Comparison of Polylactic Acid Polycondensation Using LASC $Fe(DS)_3$ Catalyst and $FeCl_3$ Metal Catalyst

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***Abstract*— Polylactic acid (PLA), also known as lactic acid, has become a promising candidate as a renewable resource for plastic production. The use of PLA as a plastic material can significantly reduce the problems caused by waste. In the production of Polylactic acid (PLA), there are byproducts such as water, while metal Lewis such as Fe (III) used in PLA production can rapidly decompose and be deactivated by water. This research aims to synthesize a water-resistant Lewis catalyst by Fe (III) Lewis metals with a surfactant called Sodium dodecyl sulfate (SDS), which will bond together to form Fe (III) dodecyl sulfate [$Fe(DS)_3$]. This catalyst will then be compared to $FeCl_3$ metal catalysts in terms of performance in PLA synthesize using the polycondensation method. The water-resistant Lewis catalyst is characterized using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). As for the PLA synthesized with $Fe(DS)_3$ and $FeCl_3$ catalysts under the same operating conditions, it is analyzed using viscometry to determine its molecular weight, Fourier Transform Infrared (FTIR), and X-Ray Diffraction (XRD). The results of the analysis of the LASC catalyst showed that FTIR spectra of $Fe(DS)_3$ and SDS show similarity in stretching and bending vibration bands.and the crystallinity indices of 36.81% and 15.82% are obtained for SDS and $Fe(DS)_3$, respectively. Results of the PLA polycondensation showed that the optimum temperature is 180 °C, as it leads to an increase in molecular weight, while at 200 °C, degradation occurs, resulting in a decrease in molecular weight. The FTIR spectra of PLA obtained in this study also showed that lactic acid polymerization was achieved which also supported by XRD spectra that showed gentle diffraction from 10° to 26° which similar with literature. The yields of PLA molecular weight synthesized by $Fe(DS)_3$ gain with higher molecular weight compared to $FeCl_3$ catalyst which showed that $Fe(DS)_3$ catalyst performed better than $FeCl_3$.**

***Keywords*— Polycondensation, Polylactic Acid, Sodium Dodesilsulfate, Water-Resistant Lewis Catalyst**

I. INTRODUCTION

Plastic plays a crucial role in modern society due to its lightweight, durability, relatively low cost, and longevity. However, most petroleum-based plastics pose environmental problems because their production generates pollutants and greenhouse gases, contributing to environmental pollution and global warming. Additionally, their high durability makes them resistant to biological degradation, leading to environmental pollution. Plastic waste has a highly detrimental impact on the environment, often considered more harmful than carbon emissions. This is why biodegradable plastics are necessary, as they can be largely converted into environmentally benign waste within a few months. Bioplastics, which function similarly to synthetic plastics but are eco-friendly, are seen as a promising solution to this issue. Bioplastics are either biodegradable or produced from biological or renewable materials, such as starch, cellulose, vegetable oil, and plant fats [1]. Polylactic acid (PLA) holds significant potential as a renewable natural resource for plastic production. Therefore, using PLA as a plastic material can help reduce the problems associated with plastic waste. However, due to its relatively high cost, the application of PLA as a substitute for conventional plastics has not been fully optimized. Hence, simplification and optimization are required in PLA production to reduce production costs.

