Synthesis of Poly Lactic Acid from Lactic Acid Using Direct Polycondensation Method Using $Al(DS)_3$ and $AlCl_3$ Catalysts

Ahmad Musonnifin Aziz, Hikmatun Ni'mah, and Tri Widjaja
Department of Chemical Engineering, Faculty of Technology Industry, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia
***triw@chem-eng.its.ac.id**

OPEN ACCESS

***Citation*: Ahmad Musonnifin Aziz, Hikmatun Ni'mah, and Tri Widjaja. 2024. Synthesis of Poly Lactic Acid from Lactic Acid Using Direct Polycondensation Method Using $Al(DS)_3$ and $AlCl_3$ Catalysts. *Journal of Research and Technology* Vol. 10 No. 1 Juni 2024: Page 35–43.

Abstract
Poly Lactic Acid (PLA) is a type of polymer that is widely researched because it can meet the requirements for biodegradable polymers and can be used in several of applications. Making PLA using the direct polycondensation method is carried out in 3 process stages, namely dehydration, polycondensation and recrystallization. Dehydration was carried out at 130℃ for 1 hour. Polycondensation was carried out at varying temperatures of 160℃, 180℃ and 200℃ with a concentration of 0.15% for 6 hours. In the meantime, 50 ml of methanol was added, and vacuum conditions were used to carry out the recrystallization process. After that, the viscosity method was used to determine PLA's molecular weight. The highest molecular weight and other properties of PLA, such as its functional groups and thermal behavior, are the aim of this study. The findings of the study indicate that PLA has its maximum molecular weight at 180°C, where it is 15576 gr/mol for PLA+$Al(DS)_3$ and 10771 gr/mol for PLA+$AlCl_3$. The PLA+$Al(DS)_3$ and PLA+$AlCl_3$ spectra display the same bands in the stretching and bending vibration modes, according to the FTIR test. Meanwhile, in the TGA analysis, the highest decomposition was shown by PLA+$Al(DS)_3$ at a temperature of 365℃.

***Keywords*:** *Poly Lactic Acid, Direct Polycondensation, $Al(DS)_3$, $AlCl_3$, Viscosity Method*.

Abstrak
Poli Asam Laktat (PLA) merupakan salah satu jenis polimer yang banyak diteliti karena dapat memenuhi persyaratan polimer biodegradable dan dapat digunakan dalam sejumlah aplikasi. Pembuatan PLA melalui metode polikondensasi langsung dilakukan dengan 3 tahapan proses yaitu dehidrasi, polikondensasi, dan rekristalisasi. Dehidrasi dilakukan pada suhu 130℃ selama 1 jam. Polikondensasi dilakukan pada variasi suhu 160℃, 180℃ dan 200℃ dengan konsentrasi 0,15% selama 6 jam. Sedangkan rekristalisasi dilakukan dengan menambahkan 50 ml metanol dan pada kondisi vakum. Kemudian dilakukan pengukuran berat molekul PLA dengan

metode viskositas. Penelitian ini bertujuan untuk mengetahui berat molekul tertinggi dan mengetahui karakteristik PLA yang meliputi gugus fungsi, dan perilaku termal. Hasil penelitian menunjukkan bahwa berat molekul PLA tertinggi berada pada suhu 180°C dengan berat molekul 15576 gr/mol untuk PLA+Al(DS)$_3$ dan 10771 gr/mol untuk PLA+AlCl$_3$. Uji FTIR menunjukkan bahwa spektrum PLA+Al(DS)$_3$ dan PLA+AlCl$_3$ menunjukkan pita yang sama pada mode vibrasi regangan dan tekukan. Sedangkan pada analisis TGA, dekomposisi tertinggi ditunjukkan oleh PLA+Al(DS)$_3$ pada suhu 365°C.

Keywords: *Poli Asam Laktat, Polikondensasi Langsung, Al(DS)$_3$, AlCl$_3$, Metode Viskositas*.

