**The Effect of NiCl2 And Si/Al Catalyst for Producing Polylactic Acid Using Ring-Opening Polymerization Method**

Hendro Juwono1,a), Reni Amalia1, Deni Setiyawati1,, Farha Hania Khaldaa1,, Kartika A. Madurani1,, Harmami1,

Author Affiliations

1Laboratory of Instrumentation and Analytical Science, Chemistry Department, Faculty of Sciences and Data Analytics, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

Author Emails

a)Corresponding author: [nehin66@chem.its.ac.id](mailto:nehin66@chem.its.ac.id)

**Abstract.** Polylactic acid (PLA) was produced using the ROP method with NiCl2 or Si/Al catalyst in concentrations of 0.3% and 0.5%. The production was conducted using lactic acid in chloroform and methanol (1:10). The dehydration step was done at 80-120°C, and the continuous polymerisation step at 160-180°C to produce oligomers. The oligomer was subjected to the depolymerisation step at 180-210°C to get lactide. The lactide was processed through ROP steps to produce PLA. The characterisation using FTIR showed that the synthesised PLA has different functional groups compared to the lactic acid. The higher crystallinity is PLA-NiCl2-0.5. The FESEM image shows that the morphology structure of both catalysts in PLA production seemed random and uneven. The thermal stability of the 0.5% catalyst is greater than 0.3% catalyst. Meanwhile, the catalytic stability of PLA-NiCl2 is better than PLA-Si/Al.

# INTRODUCTION

Polylactic acid (PLA) is a biopolyester that is used in industries including textiles, electronics, medicine, and pharmaceuticals [1]. The PLA can replace conventional plastics due to its renewability, low toxicity, energy efficiency, high mechanical and thermal strength, biocompatibility, and biodegradability[2]. Currently, PLA is produced for commercial use through various methods, such as direct condensation polymerisation, azeotropic dehydration condensation, and ring-opening polymerisation (ROP). The ROP method produces PLA with controlled molecular weight, high optical purity, and crystallised form [3]. The ROP is a better method for producing PLA with a high yield (88–92%) and a high molecular weight (Mw ≥ 100,000) [3][4].

A catalyst is needed in the ROP process. Several catalysts were reported, including complex metal catalysts (Al, Mg, Zn, Ca, Sn, Fe, Y, Sm, Lu, Ti, and Zr), cations, and organic catalysts. The use of complex metal catalysts (stannous octoate and Sn(Oct)2) on an industrial scale can lead to contamination in the PLA product[3]. To overcome this problem, researchers have been conducting studies to obtain more appropriate catalysts, i.e., heterogeneous catalysts that can be reused, sustainable, economical, and easily separated [5][6]. One of the heterogeneous catalysts is a nickel-based catalyst. Routaray et al. (2016) used nickel (II) complexes as catalysts with benzyl alcohol initiators in the lactic acid ring-opening polymerisation process [4] The results showed high reactivity, which is similar to stannous octoate, with lower cytotoxicity properties. Farquhar et al. (2020) successfully used nickel catalysts to produce oligomers and polymers from 5-ethylidene-2-norbornene with high molecular weights (from 270 Da to >100,000 Da) 7. Kang et al. (2021) used alkyl-, alkoxy, and phenylallenes polymerisations with nickel (II) catalysts and obtained high yields of polyallenes with a controlled molar mass and low molar mass distribution [8]. Furthermore, nickel catalysts have been employed in several polymerisation processes in recent years of study [9-14].

Si/Al has also been reported as a heterogeneous catalyst to increase a material's acidity in the cracking of polypropylene [15]. Si/Al catalysts have demonstrated good acidity and stability as well as comparatively large pore diameters and surface areas [16]. In PLA synthesis, Si/Al catalysts can initiate polymerisation reactions, form polymer chains, and enhance catalytic activity in ROP, thus producing PLA with shorter reaction times [17]. Nickel and Si/Al-based catalysts have been proven effective in catalysing polymerisation reactions and have high catalytic activity and good stability. In this study, NiCl2 and Si/Al catalysts were used to synthesise PLA through the ROP method. The aim is to observe the effect of both catalysts on the PLA product based on characterisation data using FTIR, TGA, XRD, and FESEM.

# EXPERIMENTAL

**Synthesis of PLA**

PLA was synthesised using an ROP method based on research [3][4]. The dehydration process of lactic acid was carried out at 80-120°C for 1 hour under nitrogen conditions. The process produces an oligomer. The oligomer was reheated at 180-210°C for 12 hours and obtained lactide. Ring-opening polymerisation is carried out by reheating the lactide at 100-140°C for 8 hours with catalysts of NiCl2 or Si/Al in a concentration of 0.3% or 0.5% (w/w). Subsequently, the mixture was dissolved in 10 mL of chloroform and then precipitated using chloroform and methanol in a 1:10 ratio. The PLA was filtered using filter paper and dried in the oven at 80°C for 4 hours until PLA powder.

