

Polymerization of Lactide to Polylactic Acid by using Homogenous and Heterogenous Catalysts

Norliza Ibrahim, Alia Syazana Mohamed



Abstract: Replacing non-biodegradable to degradable polymers are very much in concern due to reduction of petroleum supply, environment and economical related to waste disposal. Polylactic acid (PLA) shows a promising alternative to produce biodegradable plastic. The polymerization happened in homogenous phase where the catalyst, mostly used tin octoate, and the lactide are mixed in liquid phase to form PLA. However, this method become problematic for the product because the catalysts remain with the PLA and the degradation of catalyst occurred. Therefore, this study aims to convert the homogeneous catalyst to heterogeneous using ceramic waste as the support and to characterize the PLA produced by using Ultraviolet Visible (UV-Vis) Spectrometer and Fourier Transform Infrared Spectroscopy (FTIR). The experiment was carried out at different temperatures which were 110 °C, 120 °C and 130 °C. From the results obtained, the highest concentration of PLA produced is at temperature of 130 °C by using heterogenous catalyst. Therefore, it can be concluded that heterogeneous catalyst can be a new method of producing PLA.

Keywords : Catalyst, Heterogeneous, Polylactic Acid, Tin Octoate.

I. INTRODUCTION

Presently, the worldwide production of plastics had been dominated by petroleum-based polymers. Due to environmental and economical that related to waste disposal concern, the biodegradable polymers were introduced. Another reason of using biodegradable polymers is the price of petroleum nowadays is quite high and will continuously increase in the future. The first polymer that can replace the non-biodegradable polymers is Poly (glycolic acid) (PGA) then followed by Polylactic acid (PLA) [1]. The polylactic acid has received more attention time by time as it has been used in biomedical application in the form of implants due to its high biodegradability and biocompatibility. This biodegradable polymer can easily degrade and thus can save the country from the environmental pollution [2]. The polymers can be degraded by simple method which is

hydrolysis of the ester bonds that do not require the enzymes thus can prevent inflammatory reactions.

There are many ways to produce PLA. However, all the methods are not easy to perform as the PLA synthesis need rigorous control of certain condition which are temperature, pressure, pH, catalyst and time for the polymerization process. The methods are ring opening polymerization of lactide, polycondensation and enzymatic polymerization of lactic acid. The polycondensation is the cheapest routes but difficult in producing high molecular weight of PLA. Among all these methods, ring opening polymerization is widely used in industry due to its ability in achieving high molecular weight of PLA. This method used lactide as monomer to form polymer in the presence of catalyst [3].

In the production of PLA, homogeneous catalyst was introduced in the reactor in order to increase the reaction rate and increase the product yield. Previously, catalyst was fed homogeneously inside the reactor either through injection or dissolving the catalyst into the solution. This cause a major drawback since the catalyst is miscible in the reaction medium, difficult and costly process to remove and hence may defect the final product. Unfortunately, the separation of catalyst from the product still remains a challenge [4] and expensive [5]. In order to overcome this problem, heterogenization of homogeneous catalyst was introduced using solid porous support to combine the advantages of both homogeneous and heterogeneous catalyst [6]. The recover catalyst can be used further in catalytic recycle and efficient for product purification as well as catalyst residues removal especially when involving toxic metals [7]. There are many factors that can affect the polymerization process which are temperature, pressure, concentration and also type of catalyst used [8]. For each factor, there is optimum parameters and suitable catalyst in order to produce high concentration of product. In the characterization of PLA, there are many methods that can be used which are Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetric (DSC), Scanning Electron Microscope (SEM), Thermogravimetric analysis (TGA) and Ultraviolet Visible (UV-Vis) Spectroscopy.

II. METHODOLOGY

A. Materials

PLA was purchased from Goodfellow Cambridge while 3,6-Dimethyl-1,4-dioxane-2,5 dione (lactide, 99% purity) and tin octoate (Sn(Oct)₂, 92.5%-100% purity) were from Sigma Aldrich.

Manuscript published on November 30, 2019.

