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STUDYING INFLUENCES ON SYNTHESIS OF BIODEGRADABLE POLYMER POLY(L(+))LACTIC ACID) BY POLYCONDENSATION USING OF TIN BASED CATALYSTS

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Summary

There are many factors affect the polycondensation reaction of L-lactic acids (LLA) in solution such as catalysts, solvent, monomer, temperature etc. In this paper, the investigation of the influences of solvent, reaction time and tin immobilized on active carbon and titanium dioxide catalysts on the polycondensation reaction were carried out. The immobilized tin on TiO₂ can not improve the LLA polycondensation reaction rate. The reaction order of polycondensation reaction of pure tin powder catalyst was determined with the value of 3/2. The molecular construction of LLA exposures with the air in the long time is modified, consequence it can not be taken part in polycondensation reaction due to the oligomerization and intermolecular esterification to produce an ester or dilactides. Molecular weights in average number and in average weight (M_n and M_w) of PLA products were determined with the values of 11,901 and 39,320 and they can be used in the production of semi-finished articles and final products such as cast profiles, foils, packaging, and fibers.

1. INTRODUCTION

Poly(L(+))lactic acid (PLA) is a biological polymer of the third generation and having a much better potentials in production regarding raw materials (e.g. corn meal, cassava powders, sugar wastes etc.), durability and biological degradation in environment. PLA can be biodegraded more than 90% in the natural environment. In an agricultural country such as Vietnam, PLA production potential is a considerable interest.

Lactic acid (α -hydroxypropionic acid) used as a substrate in the synthesis of PLA, belongs to the hydroxyacids. Hydroxyacids are characterized by greater acidity devoid of hydroxyl groups (particularly in the α position) considerably facilitates the dissociation of carboxyl groups. For this reason α -hydroxypropionic acid is ten times stronger than propionic acid [2].

Lactic acid contains one asymmetric carbon atom, and it therefore occurs in two enantiometric forms. In the technological synthesis of poly(lactic acid), this dextrorotatory enantiomer (L(+) lactic acid) is mostly used, which gives the crystalline PLA. A mixture of enantiomers of lactic acid is applied in the food and tanning industries. The commercial lactic acid (LA), available as an 85-92% aqueous solution, contains an admixture of the linear dimer $\text{CH}_3\text{CH}(\text{OH})\text{COOCH}(\text{CH}_3)\text{COOH}$, i.e. laktyllactic acid, which is formed during the concentration of LA under atmospheric pressure. During the heating of laktyllactic acid to the temperature of 180-250°C, dehydration occurs and the cyclic diester-lactide is formed. Lactide can occur in two optic active enantiomers, a racemic mixture and in mezo form [2].

Nowadays, there are 3 main methods for PLA synthesis from lactic acid in the world: (1) The polymerization of L-lactic acid (cyclic dimer of lactic acid (Ring Opening Polycondensation)); (2) The polycondensation of L(+) lactic acid (LA), which carried out in bulk or in solution and (3) the polycondensation of LA combined with chain extended agents. So far, the synthesis of PLA from lactide is best known method of synthesis. This process is used in industry and numerous publications and patents are devoted to it. However, methods 1 and 3 used the high-cost catalysts and high pressure it can cause the side process such as reaction of depolymerization or racemization. The direct polycondensation of lactic acid in bulk is not applied on a greater scale, because of the competitive reaction of lactide formation and the simultaneously occurring degradation process. The polycondensation of lactic acid in solution gives PLA with molar masses ranging from the tens to few hundred thousand.

We chose the method 2 because of easily carry out, catalyst can be recycled and low-cost production. The main aim of this works was to investigate the factor influences such as Sn and Sn immobilized on carrier catalysts (dispersion of Sn in the system), solvents, dose of catalyst on the polycondensation and determination of PLA products.

