Microwave-Assisted Synthesis of Polylactic Acid-diol for Polyurethane as Biodegradable Packaging Material

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Abstract. Since its discovery, plastic has been a part of human life and is widely employed in our daily lives. Excessive use of plastic has raised pollution rates around the world, with plastic ending up in landfills or the sea, posing a threat to both terrestrial and aquatic life. Considering this problem, the widespread use of polyurethanes (PUs) in many industries has resulted in unavoidable PUs pollution in everyday life. A reaction involving prepolymer, isocyanate, and polyol can be used to make PUs. Petroleum-based polyl and vegetable oil-based polyl are the two types of polyls available. Isocyanate will become the hard domain of the polymer in the PUs polymer chain, while polyol will become the soft domain. Polyactic acid-diol is the prepolymer used to make PU (PLA-diol). PLA-diol was previously made using a traditional heating approach, which takes a long time. To overcome this traditional method, microwave-assisted synthesis is proposed to synthesize the PLA-diol. The synthesis process involved synthesizing PLA-diol at different microwave power (450W – 900W) and at different reaction time (1 hour – 2 hours). The peak of hydroxyl group in synthesized PLA-diol was characterized via the Fourier Transform Infrared Spectroscopy (FTIR) characterization to determine the functional groups of PLA-diol and gel permeation chromatography (GPC) characterization was done to determine the molecular weight of PLA-diol. The resulting PLA-diol will then be used to synthesis biodegradable PUs in the subsequence study.

1. Introduction
Polyurethanes (PUs) is one of the most consumed and used plastic in the world. According to statistic, 18 million tons of PUs are produced in 2016 [1]. In fact, in 2020, PU production is expected to reach 22 million tons [2]. PU is a polymer consists of organic units, combined by carbamates (urethanes) links. PU polymers are the resulting product of a step growth polymerization reaction between an isocyanates and alcohol [3]. Isocyanates can be in the form of di-isocyanates or poly-isocyanates whereas alcohol can be in the form of a diol or macro-diol. The resulting reaction between these two together with a chain extender will produce PU with a soft segment and a hard segment, where polyol as the soft segment and isocyanate as the hard segment.
Biopolymers such as polylactic acid (PLA), cellulose and polyhydroxybutyrate (PHB) have been used in producing polymers. PLA specifically has become center of interest in producing PU. PLA are used as the diol in PU synthesis. PLA can be polymerized from its monomer which is lactic acid (LA) through polycondensation and ring opening polymerization. PLA polymerized from polycondensation method typically will have low molecular weight whereas PLA polymerized from ring opening polymerization (ROP) method will have high molecular weight [4]. ROP allows higher control of polymerization hence remains as the most widely used polymerization method for synthesis of well-defined materials [5].

To obtain PLA diol, polycondensation of LA can be done in two different ways, which are through conventional heating method and microwave-assisted heating method. In conventional heating method, the heating time required to achieve reaction temperature is lengthy. As reported by Bakibaev et al., through conventional method, polycondensation require up to 16 hours of time for the process to be completed with 160°C reaction temperature [6]. Another study done by Ismail et al., 6 hours reflux time was needed to obtain PLA diol [7].

Microwave-assisted polymerization is one of the suggested alternatives to replace conventional heating method. Despite of being newly studied, microwave-assisted polymerization shows promising results of synthesizing PLA diol. By using microwave-assisted method, Bakibaev and his team manage to synthesis PLA diol at 350W microwave power with only 10 minutes reaction time [6]. In another microwave-assisted single-step polycondensation of LA, PLA diol with weight-average molecular weight of 1800 Da were produced after being irradiated with 40W microwave power, at reaction temperature of 200°C and with 30 minutes of reaction time [8]. These two studies proved that microwave-assisted polymerization of LA is possible to be done and the reaction time is significantly reduced.

Microwave irradiation is defined as radiation having a frequency ranging from 0.3 to 300 GHz. Most synthetic and home microwaves are built to function in frequencies between 2 GHz and 8 GHz to prevent interference with contemporary telecommunication and radar systems, with residential microwaves commonly operating at 2.45 GHz. [9]. To fulfil the research needs, microwave instrumentation suppliers have moved towards combinatorial or high throughput medium governs by two philosophies. These two philosophies are the actual type of the microwave itself, known as single mode (monomode) and multimode microwave reactors. Microwave heating mechanism is based on dielectric heating [10], [11]. Dielectric heating can be defined as the ability of some polar substances (liquids and solids) to absorb and convert microwave irradiation into heat [10]. The ability of these materials is closely associated with its dielectric properties and can be determined using loss tangent, tan δ which can be expressed in quotient $\tan \delta = \varepsilon' / \varepsilon''$. The dielectric loss, denote as $\varepsilon''$ indicates the efficiency in which electromagnetic is converted into heat whereas dielectric constant ($\varepsilon'$) indicates the ability of molecules to be polarized by the electric field, allowing reasonable amount of energy to be absorbed. Therefore, to obtain high absorption efficiency for fast heating, a reaction medium with high tan δ value is needed. However, the value of $\varepsilon''$ should be taken into consideration too since high tan δ value does not necessarily means the substances would allow reasonable energy absorption since it is depending on $\varepsilon'$ value.

Conventional method of producing PLA-diol requires production time up to 6 hours. Therefore, a new method which is microwave assisted synthesis of PLA-diol will be introduced in this study. The hypothesis is that by using microwave irradiation, less time will be needed to activate the reaction in PLA-diol synthesis. If this method shows a promising future, the conventional method of synthesizing PLA-diol can be replaced with a more versatile and shorter production time method.

