POLY LACTIC ACID (PLA) DEVELOPMENT USING LACTIC ACID PRODUCT FROM RICE STRAW FERMENTATION WITH AZEOTROPIC POLYCONDENSATION PROCESS

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Abstract. Polylactic acid (PLA) is the raw material for the manufacture of environmentally friendly plastics since microorganisms more easily destroy it in nature. PLA had made from renewable materials such as wood, such as agricultural waste, such as lignocellulose-containing rice straw. Azeotropic polycondensation method has been used for the processing of PLA. This method is relatively simple and can yield a high molecular weight of PLA. Xylene solvent had used to absorb water, and the SnCl2 catalyst had used to accelerate the reaction. The polymerization process lasts 30 hours. The results of the polymerization process were deposited with excess methanol and then filtered with a vacuum pump and then toasted at 80°C within 2 hours, resulting in PLA crystals in the form of yellowish-white powder. The best condition is that the 40-gram mass variation produces PLA with a yield of 49.6 per cent PLA, a molecular weight of 57066.9 g / mol and a temperature melting of 120 °C. The situation had used in the polymerization of fermented lactic acid after achieving the best conditions for the scientific lactic acid polymerization, namely at a lactic acid mass of 40 gr. PLA polymerized lactic acid fermented with rice straw has the characteristics of dark-grey powder with a molecular weight of 2310.86 g / mole and a temperature melting of 135 °C.

Keywords: lactic acid, fermented lactic acid, polylactic acid, azeotropic polycondensation

1. Introduction

Plastic is the most commonly used material for packaging. Its lightweight, robust, transparent and affordable prices are the hallmarks of plastic. So far, the raw materials used to produce plastics have typically come from non-renewable materials such as petroleum, natural gas and coal. In addition to the growing use of plastics, the supply of raw materials in nature is rapidly depleting because the nature of these raw materials had not renewed. This situation has led developed countries, such as the United States, to begin developing sustainable polymers. The polymer that had produced originated from plants in the form of starch, cellulose, with the aid of microorganisms in the form of PLA (Poly Lactic Acid). PLA had also made from animal sources in the form of chitin, chitosan, casein, gelatin (Phil and Stephen, 2008). PLA polymer can also avoid other problems caused by traditional plastic waste. Plastics have been difficulty degrading by soil, due to the existence of this PLA polymer, which can be decreased by soil microbes.
PLA had made from renewable materials such as cellulose-containing biomass, starch, agricultural waste such as lignocellulose-containing rice straw. Rice straw is an excess of agricultural waste in Indonesia. However, it is sometimes not used by society, and it is not rare for farmers to burn it, which can cause air pollution. According to Saha (2004), the essential components of rice straw are cellulose (35-50 per cent), hemicellulose (20-35 per cent) and lignin (10-25 per cent) and other ingredients that make up rice straw. Cellulose and hemicellulose are commercially useful compounds when converted to simple sugars. They can be applying to a variety of biotechnology products such as bioethanol, glutamic acid, citric acid, and the most promising today are PLA as a raw material for making biodegradable plastic. Using rice straw can minimize air pollution by CO2 gas caused by burning rice straw.

Biodegradable polymers are made from the lactic acid polymerization process to form polylactic acid. Lactic acid has been commercially produced either by chemical synthesis or by bacterial fermentation. 70-80 per cent of the world's lactic acid had formed by bacterial fermentation, and the remainder had obtained by chemical synthesis from lactonitrile hydrolysis. The benefit of the fermentation process compared to the chemical synthesis is that it can produce one form of lactic acid isomer, L(+) lactic acid, which is appropriate for the raw material for the production of PLA (Rintis, 2010).

Lignocellulose-containing rice straw had then hydrolyzed with the aid of cellulolytic microorganisms. Fermented method for the formation of lactic acid with lactic acid-producing bacteria. Lactic acid had then polymerized to form PLA. The polymerization process had done using the azeotropic polycondensation method. The reaction is a modification of a traditional polycondensation reaction that can produce a higher molecular weight. (The Averous, 2008).

Mukhamad Jaya Wardana (2012) researched the Azeotropic Poly Condensation Process in Making Biodegradable Plastic Films from Poly Lactic Acid (PLA). The results showed that the produced PLA had a molecular weight of 16,023,88, temperature melting (Tm) 136 °C, temperature glass (Tg) 38,93 °C and a yield of 37,8125 per cent. The downside of this research is that the product produced is still small because the lactic acid used as a PLA forming material is not a lactic acid but rather a scientific lactic acid and the resulting molecular weight (BM) PLA is small.

