Polymerization of Lactide to Poly (Lactic Acid): Effect of Initiators

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***Abstract*— Plastics are one of the material that responsible for countless aspects of the modern life we enjoy today. It improves our lives due to its flexibility and adaptability that enable them to provide solutions in such a complex world we live in. As the world's population continue to increase, so does the amount of plastics waste produced by people that could surely lead to massive environmental pollution. To overcome this arising problem, there is a strong need to replace the non-biodegradable plastics with the biodegradable one. Poly (Lactic Acid) (PLA) is one of the most promising and popular material of biopolymer in the production of biodegradable plastics. The aim of this study were to produce PLA by polymerization of lactide through ring-opening polymerization (ROP) method by using stannous octoate, $Sn(Oct)_2$ as catalyst and to investigate the effect of initiator towards the characteristics of the PLA produced by using UV-Visible Spectrophotometer (UV-Vis) and Fourier Transform Infrared Spectroscopy (FTIR). The experiment was conducted at constant temperature of 120°C for 3 hours in bioreactor by using different types of initiator (1-dodecanol, 1-octanol and methanol). The result obtained from UV-Vis shows that the concentration of PLA increase as the reaction time increase for reaction initiated by methanol and 1-octanol but decrease half-way for 1-dodecanol. The spectrum obtained from FTIR shows that all of the three types of initiator have successfully revealed all the functional group contained in PLA. In overall, methanol is the most effective initiator in polymerization of lactide.**

Keywords*— Poly (Lactic Acid), ring-opening polymerization, UV-Visible Spectrophotometer, Fourier Transform Infrared Spectroscopy, insertion-coordination mechanism.

I. INTRODUCTION

Plastics is a material that is made up of organic polymer that consist of long chain carbon molecules as their backbone with repeating unit of monomer that is created during polymerization process. In this modern era, plastics is gaining interest and has been extensively used in many areas due to its increasing application from time to time. With the current trends of rapid population growth and industrialization, plastics are released faster than the earth can absorb. The enormous disposal of plastic trash about 140 million tons per year causing solid waste disposal on land and ocean dumping [1]. This issue on non-biodegradable plastics waste disposal has been on rise due to its massive bad impact to environment such as contamination. This is because non-biodegradable plastics requires about 200-300 years for them to naturally decompose [2]. Hence, extensive study has been done on how to solve the arising problems and it has come to the time to replace the non-biodegradable plastics with products that can naturally degradable and environmentally safe [3].

Instead of disposal in landfills or by incineration, biodegradable plastics has the ability to naturally decompose into safe by-products with the presence of microorganisms such as bacteria and fungi [4] due to their potentially hydrolysable ester bonds. This positive characteristic of biodegradable plastics will surely help to resolve the environmental pollution such as contamination of soil.

Among the other well-known biopolymers such as polyester and starch, Poly (Lactic Acid) (PLA) is the most suitable polymer to use in the production of plastics as it has excellence characteristics in biocompatibility and biological degradation, low processing temperature and good printability [5]. Besides it environmental friendly properties, study shows that fresh products and perishable foodstuffs placed in biodegradable plastics could remain fresh for a longer period of time [6]. As such, the demand on PLA from plastics production industries has been drastically increased.

PLA can be synthesized in two ways which are through direct polycondensation (DP) and ring-opening polymerization (ROP) of lactide. DP is a low cost process that use solvent and requires high reaction time. In case of PLA, DP occurs by connecting carboxyl and hydroxyl groups and thus producing water by-products completely from the reaction mixture [7]. Thus, the resulting polymer yielded has low molecular weight and poor mechanical properties due to the difficulty in removing by-products from the reaction mixture. Since high molecular weight of PLA are needed to have good physical properties [8], ROP are the most commonly used route in PLA industrial production. In this research, the selected route for polymerization of lactide was ROP method.

ROP is the new modernize method discovered by Carothers in 1932 that requires catalyst, stannous octoate, $Sn(Oct)_2$ and results in PLA with controlled molecular weight depending on the monomer used and its reaction conditions [9]. Study stated that ROP method has various advantages such as the product yielded has high purity, produce product with wider range of molecular weight and require short reaction time [10]. Besides, the use of initiator is important in this method. According to Duda and Penzek, hydroxyl compound group is required as initiator in polymerization of lactide as it will react with stannous octoate catalyst to form tin-oxide bond [11]. The insertion of tin-oxide bond towards the opening chain of cyclic monomer will initiate the additional lactide monomer to react with the terminal end of the chain resulting in the formation of long chain of lactide monomer called PLA.