**Characterisation of PLA**

The FTIR analysis was performed to determine the effect of the catalyst on the structural changes in the synthesised PLA. The PLA function groups were analysed at the 4000-400 cm-1 using the FTIR 8400s Shimadzu. The XRD analysis was performed to determine the synthesised PLA crystallinity. XRD analysis conducted at angles between 0-90° with Cu-Kα radiation under a current of 30 mA and a voltage of 40 kV. Surface morphology of the synthesised PLA was analysed with magnifications of 500x, 9000x, 11000x, and 20,000x with an accelerator voltage of 1 kV using FESEM (REGULUS-8220 HITACHI). The thermal stability of the synthesised PLA was analysed with TGA at a heating rate of 10°C/min from 25 to 600°C under nitrogen conditions.

# RESULTS AND DISCUSSION

**Synthesis of PLA**

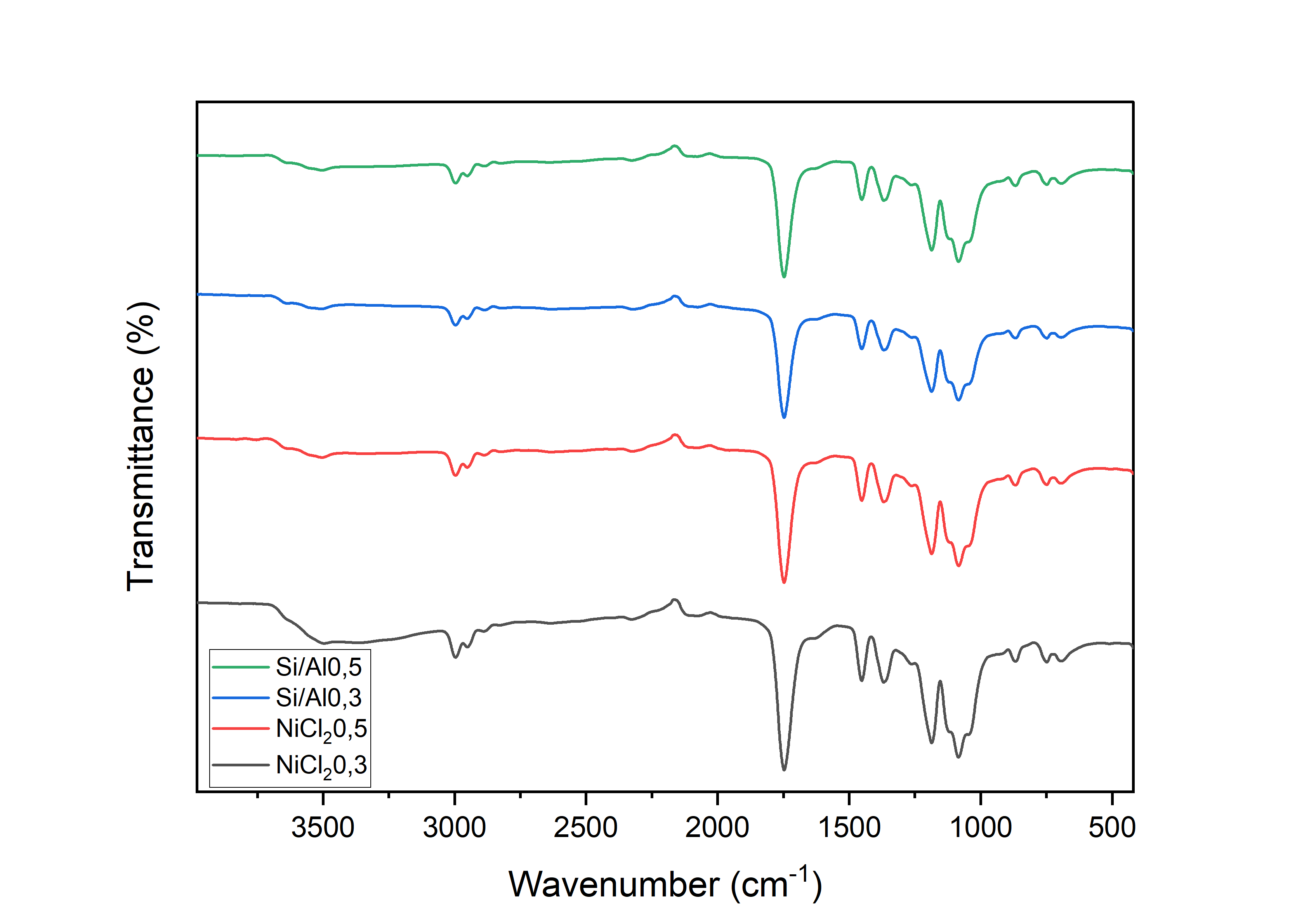
The synthesis process of PLA is carried out using the ROP method, which occurs in several stages, including dehydration and polymerisation of lactic acid to form oligomers, depolymerisation of oligomers to produce lactides, and lactide ring-opening reactions with catalysts to produce high-molecular-weight PLA. The use of reflux systems, nitrogen gas, and vacuum pumps plays a role in the water removal process and maximises the yield at each reaction stage.

The first stage is dehydration, carried out at the boiling point temperature of the water, below the boiling point of lactic acid (Tdehydration < Tboiling point of lactic acid), to produce highly viscous lactic acid liquid. This process aims to minimise the presence of water molecules so that the equilibrium reaction tends to shift towards the formation of oligomers. Next, the depolymerisation process is conducted by heating the sample at higher temperatures but not exceeding the decomposition temperature to avoid damage, resulting in solid lactide rings with a hard texture and yellowish colour.

