Effect of Pectin Variation and Sweet Orange (*Citrus sinensis)* Peel Extract on Bioplastic Synthesis

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Keywords : Plastic, Pectin, Bioplastic, Orange Peel, Extract

Abstract : Indonesia is the second largest country after China as a plastic user. The problems that occur regarding plastic waste require other alternatives by developing environmentally friendly plastics (biodegradable). One way to synthesize bioplastics is to use sweet orange (Citrus sinensis) peel pectin. The purpose of this study was to determine the bioplastic characteristics of pectin and the addition of orange peel extract with variations of 1%, 3% and 5% pectin to the resulting bioplastics and to determine the characterization of bioplastics through water absorption, tensile strength and elongation tests. Orange peel extract used as an additive for bioplastics was extracted using the maceration method with ethanol solvent. The results obtained were 0.9%, 1.7% and 3% water absorption, 1.106 and 0.9 MPa tensile strength, and 1. 8% and 0.49%.

INTRODUCTION

Indonesia is the second largest country after China as a plastic user with 700 plastic bags per person in a year. The average use of plastic waste in Indonesia reaches around 100 billion bags every year (Fatimura, 2020). The impact arising from the use of plastic is that it will produce waste which is difficult to decompose. Synthetic plastic will not disappear even if it is burned, but instead changes shape to a smaller size and is called micro plastic (Jupri *et al*., 2019). In order to decompose, synthetic plastic certainly takes a very long time, which is around 5-1000 years or even more, depending on the type of plastic. (Wijayanto & Rusdi, 2017).

In addition to burning, handling of plastic waste has also been handled by recycling. However, recycling of plastic waste is only able to process 25% of the original waste, so other efforts are needed to deal with plastic waste (Apriyani *et al*., 2015). Based on the current problems regarding plastic waste, another alternative is needed, namely the development of environmentally friendly plastics (biodegradable) and of course derived from materials that easily decompose in the environment (Sholekhahwati & Sedyadi, 2020). One of the developments in the manufacture of biodegradable plastics is through biosynthesis using materials containing pectin (Nafiyanto, 2019).

Several previous studies conducted by Ningsih *et al.*, (2019), Sholekhahwati & Sedyadi (2020) and Zuchrillah *et al.*, (2020) explained that the properties of pectin are that it can form a gel when it is mixed with certain levels of acids and sugars. This makes pectin used as a raw material for making biodegradable plastics.

The manufacture of bioplastics is still very rare with the addition of aroma. Aroma can be obtained from sweet orange peel. Sweet orange is a plant that is very suitable to be processed into various dishes, both food and drinks. From processing these oranges, it can produce waste in the form of orange peels which are generally thrown away. Whereas the peel of citrus fruit contains about 70% air, 6-8% sugar, and small amounts of organic acids. In addition, citrus fruit peels contain 30% pectin on a dry basis (M. Khan *et al.,* 2015). The purpose of this study was to determine the bioplastic characteristics of pectin and the addition of orange peel extract with variations of 1%, 3% and 5% pectin and the addition of orange peel extract as a fragrance.

METHODS

Place

The research was conducted at the Chemistry Laboratory, Basic Biology Laboratory, Concrete Laboratory and Instrumentation Laboratory, Campus II UIN Sunan Ampel Surabaya.

Tools and Materials

The tools used include scissors, blender, beaker, petri dish, hotplate, thermometer, magnetic stirrer, filter paper, Buchner funnel, dropping pipette, measuring flask, measuring cup, stirrer, spatula, test tube, analytical balance, oven, rotary evaporator, resin mold, FTIR tool, UTM tool.

The materials used included sweet orange peel, pectin obtained from the isolation, 96% ethanol, glycerin, shrimp chitosan, tissue and distilled water.

