5th ICRIEMS Proceedings
Published by Faculty Of Mathematics And Natural Sciences
Yogyakarta State University, ISBN 978-602-74529-3-0

Optimization of Plasticizer Glycerol in Edible Film Based Water Hyacinth (*Eichornia crossipes*) Starch

Abidah Walfathiyyah [1,a)], Angli Pramudita Kusuma[1,b)], Febi Nur Cahya Witana[1,c)], Nurriza Qusyairi[1,d)] and Dewi Wahyuningtyas[1,e)]

[1] *Department of Chemical Engineering, Institute of Science & Technology AKPRIND Yogyakarta, Jl. Kalisahak 28, Kompleks Balapan, Yogyakarta 55222, Indonesia*

[a)] Corresponding author: abidahfathiyyah@gmail.com, [b)] anglipramudita13@gmail.com, [c)]febi_cahyo@yahoo.co.id, [d)] nurizza75@gmail.com, [e)] dewi.wahyuningtyas@akprind.ac.id

Abstract. The biopolymers development as environment friendly plastics such as edible film is a solution of environmental problems. Edible film is a thin layer made of materials that can be consumed, but it is fragile. Therefore, to improve the mechanical characteristics of edible films required modification by addition of water hyacinth starch and glycerol plasticizer. the aim of this research is to study the addition of glycerol to the characteristic of edible film. The main components from the edible film are water hyacinth starch and glycerol. The research methods consisted of two processes: (1) making of starch from water hyacinth, (2) making of edible film with the starch-glycerol variation: 100:0; 90:10; 80:20; 70:30; 60:40 (%w/v) while the processing time-stirring speed variation: 30 minutes: 200 rpm, 1 hour: 135 rpm, and 1.5 hours: 70 rpm. The research analysis include tensile strength test, water endurance test, and compound structure test using FTIR. The results showed that the addition of glycerol (0-40% volume) causes decreasing the tensile strength value of film and increasing the percentage of film elongation. The optimum condition of starch and glycerol was obtained at 70:30 (%w/v) with stirring speed 135 rpm and 1 hour process time. The highest swelling value is 69.05%.

Keywords : edible film, water hyacinth, glycerol, tensile strength, swelling

INTRODUCTION

Water hyacinth is a pest or weed that can grow quickly. According to the survey results in Banyu Biru Village, Rawapening, water hyacinth taking by farmer groups fostered by the local government with a production rate of 4 tons per day per farmer group. However, the utilization rate of water hyacinth has not been comparable with its growth rate which is 1.9% per day and its breeding rate, These 10 plants can be 600,000 plants within 8 months [1]. Meanwhile, the content of cellulose in dry water hyacinth is quite high, which is about 64.51% [2].

Water hyacinth can be utilized as an alternative material for edible film making. Edible film is a thin layer composed of materials that can be consumed. Edible film has the potential to extend shelf life and maintain the quality of food by not changing aroma, taste, texture, and appearance [3]. Edible film from natural polymers is one of the most environmentally friendly alternative food packaging solutions because it uses renewable and relatively inexpensive materials.

Starch based of edible film is modified with the addition of glycerol. The addition of glycerol will result in a film that is more flexible, smooth, can increase film permeability to gas, water vapor and solutes [4]. The type of polymer component as an edible film will greatly affect the morphological and film structure as well as the physical, mechanical, and cross-product characteristics of the resulting packaging product. Generally, the polysaccharide component has an inhibitory trait against the gas transmission which is better than the water vapor because it has polar properties so it can interact with water. From previous research by Nahwi (2016) just studied the modification of edible film from banana peel and water hyacinth, have not studied the optimum

condition of its manufacture [6]. The authenticity of this research is to study the operating conditions of making pure film edible from water hyacinth starch with glycerol plasticizer.