In the lactide ROP stage, variations in Si/Al catalyst concentrations of 0.3% and 0.5% (w/w) are used. The results show that the ROP yield is higher at a concentration of 0.3%. But the final yield of PLA product is obtained higher rate using a catalyst concentration of 0.5% (38.847%) compared to a catalyst concentration of 0.3% (21.426%). Another catalyst, NiCl2, was also added to determine which catalyst has a good yield. The concentration variations of NiCl2 catalyst are 0.3% and 0.5% (w/w). The results showed a similar pattern with the Si/Al catalyst, but the final yield of PLA product reached up to 52.30% using a catalyst concentration of 0.5%. The catalyst acts as a coordination insertion that forms free radicals to accelerate polymer chain propagation. During the ring-opening process, the melted sample is reheated to around 90 °C (consistent with the lactide melting point of 95–98°C) to prevent compression and mix with the catalyst. Additionally, longer reaction times also increase the yield of PLA produced. Factors such as optimal oligomer and lactide formation, selection of the appropriate type and concentration of catalyst, as well as precise control of temperature, reaction time, vacuum conditions, and nitrogen amount, significantly affect the yield and success of PLA synthesis. The entire reaction series is carried out under vacuum conditions to prevent sample oxidation by air and using continuous nitrogen gas flow to accelerate water removal and reaction at each stage.

**The effect of the catalyst on PLA characterisation**

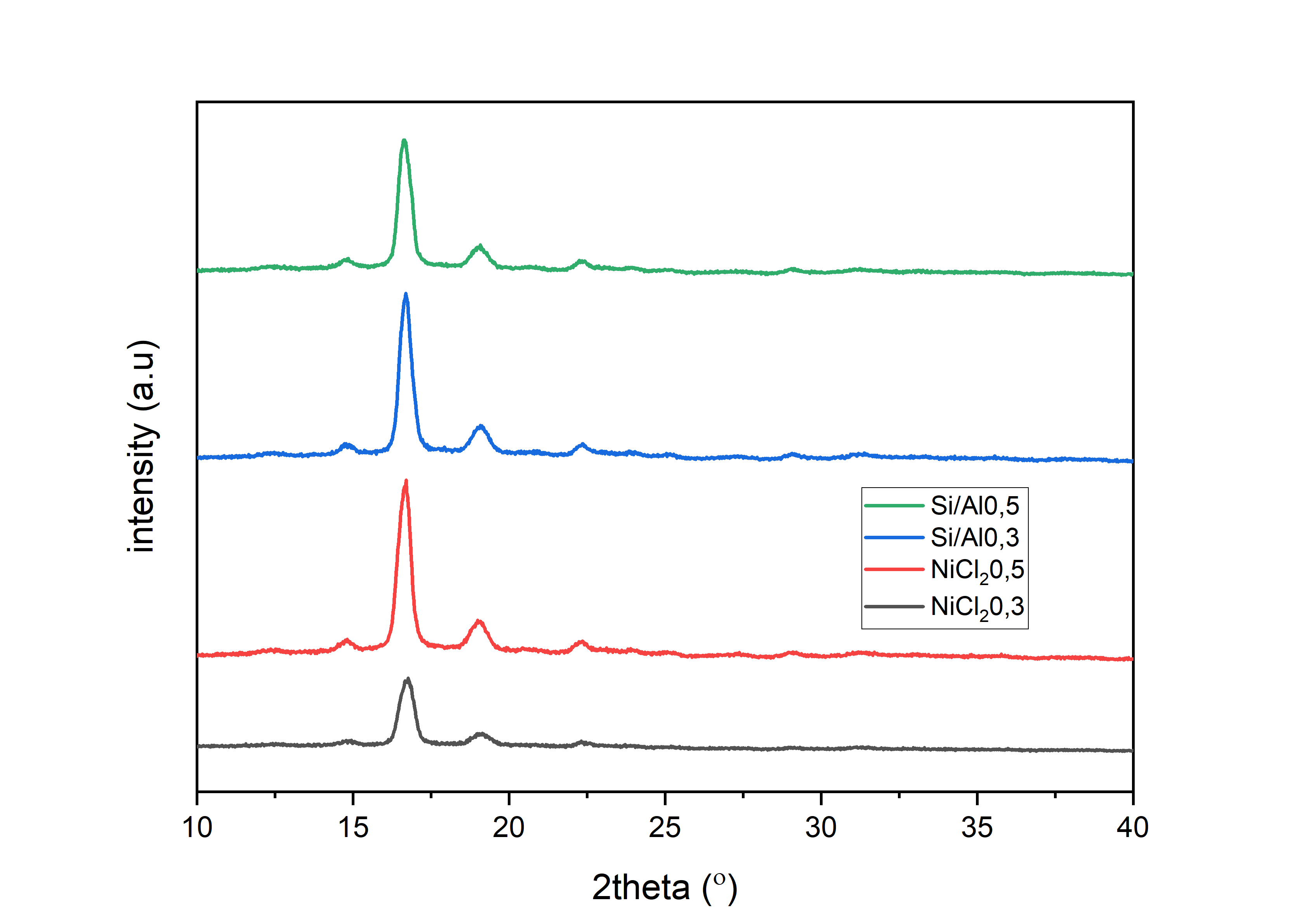
The FTIR analysis of the synthesised PLA showed its functional group characteristics different to lactic acid functional groups. The FTIR spectrum of the synthesised PLA is shown in Figure 1. The synthesised PLA have several peaks a different wavenumbers. The OH stretch is shown at 3512 cm-1, which is carboxylic acid. A wavenumber of 2995 cm-1 (asymmetrical) indicates a -CH group stretch of CH3. In addition, a carbonyl bond (C=O) appeared at 1747 cm-1, which is a C=O valence vibration of the aliphatic ester. The peak corresponding to the CH3 bending vibration is found at 1452 cm-1. A peak at 1264 cm-1 indicates C=O bending, and a peak at 1184 cm-1 shows a C-O group stretching. The FTIR spectrum of the synthesised PLA using two catalyst variations shows no significant difference. Figure 1 also gives a similar result with the FTIR spectrum of PLA standard (a molecular weight of 148,000 g/mol, which was also produced by the ROP method in previous studies) [18]. This shows that the role of the catalyst does not have a significant effect or difference on the product obtained; the catalyst only serves to accelerate the reaction during the reaction process. This comparison also shows that the synthesis carried out is indeed successful in forming PLA products, and the molecular weight produced is also not much different from standard PLA. From the FTIR analysis that has been done, the resulting spectrum resembles the PLA standard. In addition, the catalyst does not affect changes in the structure of PLA only plays a role in accelerating polymerization [18]