1. Introduction

People all across the world are now aware of the environmental issues brought on by human activity. One of them is the yearly rise in the production of biodegradable plastics. Right now, one of the biopolymers being studied is polylactic acid (PLA). This is because it is a highly biodegradable polymer, making it an environmentally friendly choice. PLA is made from renewable and environmentally friendly sources, specifically from a variety of plants with a high starch content, such as corn, cassava, sweet potatoes, bananas, and so forth, as opposed to synthetic polymers that are made from petroleum materials (Maryanty et al., 2021).

Poly Lactic Acid (PLA) has very promising potential as a renewable natural material (renewable resources) for the manufacture of plastics (Rahmayetty et al., 2018). Thus, the use of PLA as a material for making plastic is useful in reducing problems caused by waste (Kricheldorfa et al., 2019). At present, PLA has been recognized as the most potential bioplastic for application, although the amount is currently not that wide and not much is produced. However, because the price is relatively high, the application of PLA as a substitute for conventional plastics is still not optimal. Thus, simplification and optimization is needed in the manufacture of PLA to reduce the cost of making PLA.

The production of PLA can be carried out by several methods, namely polycondensation of lactic acid in solution at atmospheric and reduced pressure conditions, Ring Opening Polymerization (ROP), melt polycondensation, and direct polycondensation of lactic acid (Maharana et al., 2009). Rahmayetti et al. (2018) has carried out lactic acid polymerization using the ring opening polymerization method, but it is less efficient because it takes quite a long time and is not cheap, so an efficient method is needed, namely direct polycondensation. However, the polycondensation method still uses non-metallic catalysts that are impervious to air, so a water-resistant catalyst is needed to increase the molecular weight of PLA. Water-compatible catalysts must be used because some metal catalysts, like TiN, Sn(Oct)$_2$, and zinc salt, also have an impact due to their quick sensitivity to water, which causes decomposition and deactivation and raises the cost of producing PLA (Ye et al., 2008). Lewis Acid Surfactant Combined Catalyst (LASC), such as Fe(DS)$_3$, was created by Kitanosono et al. (2017) and is an example of an air-compatible catalyst. At the moment, LASC is being used extensively as a catalyst for water-related reactions and reactions that can happen faster by breaking water (Pradhan et al., 2013). Because LASC can be used as a heterogeneous catalyst for multiple reaction cycles and takes longer to deactivate, using it also has the benefit of being more cost-effective (Firouzabad et al., 2007).

The direct lactic acid polycondensation method, which involves polycondensation, recrystallization, and dehydration, was employed in this study (Chafran et al., 2019). The Lewis Acid Surfactant Combined Catalyst (LASC) catalyst was first made for this study (Yazdabadi et al., 2021). Because LASC is a water-compatible catalyst, the heavy metal or conventional Lewis acid will react with water quickly to decompose and deactivate, increasing the cost of PLA production (Idumah et al., 2021). In this study, Al metal was reacted with Sodium Dedosyl Sulphate (SDS), namely $Al(DS)_3$ catalyst, which will be compared with $AlCl_3$ metal catalyst performance in PLA production (Heredia-Guerrero et al., 2019). $AlCl_3$ catalyst is used because it is one of the good metal catalysts in the production of PLA, this is because the $AlCl_3$ catalyst does not include heavy metal catalysts and is environmentally friendly. The next process is polycondensation by adding 20 mL of L-lactic acid to a three neck flask with and without LASC catalyst or metal catalyst (Widjaja et al., 2023). Then recrystallization was carried out to stabilize PLA (Achmad et al., 2009). PLA results will be measured by measuring molecular weight using the Viscosity method (Hortós et al., 2019), Fourier Transform Infra-Red (FTIR), and Thermogravimetric Analysis (TGA) (Shahdan et al., 2021). This research aims to determine the comparison of PLA with $Al(DS)_3$ and $AlCl_3$ catalysts at temperatures of 160℃, 180℃, and 200℃ regarding molecular weight, functional groups, and the resulting decomposition.