Ahmad Ibrahim (2006) analyzed azeotropic polycondensation of lactic acid to lactic acid poly as a plastic packaging raw material. The plastic using pure lactic acid raw material with xylene solvent and a tin metal catalyst. The variables that changed in this analysis were fermentation time and catalytic concentration. This study resulted in PLA with a molecular weight of up to 22,000. Optimization of the lactic acid polymerization reaction in this method had achieved at a polymerization time of 30 hours and a metal catalyst concentration of 0.5 per cent. The drawback of this study is that the molecular weight of the PLA produced is small.

In connection with previous studies, this research had conducted in the form of PLA derived from lactic acid fermented with rice straw. Lactic acid from rice straw fermentation had used as a replacement for pure lactic acid, which is less economical to minimize the cost of biodegradable plastic production. It can generate a high molecular weight of PLA in a relatively simple way. This research is expected to be capable of producing PLA with a high molecular weight and has good characteristics as a material for biodegradable plastic processing. The objectives to be achieved in this study include: to determine the effect of the technical lactic acid mass on the characteristics (FTIR, Tm, and BM) of the PLA produced. The best conditions for the technical lactic acid polymerization process had founded with the variables used in this study. And we can learn about the process of lactic acid polymerization of rice straw fermentation and analyze the
characteristics (FTIR, Tm, and BM) of PLA produced under the optimum conditions of technical lactic acid polymerization.

2. Materials and Methods

2.1 Development of polylactic acid (PLA)
Lactic acid (technical lactic acid or lactic acid fermented with rice straw) of 20 grams; 25 grams; 30 grams; 35 grams; and 40 grams had been used in the polymerization reactor. Tin metal with a concentration of 0.5 per cent and 100 grams of solvent had been added, and xylene solvents reacted at 140 °C. This process has been carrying out for 30 hours. After the reaction is complete, the product had dissolved more than methanol. The precipitate is a yellowish-white powder made, washed several times with methanol and then filtered using a vacuum pump. Filtration process in the form of filtrate had discarded, and the products in the way of a PLA cake had dried in the oven (80 °C, 2 hours). The best condition of the scientific lactic acid polymerization process in the formation of PLA had used in the polymerization process of the formation of PLA using lactic acid fermented with rice straw. The PLA formed is then analyzed for its physical and mechanical properties. Tests performed include the melting temperature (Tm) test, the FTIR test, and the molecular weight test (BM).

2.2. Analysis Data
Data obtained by measuring the physical characteristics of PLA. The melting temperature (Tm), the analysis of the functional groups with and BM of each polymerization process results in certain variables used, such as the lactic acid mass ratio and the lactic acid type, in the form of technical lactic acid and lactic acid fermented rice straw. The following is a procedure to test the characteristics of the PLA produced.

a. Test of melting temperature (Tm)
The melting temperature PLA had tested using a digital melting point device of an electrothermal type. PLA samples had inserted at the sample location, then heated, and the degree of melting is known. Capillary tubes are going to suck the pieces. Then the pipe is frozen and then inserted into the sample container at the top of the tool. When the selection melts, the melting temperature of the sample had seen through the lens. Press the HOLD button and display the melting temperature of the tested PLA on the display layer.

b. FTIR test for viewing functional groups
The Poly Lactic Acid produced was tested by FTIR to determine the functional groups generated by the effects of lactic acid polymerization. The formation of PLA had known from the presence or absence of functional groups C = O, C-O-C, and OH. The infrared spectrophotometer first calibrates works performed for the FTIR test, and then the sample is mounted in the FTIR chamber. The results of FTIR tests in the form of peak functional groups had established to assess the presence of PLA functional groups, which had then compared to the literature data.

c. Molecular weight (BM) assay
The resulting polylactic acid had measured for molecular weight using the viscosity method (Ostwald viscometer). The solvent used in this test to dissolve PLA samples is chloroform. First, the chloroform has flowed into the Ostwald viscometer, and the flow period is registered. The
resulting PLA has then dissolved into a solvent of varying concentrations. The PLA, which had added to the solvent, then flowed into the Ostwald viscometer and registered the flow time (t1). From the flow time, the data can be obtained and then graphed between HSP / c and C to show the equation \( y = ax + b \). The value of b is then entered in the Mark Houwink equation to obtain the molecular weight of the PLA resulting from this study.