* Correspondence Author

Norliza Ibrahim*, Faculty of chemical engineering, Universiti Teknologi MARA, Shah Alam,

Alia Syazana Mohamed, Faculty of chemical engineering, Universiti Teknologi MARA, Shah Alam, Selangor.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an [open access](http://creativecommons.org/licenses/by-nc-nd/4.0/) article under the CC-BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Polymerization of Lactide to Polylactic Acid by using Homogenous and Heterogenous Catalysts

Lauryl alcohol, polyethylene glycol (PEG), nitric acid, ethylene glycol (EG) and dimethylformamide (DMF) were all supplied by Merck, Germany.

B. Tin octoate film preparation

The tin octoate tin film was prepared by sol gel method. One mol of Sn (Oct)₂ was added to 10 mol of ethylene glycol and heated up until it reached 90°C. Then, 0.1 molar of diluted nitric acid was added to the solution and mixed for 30 minutes to peptize the sol. 10 ml of PEG binder was added to the solution and stirred for 6 hours. After 24 hours of aging, the tin film was deposited on the ceramic support by dip coating technique at room temperature. The coated support was heated in the furnace at 200°C for 2 hours.

C. Buffer solution preparation

The polylactic acid (PLA) was prepared to become a buffer solution by melting the PLA in the solvent which was Dimethylformamide (DMF). This buffer solution was made as reference to characterize the PLA and also the concentration in the polymerization of lactide. The melting process of PLA took about 2 hours at the temperature of 100 °C. Then, the buffer solutions were diluted to create calibration curve by using the following equation:

$$M1V1=M2V2 \quad (1)$$

Where M1 and M2 are concentration of PLA at initial and desired value in mg/L while V1(L) and V2(L) are the volume of stock solution and DMF.

D. PLA production process

The method used to produce the PLA was ring-opening polymerization. For homogenous catalyst, the tin octoate was directly mixed with lactide and lauryl alcohol while for heterogenous catalyst, a ceramic support was coated with thin layer of tin octoate catalyst before the reaction occurred to form the PLA. The sample of reaction was taken for 3 hours. The temperature used for polymerization process was followed from [9] which was between 110°C to 130°C.

E. Analysis of data

The present of PLA was determined using Ultraviolet Visible Spectrophotometer (LAMBDA 750 UV/Vis/NIR, PerkinElmer, USA) and Fourier Transform Infrared Spectrometer (Spectrum One FTIR, PerkinElmer, USA). From the FTIR Spectroscopy, the active functional groups for the PLA was identified. The identification was performed within the wavelength of 2778 nm to 11534 nm. The spectrum that formed was compared with the standard for all functional groups. Furthermore, the UV-Vis Spectra was used to determine the concentration of PLA produced by interpreting the absorbance's values of PLA ester groups. The saturation of the PLA spectra was range 225 nm to 300 nm.

III. RESULTS AND DISCUSSION

By referring to calibration curve in Fig. 1, the concentration of PLA by ring-opening polymerization can be identified as the absorbance is directly proportional to the concentration.