PLA can be produced using various methods, including polycondensation of lactic acid in solution under atmospheric and reduced pressure conditions, Ring Opening Polymerization (ROP), melt polycondensation, and direct polycondensation of lactic acid [2] . The method used in this research is direct polycondensation of lactic acid, which involves dehydration, polycondensation, and recrystallization [3,4]. This research begins with the creation of a water-resistant Lewis catalyst or so called Lewis Acid Surfactant Combined Catalyst (LASC) [5,6]. LASC is chosen because it is water-compatible, meaning heavy metals or traditional Lewis acids quickly react with water, leading to decomposition and deactivation, which would increase PLA production costs [7,8]. The usage of LASC catalyst in PLA polycondesation was reported by Zuhdan et al. but they were not reported about the direct comparison of catalytic performance between LASC and traditional Lewis Acid Catalyst. In this study, iron (Fe) metal is reacted with Sodium Dodecyl Sulfate (SDS) and compared with the iron (Fe) chloride ($FeCl_3$) catalyst [9,10]. Subsequently, polycondensation is performed by using three-necked flask with the addition of LASC and metal catalysts. The resulting PLA will be analyzed using FTIR, XRD, TGA, GPC, and NMR. Meanwhile, the LASC catalyst will be analyzed using XRD, TGA, FTIR, and NMR [11,12]. The Aim of this study was to compare the catalytic performance of $Fe(DS)_3$ (as Lewis Acid Surfactant Combined Catalyst) to$FeCl_3$ Lewis Acid based catalyst on PLA polymerization via polycondensation.

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II. METHOD

a) Materials and Equipment

The materials used in this study include FeCl3, Sodium Dodecyl Sulfate, L-Lactic Acid were purchased from Sigma-Aldrich while Distilled Water and Methanol were purchased from CIMS.

b). Method

a) Catalys Synthesis

In this research, 3.4 grams of SDS (sodium dodecyl sulfate) (11.8 mmol) were mixed with 100 mL of pre-heated distilled water. The dissolved SDS was then combined with iron chloride (FeCl3) metal dissolved in 20 mL of pre-heated distilled water with a mass of 0.6384 grams (5.9 mmol). The metal was then mixed with SDS in an Erlenmeyer flask and stirred for 30 minutes. The solid catalyst was filtered and washed with distilled water before then dried for 24 hours inside the oven. Subsequently, the catalyst was analyzed using FTIR, XRD, and TGA.

b) Polycondensation

The polycondensation process was carried out by adding the catalyst. The reaction began with a dehydration process, followed by polycondensation. The reaction involved adding 20 mL of L-lactic acid to a three-necked flask along with 0.15% or 0.3% by weight of LASC (Lewis Acid Surfactant Combined Catalyst) or metal. The flask was connected to a fractionation column and a condenser to separate water vapor. The dehydration stage started by raising the temperature to 130 °C under a vacuum of 20 kPa for 1 hour, with the three-necked flask sealed tightly. This process facilitated water removal, and the resulting concentration of L-lactic acid was approximately 96%. The next stage was polycondensation, which was carried out by increasing the temperature according to the desired variable under a vacuum of 20 kPa while stirring with a magnetic stirrer at 250 rpm for 6 hours. The resulting PLA (Polylactic Acid) was then used to calculate the molecular weight using the Viscosity Method.

III. RESULTS AND DISCUSSION

A. LASC Characterization

a. FTIR Results

Fig. 1 displays the FTIR spectra of the SDS precursor and $Fe(DS)_3$. The FTIR spectra of $Fe(DS)_3$ and SDS show similar bands in stretching and bending vibration modes which shows in the Table 1. The spectrum of $Fe(DS)_3$ shows shifting bands in the symmetric and asymmetric modes compared to the SDS spectrum, which indicate the interaction between the dodecyl sulfate anion and the Fe(III) metal cation as reported[16]. Furthermore, the OSO_3 site structure has a highly asymmetric local geometry that approaches C_{2v} symmetry in the bidentate bridging complex. The spectra of $Fe(DS)_3$ and SDS generated in this study also show similarities to the spectra of cerium dodecyl sulfate and SDS from the literature [5,13].