The formation of edible films from starch, in principle is the gelatinization of starch molecules. The process of film formation is a phenomenon of gel formation due to temperature treatment, resulting in the formation of matrix or tissue [7]. In making edible film, the factors that need to be considered include:

a. Temperature
   Temperature is required to form an intact film edible, without any heat treatment the possibility of very small molecular interactions. Heat treatment is required to make the polymer sterilized. The temperature range is 64,5^{o}C - 70°C [4].
b. Polymer Concentration
   According Krochta dan Johnson (1997), polymer concentration is very influential on the physical trait of edible film [7]. The greater the polymer concentration the number of polymers making up the film matrix the more so as to produce thick film.
c. Plasticizer
   Plasticizer is influential on the mechanical and physical trait of the film because it reduces the intermolecular trait and lowered the internal hydrogen bond. Plasticizer polyols are often used such as glycerol and sorbitol [7]. Plasticizer used in this research is glycerol (propan-1,2,3-triol) with the molecular formula $C_3H_8O_3$. Glycerol is used to regulate the water content in food , preventing drought on food and glycerol as a plasticizer can improve film flexibility [8]. Increasing the amount of glycerol in a water-starch mixture reduces the value of voltage and elongation. Low glycerol content also reduces the tensile strength of edible film [9].

This research is expected to provide additional economic value from the utilization of water hyacinth for the community. Edible film products from water hyacinth can provide an environmentally friendly packaging alternative so that the use of synthetic plastics can be reduced.

RESEARCH METHODS

Research Scopes

This is an experimental research which is conducted at chemical physic and organismal chemistry lab at IST AKPRIND. The analytical of this research including tensile strength test, swelling test, durable and compound structure that shaped by FTIR. Duration of this research start from April till July 2017

Research Objective

The main raw material is water hyacinth with length of rod approximately is 30 cm that was taken in Turi Sleman. Technical Glycerol, aquadest, citric acid, and carrageenan that obtained from seller in Kotagede.

Research Instrument

Set of tools of edible film maker spatula, 20 cm x 20 cm x 2 cm glass plate, oven, mesh sieve, pipette volume, drop pipette, pan, digital scales, mortar, hot plate, FTIR, and tensile strength test (UTM) are main instrument that used in this research.

Research Variable

In this research there are two variables that used, they are :

a. Comparison between starch of water hyacinth and glycerol (%w/v) with formulation : 100:0 (F1), 90:10 (F2), 80:20 (F3), 70:30 (F4) dan 60:40 (F5)
b. Duration of process and speed of blending : 30 minutes :200 rpm (P1), 1 hour :135 rpm (P2) dan 1.5 hour :70 rpm (P3).

Data Collection Technic

The data collection technic is literature study, it means using literature (book, scientific journal about edible film maker and interviewees). And this experiments is conducted in lab included advance trial, edible film maker and result analytic.

Research Process

Starch of Water hyacinth Making

Tuber water hyacinth washed with water till clean from dirt that stick in it, and choose the best one. The clean tuber water hyacinth should be cut in tiny of each and soaked with citric acid as much 0.5% (w/v) in 10 minutes. This process is needed in order to eliminate lignin compound [10].

Tuber water hyacinth be destructed to get water hyacinth mush. Water hyacinth mush then filtered and deposition in one day. The deposition water wasted, while deposition taken and dried. Dried Starch using sun radiance with sunning it directly in the vessel in 1-2 days (depends on the weather). Starch of water hyacinth sheaved with same shaped.

Edible Film Maker

Edible film from water hyacinth made by dissolve 3 gram starch of water hyacinth and 0,5 gram carrageenan in 70 ml aquadest , and 30 minutes formulation glycerol for addition. To increase the stability, 10 ml citric acid is needed. And then the composite is heated in 70°C with blended in variety duration and speed.

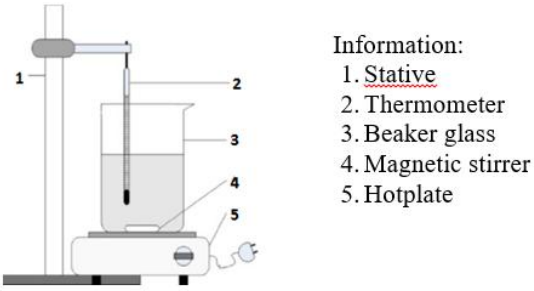


Fig 1. The series of edible film tools

Printed is performed with poured in glass plate that covered with mica. And then solvent is dried with oven in 60°C for 12 hours until forming a thin layer (edible film). After that sample result edible film need to be conducted further analytics.