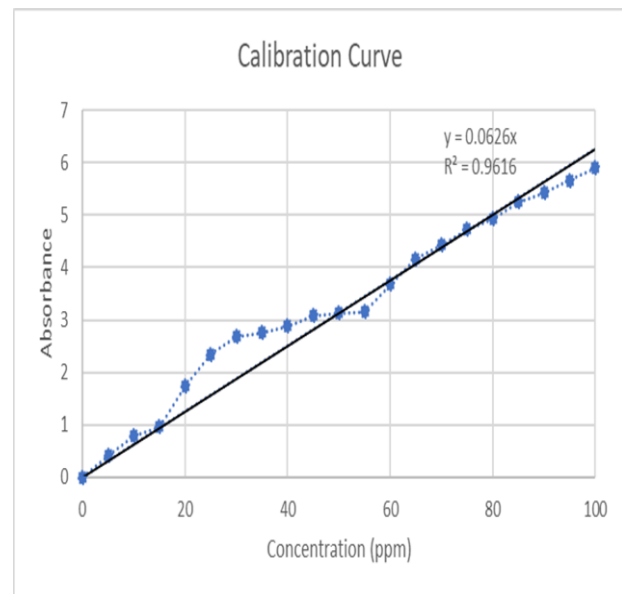


Fig. 1: Calibration curve of buffer solution

The concentration against time using homogenous and heterogenous catalysts at three different temperatures are shown in Fig. 2, 3 and 4. At temperature of 110°C, shown in Fig. 2, both catalysts show an increasing of concentration with respect to time of operation. It is seen that the concentration of heterogenous catalyst is higher than homogenous catalyst. The values obtained after 3 hours of operation is 57.4 ppm for heterogeneous while for homogeneous is 45.9 ppm. This result was also supported by Eonah Kim that proving heterogenous catalyst increased gradually and achieved higher final yield than homogenous catalyst [10]. On the other hand, although the conversion of heterogeneous (94.58%) is a bit lower than homogeneous catalyst (96.68%), reuse potential of up to 3 batches were reported for heterogeneous in biodiesel synthesis from microalgal lipids [11]

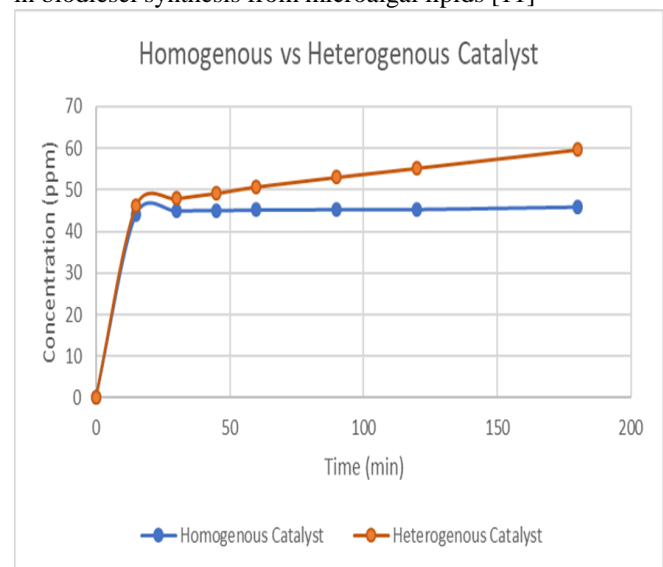


Fig. 2: Graph of PLA concentration (ppm) against time at 110°C.

Fig. 3 shows the PLA concentration against time produced from homogenous and heterogenous catalysts at 120°C. For homogenous catalyst, it is shown that the concentration of PLA produced increase from 54 ppm to 59 ppm at the first hour of operation before starting to decrease after that. While for heterogenous catalyst, the concentration keep increasing from 53 to 64 ppm. This observation is caused by the concentration of PLA produced by ROP is not a positive correlation to long heating duration as it could reach the plateau of production within a short time. Instead, long heating duration may cause degradation of PLA [12]. The reaction in homogenous catalyst seems to be faster than heterogenous catalyst at the beginning and this will cause difficulty for the monomer to access the active sites of the catalyst due to mass transfer limitations [10]. The heterogenous catalyst seems to be higher exponential phase even after longer period of reaction time. It is shown that the trend is in lag phase for 30 minutes before starting to increase until 3 hours of operation.

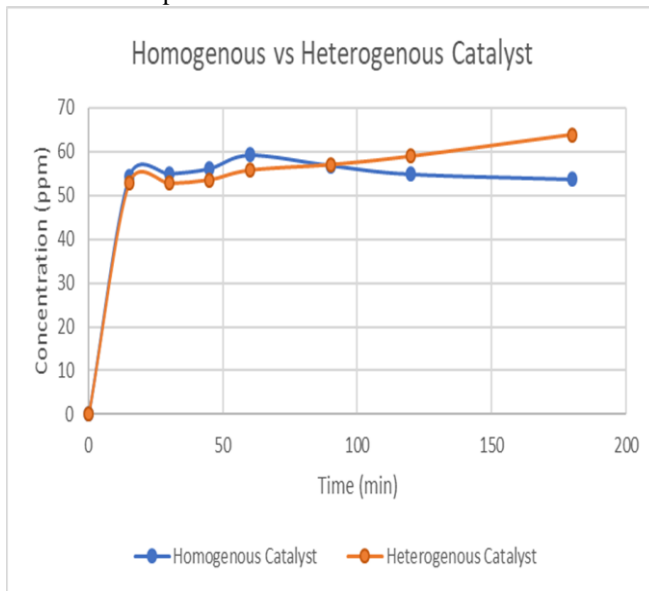


Fig. 3: Graph of PLA concentration (ppm) against time at 120°C.