However, the significant different of this research from others is that the stannous octoate catalyst used was in solid phase. The catalyst was coated in a thin layer form on the top of ceramic support and being sintered in furnace before it could be used. The main reason for this step was taken are to ease the separation process of catalyst with the reaction mixture.

Thus, the observation on the effect of initiator towards the production of PLA was conducted in this research to investigate on the ability of the initiator used to react with the thin layer solid form of stannous octoate catalyst located on the top of ceramic support in order to form tin-oxide bond.

II. METHODOLOGY

A. Materials

99% lactide and stannous octoate were supplied by Sigma Aldrich. For ring-opening initiators, 1-dodecanol, 1-octanol and methanol were purchased from Merck Group. To prepare the coating solution, ethylene glycol was used as solvent and purchased from Bendosen, nitric acid 65% and polyethylene glycol 2000 used as binder were supplied by Merck Group. In order to check the wavelength position of PLA solution, PLA granules purchased from Good Fellow was mixed with dimethyl formamide (DMF) purchased from Merck Group. Distilled water used in this research were obtained from Chemical Laboratory. Besides, the ceramic support was purchased in ready-made form.

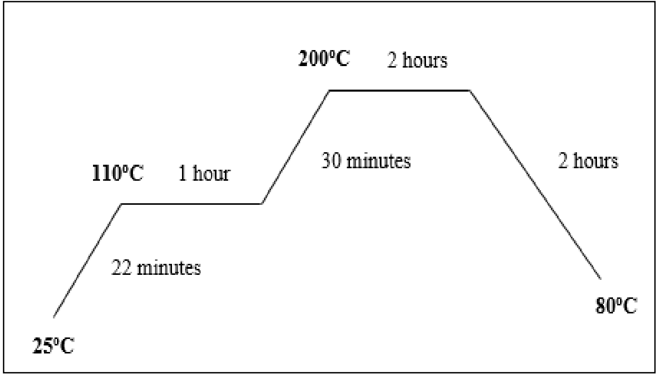
B. Synthesis of Coating Solution

A volume of 100 mL of ethylene glycol was poured in a beaker and heated up to 90°C on a hot plate. Then, 5 mL of stannous octoate was added and the solution was stirred for 2 to 3 minutes. Next, 0.1 M of nitric acid was mixed into the solution at the fume hood. The solution was continuously stirred for 30 minutes before 5 wt% of polyethylene glycol was added. Lastly, the solution was left with continuous stirring for 6 hours on a hot plate at speed of rotation of 10 rpm.

C. Sintering Process of Coating

The catalyst used in this research was solid phase of stannous octoate. Small circle-shaped of ceramic support was dipped into the solution prepared as stated in section B (synthesis of stannous octoate catalyst) for three times with duration of 30 seconds for each dip. This step was repeated for three ceramic support. Then, all of the support that were coated with stannous octoate will be put in furnace for 6 hours for coating sintering process at heating rate of 3°C/min. Figure 1 shown below is the temperature profile of the furnace.

Figure 1: Coating sintering temperature profile.



D. Polymerization of Lactide

Initially, 10.81 grams of lactide was weighed using weighing balance and mixed with 150 mL of distilled water at temperature of 90°C in a mixer. A ceramic support that was coated with stannous octoate catalyst was placed at the holder in bioreactor. The temperature of the bioreactor was set to be 120°C at the control panel of the bioreactor. Next, the lactide solution from the mixer was transferred into the bioreactor that containing the support after the temperature of the lactide solution reached 90°C. Then, 1 mL of 1-dodecanol initiator was added by using syringe through a top hole of bioreactor and the solution was let to be heated up until the temperature of the solution reached 120°C. After it already achieved temperature of 120°C, stop watch was being started up. 10 mL of product sample was taken out through bottom outlet hole at desired time interval for duration of 3 hours. All of the steps were repeated for the other two initiators, methanol and 1-octanol.