3. Results and discussion

PLA (Poly Lactic Acid) has three types of processing methods. Direct polycondensation, azeotropic polycondensation, and Ring-Opening Polymerisation (ROP). Of the three ways above, direct polycondensation is a method that needs quite a small expense, but it isn't easy to get high molecular weight PLA. The technique used to manufacture PLA with high molecular weight is the ROP process. This technique has a complicated and costly. The method of azeotropic polycondensation is comparatively more cost-effective. But PLA had produced with good characteristics and efficiency. This approach is a modification of traditional condensation, which can result in a higher molecular weight of PLA. This process, which uses xylene as a solvent, is used to facilitate the separation of water from the polymerization product. In this PLA manufacturing study, SnCl2 is also used as a catalyst to accelerate the reaction rate in the polymerization process. The SnCl2 catalyst had used because it has the advantage of not requiring extra water production. (Johan Nasir, 2008)

Hasibuan (2006), generating PLA with a molecular weight of up to 22,000 by azeotropic polycondensation method. Optimization of the lactic process at a polymerization time of 30 hours. And 0.5 per cent in the concentration of metal catalysts.

![Figure 1. The relationship between the mass of technical lactic acid and the yield of PLA produced](image-url)

In this study, the variable is the lactic acid mass of 20, 25, 30, 35 and 40 grams. And 100 grams of pure xylene solvent. From the data and graphics collected, it had shown that the yield increases with the rise in the mass of technical lactic acid. The more significant the amount of lactic acid used, the more lactic acid reacts with xylene, which then produces more PLA. From
the graph above, it had seen that the highest yield of PLA had achieved by a 40-gram lactic acid mass variation of 49.6 per cent.

As a result of this study, a lower yield had achieved compared to Hasibuan (2006), which received a product of 75.8%. Pure lactic acid was used in Hasibuan (2006) research, while technical lactic acid had used in this study. The low value of the yield of PLA due to the purity of technical lactic acid is lower than that of p.a. Technical lactic acid contains many impurities that may reduce the conversion of lactic acid to PLA during the polymerization process. Meanwhile, compared to the research conducted by Mukhamad Jaya Wardana (2012), which uses technical lactic acid and xylene pure, a yield of 37,8125 per cent is obtained, it shows that the current study has a higher product than the previous studies.

The polymerization of fermented lactic acid had carried out under the best conditions of the scientific lactic acid polymerization process using a lactic acid mass of 40 grams, a solvent in the form of xylene up to 100 grams, a tin metal catalyst of 0.5 per cent with a polymerization time of 30 hours. The yield of PLA obtained from fermentation polymerization of lactic acid is 14.43 per cent. This value had much lower compared to the product of the technical lactic acid PLA, which is equal to the PLA characterization.

(a) Physical characterization

The PLA produced by this technical lactic acid polymerization is visually a yellowish-white powder. The PLA dissolves into non-polar solvents such as chloroform and can not dissolve in polar solvents such as methanol. The essence of the solubility had calculated by the findings of Södergåd & Stolt (2002).

Although PLA had formed by the process of polymerization of lactic acid fermented in the form of blackish-grey powder, these characteristics vary from PLA in that of technical lactic acid polymerization. This product is because the fermented lactic acid is brownish-yellow, and the lactic acid content is at least 6%, so the water content and impurities are still extensive. The pollutants that result in the colour of the resulting PLA become blackish grey. The PLA formed by the polymerization process of fermented lactic acid dissolves into non-polar solvents such as chloroform and is insoluble in polar solvents such as methanol.

(b) Analysis of functional groups

Analysis of functional groups is one way of determining that these compounds are polylactic acid compounds in the presence of hydroxyl groups in these compounds. This research has carried out using a technique called FTIR. FTIR (Fourier Transformed Infrared) is a spectrum measurement technique based on electromagnetic radiation response. The FTIR test is used for qualitative analysis, molecular structure determination and groups in organic compounds or polymer compounds. The purpose of the use of FTIR in this study is to examine the functional groups of polymerization products in the form of yellowish-white powder.