**Figure 1.** FTIR spectrum of the synthesised PLA.

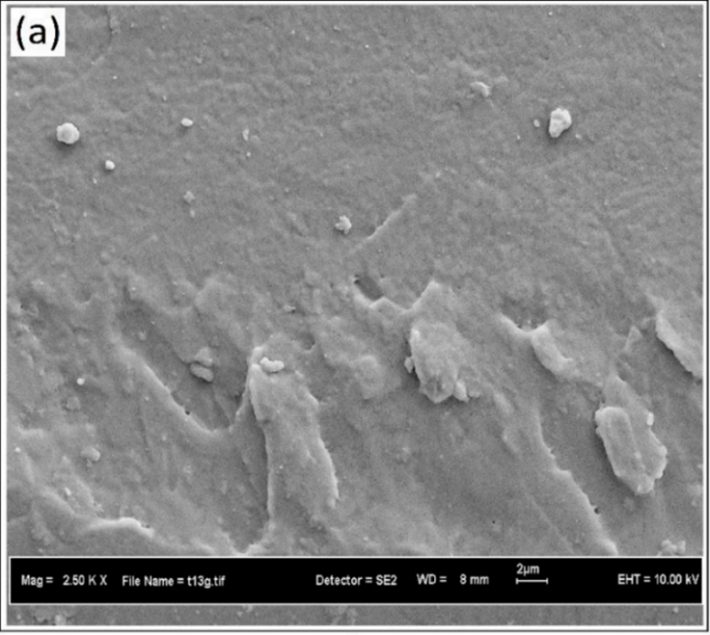
XRD analysis was performed to determine the crystallinity of the synthesised PLA. Crystallinity, which refers to the degree of order between bonding molecules in a material, has a significant impact on polymer properties such as hardness, tensile strength, stiffness, and melting point [4]. XRD diffraction results show that the synthesised PLA displays two diffraction peaks with different intensities, which are similar to the diffraction pattern of the PLA standard, indicating the crystalline phase characteristic of PLA. Highlighting the important role of NiCl2 and Si/Al catalysts as nucleating agents that promote the improvement of PLA crystallinity. In addition, the percentage of crystallinity was also affected by the polymer concentration [19]. Overall, this study shows that the synthesised PLA has a higher crystallinity than the PLA standard, indicating better applicability potential in various polymer applications.

As a result of the FTIR analysis, the PLA synthesis results showed the presence of two PLA-NiCl2-0.3 and PLA-NiCl2-0.5 diffractograms in succession of 16.75° and 19.07°; 16.71° and 19.04°. The PLA-Si/Al-0.3 and PLA-Si/Al-0.5 diffractogram in sequence of 16.69° and 19.09°; 16.65° and 19.08°. The PLA purity shows two peaks at 16.84° and 19.10°. These diphratic peaks are consistent with previous studies. The quantitative determination of PLA crystallinity is determined by XRD. Crystallinity affects various properties of polymers such as strength, gravity, stiffness, and melting point. Crystallinity is determined by comparing the size of the crystal area and the total area, where the total size is the sum of the area of the crystal and the amorphous area. Based on the calculations that have been made, PLA-NiCl2-0.3, PLA-NiCl2-0.5, PLA-Si/Al-0.3, and PLA-Si/Al-0.5 are 68.18%, 68.92%, 63.04%, and 48.05%, respectively. The highest crystallinity order obtained is PLA-NiCl2-0.5 > PLA-NiCl2-0.3 > PLA-Si/Al-0.3 > PLA-Si/Al-0.5. PLA standard has a crystallinity in the range of 0-37%. This indicates that the use of catalysts NiCl2 and Si/Al increases the crystallinity of PLA. The synthesised PLA diffractogram is shown in Figure 2.