Work Procedures

Manufacture of Orange Peel Extract

Orange peel was extracted using maceration method and 96% ethanol solvent. Preparation by washing the orange peel and cutting it into small pieces. Furthermore, the orange peel is dried in an oven at 55°C until the orange peel is dry. The dried orange peel is mashed using a chopper or blender to get orange peel powder. Orange peel powder was macerated with ethanol solvent for 2x24 hours. The maceration results are filtered, then the filtrate is stored while the residue is re-macerated again until the environment is clear. The filtrate was collected and concentrated using a rotary evaporator to obtain a concentrated orange peel extract.

Bioplastic Manufacture

The process of making bioplastics by dissolving pectin with several concentration variations (1%, 3%, 5% w/v) in 100 mL of distilled water. The mixture obtained was heated and stirred at 60˚C for 3 minutes on a hot plate equipped with a magnetic stirrer. Chitosan was dissolved using 1% acetic acid as much as 100 mL, stirred with a magnetic stirrer for 20 minutes until homogeneous. The 100 mL chitosan solution was then mixed with 10% (v/v) glycerin. Glycerol dilution process using aquadest solvent. A total of 50 mL of a mixture of chitosan and glycerin was then mixed and homogenized. Then added 1 ml of orange peel extract each and stirred until homogeneous ± 5 minutes at 80˚C. The Edible Film solution is poured into a plate mold or resin mold, then dried in an oven for 12-24 hours at 60˚C.

Data Analysis

1. **FTIR (*Fourier Transform Infrared*)**

   Bioplastic samples from sweet orange peel pectin were characterized with the FTIR spectrophotometer instrument to determine the functional groups of the compounds contained.

2. **Water Absorption Test**

   Edible Film samples were weighed to determine the initial weight. After that the samples were soaked with 3 ml of distilled water for 5 minutes. After immersion, the sample is removed and the final weight or remaining distilled water is observed.

$$absorption = \frac{\text{initial volumes}}{\text{final volume}}\ x\ 100\%$$

3. **Tensile Strength Test**

   The tensile strength test in this study was measured by UTM (Universal Testing Machine) and was guided by the ASTM D882 standard. Edible film is first cut according to the specifications of the tool.

The start button on the tool is pressed twice, the sample is clamped on the testing machine and wait until the tool pulls the Edible Film sample until it breaks (Rhim & Wang, 2013)

$$\text{tensile strength } (\sigma) = \frac{Fmaks}{A}$$

Information:
σ = strength or tensile stress (MPa)
F = pull force (N)
A = cross sectional area (mm^2)

4. Elongation

The measurement of percent elongation was carried out using the UTM (Universal Testing Instrument) and was guided by the ASTM D882 standard. The sample is cut to the size according to the specification of the tool, then the start button is pressed on the tool and the sample is clamped on the clamping machine. After that, wait for the sample to be pulled by the tool until it breaks. The output device will then read the applied force until the sample is cut and the sample length increases. Length gain is measured from the initial length before cutting (Rhim & Wang, 2013)

$$\varepsilon = \frac{\Delta L}{L_o} \times 100\%$$

Information:
ε = elongation (%)
ΔL = (L-Lo) length increase (nm)
L_o = initial length (nm)

5. Modulus Young

Young's modulus or the elasticity of a bioplastic is known from the ratio between stress and strain.

$$E = \frac{\sigma}{\varepsilon}$$

Information:
σ = voltage
ε = stretch

RESULTS AND DISCUSSION

Sweet Orange Peel Extract (*Citrus sinensis*)

This stage is to extract the orange peel powder to be used as an extract. Sweet orange peel powder is extracted using the maceration method. The maceration method was chosen because the process is quite simple and faster, but the maceration method can maximally extract chemical compounds from the extracted samples (Damanis *et al.*, 2020). The main advantage of the maceration method is that it is not heated, so it can prevent the possibility of this happening, such as the decomposition of the active substance contained in the sample due to the influence of temperature and compounds that are not resistant to heat (Sa'adah *et al.*, 2015). The process of the maceration method is carried out by soaking the sweet orange peel powder using ethanol as a solvent. Ethanol is a solvent that can attract all types of compounds including polar, semi-polar and nonpolar (Sukmawati *et al.*, 2018). The choice of ethanol solvent is because ethanol is a solvent which is certainly safe and non-toxic when used (Irawan *et al.*, 2019).