2. Method

2.1 Tools And Materials

This research was conducted at the Biochemstry Laboratory of the Chemical Engineering Department, Institut Teknologi Sepuluh Nopember. This study used metal $AlCl_3.6H_2O$, Sodium Dodecyl Sulfate (SDS), Aquadest, l-Lactic Acid 88-92%, Chloroform, Methanol, and Ethyl Acetate. All ingredients were purchased from Merc.

2.2 Preparation of $Al(DS)_3$ LASC Catalyst

In this experiment, 100 mL of heated distilled water (at 60°C) was combined with SDS ± 3.4 grams (11.8 mmol). Metal $AlCl_3.6H_2O$, which had been dissolved in 20 milliliters of heated distilled water at 60 degrees Celsius and had a mass of 0.95 grams (3.94 mmol), was added to the dissolved SDS. After that, the metal and SDS are combined in an Erlenmeyer and stirred for half an hour. After filtering and washing with distilled water, the catalyst solid is dried in the oven for a full day (Pradhan et al., 2013).

2.3 Direct Polycondensation

The three steps of the direct polycondensation process are recrystallization, polycondensation, and dehydration. To initiate the reaction, 20 milliliters of l-lactic acid and 0.15% by weight of LASC $Al(DS)_3$ or $AlCl_3$ metal catalyst are added to a three-neck flask. To separate the water vapor, the flask is attached to the condenser and fractionation column. The temperature was raised to 130°C under a 20 kPa vacuum for an hour at 200 rpm, and the three-neck flask was securely closed to begin the dehydration process. Water removal is made easier by this process, and l-lactic acid with a concentration of ± 96% is produced.

Table 1. Research variables

Catalyst	Temperature (℃)	Time (hour)
$Al(DS)_3$	160, 180, & 200	6
$AlCl_3$		

Source: Personal Research Data (2023)

The following step, called polycondensation, involves raising the temperature to the required level while stirring with a magnetic stirrer at 250 rpm for six hours under a 20 kPa vacuum each at temperature 160℃, 180℃, and 200℃ . Afterwards, 50 methanol was added to complete the recrystallization process, which was then vacuum-expelled. The resulting PLA was then weighed and the resulting molecular weight was calculated using the viscosity method (Achmad et al., 2009).

2.4 Characterization

2.4.1 Determination of PLA Molecular Weight

Determination of the molecular weight of PLA can be carried out using the Viscosity Method by measuring the flow time of ethyl acetate (t_0) and the flow time of PLA in ethyl acetate (t) in concentrations of 0.2%, 0.3% and 0.4%, using a viscometer Oswald.
Viscosity (η) is calculated through the equation:

$$\eta_{relatif} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (1)$$

$$\eta_{spesifik} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel^{-1}} \quad (2)$$

$$\eta_{reduksi} = \frac{\eta_{sp}}{C} = \frac{\eta_{rel^{-1}}}{C} \quad (3)$$

$$\eta = \frac{\eta_{sp}}{\eta_0} = \frac{t}{t_0}; \quad C = 0 \quad (4)$$

Note:
C = PLA concentration in ethyl acetate

The obtained intrinsic viscosity is used to calculate the molecular mass of PLA according to the Mark-Houwink-Sakurada equation:

$$\eta = k\, M^{\alpha} \quad (5)$$

Note:
$K = 1{,}58 \times 10^{-4}$
$\alpha = 0{,}78$

Furthermore, the PLA with the highest molecular weight was analyzed by Fourier Transform Infra-Red (FTIR) and Thermogravimetric Analysis (TGA).

2.4.2 Fourier Transform Infra-Red (FTIR) Analysis

Fourier Transform Infra-Red (FTIR) analysis is one of the analyzes used to see the movement of a molecule by describing the structure of a chemical compound. In this study, the FTIR spectrum was analyzed with Nicolet iS10 (Thermo Electron Co., USA). The spectrum was recorded in the frequency range 4000 and 400 cm^{-1}.