Analytic of Edible Film Process

Spectral analytic with Fourier Transform Infra Red (FTIR) Spectrophotometer

The purpose of FTIR calibration is to identify spectral and functional groups in edible film. The data is showed in spectrum picture between wave number and transmittance, remarkably we` could recognize the functional groups in edible film. Determination of functional groups analytical in sample which indicate optimum point in research.

Mechanic

Examination is conducted in ASTM 882-91 procedures in Agriculture Technology Faculty Lab, UGM. Tensile strength and elongation of break (E) presentations that measure twice with Universal Testing Instrument (UTI).

Swelling Test

Edible films are cut in 2cm x 2cm and weighed in advance. And put it in vessel with 15 aquadest in 10 minutes. Sample is taken and clean the water with tissue, after that do the scale. The scale and soaked is repeated until final weighed is constant. Analytics is conducted in twice.

Durability Testing

Edible film that already shaped is left in room temperature using Petridis. After 24 hours sample is observed until changes is happen. Notices every changes that happens (example: color and appearance) in edible film.

RESULT AND DISCUSSION

Field Observation

Field observation aims to looking for potential location of water hyacinth around Yogyakarta that has not been optimally utilized yet. The potential location was obtained in the area of Turi, Sleman. To get permit to take water hyacinth with landowners or residents around these area, we did it by negotiation.

Starch and Edible Film Making

The starch of water hyacinth produced is a green powder made from cobs and stems of water hyacinth. The yield of starch produced is 0,23% from 1 kg of wet water hyacinth. The edible film from water hyacinth starch formed in brown.

Testing of Edible Film Results

The edible film results afterwards were tested by mechanical properties testing, water resistance testing, FTIR testing, and durability testing.

1. Mechanical Properties of Film

The test data of the mechanical properties of edible films included 3 things such as tensile strength, elongation percentage, and film thickness. The test analysis was conducted at the Engineering Laboratory of the Faculty of Food and Agricultural Technology, Gadjah Mada University. The mechanical properties of edible films are shown in Table 1.

Table 1. Mechanical Edible Film Properties Data

Ratio Starch and Glycerol	Stirring Rate and Processing Time	Average Thickness (mm)	Average Elongation (%)	Average tensile Strength (MPa)
F1 (100:0)	200 rpm:30 minutes	0,1540	3,8706	2,7493
	135 rpm : 1 hour	0,1710	0,8934	2,9218
	70 rpm : 1,5 hours	0,1725	1,6297	4,1660
F2 (90:10)	200 rpm: 30 minutes	0,1350	6,4401	2,3451
	135 rpm : 1 hour	0,1535	6,6727	2,2285
	70 rpm : 1,5 hours	0,1370	4,5890	3,6529
F3 (80:20)	200 rpm: 30 minutes	0,1980	8,7392	1,2939
	135 rpm : 1 hours	0,2495	6,9287	1,4332
	70 rpm : 1,5 hours	0,2405	5,0159	1,6148
F4 (70:30)	200 rpm: 30 minutes	0,1805	10,9996	1,1504
	135 rpm : 1 hour	0,2110	7,6447	0,9910
	70 rpm : 1,5 hours	0,2115	8,2085	1,0873
F5 (60:40)	200 rpm: 30 minutes	0,2315	12,4987	0,8647
	135 rpm : 1 hour	0,2095	7,7095	0,9019
	70 rpm : 1,5 hours	0,2695	9,6780	0,7020

From Table 1, the more plasticizer added in edible film making then the value of tensile strength of the film was getting smaller as shown in Figure 2.