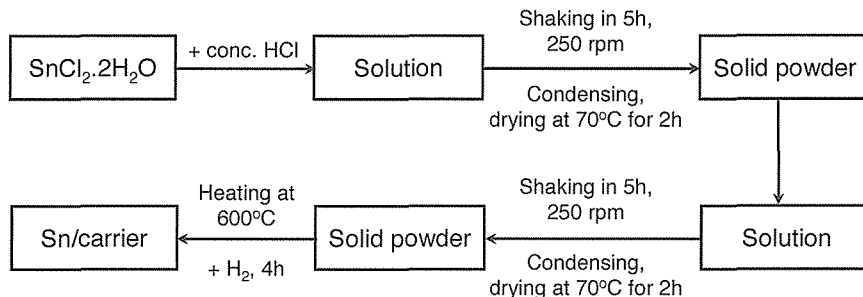
2. EXPERIMENTALS

Chemicals

- L-AL 85-92%, Wako Pure Chemical Industries
- Methanol PA
- Industrial xylene ($\geq 99\%$)
- Sn ($75 \mu\text{m}$)
- TiO_2 (P25) Degussa: 70% anatase, 30% rutile; specific area: $50\text{g}/\text{cm}^3$
- Active charcoal, TW 2 (Tra Bac, Viet Nam), average capillary diameter: 4nm, specific area: $100\text{m}^2/\text{g}$, porosity of 52%, total porous volume: $0,54\text{cm}^3/\text{g}$, specific density: $1,9\text{g}/\text{cm}^3$.
- HCl solution 36-38%
- NH_3 solution 25-28%
- Chloroform $\geq 99\%$
- $\text{Na}_2\text{SO}_4 \geq 99\%$
- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} \geq 99\%$,

Preparation of Sn on carrier materials

An appropriate Sn weight with total weight of Sn and carrier material with the ratio ($m_{\text{Sn}} : m_{(\text{Sn} + \text{carrier material})} = a\%$) is implemented the procedures of catalyst preparation as the following scheme:



Analytical methods

Titration method using phenolphthalein as an indicator at pH of 8.0 was used for determination of H^+ concentration of fresh and used LA solution after some time. After a certain time exposed with air LA could be easily esterized, especially in high concentration, to produce lactide ring and lactoyllactic acids. After esterification, H^+ concentration in LA solution decreased. Titration method could be used for determination of free H^+ in solution, therefore, equals to LA and lactoyllactic acids.

PLA product was purified and clean-up and analyzed by weighing and lectrothermal equipments for determination of polycondensation efficiency according to weight of product and melting point. Structure of PLA was identified by IR method and 1H -NMR.

Gel Permeation Chromatography (GPC) method was applied for determination of Molecular Weight in Average Number (\overline{M}_n) and Molecular Weight in Average Weight (\overline{M}_w) of PLA product. PLA samples were dissolved until 0.5% (w/v) in chloroform as the mobile phase and injected 100 μ l dissolved sample on the Shimadzu GPC equipment with Reflective Index Detector (RID-10A). Two columns Shim-pack GPC-802C (8.0mm i.d x 300 mm L.) and Shim-pack GPC-804C (8.0mm i.d x 300 mm L.) were installed consequence. Chloroform was use as mobile phase with flow rate of 1.0mL/min at temperature of 40°C. A series of polystyrene standards were prepared to get the molecular weight in the range of 580 to 1,800,000 to establish the calibration curves.

Synthesis of polymer Poly(L(+))lactic acid) by polycondensation in solution using of tin based catalysts

Based on density and weight of LA 15 g, volume of LA is calculated as 12.6 ml. The weight ratio of Sn:LA is prepared with the value of 1% for each experiment and xylene volume of 60 ml. Polycondensation of this mixture is carried out in the three-necked flask (500 ml). This reaction mixture is heated until the boiling point (140-148°C). The water was azeotropically distilled off, and fresh solvent evaporated on the top of the cooling distiller was precipitated and recycled into the mixture. Samples were taken into the 5 ml glass vial at every 5 hours. Each sample is centrifuged at the speed of 2000 rpm then decanted the mixture and throws away the catalyst at the bottom of the vial. Solvent mixture of methanol and water with the suitable ratio was added into the vial for PLA crystallization. After PLA crystallization, mixture is filtered on the glass fiber paper (porous diameter of 0.5 μ m). The PLA crystals were washed by methanol several times and then dry PLA products at 80°C for 8 hours and kept in the desiccators.

3. RESULTS AND DISCUSSION

Roles of tin on carrier material catalysts in the polycondensation

Influence of TiO_2 carrier in the catalyst

Polycondensation reactions were carried out with catalysts of Sn on TiO_2 carrier with Sn:LA ratio of 5% and 10%, respectively.