2.4.3 Thermogravimetric Analysis (TGA)

Heat is used in thermogravimetric analysis to force material reactions and physical changes. Mass changes in materials related to transitions and thermal degradation can be quantitatively measured with TGA. The TGA logs the mass change resulting from the sample's oxidation, decomposition, and dehydration as a function of temperature and time. The distinct series of physicochemical reactions that take place over a particular range of temperatures and heating rates results in the characteristics of thermogravimetric curves being provided for particular materials and chemical compounds. Characterization by thermal analysis (thermogravimetric analysis, or TGA). Thermogravimetric (TG) SDT Q600 (TA Instrument, USA) was used in this investigation to obtain the TGA curve using air as the medium. The analyses were conducted at temperatures ranging from approximately 26 °C to 600 °C, with a temperature step of 10 °C min−1 (Shahdan et al., 2021).

3. Result and Discussion

3.1 Determination of PLA Molecular Weight

Determination of the molecular weight of PLA can be measured using the viscosity method by comparing the flow time of the solvent to the polymer solution at various concentrations. The viscometer has the advantage that achieve various concentrations, the polymer solution can be diluted in the viscometer by adding a measured amount of solvent. From the obtained intrinsic viscosity, the molecular weight can be calculated and the molecular weight obtained from the research results can be seen in Molecular weight is very important in determining the characteristics of PLA. By knowing the molecular weight, the properties of PLA can be estimated, such as the ability of PLA to be degraded, which is influenced by several factors, including the higher the molecular weight of PLA, the longer it takes to degrade PLA molecules, and PLA with high molecular weight tends to have higher crystallinity (semi-crystalline). The resulting PLA is hard but brittle. This is the characteristic of Poly-L-(Lactic Acid) (PLLA).

$Al(DS)_3$ is white in color with a pleasant odor because it is formed from $AlCl_3$ and sodium dodecyl sulfate. Whereas Aluminum chloride consists of aluminum and chloride also known as aluminum trichloride or aluminum (III) chloride which has the chemical formula $AlCl_3$. the texture is white to gray powder with a pungent odor. Aluminum chloride is a strong Lewis acid and is commonly used in polymer polymerization processes, namely ring opening polymerization. Sometimes it appears yellowish due to the presence of contaminants. $Al(DS)_3$ and $AlCl_3$ both function to increase the molecular weight of PLA up to, however, it can experience decay if it reaches a temperature of 200°C because it undergoes degradation.