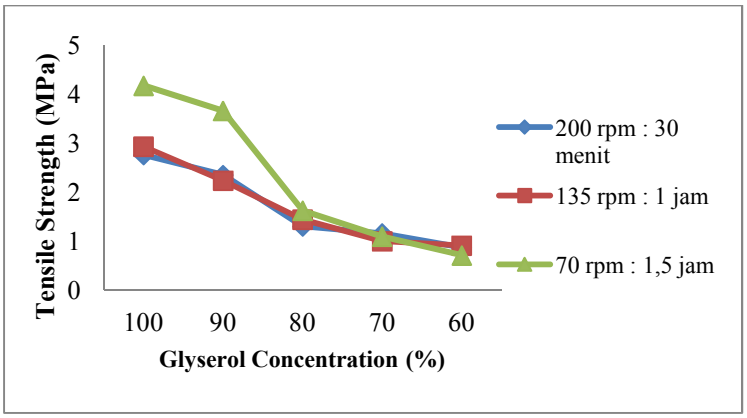


Fig 2. Tensile strength results in variation of water hyacinth starch composition

Purwanti (2010), the amount of tensile strength is closely related to the number of plasticizers added to the process of making bioplastics [11]. In this study, the more glycerol was added in edible film making which can decrease the hydrogen bonding on the plastic thereby increasing the film's flexibility, but decreasing the tensile strength value of the film. In addition, the speed of stirring and length of edible film making process influence the value of tensile strength.

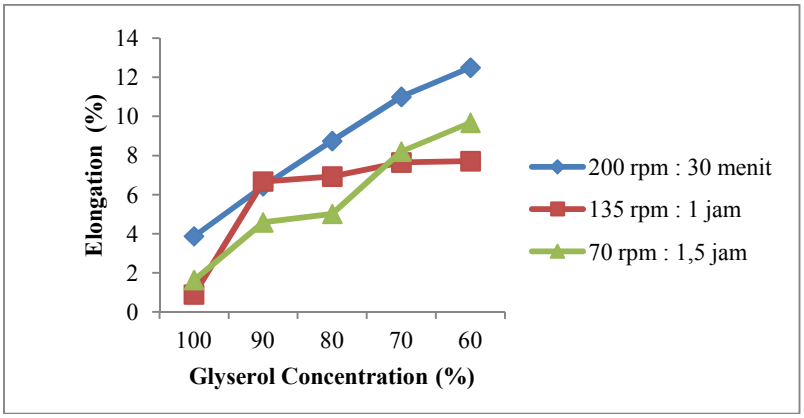


Fig 3. Elongation results in variation of water hyacinth starch composition

As a result of the effect on the tensile strength, the presence of glycerol plasticizers in the edible polymer bonding chain of water hyacinth films causes the bonding between the polymers to be reduced and makes the plastic more flexible. According to Guilbert and Biquet (1990), increased stretching forces can increase the fracture (breaking) edible film[12]. According to Damat also reported a similar phenomenon in edible film studies of starch butyricate with addition of glycerol[13].

The thickness of the film layer affects the value of the tensile strength and elongation of the edible film and the resulting water resistance. The thickness of the different film layers may be affected by the viscosity of the edible film solution, the content of the film polymer, and also the addition of plasticizers used. The thicker the edible film produced the higher its ability to inhibit the lajugas and water vapor, so the shelf life of the product is getting longer. However, if it is too thick it will affect the appearance and taste / texture of the product when it is added. Edible film thickness is usually less than 0.25mm.

2. Water Resistance Test Result Data

Water resistance testing is done at the Organic Chemistry Laboratory, Institute of Science and Technology AKPRIND Yogyakarta.

Table 2. Water resistance testing data of edible films

Ratio Starch and Gliserol	Stirring Rate and Processing Time	Average Water Resistance (%)
F1 (100:0)	200 rpm:30 menit	70,84
	135 rpm : 1 jam	69,05
	70 rpm : 1,5 jam	76,19
F2 (90:10)	200 rpm:30 menit	71,53
	135 rpm : 1 jam	80,36
	70 rpm : 1,5 jam	74,6
F3 (80:20)	200 rpm:30 menit	70,84
	135 rpm : 1 jam	60,72
	70 rpm : 1,5 jam	79,17
F4 (70:30)	200 rpm:30 menit	66,25
	135 rpm : 1 jam	69,05
	70 rpm : 1,5 jam	67,5
F5 (60:40)	200 rpm:30 menit	66,07
	135 rpm : 1 jam	81,74
	70 rpm : 1,5 jam	70,84