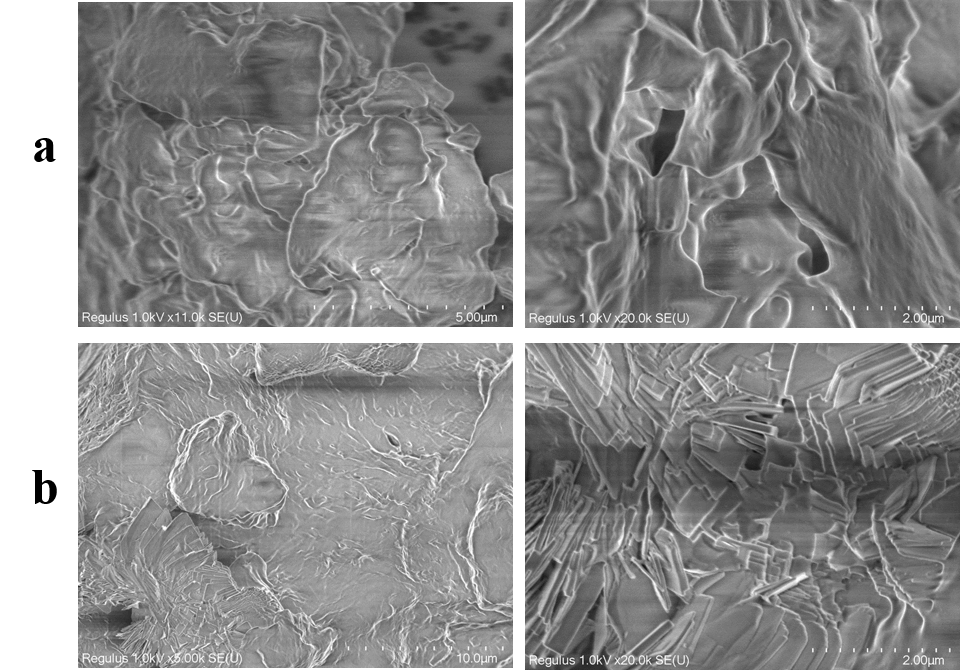
**Figure 2.** Diffractogram of the synthesised PLA.

The surface morphology of the PLA standard indicates a fairly fine surface, and there are cracks as shown in Figure 3 [20]. The results show that both variations of the catalysts appear random and irregular, except for PLA-NiCl2-0.5, where some of its surface appears elongated, thin, neat, and orderly. The morphology of synthesised PLA with the addition of NiCl2 catalysts is shown in Figure 4(a) and Figure 3(b). At a magnification of 20,000x, PLA-NiCl2-0.3 has a more random and larger surface than PLA-NiCl2-0.5. Meanwhile, the synthesised PLA with the addition of Si/Al catalysts at magnification 9000x saw more pronounced clamps and variations in PLA-Si/Al-0.3 compared to PLA/Si-Al-0.5. The yield of NiCl2 catalyst and Si/Al at 0.3% zoom 11000x appeared to be a random PLA morphology, irregular and almost similar. Meanwhile, when using NiCl2 and Si/Al catalysts of 0.5% at a magnification of 5000x, the surface of PLA-NiCl2-0.5 appears wider and larger. Morphological analysis of PLA with a Si/Al catalyst is shown in Figure 5(a) and (b).