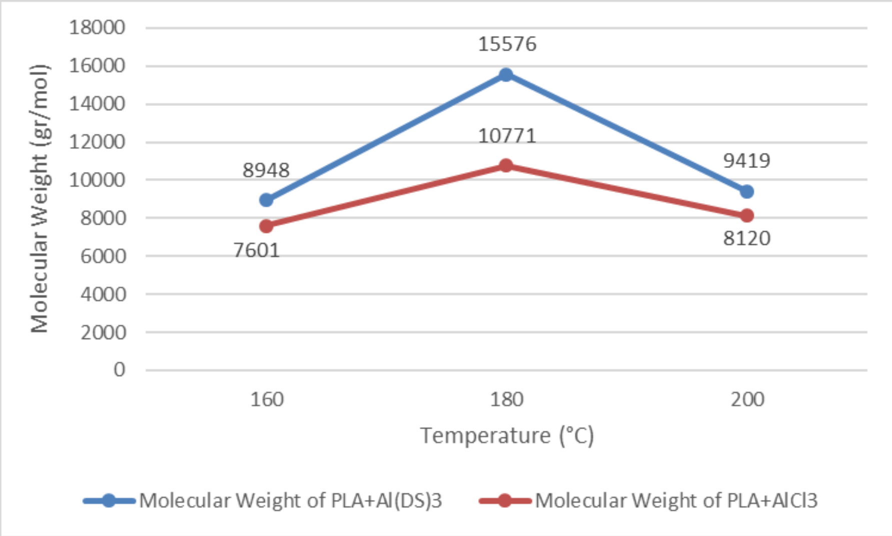

Figure 1. Graph of PLA+Al(DS)$_3$ and PLA+AlCl$_3$ Molecular Weight

The molecular weight of PLA was calculated using the Viscosity Method by measuring the flow time of ethyl acetate (t_0) and the flow time of PLA in ethyl acetate (t) at concentrations of 0.2%, 0.3% and 0.4%, using an Oswald viscometer and Each was done 3 times. The data entered is the average viscosity value and is entered into the value of equation 5 to obtain the molecular weight value. The highest PLA molecular weight was obtained in the l-lactic acid polymerization treatment at a temperature of 180°C, namely PLA+Al(DS)$_3$ of 15576 g/mol and PLA+AlCl$_3$ of 10771 gr/mol. There was a decrease in molecular weight PLA results polymerization at 200°C (Figure 1), because at high temperatures the polymerization rate is also large, after the chain extension reaction or propagation reaches a maximum, at that time depolymerization also occurs which ultimately reduces the molecular weight of PLA. This is following with the statement that the inevitable degradation that will accompany the polymerization process is caused by the additional residence time at high temperatures in which there is a catalyst (Maharana et al., 2009).

3.2 FTIR Analysis Results

The FTIR spectra of PLA+Al(DS)$_3$ and PLA+AlCl$_3$ precursors are displayed in Figure 2. The strain and bending vibration modes of PLA+Al(DS)$_3$ and PLA+AlCl$_3$'s FTIR spectra display identical bands. At 753 cm^{-1} (symmetric S–OC stretching), 1184 cm^{-1} (asymmetric S–OC stretch), 1453 cm^{-1} (slumped symmetrical OSO$_3$ stretch), and 1740 cm^{-1} (degenerate symmetrical OSO$_3$ stretching), the PLA+Al(DS)$_3$ stretching and bending vibrational modes in the anionic headgroup are observed. When compared to the PLA+AlCl$_3$ spectrum, the PLA+Al(DS)$_3$ spectrum exhibits shifts and separations in both symmetrical and asymmetrical modes. These differences can be attributed to the interaction between l-lactic lactic anions and the metal cations AlCl$_3$ (Maryanty et al., 2021). Next, the local geometry of the OSO$_3$ site structure is highly asymmetric and approaches the C_2 symmetry of the bidentate bridge complex. The resulting PLA+Al(DS)$_3$ and PLA+AlCl$_3$ spectra are generally comparable to those of standard PLA (Chafran et al., 2019).