E. UV-Visible Spectrophotometer (UV-Vis)

UV-Vis modelled *Perkin Elmer Lambda 750* in this experiment was specifically used on the investigation of the presence of PLA in the sample product obtained from bioreactor after polymerization of lactide take place. 3 mL of sample of each interval was placed in cuvette and analysis was made by observing absorbance value at specified wavelength. The programme of scan 200-800 was initially selected and auto-zeroing was done to ensure that there was no left over wavelength reading from previous usage. The absorbance value of PLA in the product samples were noted based on the wavelength of the highest peak obtained from the spectrum of UV-Vis. According to Ferry (2019), PLA shows a significant increase in UV light transmittance at wavelength ranging from 225 nm to 300 nm [12]. In this research, the exact wavelength position was obtained by mixing PLA granules with DMF solvent at temperature of 100°C. The PLA solution were then analysed and the highest peak for absorption of PLA showed around 232 nm (Λ_{max}) indicating the maximum absorption was occurred. The position of wavelength obtained was in range to the wavelength stated by Ferry.

Besides, calibration curve is a must when analyzing sample by using UV-Vis. It is normally used to understand the response of instrument towards a sample and to predict the concentration of the unknown sample [13]. A set of sample solutions were made at various range of concentration. The technique that was used to prepare the sample at different concentration is by conducting serial dilution. To construct the calibration curve, a stock solution of 100 ppm of PLA was prepared and being diluted into 20 serial dilution. Dimethyl formamide (DMF) was the solvent used to dilute the PLA and the volume of PLA and DMF required to make the serial dilution was calculated based on the equation below:

$$M_1V_1 = M_2V_2 \qquad (1)$$

Where,
M_1: Concentration of concentrated solution (mol/L)
V_1: Volume of concentrated solution (mL)
M_2: Concentration of diluted solution (mol/L)
V_2: Volume of diluted solution (mL)

By using the equation for dilution stated above, the 20 samples of serial dilution were prepared and analysed using UV-Vis. About 3 mL of solution of each concentration was put in cuvette and the sample was analysed in random order (not from highest concentration to lowest concentration) as it could help to detect any systematic error.

In order to investigate the presence of PLA in the product sample, the calibration curve of absorbance value against concentration was constructed. The presence of the PLA was observed specifically based on the concentration of PLA for each time interval. To obtain the concentration of PLA, the calibration curve was being interpolated based on the absorbance value at each time of interval, hence, the concentration of the PLA for that particular absorbance could be determined.

F. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is an instrument that offers qualitative and quantitative analysis for organic and inorganic compound. It will identify the chemical bond and functional group that presence in the sample by producing the infrared absorption spectrum. In this research, FTIR analyses were made to determine the functional groups consist in the product samples obtained in order to understand more deeply what happens in the polymerization of lactide. To analyse by using FTIR, few drops of sample taken from bioreactor was dropped using dropper on the sample placement. Next, a scan button on the software equipped for FTIR was clicked. After a few seconds of scanning, the FTIR spectrum of transmittance (%) against wavelength (cm^{-1}) will be appeared on the screen. Then, a label tool was used to label out the coordinate (wavelength, transmittance) for all the peak obtained in the spectrum. The functional group contained in the product sample were classified according to the wavelength of the peak in the FTIR spectrum. All of the steps were repeated for the sample taken at each of the time interval for all the three types of initiator.

III. RESULTS AND DISCUSSION

A. Effect of Initiators in Production of PLA

Initiator can be defined as chemical species that will reacts with monomer in order to form an intermediate compound that is capable of linking successively with a large number of other monomers to form a polymeric compound. The three different initiators used were 1-dodecanol, 1-octanol and methanol. Two characterization instruments, UV-Vis and FTIR were used to analyse the outlet samples mainly focused on the investigation of the presence of PLA and the characteristics of PLA produced focusing on functional group, respectively. In focusing to determine the effect of initiators towards the characteristics of PLA produced, this experiment has been extensively studied on two aspects, which were (a) concentration of PLA at specific time interval from UV-Vis and (b) functional group in term of band shift from FTIR.

B. Concentration of PLA

The presence of PLA in the product samples were determined based on the concentration value at the specific wavelength. As mentioned earlier in methodology section, PLA shows maximum absorption at wavelength of 232 nm when pure PLA granules was mixed with Dimethyl Formamide (DMF).

