

Polymerization of Lactide to Polylactic Acid by Using Homogenous and Heterogenous Catalysts on The Effect of Temperature

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Abstract— Polylactic acid (PLA) shows a promising alternative to petroleum-based polymers such as plastics. Catalyst such as tin octoate is most common and widely used in synthesizing of PLA in the industrial application using ring-opening polymerization method. The polymerization take place in homogenous phase where the catalyst and the lactide are mixed in liquid phase to form the PLA. However, this method become problematic for the product because the catalyst will remain in the PLA and causes the degradation of the catalyst. The objectives of the research are to investigate the production of PLA by using homogenous and heterogenous catalysts with variation of temperature from 110°C to 130°C and to characterize the PLA produced by using Ultraviolet Visible (UV-Vis) Spectrometer and Fourier Transform Infrared Spectroscopy (FTIR). From the result collected, it can be concluded that the synthesis using heterogenous catalyst is better than homogenous catalyst with high concentration and the optimum production of PLA produced is at the highest concentration which is 90.1 ppm with temperature of 130°C by using heterogenous catalyst.

Keywords— Coating, homogenous and heterogenous catalysts, lactide, polylactic acid, ring-opening polymerization

I. INTRODUCTION

Presently, the worldwide production of plastics had been dominated by petroleum-based polymers [10]. Due to environmental and economical that related to waste disposal concern, the biodegradable polymers were introduced [18]. Another reason of using the 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) [8]. The polylactic acid has received more attention time by time as it has been used in biomedical application in the form of implants because of high performances in biodegradability and biocompatibility [13, 14, 17]. This biodegradable polymer can easily degrade and thus can save the country from environmental pollution [11]. 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 the polylactic acid. However, all the methods are not easy to perform as the polylactic acid 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 (ROP) of lactide, polycondensation and enzymatic polymerization of lactic acid [3]. The polycondensation is the cheapest routes but difficult in production of high molecular weight of polylactic acid. Among all these methods, ring opening polymerization is widely used in industry due to high molecular weight that can be achieved. This method used lactide as monomer to form polymer in the presence of catalyst [7].

The production of polylactic acid can be either with homogenous or heterogenous catalyst. Commonly, production with homogenous catalyst is favorable in making pharmaceutical products because of high activity and also selectivity. Unfortunately, the separation of catalyst from the product still remains challenge [5]. Because of the issue, the production by using heterogenous catalyst is being working on nowadays in industrial. There are many factors that can affect the polymerization which are temperature, pressure, concentration and also the type of catalyst [13]. For each factor, there is optimum parameters and suitable catalyst used in order to produce high concentration of product.

In characterization of polylactic acid, there are many methods that can be used which are Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetric (DSC), Proton Nuclear Magnetic Resonance (1H NMR) Spectroscopy, Scanning Electron Microscope (SEM), Thermogravimetric analysis (TGA) and Ultraviolet-Visible (UV-Vis) Spectroscopy. FTIR Spectroscopy is used to identify an intermolecular interaction and phase behavior in the reaction process by knowing the functional groups of the products obtained by FTIR analysis while DSC is used to determine the melting and crystallization behaviors in the reactions [1]. For the discovery of stereo-sequences of the product, 1H NMR Spectroscopy is commonly used where the methine proton resonance is scanned under irradiation of the methyl protons. Besides, SEM has the potential to accurately inspect a solid surface and can observe the fractured surfaces of the composited by tensile tests. Other than that, TGA is used to analyze the thermal stability of polymers and lastly UV-Vis Spectroscopy is used to know the presence of polymer by the absorbance that was obtained.

METHODOLOGY

1. Materials

Poly(lactic acid) (PLA) was purchased from Goodfellow Cambridge while 3,6-Dimethyl-1,4-dioxane-2,5 dione (lactide, 99% purity) and tin octoate ($\text{Sn}(\text{Oct})_2$, 92.5%-100% purity) were from Sigma Aldrich. Lauryl alcohol, polyethylene glycol (PEG), nitric acid, ethylene glycol (EG) and dimethylformamide (DMF) were all supplied by Merck, Germany.