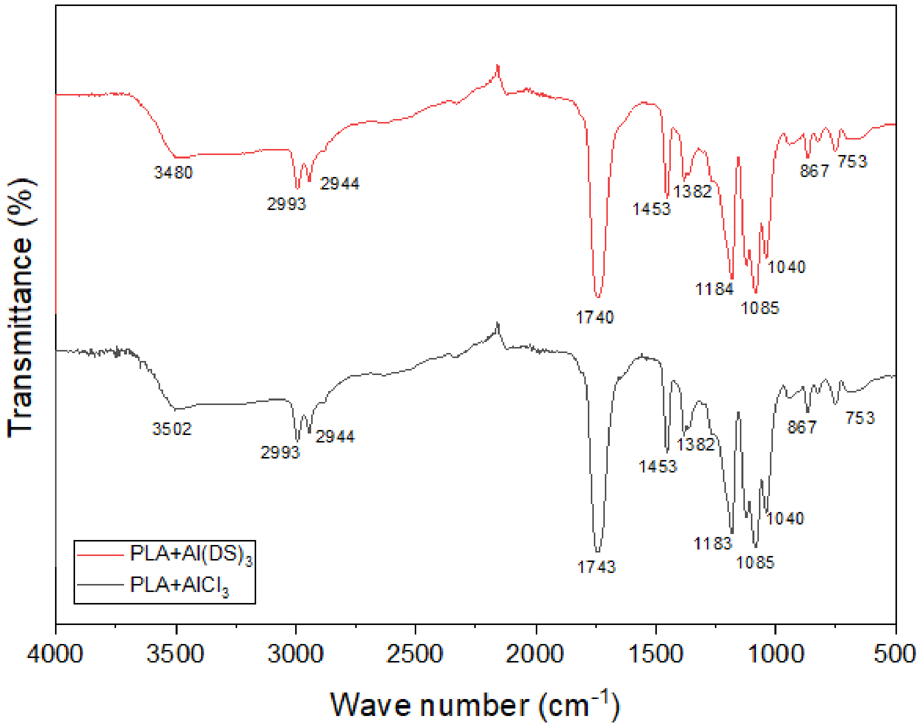

Figure 2. Graph of Analysis of PLA+$Al(DS)_3$ and PLA+$AlCl_3$ at a Temperature of 180℃

3.3 TGA Analysis

TGA analysis results on PLA + $Al(DS)_3$ and PLA + $AlCl_3$ showed that the decomposition temperature occurred at 365℃ and 350℃ respectively.

