

Effect of Polycondensation Temperature to Oligomer Yield and Depolymerisation Side Reaction

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ABSTRACT

Ring-opening polymerization reaction is the best method for producing high molecular weight polymers. The stage of manufacture of PLA from lactic acid through the lactide ring opening reaction is carried out through three stages of the process ie poly-condensation, depolymerization and polymerization. The polycondensation stage of lactic acid is the stage of oligomer formation. At the poly-condensation stage, the oligomeric molecular weight is determined by the temperature, pressure, type and concentration of the catalyst used. The purpose of this research was to obtain the effect of poly-condensation temperature without catalyst on oligomer recovery and side reactions of depolymerization. Poly-condensation is done by pretreatment of lactic acid at 120°C for 1 hour. After that, the heating lactic acid at varying temperature. OLLA yield at poly-condensation temperature 150; 180; 200°C for 4 h and gradually (at 150 °C for 2 h and 180°C for 2 h) were 96.33; 85.36; 82.13 and 88.37% respectively. The higher poly-condensation temperature, the intramolecular interactions of the molecule as a side reaction was increasing.

Keywords: lactic acid, lactide, oligomer, poly-condensation, depolymerisation

1. INTRODUCTION

Poly lactic acid (PLA) is a biocompatible, biodegradable, non-toxic polymer and derived from renewable resources (Tsukegi et al., 2007; Huang et al., 2014). PLA can be obtained from lactic acid derived from sugar, starch and cellulose. PLA has been widely used for various applications, especially in the field of biomedicine and food packaging. In the field of biomedicine, PLA is used as a sewing thread for surgical operation and capsule wrapping materials for drug delivery systems as well as repair of human tissue (a place where the growth of new cell growth). In the field of food packaging, PLA is used for food wrapping and edible films for vegetables and fruits (Madhavan Nampoothiri et al., 2010, Kamel et al., 2011).

PLA applications in the biomedical are highly determined by the molecular weight of the PLA. Molecular weight is a factor that greatly influences the nature of the polymer in the form of decomposition,

mechanical strength and crystallinity (Garlotta, 2001). High-molecular-weight PLAs (> 100,000) are used as orthopedic implant materials. Low-molecular-weight PLAs ranging from 2000-3000 and low melting temperatures are used as capsule wrapping materials for drug delivery systems (Choubisa et al., 2013). Wichert and Rohdewald (1993) used PLA with molecular weight of 2000 g/mol as a polymer material in the manufacture of microencapsules. Andreopoulos et al., (2000) used PLA with molecular weight 2000-20.000 gr/mol as an antibiotic release system (Savioli et al., 2012).

Commercial PLA preparation is generally through the lactic acid poly-condensation method and the lactide ring opening polymerization. The poly-condensation method produces low molecular weight oligomers (MW <5000) and side reactions occur, such as transesterification forming ring structures as lactides. This side reaction has a negative effect on the quality of the resulting PLA (Lopes & Jardini, 2012). Ring-opening

polymerization reactions are the best method for producing high molecular weight polymers. The stage of manufacture of PLA from lactic acid through the lactide ring opening reaction is carried out through three stages of the process i.e. polycondensation, depolymerization and polymerization. The three stages of this process determine the yield and weight of the resulting PLA molecule. The polycondensation stage of lactic acid is the stage of oligomer formation. At the polycondensation stage, the oligomeric molecular weight is determined by the temperature, pressure, type and concentration of the catalyst used (Achmad et al., 2009). The manufacture of PLA through ring opening polymerization of lactide generally uses metal catalysts such as zinc oxide (Zn) and tin (Sn). The disadvantages of using metal catalysts are the contamination of polymer products by which metals are used so that when products are used for biomedical applications and food may be harmful to health (Yu et al., 2004). The US Food and Drug Administration (US-FDA) has set a maximum allowable tin limit in commercial products and for medical needs of 20 ppm. In the ring-opening reaction, the reduction of the tin catalyst is not possible because of the tin function as the initiator of the reaction (Stjerndahl et al., 2008).

Based on the description above, in this research will be explained the influence of polycondensation temperature of lactic acid without using catalyst to yield oligomer and side reaction of depolymerization.

2. LITERATURE REVIEW

Lactic acid polycondensation is a simple process for producing PLA. The presence of hydroxyl function groups (-OH) and carbonyl (-COOH) in lactic acid, results in esterification reactions due to intermolecular and intramolecular interactions. Intermolecular interactions enable the formation of dimers, trimers and oligomers by the condensation reaction of lactic acid and produce water molecules (H₂O), as shown in Fig. 1. This lactic acid dimer is often referred to as lactic acid lactate (Groot et al., 2010). Intramolecular interactions may result in deformation by the condensation reaction in the lactic acid lactate molecule. The product resulting from the intramolecular interaction of lactic acid lactate is lactide which also has different enantiomer types.