Bioplastic

The results of bioplastics obtained in this study can be seen in the image below.

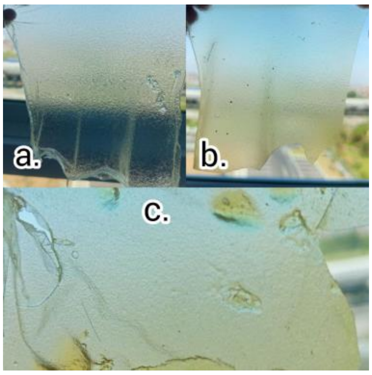


Figure 1: a. pectin 1%, b. pectin 3%, c. pectin 5%

Based on the physical appearance of the three pectin concentrations, the three of them do not have completely transparent colors. In the picture, Bioplastic has a clear, slightly opaque color and has a sticky texture. In figure

B, bioplastic has a slightly clear yellow color and has a slightly sticky texture, but is still easy to pick up from the mold. In figure C bioplastic has a brownish yellow color and has a very sticky texture.

FTIR (*Fourier Transform Infrared*) Bioplastic

FTIR analysis of orange peel pectin bioplastic aims to determine the functional groups contained in the bioplastic. The bioplastics tested by FTIR were bioplastics with 1 gram pectin variation with glycerol: chitosan = 1: 1, 3 gram pectin variation with glycerol: chitosan = 1: 1, and 5 gram pectin variation with glycerol: chitosan = 1: 1. Each bioplastic concentration added orange peel extract as scent.

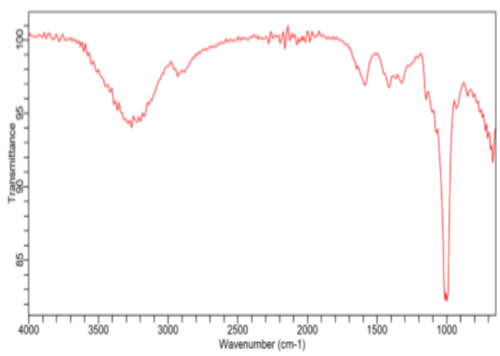


Figure 2: FTIR Results of Bioplastics with 1% Pectin

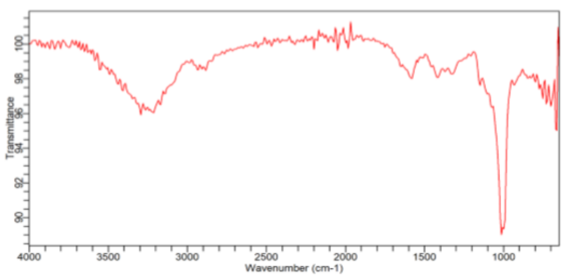


Figure 3: FTIR Results of Bioplastics with 5% Pectin

FTIR test on bioplastics uses wave numbers with a range of 1000 to 4000 Cm^{-1}. The results obtained were not much different from the FTIR results on orange peel pectin and orange peel extract, because the bioplastic constituents in this study were pectin and orange peel extract.

Table 1: Absorption Result of Bioplastic Pectin 1% FTIR Wave

Peak Number	Wavemeter (Cm^{-1})	Intensity
1	670,92081	91,63981
2	849,83303	96,15819
3	1013,83589	82,26233
4	1416,38838	96,75489
5	1587,84592	96,89380
6	2929,68754	97,54326
7	3265,14795	94,03837

Table 2: Absorption Result of Bioplastic Pectin 3% FTIR Wave

Peak Number	Wavenumber (Cm^{-1})	Intensity
1	1013,83589	86,69591
2	1416,38838	97,78718
3	1587,84592	97,88665
4	2907,32351	98,37135
5	3220,41989	95,79310
6	3280,05730	96,02525
7	3444,06016	97,44614