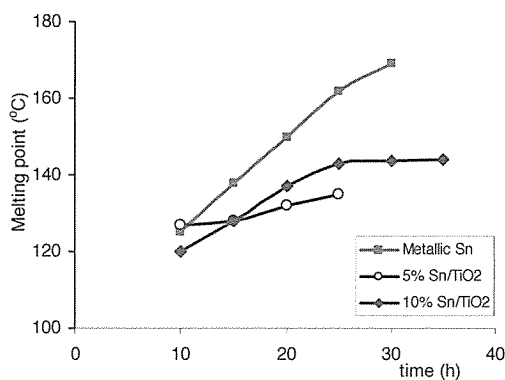


Figure 1. Melting point of PLA products due time course

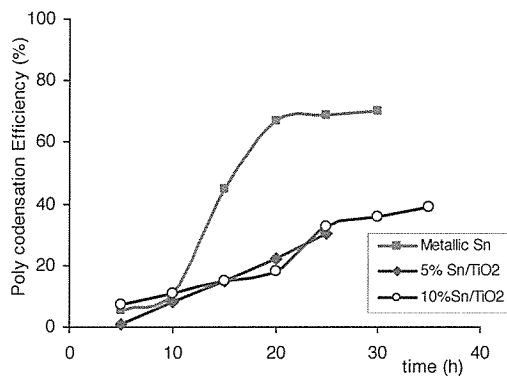


Figure 2. Comparison of the poly condensation of LA reaction efficiency using catalysts with and without carrier TiO₂ (Sn/AL =1%)

Melting point of product shows the quality of PLA regarding the molecular weight of PLA (figure 1). Melting point is higher the higher molecular weight of PLA achieved. In this research, melting point was used as a parameter to investigate the quality of PLA molecular weight. The melting points of PLA products were increasing when increasing reaction time. The polycondensation reaction using the powder Sn catalyst always give the higher melting point of PLA products in compare to the Sn on carrier TiO₂ catalysts.

The polycondensation reaction efficiency was determined by the ratio of weight of the PLA product weight and theoretical LA weight.

Sn was coated on the TiO₂ with the aim of improving of Sn dispersion in the polycondensation reaction. Figure 2 showed that Sn/TiO₂ catalyst effected to the PLA condensation reaction only in the beginning period (5-10h). In this period the dispersion of Sn only effected in the oligomer reaction stage. Then the efficiency of polycondensation showed that after the low oligomer appearance, reaction rate was not depended on the Sn dispersion. The low dispersion of free Sn is low but highest reaction rate. It can be explained that due to the Sn-lactate mechanism. In the beginning stage, the high Sn dispersion caused the formation of Sn-lactate complexes. Consequence, the reaction rate is higher. In the second periods, Sn dispersion did not play the important role when the number of sites of Sn-lactate appeared.

Effect of charcoal carrier in the catalyst

Active charcoal was coated with Sn could not improve the efficiencies of LA polycondensation reaction. Charcoal is multi size capillary material. In the immobilization of Sn on charcoal, a part of Sn powder is “sneaked” into the capillary pores. In the reaction LA monomer need to take a certain time to diffuse into the catalyst sites on charcoal. It showed on the first 20h period.

PLA product gained in the reaction with the Sn/C catalyst is low because the diameter of capillary of charcoals interfered the polycondensation of and separation of PLA out of catalyst.

Table 1. Efficiency of polycondensation reaction and melting point of PLA products when using Sn catalyst and Sn on active charcoal.

Time (h)	Sn		5% Sn/C		10% Sn/C	
	Efficiency (%)	T _{melt} (°C)	Efficiency (%)	T _{melt} (°C)	Efficiency (%)	T _{melt} (°C)
5	5,34	-	-	-	-	-
10	10,75	124-126	-	-	-	-
15	44,83	125-127	-	-	11,7	120-121
20	66,84	149-151	-	130-132	29,91	122-124
25	68,59	160-164	11,11	142-144	-	-
30	70,05	-	28,52	-	-	-

Influence of the Sn:LA ratio in the polycondensation

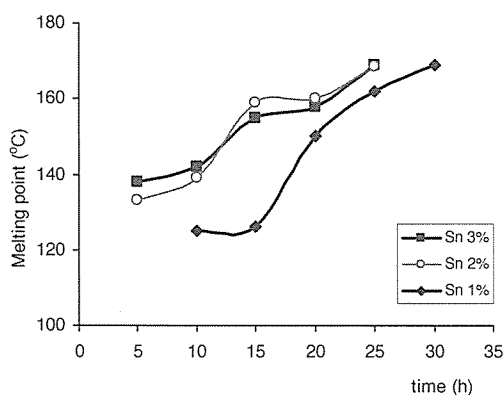


Figure 3. Melting points of PLA in the polycondensation reactions using different amount of Sn catalyst