The esterification reaction due to intermolecular interaction is an equilibrium reaction so that the water molecules formed must be removed in order to favor the polycondensation reaction to the right side (Sinclair et al., 1993). The imperfection of removal of water molecules will cause the hydrolysis of the PLA formed. Water in the feed needs to be removed by evaporation at temperatures above the boiling point of water and atmospheric pressure. After the evaporation stage, an oligomerization stage is performed. At this stage, lactic acid undergoes a polycondensation reaction into a low molecular weight lactic acid (PLA) acid. This stage does

not require a solid catalyst because the acidic feed can be act as catalyst for the polycondensation reaction. Low molecular weight oligomers or PLAs can be produced from simple systems in stirred reactors combined with heating and condensers (Maharana et al., 2009).

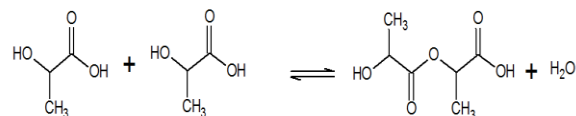


Fig. 1. Polycondensation reaction of lactic acid

Depolymerization of lactic acid oligomers is a cyclic diester forming reaction. Masaki & Okuyama (1999) studied the effect of different metal catalysts in thermal catalytic depolymerization of lactic acid oligomers to produce L-lactide. The formation of lactide involves back-biting and end-biting reactions. Back-biting reactions are also called transesterification reactions that refer to the formation of cyclic compounds (lactides). The formation of lactide occurs by an intramolecular reaction between the carboxylate group at the end chain and the ester bond in the first group chain in the PLA, as shown in Fig. 2. The end-biting reaction is a ring closure reaction of the oligomer dimer chain. Back-biting reactions produce cyclic and linear and end-biting compounds produce cyclic and water (Sinclair, 1993). Both of these reactions are equilibrium reaction that highly influenced by temperature, so that appropriate operating conditions are required for the reaction to go to the right.

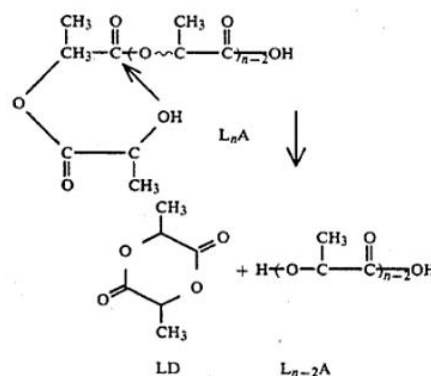


Fig. 2. Back-biting reaction to lactide synthesis (Sinclair, 1993)

3. RESEARCH METHODOLOGY

This research was conducted at Chemical Engineering Operations Laboratory of Universitas Sultan Ageng Tirtayasa. The materials and procedures are described in this section.

3.1 Materials and Tools

The materials used in the study of the preparation of lactic acid oligomers are listed in Table 1.

Table 1. Material of oligomer synthesis

No.	material
1.	Lactic acid with a purity of 90% from PT. Merck, Indonesia
2.	Nitrogen from PT. Windu Prasetya Manunggal, Cilegon, Indonesia

The equipment used during the preparation of lactic acid oligomers is shown in Table 2.

Table 2. Tools used in the synthesis of oligomers

No.	Tools	No.	Tools
1.	Four neck flask, 500 ml	6.	Magnetic stirrer
2.	Threaded condenser	7.	Condensate container
3.	Water trap	8.	Thermometer
4.	Hotplate	9.	Circulation pump
5.	Erlenmeyer		

3.2 Arrangement of equipment

Arrangement of research equipment is shown Fig. 3.