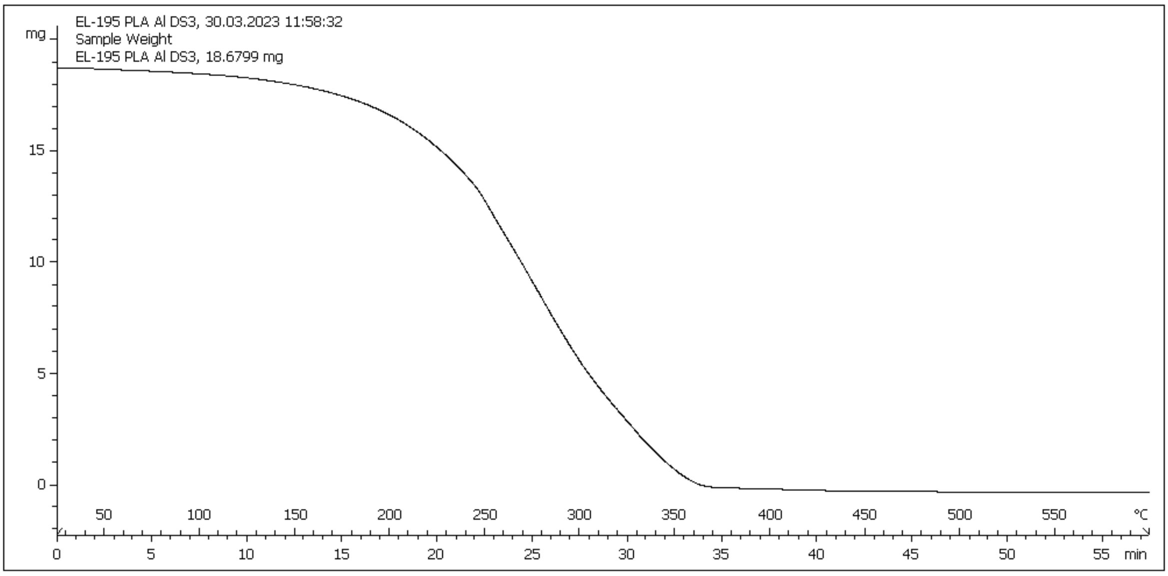

Figure 3. Graph of TGA Analysis on PLA + $Al(DS)_3$

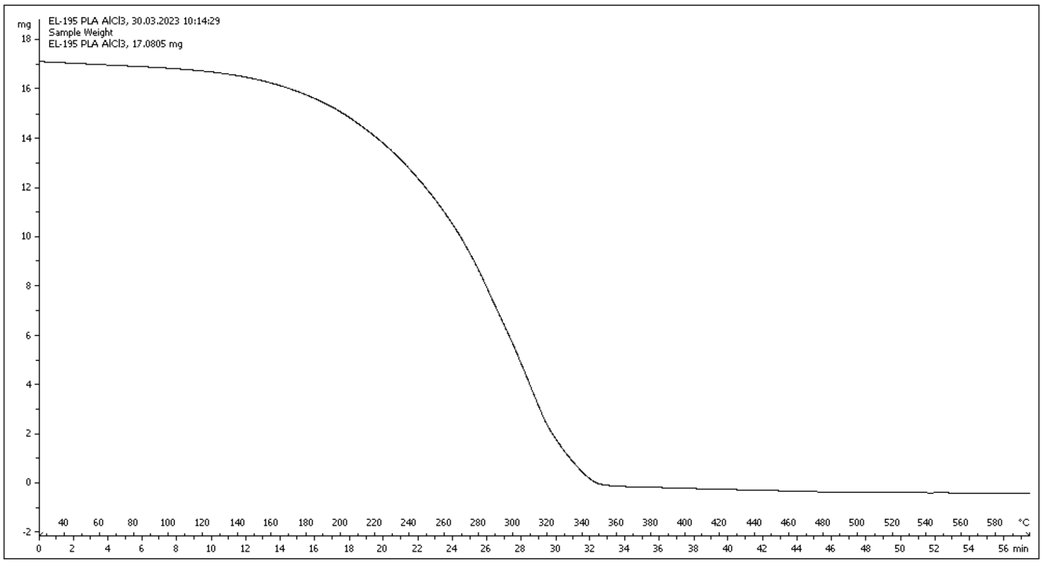

Figure 4. Graph of TGA Analysis on PLA + $AlCl_3$

In detail, for PLA + $Al(DS)_3$, there was a decrease in mass due to a reduction in water content at temperatures below 270℃ and in the temperature range of 270℃ - 365℃, there was decomposition of the long PLA chains. Whereas in PLA + $AlCl_3$ there is a decrease in mass caused by a reduction in water content at temperatures below 220℃ and in the temperature range 220℃ - 240℃ decomposition of long PLA chains occurs. When looking at the decomposition temperature, PLA + $Al(DS)_3$ is the best PLA using the direct polycondensation method because in the direct polycondensation method the higher the operating temperature, the resulting PLA has a higher level of viscosity or viscosity, this is also an indication that PLA produced has a larger molecular weight (Shahdan et al., 2021).

4. Conclusion

PLA experienced an increase in weight at 180℃ respectively on PLA+$Al(DS)_3$ of 15576 gr/mol and PLA+$AlCl_3$ of 10771 gr/mol. Whereas at 200℃ PLA decreased in molecular weight, this was because at that temperature PLA experienced degradation. FTIR analysis shows that PLA+$Al(DS)_3$ and PLA+$AlCl_3$ have the same spectrum. Meanwhile, in the TGA analysis, PLA+$Al(DS)_3$ experienced the greatest degradation because it could survive up to 265℃. Meanwhile, PLA+$AlCl_3$ can only survive up to 240℃.

Appreciation

The author expresses sincere gratitude to the Biochemistry Laboratory of Institut Teknologi Sepuluh Nopember for generously providing the research funding.

REFERENCES

Achmad, F. Yamane, K. Quan, S. & Kokugan, T. (2009), Synthesis of Polylactic Acid by Direct Polycondensation Under Vacuum Without Catalysts, Solvents and Initiators, *Chemical Engineering Journal*, 151 342–350.

Chafran, L.S. Paiva, M.F. França, J.O.C. Sales, M.J.A. Dias, S.C.L. Dias, J.A. (2019).

Preparation of PLA Blends by Polycondensation of D,L-Lactic Acid using Supported 12-Tungstophosphoric Acid as a Heterogeneous Catalys, *Heliyon,* 5 e01810.

Firouzabadi, H. Iranpoor, N. Khoshnood, A. (2007). Aluminum Tris (Dodecyl Sulfate) Trihydrate Al(DS)3·3H2O as an Efficient Lewis Acid-Surfactant-Combined Catalyst for Organic Reactions in Water. Efficient Conversion of Epoxides to Thiiranes And To Amino Alcohols at Room Temperature. J. Mol. Catal, *A Chem.* 274 109–115.