To support the finding, the product samples obtained from bioreactor after polymerization reaction of lactide took place were analysed by using UV-Vis Spectrophotometer (UV-Vis). As results, the UV-Vis spectrum for all the product samples showed obvious peak around 230 nm indicated that PLA was present. Hence, the absorbance value of all product samples for each time interval at wavelength around 230 nm were noted.

Figure 2 below shows the shows the calibration curve of PLA where absorbance value obtained was plotted against its respective concentration. The coefficient of determination value, R^2 that was obtained from the curve is 0.9773 which is quite good and acceptable as it is nearly closed to the theoretical value of 1. The interpolation of calibration curve was conducted in order to determine the concentration of samples for its respective absorbance value at each time of interval for all of the three types of initiator.

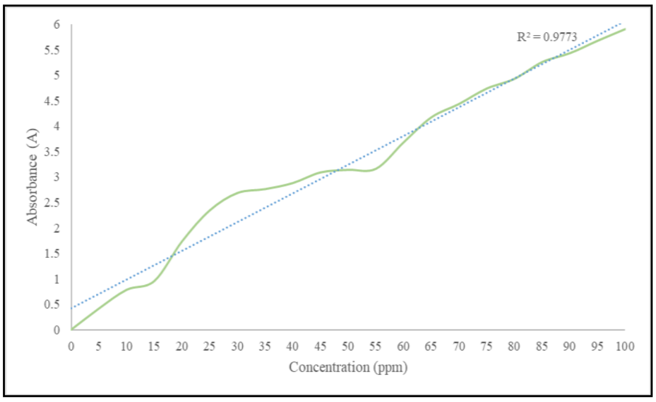


Figure 2: Calibration curve of PLA.

In addition, as the trend of absorbance value against time shown in *Figure 3* and concentration of PLA against time shown in *Figure 4* have the same trend and are correlated to each other, these two parameter will be simultaneously discussed in investigating the effect of initiator towards the production of PLA. The PLA are said to be successfully present if there was a continuous increment of concentration throughout the 3 hours of reaction.

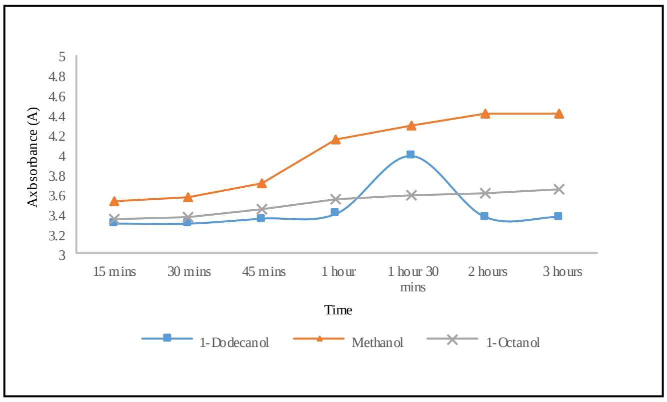


Figure 3: Graph of absorbance value against time (reaction period 3h; temperature 120ºC).

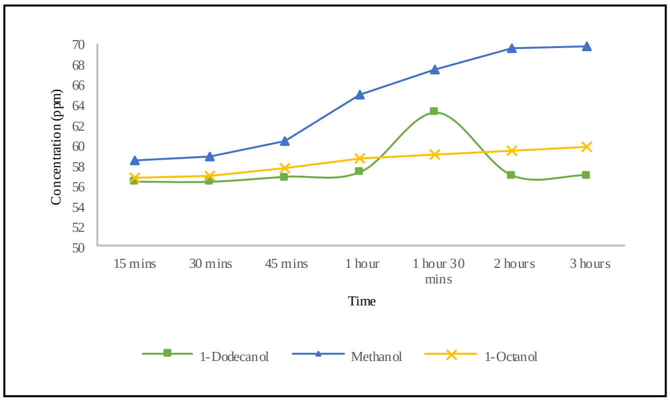
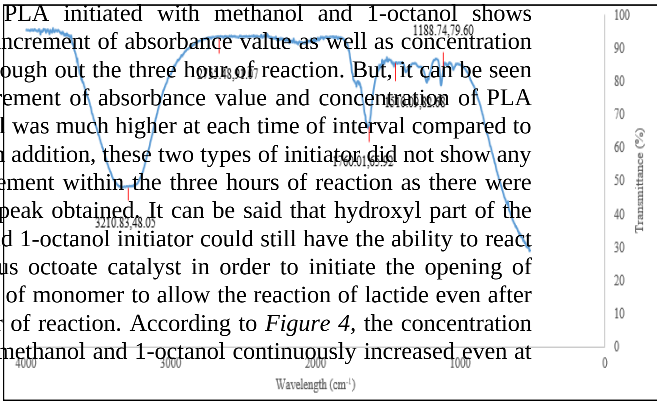