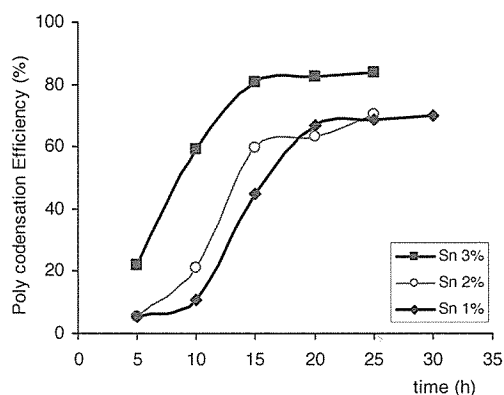


Figure 4. LA polycondensation efficiencies in reactions using different amount of Sn catalyst

The polycondensation reactions were carried out with the Sn:LA ratios of 1, 2 and 3% (in weight ratio). The melting points of PLA products were increased in the polycondensation which used the higher Sn:LA ratio (figure 3). Increasing reaction time, PLA products with different doses of catalyst will reach the similar molecular weight. When the reaction reached to the equilibrium state the melting points of PLA products is still increasing.

The higher amount of Sn catalyst in the reaction the higher efficiency and reaction rate of the polycondensation were achieved (figure 4). The efficiency of PLA products reached the stable value after 20h. This means the polycondensation reaction approached the equilibrium state.

Determination of reaction order of Sn in the polycondensation reaction

The equation of chemical reaction rate of the polycondensation is as follows:

$$\frac{w}{w} = \frac{\Delta C}{\Delta t} \quad (1)$$

Where, ΔC is difference of PLA concentration

$$\text{Otherwise, } \overline{w} = k \cdot [C_{\text{cat}}]^n \cdot [C_{\text{AL}}]^m \quad (2)$$

Where C_{cat} is concentration of Sn catalyst

C_{LA} is concentration of LA

In the polycondensation LA concentration was maintained constant, so the equation 2 is written as follows:

$$\overline{w} = k' \cdot [C_{\text{cat}}]^n \quad (3)$$

where $k' = k \cdot [C_{\text{AL}}]^m$

Logarite two part of the equation 3, it become

$$\lg \overline{w} = \lg k' + n \lg C_x \quad (4)$$

The reaction order of catalyst in the reaction can be achieved from the slope of the linear curve in the graph between $\lg \overline{w}$ versus $\lg C_{\text{cat}}$.

$$\Delta C = \frac{\Delta m}{V_0}; V_0 = 8\text{ml}; \Delta m: \text{ where } \Delta m \text{ is difference of PLA product weight (g)}$$

$$C_{\text{cat}} = \frac{m_{\text{cat}}}{V} = \frac{m_{\text{cat}}}{70.2 - 8.0} = \frac{m_{\text{cat}}}{62.2} \text{ (g/ml) (8ml is volume of PLA taken at 5h)}$$

Considering the reaction time after 10 h, so $\Delta t = 10\text{h}$:

Catalyst ratio	Sn 1%	Sn 2%	Sn 3%
M_{cat} (g)	0.15	0.3	0.45
Δm (g)	0.147	0.287	0.781
\overline{w}	$1.8375 \cdot 10^{-3}$	$3.5875 \cdot 10^{-3}$	$9.7625 \cdot 10^{-3}$
C_{cat} (g/ml)	$2.4116 \cdot 10^{-3}$	$4.8232 \cdot 10^{-3}$	$7.2348 \cdot 10^{-3}$
$\lg C_{\text{cat}}$	-2.6177	-2.3167	-2.1406
$\lg \overline{w}$	-2.7358	-2.4452	-2.01055

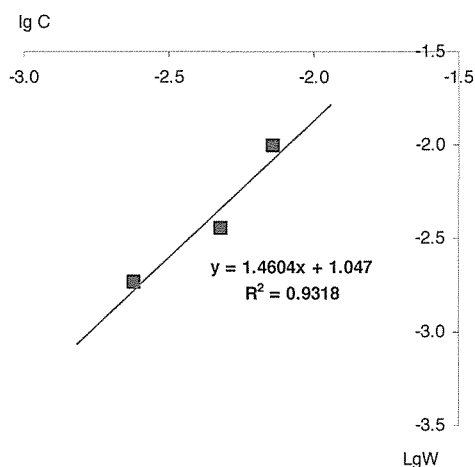


Figure 5. Slope of the linear curve between $\lg \overline{w}$ and $\lg C_{\text{cat}}$

The value of slope of the curve (figure 5) is 1.5 and the value of apparent k' of 1.047 h^{-1} . According to the Langmuir law for the absorption of the reaction on the surface of catalyst is mono layer absorption. Therefore, the order of reaction should be less than 1. But the found value of the

reaction order of catalyst is higher than 1. So, the mechanism of the Sn catalyst reaction is not only the absorption and desorption. This confirmed that the LA polycondensation reaction occurred obeying both 2 mechanisms: Reaction rate depended on the Sn dispersion and active Sn-lactate sites.