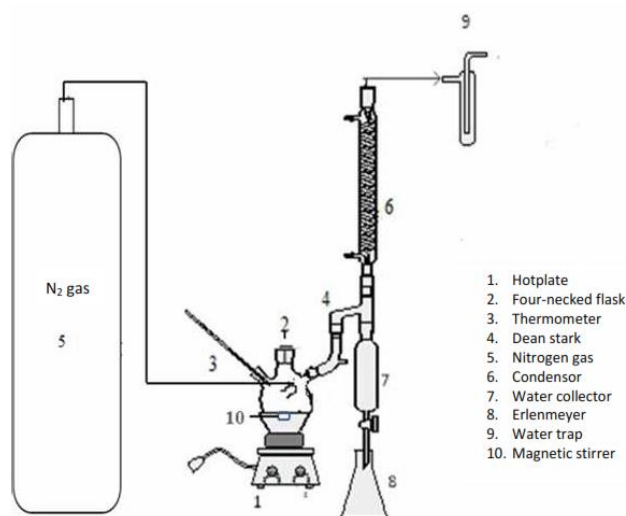


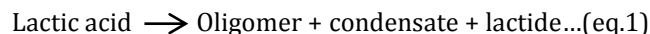
Fig. 3. Arrangement of equipment

3.3 Procedure

L-lactic acid (50 ml) was put in a four-necked flask equipped with a magnetic stirrer, a temperature controller, and a condenser, which was connected to a collector distilled. The reaction was carried out at 120°C for 1 h with continuous nitrogen gas flow to push evaporative water into the condenser. Afterwards, the oligomerization stage held at 150°C for 4 h, 180°C for 4 h and gradually at 150°C for 2 h and at 180°C for 2 h without nitrogen gas flow.

4. RESULTS AND DISCUSSION

The poly-condensation stage is the stage of bond of lactic acid molecules into larger molecules (oligomers) in the presence of heat. At the polycondensation stage an oligomer (OLLA), condensate and polycondensation temperature > 180°C will form a small amount of lactide.



The OLLA yield produced in the polycondensation temperature variation is calculated using Eq.2.

$$\text{Yield of OLLA} = \frac{\text{weight of OLLA}}{\text{lactic acid weight (theoritis)}} \times 100\% \dots \text{(eq.2)}$$

The calculation results show that the yield of OLLA at polycondensation temperature 150, 180, 200°C and gradually were 96,33; 85,36; 82,13 and 88,47% respectively, as shown in Figure 4.

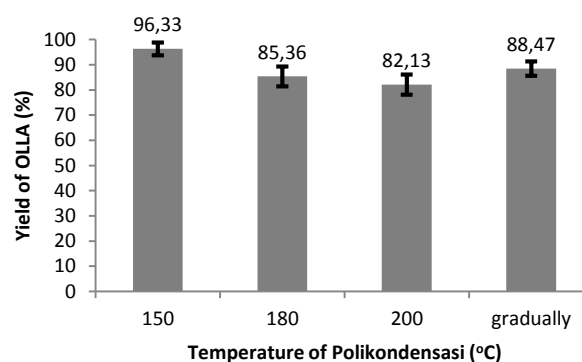


Fig. 4. Yield of oligomers in poly-condensation temperature variations

Decreased yield of OLLA along with increasing poly-condensation temperature due to the presence of lactic acid that is evaporated with water and other components and the occurrence of intramolecular interactions during the condensation process. At high temperatures lactic acid will react quickly to extend the bond, but high temperatures cause unreacted lactic acid to evaporate. At a pressure of 1 atm the boiling point of lactic acid at a temperature of 217°C (Upare et al., 2012). In this study polyc-ondensation takes place at a temperature of 150; 180; 200°C and 150-180°C and a pressure of 1 atm so that lactic acid may be evaporate with water and found in the condensate. Difference of Poly-condensation temperature produce different condensate volumes, as shown in Figure 5. The higher the poly-condensation temperature, the higher the amount of condensate produced.

The weight measurement of the condensate volume is performed to determine whether or not lactic acid is involved. The result of the measurement shows that condensate density exceeds water density and less than lactic acid density (1.224 g/ml at 20°C). From these measurements, the presence of lactic acid in small amounts is evaporated during the oligomer formation stage. In this study, condensate which is a mixture of

water and lactic acid, was not separated and processed, but directly discharged into the environment. Lactic acid is a decomposable and non-toxic compound and is very small in condensate, so it does not harm the environment.

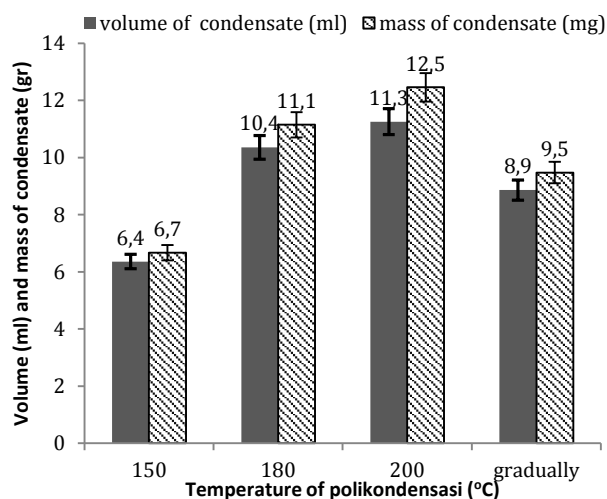


Fig. 5. Volume and mass of condensate for proses poly-condensation process with temperature variation