2. Tin octoate film preparation

The tin octoate tin film was prepared by sol gel method [12]. One mol of $\text{Sn}(\text{Oct})_2$ 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 binder which was PEG was added to the solution and stirred for 6 hours. After 24 hours aging of solutions, 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.

3. Preparation of buffer solution

The poly(lactic acid) (PLA) was prepared to become a buffer solution by dissolving 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 process took about 2 hours at the temperature 100°C . Then, the buffer solutions were diluted to create calibration curve by using following equation:

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

Where M_1 and M_2 are concentration of PLA at initial and desired value in mg/L while $V_1(\text{L})$ and $V_2(\text{L})$ are the volume of stock solution and DMF.

4. 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 and then the reaction occurred with lactide and lauryl alcohol to form the PLA. The sample of reaction was taken with desired time interval for 3 hours. The temperature used for polymerization process was 110°C , 120°C and 130°C .

5. Analysis of data

The present of PLA was determined by 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 3500 cm^{-1} to 500 cm^{-1} . 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 [15].

II. RESULTS AND DISCUSSION

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

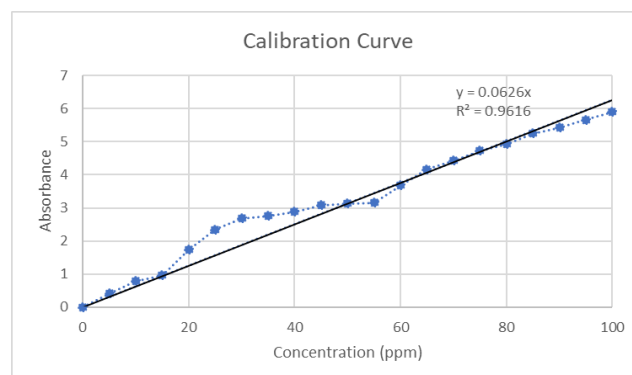


Figure 1: Calibration curve of buffer solution

1. Effect of catalyst phase on PLA production

The graph of absorbance against time (min) by homogenous and heterogenous catalysts as figures 2(a), 3(a) and 4(a) have been plotted for each temperature. From these graphs, the graph of concentration versus time are plotted based on the calibration curve. At the temperature of 110°C in figure 2(b), the result shows that the concentration of heterogenous catalyst is higher than homogenous catalyst at 3 hours which is 59.7 ppm while the other one is 45.9 ppm. This result supported by Eonah Kim proving that heterogenous catalyst increased gradually and achieved higher final yield than homogenous catalyst [4].

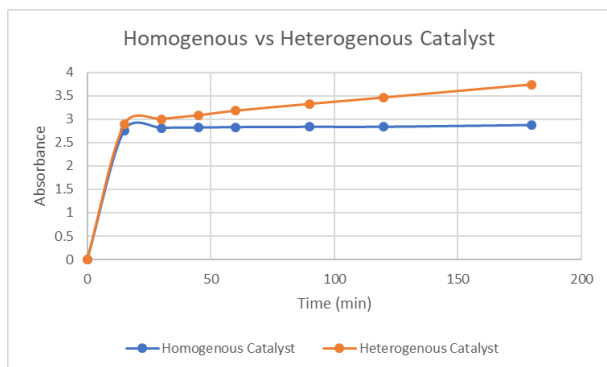


Figure 2 (a): Graph of absorbance against time (min) of PLA at 110°C.

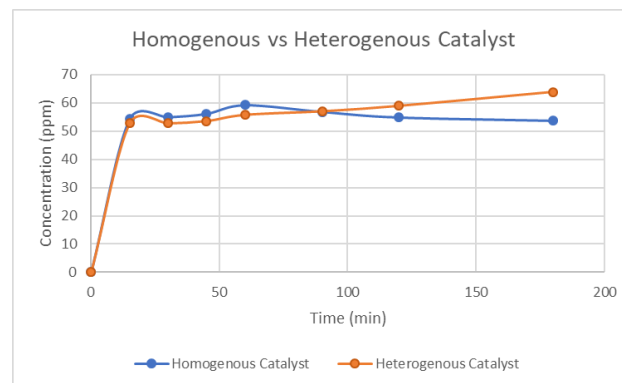


Figure 3 (b): Graph of concentration (ppm) against time of PLA at 120°C.