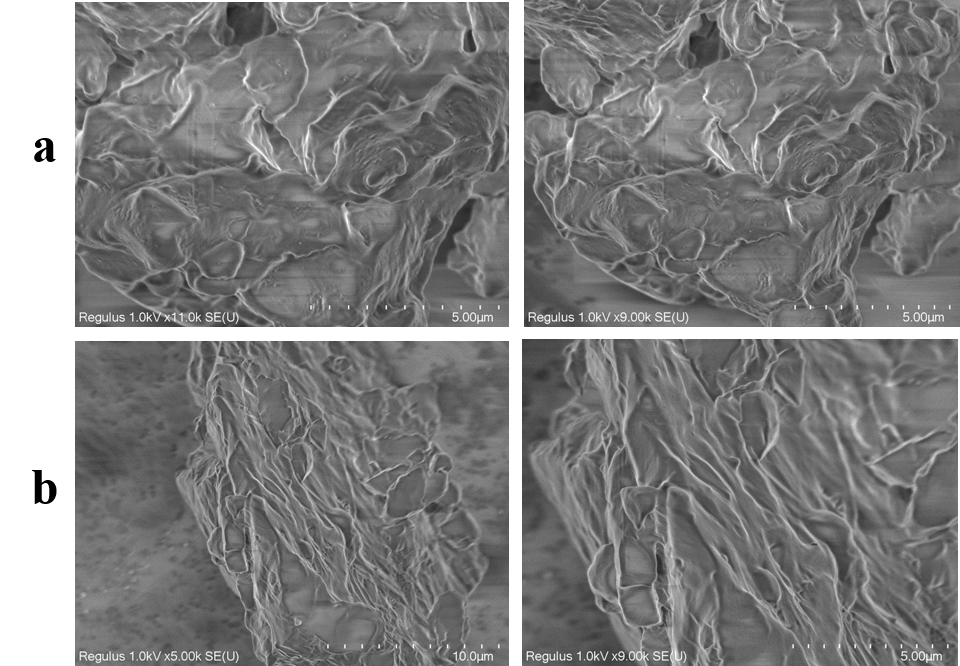


**Figure 3.** Image of PLA standard.

The FESEM (Figure 4) analysis shows that the morphology structure of the synthesised PLA looks slightly different. The morphology of 0.3% NiCl2 looks like an amorphous structure where the surface looks random and irregular, and the surface of 0.5% NiCl2 is also the same, but there is a slight difference in the 0.5% NiCl2 variation where the surface of PLA looks elongated, neat, and orderly, similar to the surface of crystalline polymers. It can be learned that the role of the nickel (II) chloride catalyst in PLA synthesis will give a slightly different morphological structure. This difference will affect the physical properties of PLA. In general, the crystallinity of PLA also affects the molecular weight of PLA. PLA with a crystalline structure will have a larger molecular weight than PLA with an amorphous structure. Crystalline PLA will be physically strong, stiff, and hard, but easily broken and brittle. The amorphous structure will produce plastic properties that are more flexible, elastic, and soft. It can be learned that a large catalyst concentration with the same manufacturing method and time estimation will accelerate the formation of PLA with a crystalline structure.



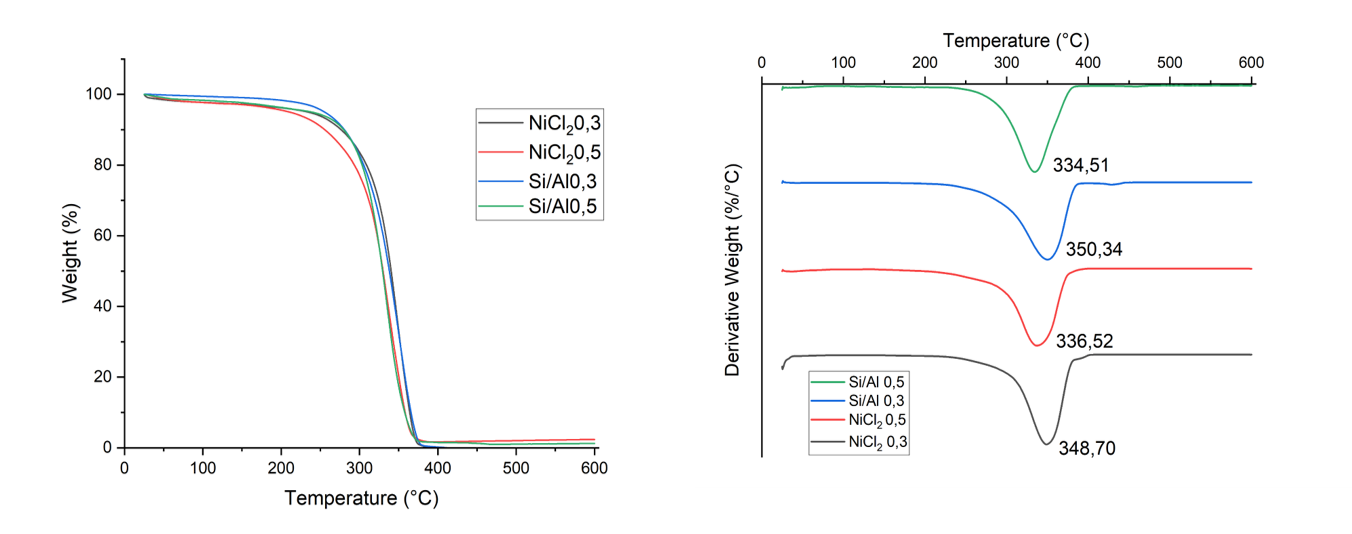
**Figure 4.** Images of the synthesized PLA-NiCl2-0.3 (a) and PLA-NiCl2-0.5 (b) in different magnification.



**Figure 5.** Images of the synthesized PLA-Si/Al-0.3 (a) and PLA-Si/Al-0.5 (b) in different magnification.

The thermogram of the synthesised PLA is shown in Figure 6. The decomposition of PLA-NiCl2-0.3 starts at 250.22℃ and ends at 374.09℃. In addition, the DTG curve of PLA-NiCl2-0.3 shows a single peak at 348.70℃. The decomposition of PLA-NiCl2-0.5 starts at a temperature of 239.87℃ and ends at 367.19℃, and the DTG curve shows a single peak at 336.5℃. The decomposition of PLA-Si/Al-0.3 starts at a temperature of 255.32℃ and ends at 376.43℃, and the DTG curve shows a single peak at 350.34℃. The decomposition of PLA-Si/Al-0.5 starts at a temperature of 246.91℃ and ends at 370.50℃, and the DTG curve shows a single peak at 334.51℃. The synthesised PLA with a catalyst concentration of 0.3% has a higher decomposition temperature than catalyst concentration of 0.5% with a faster decomposition rate. Meanwhile, PLA-Si/Al has a higher decomposition temperature with a faster decomposition rate compared to PLA-NiCl2. Percent decomposition of PLA-NiCl2-0.3; PLA-NiCl2-0.5; PLA-Si/Al-0.3; PLA-Si/Al-0.5 are 92.78%; 89.05%; 93.72%; and 91.98%, respectively. After heating to the maximum temperature of 600 ℃, the sample degraded and left a residue with the % residue obtained by PLA-NiCl2-0.3; PLA-NiCl2-0.5; PLA-Si/Al-0.3; PLA-Si/Al-0.5 are 0% (w/w); 2.37% (w/w); 0% (w/w), and 1.23 % (w/w). In this study, the catalyst concentration of 0.3% had a higher decomposition temperature with a greater %decomposition. The result also shows that PLA-Si/Al has a higher decomposition temperature (with a greater %decomposition) than PLA-NiCl2.