Table 3: Absorption Result of Bioplastic Pectin 5% FTIR Wave

Peak Number	Wavenumber (Cm^{-1})	Intensity
1	670,92081	95,12218
2	1013,83589	89,00357
3	1416,38838	98,06652
4	1580,39124	98,00646
5	2884,95949	98,48126
6	3220,41989	96,09552
7	3675,15511	99,67255

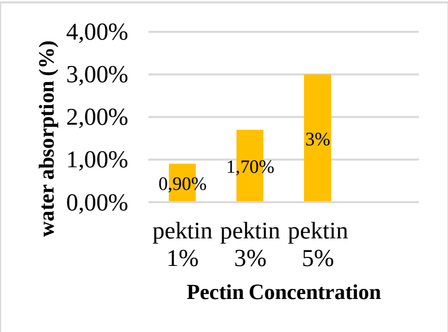
Absorption at a distance of 3000 to 3400 Cm-1 indicates the presence of OH groups. The OH group in bioplastics comes from glycerin which is mixed into the bioplastics. Glycerol or glycerin (C3H8O3) is a viscous liquid that has a sweet taste, colorless, odorless, dissolves easily in air, increases solution viscosity, binds air, and reduces air activity (aw). Glycerol has the chemical name

1,2,3-propanetriol. The molecular weight of glycerol is 92 g/mol, the density is 1.261 g/mL, the viscosity is 1.5 Pa.s, the melting point is 17.8°C and the flash point is 290°C (Wahyuni *et al.*, 2016)

At wave numbers 1000 to 1300 Cm-1 there is a very strong wave absorption. The absorption of these waves indicates the presence of a middle group (C-N). Amides are compounds that have a carbonyl group attached directly to a nitrogen atom (Nugraha, 2018). The amide group comes from citrus pectin as the main ingredient in the manufacture of bioplastics, because pectin consists of functional groups, namely carboxyl, hydroxyl, mide and methoxyl (Khotima *et al.*, 2020).

Water Absorption Test

Water absorption is the ability of bioplastics to absorb and hold air without reducing the quality of the bioplastics. The test was carried out aiming to determine the value of air absorbed by bioplastics. The smaller the value of air absorption, the higher the resistance of bioplastics to air. The results obtained are the remaining water of 1%, 3% and 5% is 0.9%, 1.7% and 3%. The data has been presented in Graph 1.

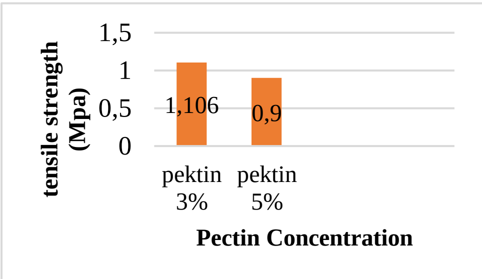


Graph 1: Bioplastic Water Absorption Test Results

Based on these data, the results showed that it increased with the addition of pectin concentration. The percentage value of air absorbed by bioplastic will be inversely proportional to the air resistance of the plastic. So, the smaller the percentage value of air absorbed by the plastic, the greater the air resistance possessed by the plastic. The addition of pectin affects the value of air resistance to bioplastics. The lower the pectin concentration, the smaller the air content in the bioplastic (Isnanda *et al.*, 2016). This happens because pectin can bind air so that free air is reduced. Pectin is a polymer compound that can bind air, and form a gel or thicken the liquid.

Tensile Strength Test

The tensile strength test was carried out on 2 samples, namely pectin with a concentration of 3% and 5%. Pectin with a concentration of 1% was not subjected to a tensile strength test because the sample was not possible to be tested. Physically, samples with 1% pectin were too thin and very sticky for testing. This is most likely due to the less pectin concentration and higher glycerol concentration. Glycerol can cause a decrease in intermolecular attractions. Therefore, it can reduce the resistance to mechanical treatment of bioplastic films. The plasticizer used is glycerol. Glycerol will reduce intermolecular forces which can cause an increase in molecular space and mobility of the biopolymer. The polar groups (-OH) around the plasticizer chain lead to the development of polymer-plastic hydrogen bonds that replace polymer-polymer interactions in the biopolymer film. An increase in glycerol concentration will result in a decrease in intermolecular interactions so that the movement of the molecular chains will decrease (Radhiyatullah *et al.*, 2015).