For the temperature of 130°C as shown in Fig. 4, the concentration of homogenous catalyst is higher at the first 15 minutes which is 68.5 ppm and start to decrease until reaching 42 ppm at the end. The reaction is vigorous at high temperature and this causes faster degradation of PLA. For the heterogenous catalyst, it keeps increasing from 60 ppm and reach plateau of production at 90.1 ppm. The trend is observed as the result of optimum temperature for the production of PLA is at 130°C. It is also reported by Lopes et.al (2014) that PLA was able to be produced at temperature of 140°C for two hours [13].

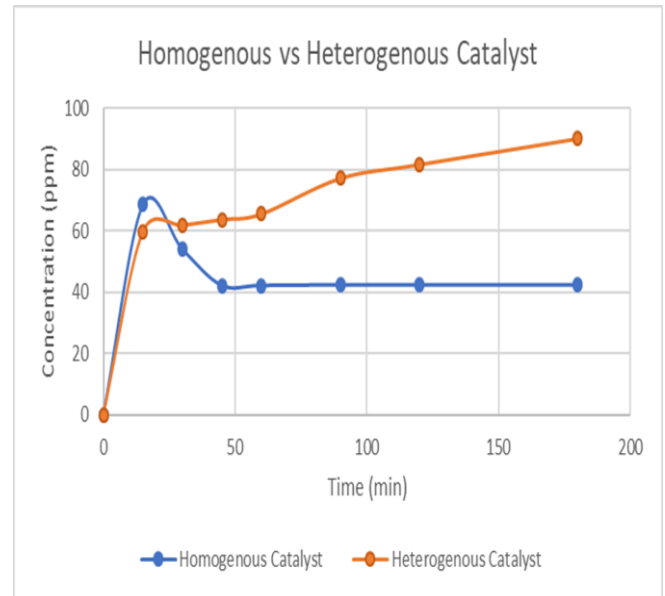


Fig. 4: Graph of concentration (ppm) against time of PLA at 130°C.

Table I concludes the effect of temperature on the production of PLA using two different phase of catalyst. It shows that the concentration of PLA from both catalysts at temperature of 130°C is the highest among other temperature. However, for homogenous catalyst, the concentration drastically decreased due to degradation of PLA after achieving the optimum concentration at 15 minutes. For the temperature of 120°C, the optimum concentration is lower than 130°C and has slower rate of reaction. The optimum concentration for 110°C is the lowest and takes 3 hours to achieve it. Meanwhile, for the heterogenous catalyst, the optimum concentrations of PLA keep increasing with the increment of the temperature. All values are obtained after 3 hours of operating. This finding was comparable to that of Singh et.al [14], where 2.5 hours was optimum for yield of 97% using heterogenous catalyst, while only 1 hour for homogeneous catalyst.

Table I: The optimum concentration of PLA by homogenous and heterogeneous catalyst at different temperature.

Temperature (°C)	Homogeneous		Heterogeneous	
	Time (min)	Optimum Concentration (ppm)	Time (min)	Optimum Concentration (ppm)
110	180	45.9	180	57.4
120	60	59.1	180	63.8
130	15	68.5	180	90.1