Reuse of catalyst after polycondensation

Sn catalyst was recycled after taking part the polycondensation reaction with the ratio of 3% in compare to LA by rinsing used catalyst and washing several times by chloroform solution. Sn catalyst is resin with diameter of 75 μm . After the polycondensation Sn catalyst is modified not the same with the original structure (see SEM photo, figure 6). There is non-crystallized part stucked on metallic Sn catalyst. This can be explained that Sn catalyst took part in to the reaction with LA to produce Sn-lactide.

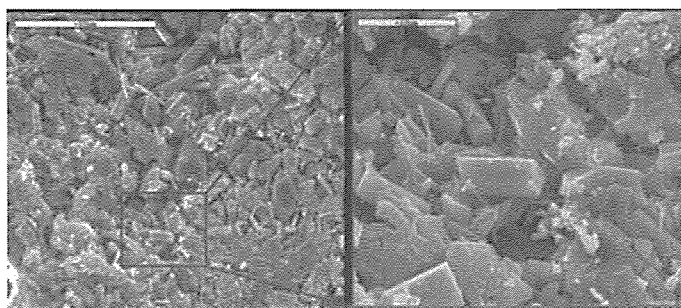


Figure 6. SEM photo of Sn catalyst after polycondensation reaction

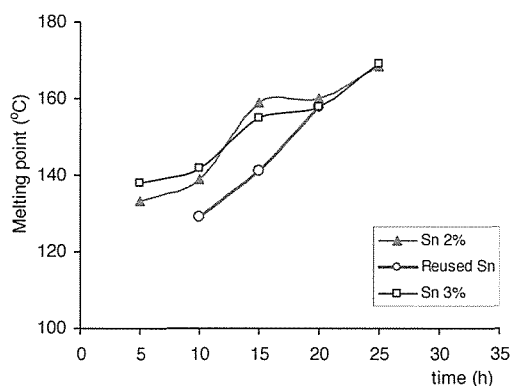


Figure 7. Comparison of PLA products in the polycondensation using powder and recycled Sn catalysts

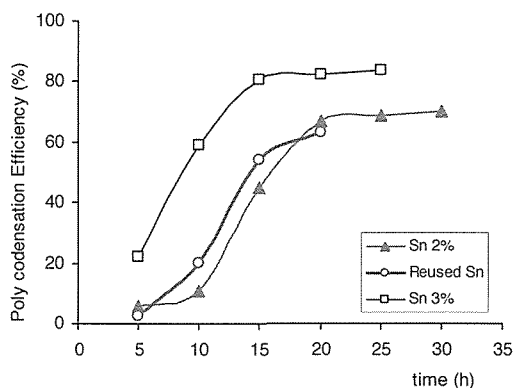


Figure 8. Comparison of polycondensation efficiency using powder and recycled Sn catalysts

From the experimental data showed that the weight of Sn catalyst was reduced after each polycondensation batch. This can be explained the polycondensation reaction followed the Sn-lactide formation mechanism. In the reused Sn catalyst Sn:LA ratio was $0.38:15 \approx 2.5\%$. The melting point curve of PLA product of the reaction with used Sn catalyst is in the middle of catalyst does of 2% and 3% (see figure 7) The comparison of polycondensation efficiencies with used and powder Sn (2% and 3%) catalysts are shown in the figure 8.

The catalyst activity of used Sn was less than powder Sn in the period of the first 15 hours. But the reaction time was prolonged (after 15 hours) the activity of used Sn did not influenced on the quality of PLA regarding melting points and polycondensation efficiencies.

Change of LA structures according to using time

Among the experiments, phenomena of PLA could not crystallize after polycondensation reaction was found. So LA was needed to check the H⁺ concentration and structure of LA after certain time used.

Free H⁺ in LA solution, which was determined by titration method, decreased significantly to using time while H⁺ after hydrolyzation are similar. This shows that LA is esterized to produce lactides or lactoyllactic acids. Especially, LA is easily hydrolyzed in anhydriization condition (high LA concentration). It is also observed that the viscosity of AL is increased when LA bottle was opened to use for a certain time. That means higher molecular weight of lactides or lactoyllactic acids.