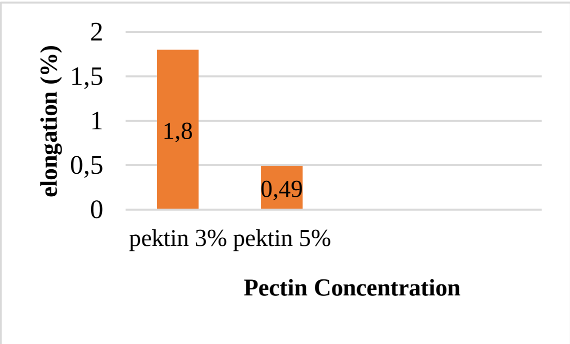


Graph 2: Tensile Strength Test Results

The tensile strength test at 3% and 5% pectin concentrations can be seen in Graph 2. Based on these data, the tensile strength has decreased. The best results are at 3% pectin concentration. This is because the decrease in tensile strength is due to reduced protein chains between molecules, so that less bioplastic matrix is formed. This happens because due to the addition of glycerol, the nature of the plasticizer molecule will reduce intermolecular interactions, disrupt the cohesiveness of starch, and increase the mobility of bioplastics. Another factor that causes the decrease in the tensile strength value is possibly due to the inhomogeneity of the distribution of the boplastic molecules (Sholekhahwati & Sedyadi, 2020).

Elongation

The percent elongation test was carried out on 2 samples, namely pectin with a concentration of 3% and 5%. Similar to the tensile strength test, in the percent elongation test for pectin with a concentration of 1%, a tensile strength test was not carried out because the sample was not possible to be tested. The percent elongation indicates the film's ability to elongate. Plastic elasticity is shown by increasing the elongation of the plastic film. The greater the tensile strength value, the lower the elasticity of the plastic. Vice versa, the higher the percentage of elongation, the lower the tensile strength (Haryati *et al.*, 2017).



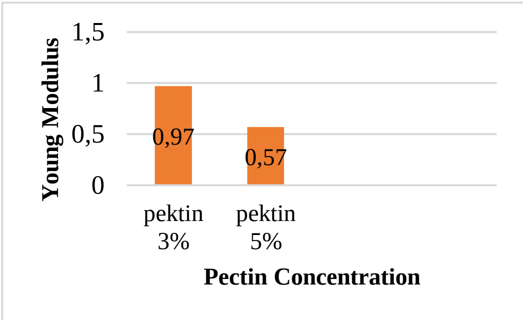
Graph 3: Elongation Test Results

The elongation test at 3% and 5% pectin concentrations can be seen in Graph 3. The value in the data tends to decrease, namely at 3% pectin concentration is 1.8% and 5% pectin concentration is 0.49% which indicates that the more pectin added, the smaller the elongation value produced. The best percent elongation is the variation of 3% pectin concentration. This is caused by the formation of hydrogen bonds between orange pectin molecules and glycerol molecules. The more hydrogen bonds that are formed in the polymer causes the chain to get longer and the dependency increases.

This research is different from previous research, namely the research of Sholekhahwati & Sedyadi, (2020). In this study explained that the addition of pectin concentration, the greater the resulting elongation value. This could have been because in this study, pure sweet orange peel extract was added. The menis orange peel extract may also affect the percent elongation of bioplastics.

Modulus Young

Young modulus value is obtained from the comparison between tensile strength and percent elongation.



Graph 4: Young's Modulus Test Results

Based on the results obtained, it shows that Young's modulus values range from 0.57 to 0.97 MPa. With decreasing tensile strength, the value of Young's modulus also decreases. The decrease in the value of Young's modulus indicates that the plasticity produced is increasing (Nahwi, 2016).