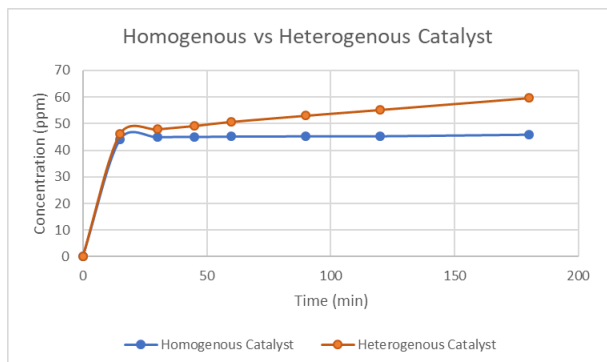


Figure 2 (b): Graph of concentration (ppm) against time of PLA at 110°C.

Figure 3(b) shows the graph of concentration of PLA against time produced from homogenous and heterogenous catalysts at 120°C. For homogenous catalyst, it is shown that the concentration of PLA produced increase at an hour and start to decrease. It is because 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 the short time. Instead, long heating duration may cause degradation of PLA [16]. 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 [3]. The heterogenous catalyst seems to be higher exponential phase even longer period time of reaction. It is shown that the trend is in lag phase for 30 minutes and start to increase until 3 hours until reach the maximum concentration which is 63.8 ppm.

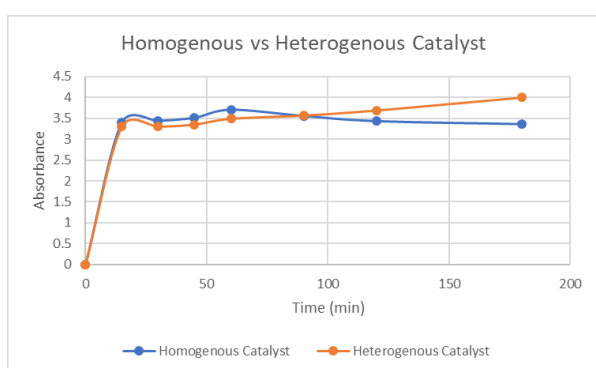


Figure 3 (a): Graph of absorbance against time (min) of PLA at 120°C.

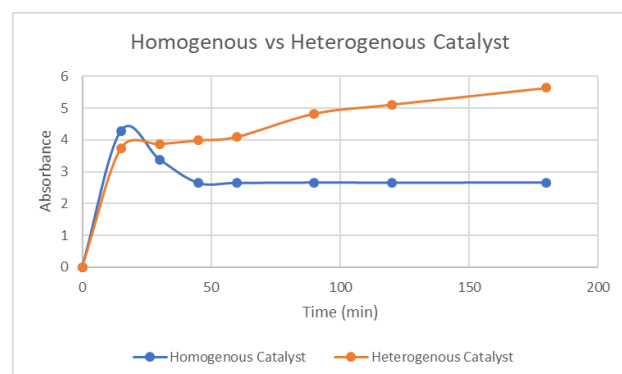


Figure 4 (a): Graph of absorbance against time (min) of PLA at 130°C.

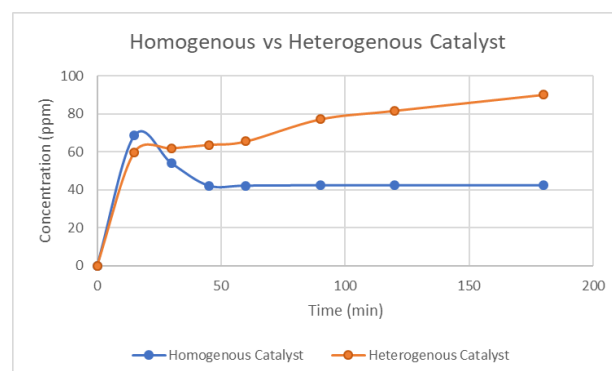


Figure 4 (b): Graph of concentration (ppm) against time of PLA at 130°C.