Heredia-Guerrero, J.A. Caputo, G. Guzman-Puyol , S. Tedeschi, G. Heredia, A. Ceseracciu, L. Benitez, J.J. Athanassiou, A. (2019). Sustainable Polycondensation of Multifunctional Fatty Acids from Tomato Pomace Agro-Waste Catalyzed by Tin (II) 2-Ethylhexanoate, *Materials Today Sustainability*. 3-4 100004.

Hortós, M. Viñas, M. Espino, S. & Bou, J.J. (2019). Influence of Temperature on High Molecular Weight Poly (Lactic Acid) Stereocomplex Formation, *eXPRESS Polymer Letters*, 13 (2) 123–134.

Idumah, C.I. Nwabanne, J.T. Tanjung, F.A. (2021). Novel Trends in Poly (Lactic) Acid Hybrid Bionanocomposites, *Cleaner Materials*. 2 100022.

Kitanosono, T., Kobayashi, S. (2017). Water-Compatible Chiral Lewis Acids, *Chiral Lewis Acids in Organic Synthesis*, 1 299–344.

Kricheldorfa, H.R. Weidner, S., M. (2019). About the Influence of Salicylic Acid on tin(II)Octanoate-Catalyzed Ring Opening Polymerization of L-lactide, *European Polymer Journal* . 119 37-44.

Maharana, T. Mohanty, B. Negi, Y.S. (2009). Melt-solid Polycondensation of Lactic Acid and Its Biodegradability, *Progress in Polymer Science (Oxford)*, 34 99–124.

Maryanty, Y. Hadiantoro, S. Widjajanti, K. Putri, D.I.K. & Nikmah, L. (2021), Poly Lactic Acid (PLA) Development Using Lactic Acid Product from Rice Straw Fermentation with Azeotropic Polycondensation Process, *IOP Conf. Series: Materials Science and Engineering*, 1053 012043.

Pradhan, K., Paul, S., Das, A.R. (2013). Fe(DS)3, an efficient Lewis Acid-Surfactant-Combined Catalyst (LASC) for the One Pot Synthesis of Chromeno[4,3-b]Chromene Derivatives by Assembling the Basic Building Blocks, *Tetrahedron Lett.* 54 3105–3110.

Rahmayetty, Whulanzaa, Y. Sukirnoc. Rahmana, S.F. Suyono, E.A. Yohda, M. Gozana, M. (2018). "Use of Candida Rugosa Lipase as a Biocatalyst for L-lactide Ring-Opening Polymerization and Polylactic Acid Production, *Biocatalysis and Agricultural Biotechnology*, 16 683-691.

Shahdan, D. Chen, R.S. Ahmad, S. (2021). "Optimization of Graphene Nanoplatelets Dispersion and Nano-Filler Loading in Bio-Based Polymer Nanocomposites based on Tensile and Thermogravimetry Analysis, *Journal of Materials Research and Technology.* 15 1284-1299.

Widjaja, T. Hendrianie, N. Nurkhamidah, S. Altway, A. Yusuf, B. Fakhrizal, F. Alifatul, A. Pahlevi, A. (2023). "Poly Lactic Acid Production using the Ring Opening Polymerization (ROP) Method using Lewis Acid Surfactant Combined Iron (Fe) Catalyst ($Fe(DS)_3$)", *Heliyon.* 9 e17985.

Yazdabadi, S.H. Farrokhpour, H. Tabrizchi, M. (2021). Using Surfactants as Matrix for the Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) of amino acids: Sodium dodecyl sulfate (SDS) and sodium octyl sulfate (SOS), *Biophysical Chemistry.* 278 106667.

Ye, Y. Ding, Q. Wu, J. (2008). Three-Component Reaction of 2-Alkynylbenzaldehyde, Amine, and Nucleophile using Lewis Acid-Surfactant Combined Catalyst in Water", *Tetrahedron*. 64 1378e1382.