Figure 4: Graph of concentration of PLA against time (reaction period 3h; temperature 120ºC).

Referring to *Figure 3*, it illustrated the relationship between absorbance value with time interval for all three types of initiator. It shows that PLA initiated with different initiator results in different absorbance value at same time of interval. For PLA initiated with 1-dodecanol, there was no changes on absorbance at time interval of 15 minutes to 30 minutes. This indicated that the polymerization using this initiator has a slow rate of reaction. However, the absorbance value increased drastically at time interval of 1 hour 30 minutes and sudden decreased at the 2nd hour of the reaction with value of 3.996 and 3.367, respectively and thus resulting in obvious curve. Based on *Figure 4*, the concentration of PLA initiated with 1-dodecanol at 1 hour 30 minutes was 63.235 ppm and decreased to 57 ppm at the 2nd hour and remained constant until the last hour of interval. The decrement of the concentration might happen because of the stannous octoate catalyst has been fully utilized by the hydroxyl group of 1-dodecanol initiator for the production of PLA before the 2nd hour interval. As the reaction proceed, 1-dodecanol initiator did not have the ability to conduct insertion-coordination mechanism for further polymerization reaction. Hence, the concentration decreased.

Besides, PLA initiated with methanol and 1-octanol shows continuous increment of absorbance value as well as concentration of PLA thorough out the three hour of reaction. But, it can be seen that the increment of absorbance value and concentration of PLA for methanol was much higher at each time of interval compared to 1-octanol. In addition, these two types of initiator did not show any drastic decrement within the three hours of reaction as there were no obvious peak obtained. It can be said that hydroxyl part of the methanol and 1-octanol initiator could still have the ability to react with stannous octoate catalyst in order to initiate the opening of cyclic chain of monomer to allow the reaction of lactide even after the 3rd hour of reaction. According to *Figure 4*, the concentration of PLA for methanol and 1-octanol continuously increased even at



the 3rd hour of reaction with the value of 69.901 ppm and 59.75 ppm, respectively. It can be said that reaction initiated with methanol yielded the highest concentration of PLA until the last interval as compared to the other two initiators. However, reaction initiated by 1-octanol was resulted in higher concentration than 1-dodecanol.

Theoretically, the higher the concentration of PLA initiated by methanol indicated a more complete reaction. This is because it related to effect of initiators' initiation step towards polymerization reaction as the reaction conditions such as ratio of monomer to initiator, reaction time, reaction temperature, amount and type of catalyst were kept the same except for the type of initiator. Besides, the more complete reaction by methanol is due to its smallest alcohol characteristics, so it has lower steric hindrance when attacking the octoate ligand and can attack the substrate much more easily compared to longer primary alcohol such as 1-dodecanol and 1-octanol.

In overall, it can be said that methanol was the most effective initiator in the production of PLA as it attributed highest initiation rate [14]. Based on ROP method through the insertion-coordination mechanism, the propagation step occurs by repeatedly adding the lactide monomer into the tin-oxygen bond, so all of the propagation rates are expected to be the same since all factors governed are similar. Therefore, the high initiation rate contributed by methanol is the only variable affecting the concentration of PLA. The statement on saying that methanol was the most effective initiator in polymerization was also being supported by a research conducted by Pholharn et al., (2017) as methanol initiator could produce highest molecular weight of PLA (14,400 g/mol) through ROP method compared to the other initiator [14].