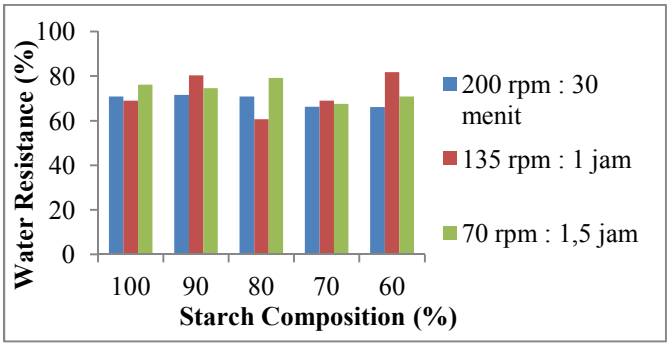


Fig 4. Water resistance results in variation of water hyacinth starch composition

Figure 4 shows the water absorption rate of the edible film of each of the different variations. The film ions made from starch with the addition of glycerol have the highest percentage of water absorption value of 81.74% in the 60% variable starch: 40% glycerol with stirring speed 135 rpm for 1 hour. High water absorption values indicate that edible film can be degraded naturally so it can be used as an alternative to plastic food wrappers. In all cases, the material with 30wt.% plasticizer was more permeable than the material with 20wt.% plasticizer[15]. The vapour transport through the polymer also increases, based on the relative humidity, which brings as a consequence the swelling of the material and, therefore, the permeability increases rapidly[16][17].

3. FTIR Test Result Data

The result of spectral analysis with Fourier Transform Infra Red (FTIR) spectrophotometer shows the addition glycerol into edible film did not result new peaks. This indicates no new functional groups due to the interaction of starch with the plasticizer, but only the interaction of van der wall bonds of hydrogen intermolecular constituents edible film. For a thorough understanding of these interactions, FTIR spectra of all prepared blends were recorded. In this, two regions are of great importance, that is, the carbonyl group situated between 1600 and 1750 cm^{-1} and the respective of the hydroxyl groups at 3350–3700 cm^{-1} [19]. The resulting peak has almost the same spectrum, only the top position of the hydroxyl group with the addition of 30% wider glycerol and shiftus to the right than the edible film peak with 20% glycerol addition. The characteristic peaks of glycerol are at 3425.58 cm^{-1} . From the FTIR spectra of the prepared blends it can be seen that, as the amount of glycerol increases, the hydroxyl band moves to lower wave. The absorption of O-H group was widened due to the interaction of hydroxyl compounds between water, starch, and glycerol in the edible film. The spread of the spectrum in the hydroxyl group is influenced by the addition of glycerol and the effect on the mechanical properties of the edible film. No significant differences in the positions and intensities of the bands of all the samples were observed. It means that polysaccharides were not degraded by citric acid. Despite the fact that citric acid has low pH, basically it is a weak acid [18].

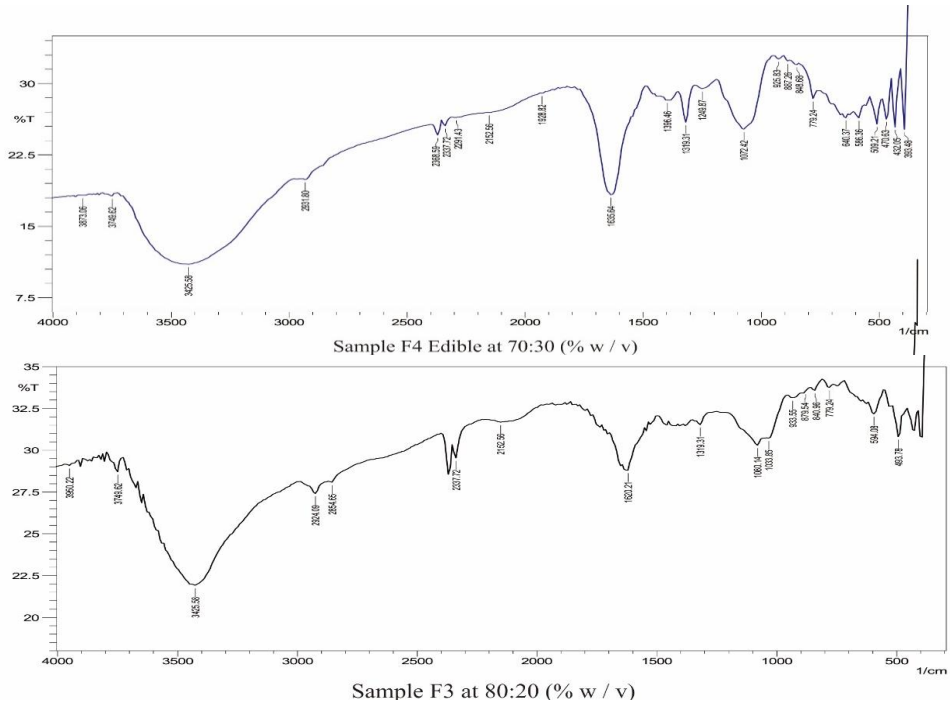
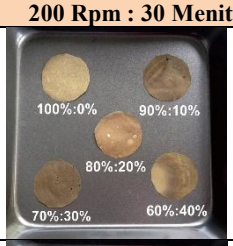
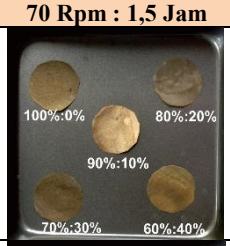
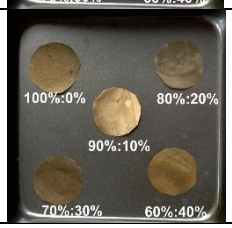