FTIR spectroscopy gives the qualitative information where the Sn (Oct)₂ molecules are bonded to the lactide molecules. Fig. 5 and 6 show the comparison of FTIR spectrums of PLA that presence in the solutions that have been polymerized using homogenous and heterogenous catalysts. These data were collected after 3 hours of operation and for all temperatures. The FTIR analysis was recorded using a FTIR spectrometer in a range between 3500 cm⁻¹ to 500 cm⁻¹. Both figures give approximately the same trend of peaks due to similar molecular structure of PLA that presence in the solutions. The PLA spectrum shows the bands at 1047.82 cm⁻¹ to 1236.88 cm⁻¹ from C-O-C stretching vibration. The bands around 3300 cm⁻¹ is related to the stretching of OH group which is the highest peak because OH bond is polar, thus show intense absorption bands. This OH bond also depends on the concentration. The higher concentration of solution contributed to more OH containing molecules. Therefore, PLA at all temperatures give the highest stretch peak. This result was supported by Iriswguo [15] that O-H stretch in a concentrated hydrogen bonded solution of an alcohol occurs at 3550-3200 cm⁻¹. Although the C-H and C-C bond are not showed in the spectrum, it definitely presence in the molecule of PLA. Based on the theory from Dr. A. Bacher [16], groups with a small difference in electronegativity such as C-H and C-C bond will usually show weak or medium sized peaks in the spectrum. Thus, that is the reason of the absence of peak for C-H and C-C bond. It is observed that a band shift related to the C=O stretch at 1636.11-1635.31 cm⁻¹ in the polymer. These bands that show shifts of monomer to polymer present difference in peak intensity which suggests the arrangement of molecules in the polymer chain [13].

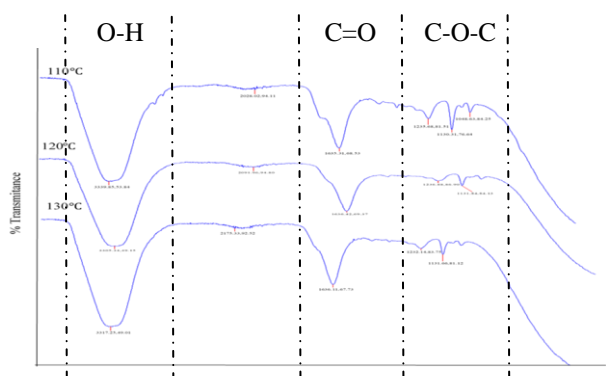


Fig. 5: FTIR spectrum of PLA by homogenous catalyst

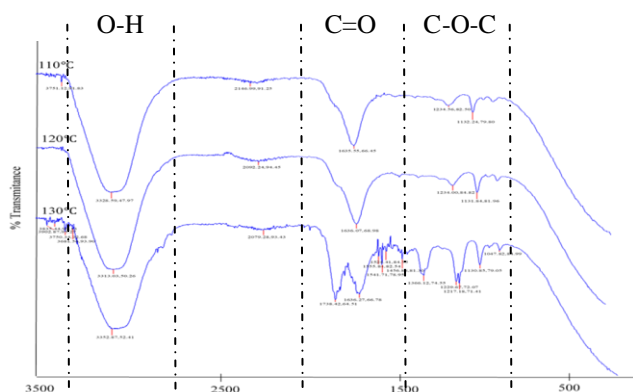


Fig. 6: FTIR spectrum of PLA by heterogenous catalyst

IV. CONCLUSION

This experimental set up is to investigate the production of PLA by using homogeneous and heterogenous catalyst. From the results, it can be concluded that the production of PLA exists in the solutions by both catalysts as the FTIR and UV-vis spectra shows a positive result of characterization. The results show that heterogenous catalyst produces higher concentration than homogenous catalyst even it takes long time to achieve. In homogenous catalyst, the concentration increased with increasing temperature. The highest concentration is at temperature of 130°C which is 68.5 ppm for homogenous catalyst while for the heterogenous catalyst, the highest concentration is 90.1 ppm.

V. ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Education for financial support via Fundamental Research Grant Scheme (600-IRMI/FRGS 5/3 (93/2016)). The authors gratefully acknowledged use of services and research facilities available at the Faculty of Chemical Engineering, Universiti Teknologi Mara, Shah Alam. The authors would also like to thank all people who have been directly and indirectly contributed and helped throughout the work.