Before the decomposition of PLA, at NiCl2 0.3% and NiCl2 0.5% (Figure 6), a slightly sloping curve is seen around the temperature of 50–150°C. This is due to the volatile condition of the sample. The decrease in mass at that temperature is the result of the degradation of water and solvent content that is still present in the sample. In the PLA-NiCl2-0.3, PLA decomposition began to occur at a temperature of 282.10°C to 375.60°C, while PLA-NiCl­2-0.5 occurred at a temperature of 245.30°C to 366.70°C. PLA-NiCl2-0.3 has a higher degradation temperature than PLA-NiCl2-0.5; this high temperature means that PLA can maintain thermal stability well. However, PLA-NiCl2-0.3 has a faster degradation rate than PLA-NiCl2-0.5, with percent degradation of 98.92% and 88.00%, respectively. After heating to the maximum temperature of the TGA process, which is 600°C, at the end of the sample, PLA-NiCl2-0.3 was completely degraded, while PLA-NiCl2-0.5 left a residue of 3.7%. The higher the percent of residue produced at a certain temperature, the better and stable PLA.



**Figure 6.** Thermogram of the synthesised PLA.

PLA generally has a maximum degradation temperature in the range of 220–390°C [21]. PLA standard itself degrades at a peak of 352.50°C, and the degradation ends completely (with 0% w/w residue) at 376.20°C 22. The results show that the PLA standard has better stability but is still close to the synthesised PLA. One of the factors influencing thermal stability is molecular weight and end groups. The PLA with Mw of about 30,000 and -Cl end groups (Tmax = 360–370°C) is much more stable than the PLA with hydroxyl end groups (Tmax = 240°C) [21]. The role of the catalyst as a component is to accelerate the reaction in the lactide ring-opening process, but the catalyst residue itself is the main impurity that determines the thermal stability of PLA. Thermal degradation was also observed in previous studies on stannous octoate catalysts; decreasing the concentration of catalyst residue led to an increase in thermal degradation temperature [21].

The decomposition of the PLA standard started at 265.38°C to 380.97°C, with a total mass decomposition of 98.41%. The DTG curve of PLA showed a single peak at 337.49°C [23]. The decomposition of PLA-0.3 started at 241.11°C, ended at 377.64°C, and showed a single peak of the DTG curve at 350.39°C. Meanwhile, the decomposition of PLA-0.5 started at 209.55°C, ended at 372.46°C, and showed a single peak on the DTG curve at 335.14°C. The total decomposition of PLA-0.3 and PLA-0.5 variations was 98.44% and 97.98%, respectively. These results are close to the total mass decomposition of the PLA standard. It shows that the decomposition can start at a lower temperature compared to the reaction without a catalyst. It can be seen that PLA-0.3 has high thermal stability compared to PLA-0.5. High thermal stability indicates that the material can resist degradation at high temperatures.

# CONCLUSION

The PLA has been successfully synthesised with NiCl2 and Si/Al catalysts using the ROP method. The use of nitrogen, the amount of catalyst, temperature, reaction time, temperature, vacuum conditions, and amount of nitrogen are important factors in PLA synthesis. Differences in variations in catalyst concentration in the FTIR spectrum do not affect the PLA structure. The addition of catalyst concentration affects the crystallinity of the PLA. The surface morphology of both catalysts showed similar results, appearing random and irregular, except for PLA-NiCl2-0.5. The surface morphology of PLA-NiCl2-0.5 shows some surfaces that look elongated, thin, neat, and regular. Based on the TGA/DTG results, it shows that variations in catalyst concentration of 0.5% produce PLA, which has better stability than 0.3%. Meanwhile, judging from the type of catalyst, PLA-NiCl2 produces better stability.

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# References

[1] A. Jiménez, M. Peltzer, and R. Ruseckaite, Poly(Lactic Acid) Science and Technology: Processing, Properties, Additives and Applications (The Royal Society of Chemistry, 2014).

[2] V. Vatanpour, A. Dehqan, S. Paziresh, S. Zinadini, A.A. Zinatizadeh, and I. Koyuncu, “Polylactic acid in the fabrication of separation membranes: A review,” Sep Purif Technol 296, (2022).

[3] Rahmayetty, Y. Whulanza, 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,” Biocatal Agric Biotechnol 16, 683–691 (2018).

[4] A. Routaray, S. Mantri, N. Nath, A.K. Sutar, and T. Maharana, “Nickel(II) complex catalyzed ring-opening polymerization of lactide,” Polyhedron 119, 335–341 (2016).