¹³C-NMR was applied to observe the change of structure of LA due time course. ¹³C-NMR spectrograms of fresh LA and LA, which had been opened 6 months ago showed that there were specific picks of CH₃, CH and C=O groups in each spectrogram. However, the change of relative height of each pick showed that LA had been modified. 4 different specific picks of C=O bonds in ¹³C-NMR spectrogram of old LA were found. The solution of old LA contained 4 C=O groups belonged to the LA, lactide and lactoyllactic acid molecules.

Determination of chemical structure of PLA product

PLA product was analyzed by IR and ¹H-NMR spectrograph methods. IR spectrogram contained specific valent picks at 1751 cm⁻¹, 1188 cm⁻¹, 2991 cm⁻¹, 2939 cm⁻¹ and 3632 cm⁻¹ corresponding to groups of ester CO, C-O-C, saturated CH and OH, respectively. The doublet pick at 1.579 ppm in the ¹H-NMR spectrogram and the integration of 3 protons improved the CH₃ beside CH group. The quartet pick at 5.167 and the integration of 1 proton improved the CH beside CH₃ group.

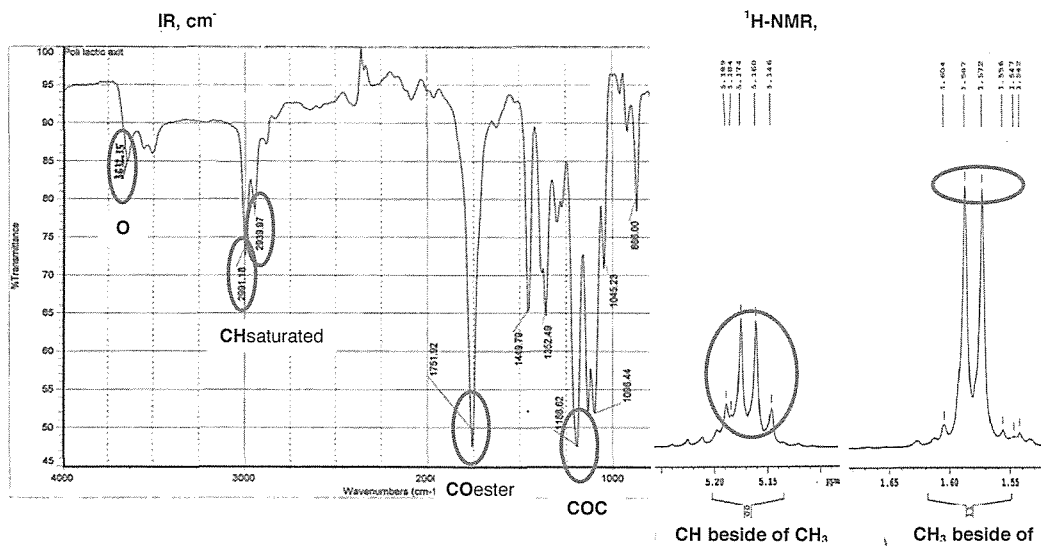
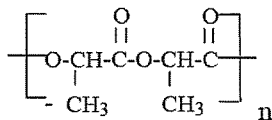
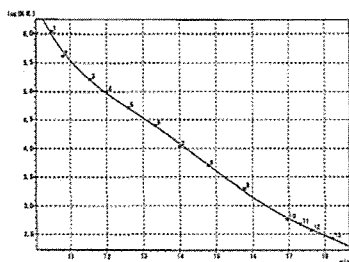


Figure 9. IR and ¹H-NMR spectrogram of PLA product

Data collection from IR and ¹H – NMR allowed to determine the structure of PLA product is as follows:



Determination of PLA molecular weight in average number and molecular weight in weight by GPC method



Calibration curve of polystyrene . $F(x) = -4.918969e-0.04 \cdot X^5 + 3.728329e-0.02 \cdot X^4 - 1.11892 \cdot X^3 + 16.62887 \cdot X^2 - 122.8958 \cdot X + 367.9137$, $R^2 = 0.9990851$