2. Effect of temperature on PLA production

From figure 5 and 6, the result shows that the concentration of PLA from both catalysts at temperature 130°C is the highest among other temperature after first hour of operation in homogenous catalyst while after 3 hours operation in heterogenous catalyst. However, for homogenous catalyst, the concentration drastically decreased due to degradation of PLA after achieve the optimum concentration at time 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 take 3 hours to achieve it. By comparing all temperatures in homogenous catalyst, temperature at 130°C is slightly different in terms of time to reach high concentration. The reaction reaches the optimum concentration after 15 minutes and start to decrease. This is because the high temperature aggravates the chain growth polymerization and heat accumulation make the decomposition to dominate the reaction balance and thus decrease the polymer concentration [16]. In contrast, the concentration of PLA by heterogenous catalyst increase smoothly due to effectiveness of production. This is because the catalyst is not remained in the product and thus unaffacting the concentration of PLA. These optimum concentration for homogenous and heterogenous catalyst can refer to table 1 and 2 below.

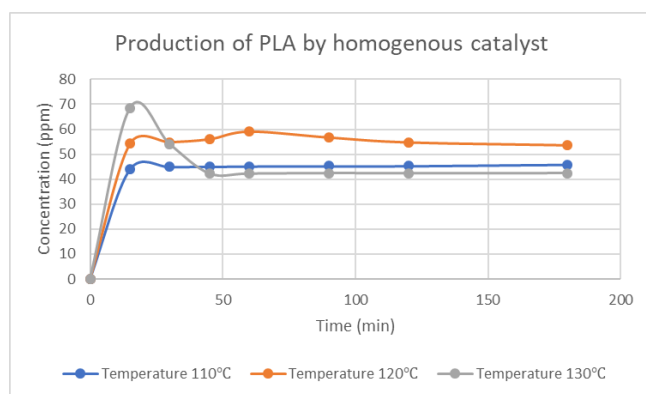


Figure 5: Graph of concentration (ppm) against time of PLA by homogenous catalyst at different temperature.

Table 1: The optimum concentration of PLA by homogenous catalyst at different temperature.

Temperature (°C)	Time (min)	Optimum Concentration (ppm)
110	180	45.9
120	60	59.1
130	15	68.5

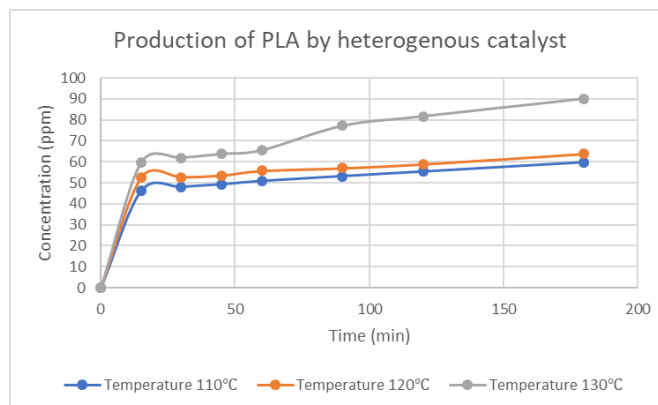


Figure 6: Graph of concentration (ppm) against time (min) of PLA by heterogenous catalyst at different temperature.

Table 2: The optimum concentration of PLA by heterogenous catalyst at different temperature

Temperature (°C)	Time (min)	Optimum Concentration (ppm)
110	180	59.7
120	180	63.8
130	180	90.1

