit seed (Artocarpus heterophyllus) as raw material for bioplastics manufacturing using sorbitol as plasticizer and chitosan as filler. J. Phys.: Conf. Ser. 801 012014