Plastic Properties According to ASTM D 882 Year 2012

Table 4: Plastic Properties According to ASTM D 882 Year 2012

No	Characteristics	LDPE	HDPE	PP
1	Tensile Strenght (MPa)	0,02358	0,047367	0,195811
2	Break Elongation (%)	205	570	57,8
3	Elasticity Modulus (MPa)	0,372	1,31	2,93

HDPE (*High Density PolyEthylene*) is a hard plastic, resistant to chemicals and moisture, easy to color, shape and process. Usually used for liquid milk bottles, juices, drinks and plastic lids. It is recommended for single use only because if used repeatedly, the constituent ingredients will transfer into the food. **LDPE** (*Low Desnity PolyEthylene*) is a plastic with a material that is easy to process, flexible, waterproof, not clear but translucent and is usually used for plastic bags. **PP** (*PolyPropylene)* is a plastic that has the characteristics of being transparent but colorful, hard but flexible, strong, heat resistant, chemicals and oil, so PP is a good choice of plastic material for food packaging such as medicine containers, milk bottles and straws.

In accordance with ASTM (*American Standard Testing and Materials*), the tensile strength test of bioplastics in this study complied with ASTM on the third component, namely LDPE, HDPE and PP with a 3% pectin variation of 1.106 MPa and a 5% pectin variation of 0.9 MPa. In percent elongation, the bioplastics in this study did not meet ASTM, both at 3% and 5% pectin variations. Whereas at Young's Modulus, the bioplastics in this study met ASTM, namely LDPE and HDPE with a 3% pectin variation of 1.84 MPa and a 5% pectin variation of 0.97 MPa.

CONCLUSIONS

Based on the research that has been done, the best results were obtained for bioplastics, namely the 3% pectin variation. In accordance with ASTM (American Standard Testing and Materials), the tensile strength test of bioplastics in this study complied with ASTM on the third component, namely LDPE, HDPE and PP with a 3% pectin variation of 1.106 MPa and a 5% pectin variation of 0.9 MPa. In percent elongation, the bioplastics in this study did not meet ASTM, both at 3% and 5% pectin variations. Whereas at Young's Modulus, the bioplastics in this study met ASTM, namely LDPE and HDPE with a 3% pectin variation of 1.84 MPa and a 5% pectin variation of 0.97 MPa.

REFERENCES

Apriyani, M., dan Endaruji, S. (2015) 'Sintesis Dan Karakterisasi Plastik Biodegradable Dari Pati Onggok Singkong Dan Ekstrak Lidah Buaya Dengan Platisizer Gliserol', *Jurnal Sains Dasar*, 2(4), pp. 145-152.

Damanis, F. V., Wewengkang, D. S., & Antasionasti, I. (2020) 'Uji Aktivitas Antioksidan Ekstrak Etanol Ascidian Herdmania Momus Dengan Metode Dpph (1, 1-Difenil-2-Pikrilhidrazil)', *Pharmacon*, 9(3), pp. 464-469.

Fatimura, M. (2020) 'Evaluasi Kinerja Reaktor Pirolisis Non Katalis dalam Mengkonversikan Limbah Plastik Menjadi Bahan Bakar Minyak', *Jurnal Ilmiah Teknik Kimia*, 4(1), pp. 1-7.

Haryati, S., Rini, A. S., & Safitri, Y. (2017) 'Pemanfaatan biji durian sebagai bahan baku plastik biodegradable dengan plasticizer giserol dan bahan pengisi CaCO3', *Jurnal Teknik Kimia*, 23(1), pp. 1-8.

Irawan, H., Agustina, E. F., & Tisnadjaja, D. (2019) 'Pengaruh Konsentrasi Pelarut Etanol terhadap Profil Kromatogram dan Kandungan Senyawa Kimia dalam Ekstrak Daun Pepaya (*Carica papaya* l.) dan Daun Patikan Kebo (*Euphorbia hirta* l.)', *Prosiding Seminar Nasional Kimia*, pp. 40-45.

Isnanda, D. Novita dan M. Rohaya, S. (2016) 'Pengaruh Konsentrasi Pektin dan Karagenan terhadap Permen Jelly Nanas (*Ananas comosus* L. Merr)', *Jurnal Ilmiah.* Universitas Syah Kuala. Aceh.