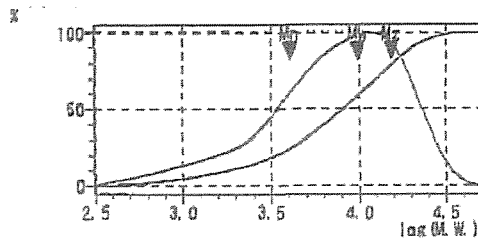
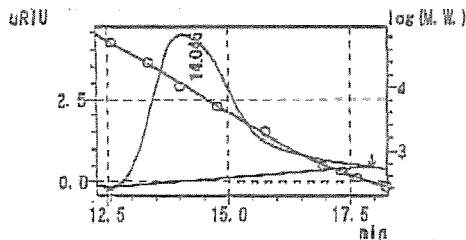
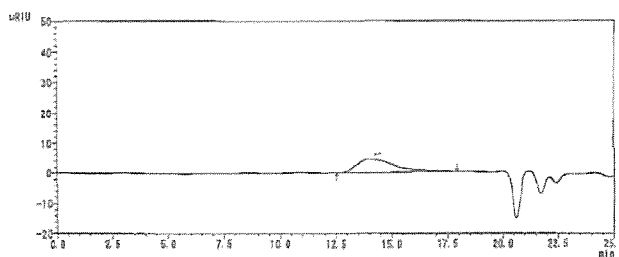


Figure 10. Chromatogram and distribution pick of PLA molecular weight of the polycondensation using Sn catalyst with Sn:LA = 1%, reaction time of 30h, temperature of 150-151°C

Table 2. Molecular weights of PLA products

No.	PLA using catalyst	Molecular Weight in Average Number (\overline{M}_n)	Molecular Weight in Average Weight (\overline{M}_w)	Distribution of molecularweight (n)
1	PLA1 (Sn/LA = 1%, 30h, t=150-151oC)	11.901	39.320	0.3
2	PLA2 (10%TiO ₂ : Sn/LA = 1%, 35h, t=140-148°C)	4.055	9.843	0.4

Where, PLA1 is products of LA polycondensation using powder Sn catalyst and Sn/TiO₂ with the same ratio of catalyst:LA of 1%.

M_n, M_w and n of PLA1 using powder Sn catalyst are 11,901, 39,320 and 0.3, respectively, are higher than those of PLA2 which using Sn/TiO₂ catalyst (4,055, 9,843 and 0.4). This can be explained that the dispersion of active Sn sites on carrier material were more active and regular in the reaction solvent mixture, the polycondensation rate will be slower to support the suitable condition for the formation of oligomer occurred simultaneously. Consequence, the distribution of polymer chains in the PLA is more regularly.

The polymerisation rate occurred and molecular weight of PLA product increased formed relatively fast but the chain distribution in PLA are not regular in the case of using powder metallic Sn catalyst. Therefore, the molecular weight distribution n is smaller than those in the case of Sn/TiO₂ catalyst. If the distribution of molecular weight n closer 1, PLA polymer will have higher physico-mechanically persistence and durable.

According to the literature [24] Slawonmir produced PLA with M_n of 2.6x10⁴ to 4.0x10⁴ from LA in the pure p-xylene solvent. But in this work we used the industrial xylene solvent so PLA achieved M_n of only 1.1x10⁴. This can be improved when the polycondensation of LA is applied in the pure p-xylene.

CONCLUSION

- The research carried out the investigation of Sn on carrier such as active charcoal and TiO₂ on the poly condensation reaction from l-lactic acid. Sn immobilized on carriers decreased the polycondensation reaction rate in comparison of Powder Sn catalyst. Sn immobilized on none-capillary TiO₂ carrier catalyst give the higher polycondensation reaction efficiency then Sn immobilized on medium-capillary catalyst with the same reaction time. However, the longer reaction time, Sn on capillary carrier catalyst can give the higher melting point of the PLA product. This means PLA has the higher molecular weight in average weight (M_w).
- Content of Sn in the catalysts are investigated in the L-lactic acid polycondensation reaction. In the beginning the higher content of Sn catalyst advantaged the polycondensation reaction but it will give the lower M_w. This can be presented in the lower melting point.

- Reaction order of the Sn catalyst in the L-lactic acid (LLA) polycondensation reaction was determined with the value of 3/2. The higher content of Sn the higher reaction efficiency and consequence of higher reaction rate. The longer reaction time the melting point of PLA products will have the similar value.
- H^+ concentration in the LLA exposed longer time in the air is decreased due to LLA participated in the esterisation reaction to produce lactides and lactoyllactic acids (opened chain dime), especially drying condition (higher LLA concentration). Consequence, polycondensation reaction is decreased.
- Suggestion of two hypotheses of Sn catalyst roles in the mechanisms of the polycondensation, possibly a Lewis acid or reaction with acid to produce lactate.
- The difference of M_n and M_w of PLA1 and PLA2 using Sn and Sn/TiO₂ catalysts can be explained based on the roles of powder Sn and Sn/TiO₂ catalysts. Molecular weights in average number and in average weight (M_n and M_w) of PLA products were determined with the values of 11,901 and 39,320 and they can be used in the production of semi-finished articles and final products such as cast profiles, foils, packaging, and fibers.