Intramolecular interactions occur during high-temperature poly-condensation. Groot et al., (2010) states that lactic acid molecules having hydroxyl functional groups (-OH) and carboxylic acids (-COOH) undergo esterification reactions due to inter- and intramolecular interactions, as shown in Figure 4.11. Intermolecular interactions of lactic acid molecules at the poly-condensation stage cause the formation of dimers, trimers and oligomers and produce water molecules (H₂O). In intramolecular interaction there will be a change in the form of lactic acid dimer into lactide. The intramolecular interaction is caused by the thermal degradation of lactic acid oligomers into short chain or lactid molecules (Achmad et al., 2009).

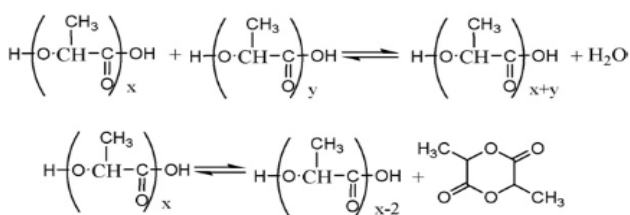


Fig. 6. Dua reaksi yang terlibat dalam polikondensasi (Maharana et al., 2009)

The intramolecular interactions in this study were seen with the formation of white powder (lactide) attached to the reactor connecting pipe wall (four neck flask) and the condenser and the condenser wall, as shown in Figure 6. At the temperature of poly-condensation 150°C there is no white lactide powder, but there is a small amount of glass-shaped crystals attached to the connecting pipe between the four-neck flask and the condenser. At a gradual temperature,

180°C and 200°C are formed of small amounts of lactide attached to the condenser during the poly-condensation process. The formation of lactide as a byproduct of this poly-condensation leads to reduced yield of OLLA.

The weight of lactide formed during the intramolecular interaction of molecules is very difficult to measure. This is because the amount of lactide attached to the wall of the reactor connecting pipes with the condenser and on the condenser thread. The weight of the lactide is estimated by calculating the difference between the weight of the initial reactant with the OLLA and the condensate formed.

Based on the calculation results obtained that the higher temperature poly-condensation, molecular intramolecular interaction as a side reaction is increasing, as shown in Figure 7. The intramolecular interactions of molecules or back biting reactions usually occur at temperatures above 180°C (Yang & Liu, 2008). Similar results are also reported by Achmad et al. (2009), that the higher the poly-condensation temperature the lower the yield of the polymer product, the higher the condensate and yield of the lactides being produced.

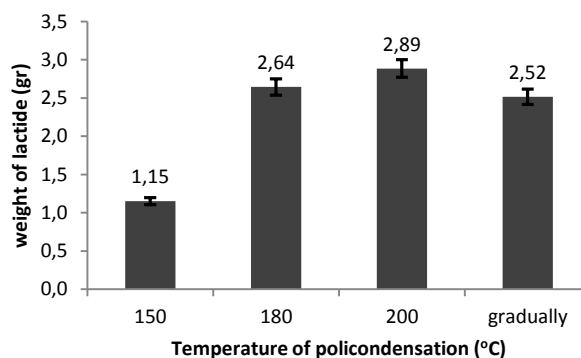


Fig. 7. Lactide production for poly-condensation step with temperature variation

Material balance at poly-condensation step with temperature variation was shown in Table 3.

Table 3. Material balance at poly-condensation step

Compound	Input		Output (150°C)		Output (180°C)		Output (200°C)		Output (bertahap)	
	gr	mol	gr	mol	gr	mol	gr	mol	gr	mol
Lactide acid	53,10	0,59	0,80	0,01	5,20	0,06	6,60	0,07	3,60	0,04
H ₂ O	5,90	0,33	5,90	0,33	5,90	0,33	5,90	0,33	5,90	0,33
OLLA	-	-	51,15	0,14	45,33	0,05	43,62	0,03	46,98	0,02
lactide	-	-	1,15	0,01	2,64	0,02	2,88	0,02	2,52	0,02
Total	59,00	0,92	59,00	0,49	59,07	0,46	59,00	0,45	59,00	0,41

4. CONCLUSION

OLLA yield at poly-condensation temperature 150; 180; 200°C for 4 h and gradually (at 150 °C for 2 h and 180°C for 2 h) were 96.33; 85.36; 82.13 and 88.37% respectively. The higher poly-condensation temperature, the intramolecular interactions of the molecule as a side reaction was increasing. The highest lactides are

produced as a side reaction at a poly-condensation temperature of 200°C.

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