FTIR spectroscopy gives the qualitative information where the $\text{Sn}(\text{Oct})_2$ molecules are bonded to the lactide molecules. Figure 7 and 8 show the comparison of FTIR spectrums of PLA that presence in the solutions that have been polymerized by using homogenous and heterogenous catalysts after 3 hours for desired temperatures. The FTIR analysis was recorded using a FTIR spectrometer in a range between 3500 cm^{-1} to 500 cm^{-1} . Both figures give the approximately same trend of peaks due to similar molecular structure of PLA that presence in the solutions. The PLA spectrum shows the bands at 1236.88 cm^{-1} to 1047.82 cm^{-1} from C-O-C stretching vibration. The bends 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, the more OH containing molecules. Therefore, the PLA in all temperature give the highest stretch peak. This result also supported by Iriswguo that O-H stretch in a concentrated hydrogen bonded solution of an alcohol occurs at $3550\text{--}3200\text{ cm}^{-1}$ [6]. Although the C-H and C-C bond which are related to PLA compound are not showed in the spectrum, it definitely presence in the molecule of PLA. Based on the theory from Dr. A. Bacher in Infrared Spectroscopy website, 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 [2]. It is observed that a bend shift related to the C=O stretch at $1636.11\text{--}1635.31\text{ cm}^{-1}$ in the polymer. In heterogenous catalyst at temperature 130°C , the bend shift is a bit different with others due to repeated C=O and C-O-C bond

that gives higher number (n) of polymer. These bands that show shifts of monomer to polymer show difference in peak intensity which suggests the arrangement of molecules in the polymer chain [9].

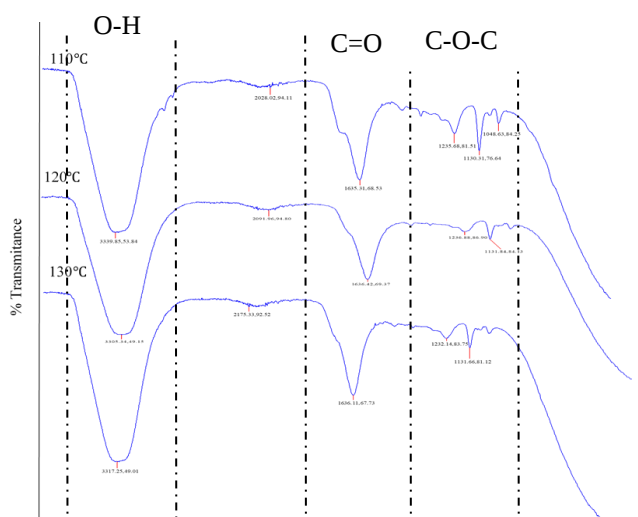


Figure 7: FTIR spectrum of PLA by homogenous catalyst

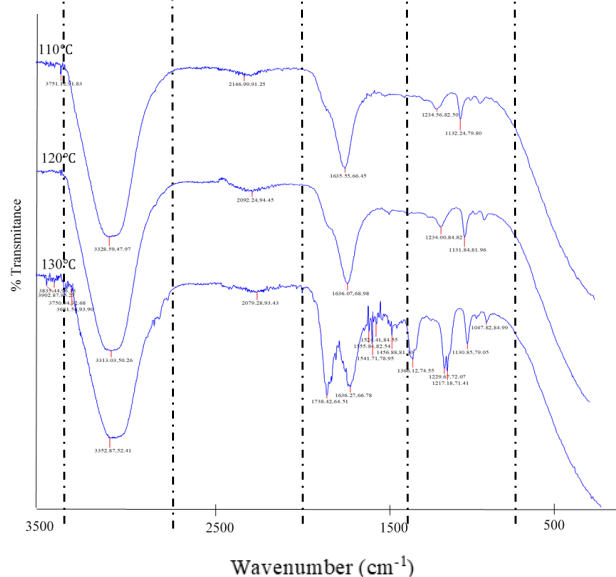
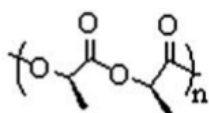


Figure 8: FTIR spectrum of PLA by heterogenous catalyst



PLA Compound

III. CONCLUSION

The experimental was set up to investigate the production of PLA using ring opening polymerization method with different temperatures of difference catalyst phases. From the results, it can be concluded that the PLA were exists in the solutions by both catalysts as the FTIR and UV-vis spectra shows a positive result of characterization. From the FTIR, it shows that the PLA compound is formed from the stretching and bending of O-H, C=O, C-O-C, C-C and C-H groups. By UV-vis spectrophotometer, the results show that heterogenous catalyst produces higher concentration than homogenous catalyst even it takes long time to achieve it. In both catalysts, the concentration of PLA 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. Therefore, production by heterogenous catalyst is more preferable due to high concentration of the PLA other than ease in separation process of catalyst from the product.

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