Fig 5. FTIR Test Results

4. Durability Testing

This test aims to determine the edible film resistance from the influence of temperature and environment to the growth of fungi. Generally, the biopolymer making from organic materials have a short durability and easily moldy. From the observation for 7 days, the films were indicated the growth of fungi or physical changes into them.

Table 3. Durability test result

Time	200 Rpm : 30 Menit	135 Rpm : 1 Jam	70 Rpm : 1,5 Jam	Keterangan
24 hours				Fungi do not growht and no physical change
7 days				The growth of fungi in surface

5. Comparison of Standards with Results

From all mechanical properties results in this study such as thickness, tensile strength, and elongation of edible films, they can be compared with mechanical properties results in other edible film research which various methods and materials. In this research, the edible films made from water hyacinth starch. The comparison of mechanical properties in the films can be seen in Table 4.

Table 4. The comparison of mechanical properties in films with previous research and standard edible film

No	Sifat	Nilai Standar JIS	Edible film from water hyacinth starch	Edible film from banana starch, Wulansari (2016)	Edible film from HPMC/PVP, Somashekarappa (2013)
1.	Thickness (mm)	0,25	0,137 - 0,2695	0,22	-
2.	Tensile strength (MPa)	3,92266	0,702 – 4,17	0,98	6,60-22,90
3.	Elongation (%)	Bad < 10 Good >10	0,89 – 12,49%	8,2%	3,12-9,45 %

CONCLUSION

The edible films can be made from water hyacinth starches. The addition of glycerol had an effect on the physical characteristics of edible film from the water hyacinth starch. When glycerol (in the range 0-40% volume) was added increasingly, the tensile strength values were decreased and the elongation values were increased. The spectral analysis results with FTIR spectrophotometer resulted the peak has almost the same spectrum, only the top position of the hydroxyl group was widened to the right when the glycerol was added.
The optimum condition of ratio starch and glycerol starch was obtained at 70:30 (%w/v) composition with stirring rate 135 rpm for 1 hour. The largest swelling value (water resisante) is 69.05%.

ACKNOWLEDGMENTS

The authors are grateful to Institute of Science & Technology AKPRIND Yogyakarta for supporting this research and the Ministry of Research, Technology and Higher Education (Kemenristekdikti - Indonesia) for the grant fundings through the Student Creativity Program - Research in 2017.