REFERENCES

1. Sang Y.Lee, Soon H. Hong, Seung H.Lee, Si J.Park (2004), "Fermentative Production of Building Blocks for Chemical Synthesis", *Macromol, Biosci*, pp.157-164.
2. Slawomir Dutkiewicz, Dienla.Grochowska lapienis, Wailaw Tomas Zewski (2003), "Synthesis of poly(LCT) lactic by Polycondensation Method in Solution", *Fibers & Textiles in Eastern Europe*, Vol. 11, No 4, pp. 60 – 70.
3. Williams, Chorlottek, Laurie.F, Choi Sun Kyung, Nam, Wonwoo, Tolman (2003), "A highly active zinc catalyst for the controlled polymerization of lactide", *J. AM. Chem. Soc*, Vol 125, pp. 11350 – 11359.
4. Zhiyuan Zhong, Piter J. Dijkstra, and Jan Feijen (2003), "Controlled and Stereoselective polymerization of lactide kinetics, Selectivity and Microstructures". *J. AM. Chem. Soc*, Vol 125, pp. 11291 – 11298.
5. Jukka Tuomien (2003), "Chain linked lactic acid polymers polymerization anih biodegradation", *Polymer technology Publication*, Series.No.25.
6. Mc Guinness, Davids, Marrall, Eward.L, gibson, Steed (2003), "Anionic Iron(II) alkoxides as initiators for the controlled ROP of lactide". *J.AM.Chem.Soc*, Vol. 41, pp. 3498 – 3803
7. Youngjo Kim, G.K. Jnaeshwara, John G.Verkaide (2003), "Titanium alkoxides initiators for the controlled polymerzation of laciide", *Inorganic chemistry*, Vol 45, No 5, pp. 1437 -1447.
8. O'Brien, Micheal and Gray, Genifer, "Federal trade commission Annouces Men Fiber Generic: Cargill Dow's Natureworks TM fibers Receive Fist designation of the century" Internet (2002) Available [March 2002] <http://www.cargilldow.com>
9. Ricard Gattin, Alain Copinet, Celine Bertrand and Yces Couturier (January 2001), "Comparative biodegradation study of starch and polylactic acid basedmaterials", *Journal of polymer and the Environment*, Vol. 9, No.1, pp.11 – 17.
10. Ray E. Drumright, Patrick R. Gruber, and David E. Henton (2000), "Polylactic acid Technology", *Advance Materials*, 12, No 23, pp. 1841-1845.
11. "Ullmann's Encyclopedia of Industrial Chemistry" (2000), CD.
12. Harper, Charles A (2000), *Modern Plastic Handbook*, New York: Mc Graw-Hill.
13. Uhrich, K.E; Cannizzaro, S.M; Langer, R.S; Sakesheff, K.M (1999), *Chem.ReV*, 99, pp.3181- 3198.
14. James Lunt (1997), "Large-scale production, properties and commercial applications of polylactic acid polymers", *Polymer Degration and Stability*, Vol 59, pp. 145-152.
15. Loontjens. T, Pauwels. K, Derks. F, Neilen. M (1997), "The action of chain extenders reaction in nylon-6, PET and model compounds". *J. Appl. Polym. Sci*, Vol 65, pp.1813 – 1819.

16. Inata.H and Matsumura.S (1995), "Chain extender for polyesters.I.addition – type chain extenders reactive with carboxyl end groups of polyesters", *J. APPL polymer. Sci*, Vol 30, pp. 3325 – 3337.
17. Lanza. R. P; Langer. R; Vacanti. J, "Principles of tissue Engineering"; *Academic Press*, pp. 1292 – 1301.
18. Mclain, SteveJ, Ford, Thomas M. Drysdale, Jones, Mancy (1994), "ROP of lactice by Yttrium and lanthanum complexes". *J. AM. Chem. Soc, Division of polymer chemistry*, Vol 35, pp. 534 – 540.
19. Carothers, W.Dorough, and Van Natta.F (1932), "Studies on polymerization and ring Formation.X.The reversible polymersation of six membered cyclic esters", *J. Am. Chem. Soc.*, Vol. 51, pp. 761 – 772.