[5] L.S. Chafran, M.F. Paiva, J.O.C. Freitas, M.J.A. Sales, S.C.L. Dias, and J.A. Dias, “Preparation of PLA blends by polycondensation of D,L-lactic acid using supported 12-tungstophosphoric acid as a heterogeneous catalyst,” Heliyon 5(5), (2019).

[6] V. Gupta, and K. Pal Singh, “The impact of heterogeneous catalyst on biodiesel production; a review,” Mater Today Proc 78, 364–371 (2023).

[7] A.H. Farquhar, M. Brookhart, and A.J.M. Miller, “Oligomerization and polymerization of 5-ethylidene-2-norbornene by cationic palladium and nickel catalysts,” Polym Chem 11(14), 2576–2584 (2020).

[8] S.-M. Kang, X.-H. Xu, L. Xu, L. Zhou, N. Liu, and Z.-Q. Wu, “Highly 2,3-selective and fast living polymerization of alkyl-, alkoxy- and phenylallenes using nickel(ii) catalysts,” Polym Chem 12(33), 4822–4828 (2021).

[9] Q.H. Tran, X. Wang, M. Brookhart, and O. Daugulis, “Cationic α-Diimine Nickel and Palladium Complexes Incorporating Phenanthrene Substituents: Highly Active Ethylene Polymerization Catalysts and Mechanistic Studies of syn/anti Isomerization,” Organometallics 39(24), 4704–4716 (2020).

[10] J. Wang, L. Wang, H. Yu, R.S. Ullah, M. Haroon, Zain-ul-Abdin, X. Xia, and R.U. Khan, “Recent Progress in Ethylene Polymerization Catalyzed by Ni and Pd Catalysts,” Eur J Inorg Chem 2018(13), 1450–1468 (2018).

[11] D. Li, F. Li, H. Yu, L. Guo, J. Huang, J. Li, and C. Li, “Nickel-modified triphenylamine-based conjugated porous polymers as precatalyst for ethylene oligomerization,” Inorganica Chim Acta 544, (2023).

[12] T. V Tran, Y.H. Nguyen, and L.H. Do, “Development of highly productive nickel–sodium phenoxyphosphine ethylene polymerization catalysts and their reaction temperature profiles,” Polym Chem 10(27), 3718–3721 (2019).

[13] L. Zhong, H. Zheng, C. Du, W. Du, G. Liao, C.S. Cheung, and H. Gao, “Thermally robust α-diimine nickel and palladium catalysts with constrained space for ethylene (co)polymerizations,” J Catal 384, 208–217 (2020).

[14] Z. Hai, Z. Lu, S. Li, Z.-Y. Cao, and S. Dai, “The synergistic effect of rigid and flexible substituents on insertion polymerization with α-diimine nickel and palladium catalysts,” Polym Chem 12(32), 4643–4653 (2021).

[15] K. Katalitik Limbah Plastik Polipropilen dengan Katalis Silica Alumina Keramik Menghasilkan Bahan Bakar Alternative Fraksi Hidrokarbon, H. Juwono, S. Ismada, Ma. tri Sujadmiko, L. Fauziah, and I. Qurrota Ayyun, Catalytic Conversion From Plastic Waste by Silica-Alumina-Ceramic Catalyst to Produce an Alternative Fuel Hydrocarbon Fraction (2019).

[16] L. Fu, C. Huo, X. He, and H. Yang, “Au encapsulated into Al-MCM-41 mesoporous material: in situ synthesis and electronic structure,” RSC Adv 5(26), 20414–20423 (2015).

[17] A.L. Kocen, M. Brookhart, and O. Daugulis, “A highly active Ni(II)-triadamantylphosphine catalyst for ultrahigh-molecular-weight polyethylene synthesis,” Nat. Commun. 10, 438 (2019).

[18] H.W. Lee, R. Insyani, D. Prasetyo, H. Prajitno, and J. Sitompul, “Molecular weight and structural properties of biodegradable PLA synthesized with different catalysts by direct melt polycondensation,” Journal of Engineering and Technological Sciences 47(4), 364–373 (2015).

[19] N. Yadav, L. Nain, and S.K. Khare, “Studies on the degradation and characterization of a novel metal-free polylactic acid synthesized via lipase-catalyzed polymerization: A step towards curing the environmental plastic issue,” Environ Technol Innov 24, (2021).

[20] R. Arjmandi, A. Hassan, M.K.M. Haafiz, Z. Zakaria, and I.M. Inuwa, Characterization Of Polylactic Acid/Microcrystalline Cellulose/Montmorillonite Hybrid Composites (Pencirian Komposit Polilaktik Asid/Selulosa Mikrohablur/ Hibrid Montmorilonit) (2014).

[21] E. Wojtczak, P. Kubisa, and M. Bednarek, “Thermally stability of polylactide with different end-groups depending on the catalyst used for the polymerization,” Polym Degrad Stab 151, 100–104 (2018).

[22] A. Mohamed, S.H. Gordon, and G. Biresaw, “Poly(lactic acid)/polystyrene bioblends characterized by thermogravimetric analysis, differential scanning calorimetry, and photoacoustic infrared spectroscopy,” J Appl Polym Sci 106(3), 1689–1696 (2007).