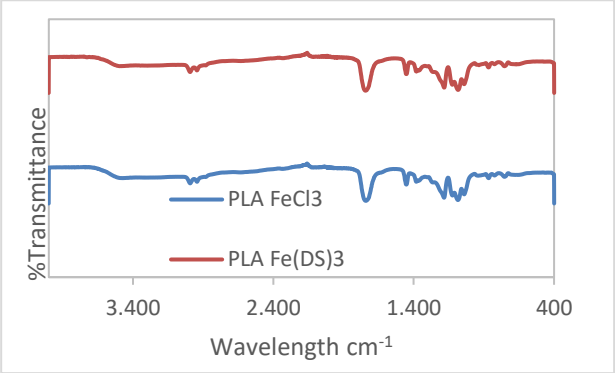

Fig. 1: FTIR result of SDS vs $Fe(DS)_3$

Table I.
FTIR bands of $Fe(DS)_3$ and SDS in cm^{-1}

Functional Group Bands	SDS	$Fe(DS)_3$
Symmetric;Asymmetric stretching of SOC	822.9;1015.6	826.6;982.4
Symmetric;Asymmetric stretching of OSO_3	1079.5;1217	1067.3;1205.7

b. XRD Results

Materials with a crystalline structure can be diffracted using X-rays, which can be used to determine their structure. The crystallinity index (CrI) is the ratio of the area under the crystalline peaks to the total area under all peaks, including both crystalline and amorphous regions. Amorphous compounds, such as lignin and hemicellulose, are removed during pretreatment, leaving behind the crystalline fraction and increasing the crystallinity index [14]. The following figure was the XRD analysis results for $Fe(DS)_3$.

The areas of the crystalline peaks and the areas of all peaks were obtained using Origin software, resulting in crystallinity percentages of 36.81% and 15.82% for SDS and $Fe(DS)_3$, respectively. The XRD pattern (**Fig. 2)** of SDS shows strong reflections at lower diffraction angles of $2\theta = 2.39°$, 4.57°, and 6.74°. There is a slight difference with $Fe(DS)_3$, where the interplanar spacing (dhkl) obtained from the lower diffraction angles indicates periodicities of 3.69 nm and 4.4 nm for SDS and $Fe(DS)_3$, respectively. The results of XRD SDS and $Fe(DS)_3$ in this study also similar with literature [13,15]. According to XRD result it showed that $Fe(DS)_3$ catalyst phase was amorf compared to its pre-cursor(SDS), which could improve catalytic activity since the amorf phase increase the catalytic surface and catalytic site activity [16].

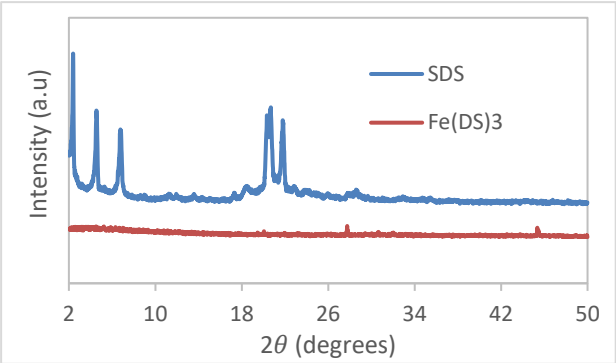

Fig. 2: XRD result of SDS vs $Fe(DS)_3$

c. TGA Results

Thermogravimetric analysis (TGA) was employed to study the thermal behavior of $Fe(DS)_3$ and SDS. **Fig. 3** shows the TGA results for SDS and $Fe(DS)_3$.