The infrared spectrum of the lactic acid monomer analyzed in the Hasibuan (2006) study (Figure 4.2) shows that the O-H strain of the hydroxyl group is indicated by the strong formation of hydrogen bonds as seen from the peak width in the 3500 cm-1 wave region. The carbonyl group
$C = O$ has shown in wave number 1735 cm$^{-1}$. The hydroxyl group and the hydrogen bonds present in the lactic acid monomer will disappear if the PLA has formed. This result is because polymerization has occurred.

![Figure 2 FTIR Results (a) Lactic Acid Monomers (b) PLA from Hasibuan Research (2006)](image)

The FTIR test had performed to analyze the presence of PLA compounds produced in this study. PLA formed by the reaction of technical lactic acid and solvent in the form of xylene p.a with SnCl2 catalyst has white PLA powder. The powder had then analyzed for the functional groups of PLA. This test had based on the Shimadzu 8400S FTIR device. The results of the assay had shown in Figure 4.

![Figure 3 Results of FTIR PLA synthesis of research results by Mukhamad Jaya Wardana (2012)](image)
Figures 3 and 4 are the results of the PLA synthesis FTIR synthesis in the Mukamad Jaya Wardana study and the results of the PLA synthesis FTIR in this study. The presence of had shown by the fact of alkyl groups (C-H) and carboxyl groups (C = O). The results of the PLA synthesis of FTIR from this analysis showed that the peak of the hydroxyl group (O-H) was at wave number 3508.28 cm<sup>-1</sup>. The peak formed by the hydroxyl group had widened by the polymerization process that releases the hydroxyl group. The alkyl group (C-H) looks more clearly at wave number 2997.18 cm<sup>-1</sup>, and the carboxyl group (C = O) is at wave number 1760.89 cm<sup>-1</sup>. The presence of alkyl groups and carboxyl groups indicates that this research produces the desired PLA compound.

The graph obtained from the results of the PLA FTIR synthesis is almost the same as the Hasibuan research results (2006). The carboxyl group, which is the leading group in the PLA, is within the same wave spectrum. The FTIR results of the Hasibuan PLA synthesis indicate that the carboxyl group is at wave number 1758 cm<sup>-1</sup>, and in this analysis, the wavenumber is 1760.89 cm<sup>-1</sup>. The disparity in the value of the wavenumber is due to the variations in the FTIR equipment used. In the Hasibuan analysis, the FTIR test had carried out using 37 bunker voltages, while the Shimadzu 8400S had used in this study. The different types of tools can influence the reading of the equipment on the sample has been testing based on other system specifications. However, the various operating conditions of this study have the findings of FTIR, which are almost the same as those of Mukhammad and Romadhon (2012) since they use the same methods to test the FTIR PLA synthesis as shown in Figure 3.

Next is the product of the FTIR PLA formed by the polymerization of fermented lactic acid shown in Figure 5.
Figure 5 Results of FTIR PLA synthesis of fermented lactic acid
Figures 5 and 6 present the results of the PLA FTIR synthesis on fermented lactic acid and the results of the PLA FTIR experiments resulting from the polymerization of technical lactic acid and fermented lactic acid. Figure 5 indicates the presence of PLA, which is shown by the fact of an alkyl group (C-H) and a carboxyl group (C = O). The FTIR results of this analysis showed that the peak alkyl group (CH) looks stronger at wave number 2997 cm⁻¹ and the carboxyl group (C = O) is at wave number 1758.96 cm⁻¹. The presence of the alkyl and carboxyl groups shows that this study created the desired PLA compound.

Figure 6 shows that the results of the FTIR test in the PLA study of technical lactic acid with PLA of fermented lactic acid showed the same results. This result had seen the carboxyl group, which is the leading group in the PLA in the same wave number range, as well as in the alkyl group wave number. This figure shows that the PLA formed by the polymerization of fermented lactic acid and technical lactic acid can be said to be the same when viewed from the functional groups.

(c) Molecular Weight

The next feature of PLA is the molecular weight of PLA. Molecular weight is a critical polymer feature since it affects the physical properties of the polymer. Measuring the viscosity of the aqueous solution is the most comfortable and most commonly used form of molecular weight determination.

This time, the viscosity value of the PLA synthesis powder had achieved using the Ostwald viscometer. The first PLA powder is dissolved into chloroform to measure the viscosity of the PLA formed. The mixture had moved to the capillary tube in the Ostwald Viscometer, and the flow time is then measured. The viscosity calculation had performed on all scientific lactic acid mass variables of 20, 25, 30, 35 and 40 grams. The calculation results for each of these variables in the form of flow time has shown in tables 2, 3, 4, 5 and 6.