Jupri, A., Prabowo, A. J., Aprilianti, B. R., & Unnida, D. (2019) 'Pengelolaan Limbah Sampah Plastik Dengan Menggunakan Metode Ecobrick di Desa Pesanggrahan', *Prosiding PEPADU*, 1, pp. 341-347.

Khotima, K., & Santoso, T. (2020) 'Pemanfaatan Pektin Kulit Nangka (*Artocarpus heterophyllus*) Sebagai Adsorben Logam Cu (II)', *Media Eksakta*, *16*(2), pp. 105-112.

M. Khan, N. Bibi, & A. Zeb. (2015) 'Optimization of Process Conditions for Pectin Extraction from Citrus Peel', *Science, Technology and Development,* 34(1), pp. 9-15.

Nafiyanto, Indra. (2019) 'Pembuatan Plastik Biodegradable dari Limbah Bonggol Pisang Kepok dengan Plasticizer Gliserol dari Minyak Jelantah dan Komposit Kitosan dari Limabah Cangkang Bekicot (*Achatina fulia*)', *Intergrated Lab Journal*, 7(1), pp. 75-89.

Nahwi, N.F. (2016) 'Analisis Pengaruh Penambahan Plasticizer Gliserol pada Karakteristik Edible Film dari Pati Kulit Pisang Raja Tongkol Jagung dan Bonggol Enceng Gondok. Skripsi Program Studi Kimia. Fakultas Sains dan Teknologi. UIN Maulana Malik Ibrahim Malang.

Ningsih, A. S., Dewi, E., Kalsum, L., & Margaretty, E. (2019) 'Karakteristik Bioplastik Dari Pektin Kulit Pisang Kepok (*Musa paradisiaca* formatypica) dengan Penambahan Kasein', *Prosiding SENIATI*, *5*(1), pp. 190-198.

Radhiyatullah, A., Indriani, N., & Ginting, M. H. S. (2015) 'Pengaruh Berat Pati Dan Volume Plasticizer Gliserol Terhadap Karakteristik Film Bioplastik Pati Kentang', *Jurnal Teknik Kimia USU*, *4*(3), pp. 35-39.

Sa'adah, H., Nurhasnawati, H. (2015) 'Perbandingan Pelarut Etanol Dan Air Pada Pembuatan Ekstrak Umbi Bawang Tiwai (*Eleutherine americana* Merr) Menggunakan Metode Maserasi', *Jurnal Ilmiah Manuntung*, 1(2), pp. 149-153.

Sholekhahwati, S., & Sedyadi, E. (2020) 'Effect of Addition Bali Orange Peel Pectins on The Mechanical Properties of Garut Starch Bioplastic', *Gontor AGROTECH Science Journal*, *6*(3), pp. 369-391.

Sukmawati, I., Susilawati, E. dan Putri, S. (2018) 'Antibacterial Activity of Extracts and Fractions of Wood Ear Mushroom (*Auricularia auricula*)', *Pharmaciana*, 9 (1), pp. 162.

Wahyuni, S., Hambali, E., & Marbun, B. T. H. (2016) 'Esterifikasi gliserol dan asam lemak jenuh sawit dengan katalis MESA', *Jurnal Teknologi Industri Pertanian*, *26*(3).

Wijayanto, A., & Rusdi, R. (2017) 'Pendampingan Kelompok Usaha Pencacahan Limbah Plastik di Kabupaten Malang', *JPM PAMBUDI*, 1(1), pp. 11-11.

Zuchrillah, D. R., Pudjiastuti, L., Puspita, N. F., Hamzah, A., Karisma, A. D., Surono, A., ... & Ningrum, E. O. (2020) 'Karakteristik Biokomposit Edible Film dari Campuran Kitosan dan Pektin Limbah Kulit Pisang Kepok (*Musa acuminata*)', *Chemical Engineering Research Articles*, *3*(1), pp. 33-41.