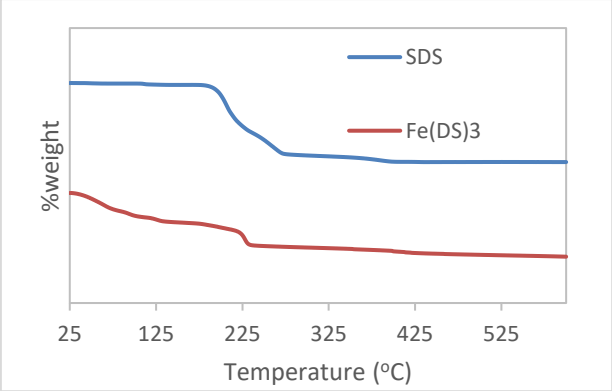

Fig. 3: TGA result of SDS vs $Fe(DS)_3$

The decomposition of SDS in the TGA test, with weight reduction under 200 °C, indicates the elimination of water. The $Fe(DS)_3$ samples exhibit a similar curve although mass reduction was taken place earlier. It seems that water binding force in $Fe(DS)_3$ is weaker than SDS. As more dodecyl sulfate binds with Lewis acid, the water concentration increases, resulting in a higher percentage of weight loss. This is supported by the data showing that the residue weight percentage of SDS is 34.35%, and for $Fe(DS)_3$, it is 73.25%. The loss of alkyl chain groups is taken place above 200 °C and it shows carbon residue combustion (weight loss found to be 68.42%). The total mass loss from 120 °C to 600 °C is 6.26% for SDS and 31.13% for $Fe(DS)_3$. The remaining dodecyl sulfate molecules can form templates with strong bonds with metals [17].

B. PLA Characterization

a. FTIR Results

The FTIR analysis aims to determine the presence of functional groups in the PLA compounds produced in this study. Based on **Fig. 4** and **Table 2.** the presence of alkyl and carbonyl groups indicates that this research has produced the expected PLA compounds this result also parallel with literature [18].

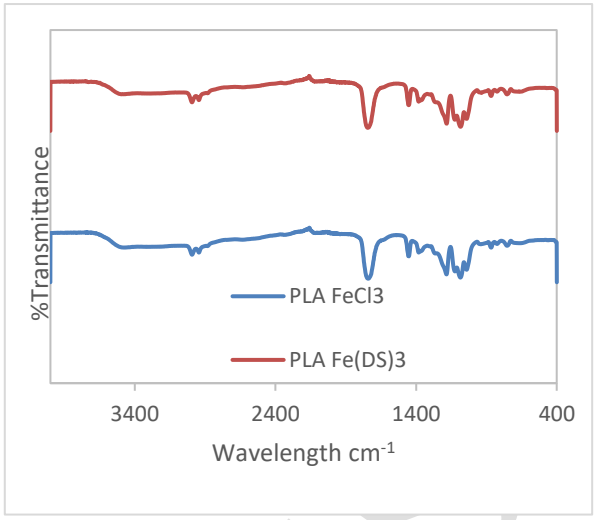

Fig. 4: FTIR result of Synthesized PLA

Table II.
FTIR bands of Synthesized PLA in cm^{-1}

Functional Group Bands	PLA $FeCl_3$	PLA $Fe(DS)_3$
O-H group (hydroxyl)	3469	3503
C-H group (alkyl)	2993	2993
C=O group (carbonyl)	1740	1743

b. XRD Results

Fig. 5 shows the XRD patterns for the synthesized PLA from the research using two different catalysts.

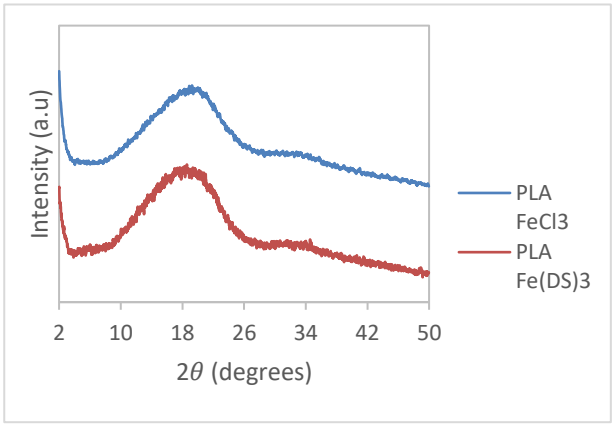

Fig. 5: XRD result of Synthesized PLA

The broad diffraction from 10° to 50° caused by scattering of the PLA compound matrix. Sharp diffraction is observed in the range of 10° to 26°, corresponding to a layer spacing of 5.29 nm based on Bragg's law, which is associated with the graphite plane (002) [11]. In the XRD patterns for PLA+$Fe(DS)_3$ and PLA+$FeCl_3$, no sharp or broad peaks were found. The result in this research also has similarities with literature [19].