REFERENCES

1. E. E. Schmitt and E.J. Frazza "A new absorbable suture," *Journal of Biomedical Materials Research*, vol. 5, no. 2, 1971.
2. R. Mehta, V. Kumar, H. Bhunia and S.N. Upadhyay "Synthesis of Poly (Lactic Acid): A Review," *Journal of Macromolecular Science, Part C: Polymer reviews*, vol. 45, no. 4, 2005, pp. 325-349.
3. A.J.R. Lasprilla, G.A.R. Martinez, B.H. Lunellia, A.L. Jardini and R. Maciel Filho, "Poly-lactic acid synthesis for application in biomedical devices — A review," *Biotechnology Advances*, vol. 30, no. 5, 2012, pp. 321-328.
4. A. Guldhe, P. Singh, F. Ahmad Ansaria, B. Singh and F. Bux "Biodiesel synthesis from microalgal lipids using tungstated zirconia as a heterogeneous acid catalyst and its comparison with homogeneous acid and enzyme catalysts," *Fuel*, vol. 187, 2017, pp. 180-188.
5. J. Govan and Y.K.Gun "Recent advances in the application of magnetic nanoparticles as a support for homogeneous catalysts," *Nanomaterials*, vol. 4, no. 2, 2014, pp. 222-241.
6. L. Carneiro, A.R. Silva, P.S. Shuttleworth, V. Budarin and J.H. Clark "Synthesis, immobilization and catalytic activity of a copper (II) complex with a chiral bis(oxazoline)," *Molecules*, vol. 19, no. 8, 2014, pp. 11988-11998.
7. L. Wei "Designing immobilized catalysts for chemical transformations: New platforms to tune the accessibility of active sites," *Georgia Tech Library*, July 3, 2012. Accessed on Aug. 3, 2019 [online]. Available: <https://smartech.gatech.edu/handle/1853/49017>.
8. S. Rahmayetty, B. Prasetya, and M. Gozan "Synthesis and characterization of L-lactide and polylactic acid (PLA) from L-lactic acid for biomedical applications," *AIP Conference Proceedings*, vol. 1817, no. 1, 2017.
9. Rahmayetty, W. Yudan, Sukirno, S.F. Rahman, E.A. Suyono, M. Yohda and M. Gozan "Use of *Candida rugosa* Lipase as a Biocatalyst for L-lactide Ring-Opening Polymerization and Polylactic Acid Production," *Biocatalysis and Agricultural Biotechnology*, vol. 16, 2018, pp. 683-691.
10. E. Kim, E. Woo Shin, Ik-K. Yoo and J. Suk Chung "Characteristics of heterogeneous titanium alkoxide catalysts for ring-opening polymerization of lactide to produce polylactide," *Journal of Molecular Catalysis A: Chemical*, vol. 298, no. 1-2, 2009, pp. 36-39.
11. I. Vural Gursel, Q. Wang, T. Noel and V. Hessel "Separation/Recycling methods of homogeneous transition metal catalysts in continuous flow," *Green Chemistry*, vol. 17, no. 4, 2015, pp. 2012-2026.

12. Y. Hu, W. A. Daoud, K. K. L. Cheuk and C. S. K. Lin, "Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: focus on poly(lactic acid)," *Materials*, vol. 9, no. 133, 2016, pp. 1-14.
13. M. S. Lopes, A. L. Jardini and R. M. Filho "Synthesis and Characterizations of Poly (Lactic Acid) by ring-opening polymerization for biomedical applications," *Chemical Engineering Transactions*, vol. 38, 2014, pp. 331-336.
14. B. Singh, F. Bux and Y.C. Sharma "Comparision of homogeneous and heterogeneous catalysis for synthesis of biodiesel from madhuca indica oil," *Chemical Industry & Chemical Engineering Quarterly*, vol. 17, no. 2, 2011, pp. 117-124.
15. Iriswguo "O-H and N-H absorption bands because O-H bonds are polar," Chapter 14, University of Connecticut. Accessed on Aug. 3, 2019 [online]. Available: Coursehero: <https://www.coursehero.com/file/p50s0n1/O-Hand-N-H-Absorption-Bands-Because-O-H-bondsare-polar-they-show-intense/>
16. A. Bacher, "Infrared Spectroscopy", April 1, 2002. Accessed on Aug. 3, 2019 [online]. Available: <http://www.chem.ucla.edu/~bacher/spectroscopy/IR1.html>

AUTHORS PROFILE



Norliza Ibrahim PhD (Chem. Eng) (UiTM), MSc (Chem Eng) (USM), B.Eng (Chemical)(Hons)(USM). BEM Member, research focus on surface coating and ceramic membrane.



Alia Syazana Mohamed B.Eng (Hons) Chemical (UiTM), research focus on comparison between homogeneous and heterogeneous catalyst in polylactic acid production.