C. Functional Group of PLA

The FTIR spectrum of PLA initiated with methanol, 1-octanol and 1-dodecanol respectively at 120°C at 3 hours of reaction was illustrated in *Figure 5*, *Figure 6* and *Figure 7*. **T**he FTIR spectrum that revealed the characteristics of functional group contained in the products of PLA according to its absorption peaks in terms of wavelength. The PLA spectrum shows the band shift at 3210.94 cm^{-1}, 3210.48 cm^{-1} and 3208.03 cm^{-1} for methanol, 1-octanol and 1-dodecanol, respectively indicating that there were OH group found.

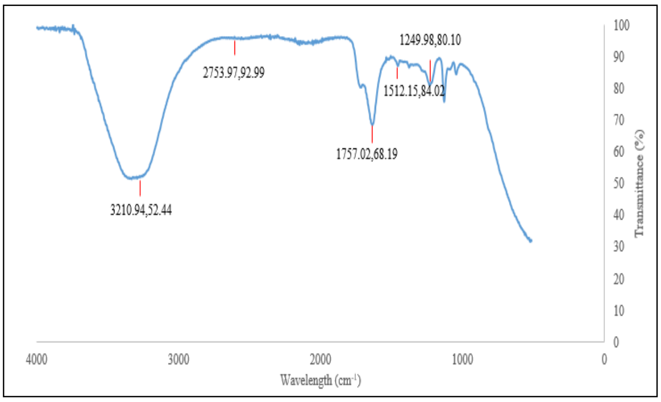


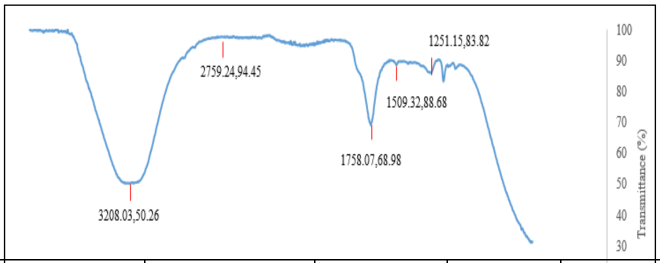
Figure 5: FTIR spectrum of PLA initiated with methanol (reaction period 3h; temperature 120°C).

Figure 6: FTIR spectrum of PLA initiated with 1-octanol (reaction period 3h; temperature 120°C).

Figure 7: FTIR spectrum of PLA initiated with 1-dodecanol (reaction period of 3h; temperature 120°C).

According to Gangopadhyay et al., (2001), the band shift located around 3220 cm^{-1} was related to the stretching of OH group [15]. Besides, the band shift around 2750 cm^{-1} for all the three initiators shows that there were valence vibrations of C-H from CH$_3$. A research on PLA shows that the location of C-H from CH$_3$ on FTIR spectrum located at 2781.81 cm^{-1} which was not much different from what the results shown [16]. It is possible to observe a band shift related to C=O in PLA at 1757.02 cm^{-1} for methanol, 1760.01 cm^{-1} for 1-octanol and 1758.07 cm^{-1} for 1-dodecanol [4].

In addition, banding vibration for all those three initiators related to functional group of CH$_3$ were found around 1510 cm^{-1}. As for C-O-C, research shows that it located at the band shift of 1200.59 cm^{-1}. This statement was similar to those stated by R. Crockett et al., (2017) [17] and Gangopadhyay et al., (2001) [15]. Based on the results obtained, the band shift for C-O-C is 1249.98 cm^{-1} for methanol, 1188.74 cm^{-1} for 1-octanol and 1251.59 cm^{-1} for 1-dodecanol. Table 1 below shows the summary of functional group contained in PLA according to its wavelength that successfully obtained in this research.



Functional Group	Standard Wavelength (cm^{-1})	PLA with Methanol (cm^{-1})	PLA with 1-Octanol (cm^{-1})	PLA with 1-Dodecanol (cm^{-1})
OH	3220	3210.94	3210.83	3208.03
C-H from CH$_3$	2781.81	2753.97	2755.48	2759.24
C=O	1757.92	1757.02	1760.01	1758.07
CH$_3$	1511.08	1512.15	1510.09	1509.32
C-O-C	1200.59	1249.98	1188.74	1251.15

Table 1: Summary of PLA functional group.