Further measurements are made to achieve reduced viscosity (HSP) and then divided by concentration (C). This value had then graphed hs / C vs C. From this graph, we can get the value of the inherent viscosity [h] PLA. The molecular weight value has obtained, the value of the intrinsic viscosity has entered in the Mark Houwink equation, which states as follows:

\[ \eta = K M^\alpha \]

With a value of \( K = 2.21 \times 10^{-4} \) and \( \alpha = 0.77 \) (Hasibuan, 2006).

The results of PLA synthesis molecular weight measurements in this study are shown in Figure 5 below.
The graph above shows the relationship between the mass of technical lactic acid and PLA molecular weight, where the more significant the mass of technical lactic acid, the greater the molecular weight of PLA produced. That's because the more technical lactic acid mass, the more lactic acid will react with the solvent to form a polymer so that more carboxyl groups have formed, including a polymer chain that results in a massive molecular weight of PLA. From this graph, it had shown that the maximum molecular weight has obtained in the 40-gram technical lactic acid mass variable at 57,066.9 g / mol. This molecular weight had much better compared to the results of Hasibuan (2006) research which produced 22,000 g / mol molecular weight PLA using p.a and xylene p.a. And also better compared to the study by Mukhamad and Romadhon (2012) which provided BM of 16,023,88. However, this research is no better than that of Ajioka et al., who obtained a PLA molecular weight of up to 240,000 using solvents such as diphenyl ether at a polymerization temperature of 130 °C for 24 hours. This result is because this analysis uses a low xylene solvent as an azeotropic solvent. It is, after all, much lower than the boiling point of specific volatile oligomers.

In the PLA results of the polymerization of lactic acid fermented with 40 grams of lactic acid, the mass obtained a molecular weight value of 2,310,86 g / mole. The BM value is much lower than the BM value of the scientific lactic acid PLA with a pack of 40 grams, which reaches 57,066.9 g / mol. The low BM value is due to the low concentration of lactic acid fermented before polymerization, which is only 6 per cent so that the polymer chain produced by lactic acid monomers is not long enough and the molecular weight of PLA is small.

**The temperature of melting (Tm)**

The next feature is the testing of thermal properties using an electrothermal DMPA system. The Tm value for PLA resulting from technical lactic acid polymerization is 120 °C, where the findings of this study are different from those of Hasibuan (2006), which obtained a Tm value of 146 °C. These data show that the results of our analysis have a lower Tm value. This disparity in
the Tm value had calculated due to variations in the raw material used by lactic acid, Hasibuan (2006) using pure lactic acid, which has a higher purity such that the resulting PLA had melted at uniform temperatures due to minimal impurities. The result is a higher Tm PLA Hasibuan value compared to this study using technical lactic acid. Technical lactic acid produces several contaminants resulting in a lower melting point for PLA. Besides, the PLA obtained a Tm value of 135 °C from the fermentation of lactic acid polymerization. This Tm value is higher compared to the PLA resulting from technical lactic acid polymerization.

4. Conclusion
The process of PLA from technical lactic acid using the azeotropic polycondensation method produces PLA. PLA with the characteristics of a white-yellow powder. The yield of PLA increases with the increasing mass of lactic acid and its molecular weight. The best-operating conditions for technical lactic acid polymerization have been obtaining at a technical lactic acid value of 40 grams. Xylene solvent up to 100 grams, 0.5-per cent SnCl2 catalyst and 30-hour polymerization time, resulting in a PLA yield of 49.6 per cent, a molecular weight of 57,066.9 g / mol, and a melting temperature of 120 ° C. The fermentation process of lactic acid polymerization with the best conditions of the technical lactic acid polymerization process produces PLA with the characteristics of blackish-grey powder with a molecular weight of 2,310,86 g / mol and a melting temperature of 135 ° C. For good PLA results, the lactic acid levels for the PLA manufacturing process should be high. PLA thermal analysis should have performed using a DSC tool because it is more sensitive to low temperatures and can detect the melting temperature and glass temperature of the resulting PLA. The method for purifying fermented lactic acid must be further improved for the production of high purity lactic acid to enhance the characteristics of the PLA produced.

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