c. PLA Molecular Weight

The rise of PLA molecular weight taken place at polymerization temperature of 160°C to 180°C, and then decreased after reaching 200°C. The highest molecular weight of PLA was obtained in PLA+Fe(DS)$_3$ with a catalyst loading of 0.15% at a temperature of 180°C, which is 10,395.51 g/mol. The decrease in the molecular weight of the polymerized PLA at 200°C is because high temperatures result in a faster polymerization rate but it also increase the rate of lactide formation which lead to lower yield of PLA molecular weight since some of dimer/trimer were converted into lactide as result of this side reaction during polycondensation.

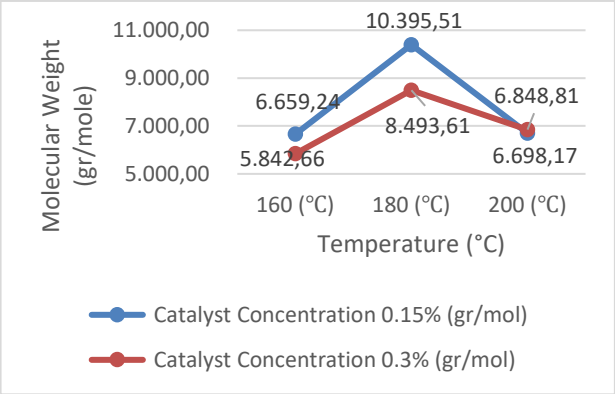

Fig. 6: MW result of PLA Synthesized by Fe(DS)$_3$

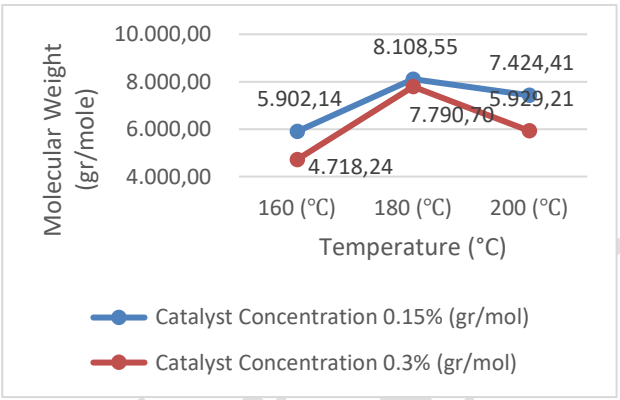

Fig. 7: MW result of PLA Synthesized by FeCl$_3$

After the chain extension or propagation reaction reaches its maximum, depolymerization also occurs, ultimately reducing the molecular weight of PLA [17]. This is in line with the statement that unavoidable degradation accompanies the polymerization process due to prolonged exposure to high temperatures, which includes the presence of a catalyst [20].

Fig. 6 and **7** show the influence of catalyst loading and temperature on the PLA molecular weight. At catalyst concentration of 0.15%, the molecular weight is higher than at 0.3%. This indicates that a catalyst loading of 0.15% is the optimum loading for the molecular weight of the polymerized PLA [21]. The physical appearance of the PLA produced in the study, using a catalyst loading of 0.15% with the highest molecular weight, exhibits characteristics similar to PLLA, which is hard but brittle. From **Fig. 6** and **7** also showed that Fe(DS)$_3$ catalyst has better activity towards polymerization of lactic acid rather than FeCl$_3$ which shown by significant decrease at higher polymerization temperature.

IV. CONCLUSION

The synthesized LASC with Fe(III) metal, which is a water-resistant Lewis catalyst, yields higher molecular weight PLA compared to FeCl3. The catalyst concentration and temperature shows impact on the PLA molecular weight. At a temperature of 180°C with a catalyst loading of 0.15% w/w, the optimum conditions were observed, characterized by higher PLA molecular weight. However, the molecular weight decreased at 200°C and a catalyst concentration of 0.3% w/w.

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