IV. CONCLUSION

Based on the studies conducted, it can be concluded that all of the three types of initiator used which were 1-dodecanol, 1-octanol and methanol has the ability to initiate the polymerization reaction of lactide. Based on UV-Visible Spectrophotometer (UV-Vis) analysis, reaction initiated with methanol has the highest concentration of PLA throughout the 3 hours of reaction time at constant temperature of 120°C followed by 1-octanol and 1-dodecanol. As for Fourier Transform Infrared Spectroscopy (FTIR), the spectrum proved that when the reactions were initiated with those three types of initiator, it achieved a complete polymerization as the spectrum consist of complete functional groups of PLA that was investigated based on the wavelength value of each peak obtained in the spectrum. In conclusion, it can be said that methanol was the most effective initiator as it led to the highest concentration of PLA throughout the 3 hours of reaction time at constant temperature of 120°C and could revealed complete functional groups of PLA.

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REFERENCES

[1] Madhavan Nampoothiri, K., Nair, N. R., & John, R. P. (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology*, *101*(22), 8493–8501. https://doi.org/10.1016/j.biortech.2010.05.092

[2] Song, J. H., Murphy, R. J., Narayan, R., Davies, G. B. H., Engineering, M., & Ub, M. (2009). *Biodegradable and compostable alternatives to conventional plastics*. 2127–2139. https://doi.org/10.1098/rstb.2008.0289

[3] Liu, C., Jia, Y., & He, A. (2013). Preparation of higher molecular weight poly (L - lactic acid) by chain extension. *International Journal of Polymer Science*, *2013*(March 2015). https://doi.org/10.1155/2013/315917

[4] Choksi, N., & Desai, H. (2017). Synthesis of Biodegradable Polylactic Acid Polymer By Using Lactic Acid Monomer. *International Journal of Applied Chemistry*, *13*(2), 377–384.

[5] Lim, L., Auras, R., & Rubino, M. (2008). *Progress in Polymer Science Processing technologies for poly (lactic acid). 33*, 820–852. https://doi.org/10.1016/j.progpolymsci.2008.05.004

[6] Van Den Oever, M., Molenveld, K., Van Der Zee, M., & Bos, H. (2017). *Bio-based and biodegradable plastics - Facts and figures*. Retrieved from http://edepot.wur.nl/408350

[7] Zhang, X., Liu, C., Zhang, A., & Sun, R. (2017). Organic catalysis for the ring-opening graft polymerization of p-dioxanone with Xylan in ionic liquid. *Polymers*, *9*(8). https://doi.org/10.3390/polym9080345

[8] Robert, J. L., & Aubrecht, K. B. (2008). Ring-Opening Polymerization of Lactide To Form a Biodegradable Polymer. *Journal of Chemical Education*, *85*(2), 258. https://doi.org/10.1021/ed085p258

[9] Gupta, B., & Revagade, N. (2007). *Poly (lactic acid) fiber : An overview. 32*, 455–482. https://doi.org/10.1016/j.progpolymsci.2007.01.005

[10] Hu, Y., Daoud, W. A., Cheuk, K. K. L., & Lin, C. S. K. (2016). Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: Focus on poly(lactic acid). *Materials*, *9*(3). https://doi.org/10.3390/ma9030133

[11] S. Slomkowski and A. Duda, in *Ring-Opening Polymerization: Mechanisms, Catalysis, Structure, Utility*, D. J. Brunnell, Ed., Henser, Munich, 1993.

[12] FERRY, D. K. (2019). Optical properties. *Semiconductor Transport*, 277–323. https://doi.org/10.4324/9781315267548-6

[13] *Basic Calibration of UV / Visible Spectrophotometer*. (2013). *2*(3), 247–251.

[14] Pholharn, D., Srithep, Y., & Morris, J. (2017). Effect of initiators on synthesis of poly(L-lactide) by ring opening polymerization. *IOP Conference Series: Materials Science and Engineering*, *213*(1). https://doi.org/10.1088/1757-899X/213/1/012022

[15] Gangopadhyay, R., De, A., & Ghosh, G. (2001). Synthesis and Characterization of Poly (Lactic Acid) for Use in Biomedical Field Astrid. *Polymer Journal*, *123*, 21–31. https://doi.org/10.3144/expresspolymlett.2011.29

[16] El, A. L. F. (2010). *S Ens or S I I*. 5346–5358.

[17] R. Crockett. (2017). *Biochemical composition of the superficial layer of articular cartilage*. *67*(8), 1180–1185. https://doi.org/10.1002/jbm.a