REFERENCES

1. Van Steenis, C.G.G.J., *Flora* (PT Pradnya Paramita, Jakarta Pusat, 2008).
2. Farida, Pemanfaatan Serat Enceng Gondok dan Kitosan Sebagai Bahan Baku Untuk Pembuatan Poly Lactic Acid Sebagai Kemasan Ramah Lingkungan*, Thesis*, (Sumatera Utara University, Medan, 2012)
3. Kusumawati, D.H. and Putri, W.D.R., Karakteristik Fisik dan Kimia Edible Film Pati Jagung yang Diinkorporasi dengan Perasan Temu Hitam*, Jurnal Pangan dan Agroindustri*, 1, 90-100 (2013).
4. Krochta, J.M., Baldwin, E.A., and Nisperos-Carriedo, M.O., *Edible Coatings and Film to Improve Food Quality* (Echnomic Publishing Company Inc, USA, 1994)
5. Hught, T.H. Mc. and Krochta, J.M., Sorbitol vs Glyserol Plasticized Whey Protein Edible Films : Integrated Oxygen Permeability and Tensile Property Evaluation, *Journal of Agricultural and Food Chemistry*, 42, 841-845 (1994).
6. Nahwi, N.F., Analisis Pengaruh Penambahan Plastisizer Gliserol pada Karakteristik Edible Film Dari Pati Kulit Pisang Raja, Tongkol Jagung dan Bonggol Enceng Gondok, *Thesis,* (UIN Maulana Malik Ibrahim. Malang, 2016)
7. Krochta, J. M. and Johnson, C.M., Edible Film and Biodegradable Polymer Film Challenger and Opportunities, *Journal Food Technology*, 51 (2), 61-74 (1997).
8. Ginting, A., Pemanfaatan Gliserol dan Turunannya Sebagai Plastisizer Pada Edible Film Gelatin yang Diinkorporasi Dengan Minyak Atsiri Kulit Kayu Manis (Cinnamomum Burmamii) Sebagai Antimikroba*, Thesis*, (Universitas Sumatera Utara. Medan, 2012).
9. Larotonda, F.D.S., Matsui, K.N., and Laurindo, J.B., Biodegradable Films Made From Raw and Acetylated Cassava Starch, *The Journal Brazilian Archives of Biology and Technology*, 47, 477-484 (2004).
10. Wardah, I., Pengaruh Variasi Komposisi Gliserol Dengan Pati dari Bonggol Pisang, Tongkol Jagung dan Eceng Gondok Terhadap Sifat Fisis dan Mekanis Plastik Biodegradable, *Thesis*, (UIN MaulanaMalik Ibrahim, Malang, 2014).
11. Purwanti, A., Analisis Kuat Tarik dan Elongasi Plastik Kitosan Terplastisasi Sorbitol, *Jurnal Teknologi Institut Sains dan Teknologi AKPRIND,* 3 (2), 99-106 (2010).
12. Guilbert, S, and Biquet, B., *Edible films and coatings*, (VCH Publishers. New York, 1990)

13. Damat, Efek jenis dan konsentrasi plasticizer terhadap karakteristik edible film dari pati garut butirat, *Jurnal Agritek,* 16 (3), 333-339, (2008).
14. Wulansari, W., Analisis Pengaruh Variasi Komposisi Pati Bonggol Pisang, Antioksidan Jahe dan Gliserol terhadap Karakteristik Edible Film*, Thesis*, (UIN Maulana Malik Ibrahim. Malang, 2016).
15. Cho, S.W., Blomfeldt, T.O.J., Halonen, H., Gallstedt, M., and Hedenqvist, M.S., Wheat Gluten-Laminated Paperboard with Improved Moisture Barrier Properties: A New Concept Using a Plasticizer (Glycerol) Containing a Hydrophobic Component (Oleic Acid), *International Journal of Polymer Science*, (2012).
16. Karel, M. and Lund, D.B., *Physical Principles of Food Preservation*, (Marcel Dekker, New York, NY USA, 2003).
17. Del Nobile, M. A.and Conte, A. *Packaging for Food Preservation,* (Springer, Berlin, German, 2013).
18. Hati, S., Mandal, S., and Minz, P.S., Electrolyzed Oxidized Water (EOW): non-thermal approach for decontamination of food borne microorganisms in food industry, *Food and Nutrition Sciences*, 3 (6), 760–768 (2012).
19. Somashekarappa, H., Prakash, Y., Hemalatha, K., Demappa, T., and Somashekar, R., Preparation and Characterization of HPMC/PVP Blend Films Plasticized with Sorbitol, *Indian Journal of Materials Science*, (2013)