### 2. Experimental Procedures

#### 2.1. Material & Instrumentation

**2.1.1. Material.** L-lactide (98%), 1,4-butanediol (99%), stannous octoate (95%), and dichloromethane (99%) were purchased from Sigma Aldrich. Toluene (99.8%) were used as the solvent in the reaction
whereas methanol was used as it is in the purification process. Both toluene and methanol are from analytical grade and were used as is.

2.1.2. **Instrumentation.** The microwave used in the polymerization experiment was a modified domestic microwave oven, SAMSUNG MC455THRCRSR (2450 MHz, 900W), with different power level (100W – 900W). The microwave was modified so that a 250 mL three neck flask, an overhead stirrer, a reflux condenser, and a nitrogen gas flow system could be introduced into the cavity of the microwave oven where appropriate additional safety steps were taken to avoid radiations leakages.

2.2. **Synthesis of PLA-diol via Microwave assisted synthesis**

Prior to experiment, an adequate amount of L-lactide was dried in vacuum oven at 45°C for a few hours to remove existing moisture. 1g of L-lactide (6.94 x 10^3 mol) was mixed with 42 mL anhydrous toluene in a 250mL three-neck round bottom flask. The mixture was purged with nitrogen gas for a few minutes. Next, 1,4-butandiol (4.16 x 10^4 mol) was added to the mixture while still being purged by nitrogen gas. Finally, stannous octoate (3.47 x 10^5 mol) was added into the mixture. After that, the flask was placed into microwave oven cavity. The flask was securely connected to an overhead stirrer, a reflux condenser, and a nitrogen gas flow system. All the connections were checked to be secured and safe before operating the microwave synthesizer. The microwave synthesizer was operated at 450W for 2 hours. After reaction completed, the solvent was removed via separation process. The product was dissolved in dichloromethane and then precipitated in methanol. The remaining moisture in the precipitate was removed by vacuum oven, yielding white powder. The experiment was repeated with different microwave operating conditions so that an optimum condition could be identified. Figure 1 illustrated the schematic of the experimental procedure.

![Figure 1. Synthesis pathway and the experimental set up of the experiment.](image)

2.3. **Characterization**

The resulting PLA-diol samples were characterized for gel permeation chromatography (GPC) to determine its molecular weight. During GPC analysis, the elution phase was tetrahydrofuran (THF) and was calibrated with polystyrene standard. The peak of hydroxyl group in PLA-diol was characterized by Fourier Transform Infrared Spectroscopy (FTIR) spectra, taken at 650 cm\(^{-1}\) – 4000 cm\(^{-1}\) spectral resolution.
3. Results and discussion

3.1. Microwave-assisted synthesis of PLA-diol optimization
PLA diol was synthesized via microwave-assisted synthesis at different microwave power and reaction time to find optimum synthesis reaction condition. Table 1 illustrates the optimization runs done during the experiment and the resulting PLA diol obtained in weight.

| Microwave Power (W) | Reaction time (mins) | Weight (g) |
|---------------------|----------------------|------------|
| 600                 | 45                   | N/A        |
|                     | 60                   | N/A        |
|                     | 90                   | 0.54       |
|                     | 120                  | 0.65       |
| 900                 | 45                   | 0.52       |
|                     | 60                   | 0.93       |
|                     | 90                   | 1.21       |
|                     | 120                  | 0.19       |

The weight from reactions from 600W at 45 minutes and 60 minutes could not be computed because the samples were dissolved in methanol during precipitation process which means PLA-diol did not form. From the resulting PLA-diol weight, it can be said that PLA-diol was successfully synthesized via microwave-assisted synthesis starting from 600W at 90 minutes. On the other hands, it clearly showed that when reacted at 900W for 90 minutes, the weight of PLA-diol produced was the highest. However, when reacted at 900W for 120 minutes, the weight of PLA-diol produced was the least among all runs. The weight of PLA-diol produced at 120 minutes, 900W power was lost due to extensive evaporation of water molecule and intensified polycondensation process [12]. Therefore, it can be concluded that the reaction between l-lactide, 1,4-butanediol and stannous octoate was at optimum condition when reacted at 900W for 90 minutes. Figure 2 shows the relation between microwave power, reaction time and weight of PLA-diol produced.

Figure 2. The relation between the weight of PLA-diol produced with microwave power and reaction time.

Figure 3 shows GPC chromatogram. GPC was done on samples for molecular weight determination. The samples were eluted in THF, and the system was calibrated with polystyrene standard. From the chromatogram, the samples showed peaks at the retention time of 28 minutes.
3.3. Fourier Transfer Infrared Spectroscopy (FTIR)

Figure 4 shows FTIR spectra for PLA-diol synthesized via microwave-assisted synthesis method. The broad peak of hydroxyl group of PLA-diol produced can be observed at 3500 cm\(^{-1}\). A similar peak for PLA-diol was reported by previous studies [7], [13]–[15]. This high hydroxyl absorption peak is expected to disappear when reacted with isocyanate in polyurethane synthesis. [7], [13]. The peak at 2995 cm\(^{-1}\) indicated -CH\(_3\) end groups and the peak at 1759 cm\(^{-1}\) indicated C=O end groups. A similar finding was reported by Luo et al., [16]. From the FTIR spectra, it can be concluded that PLA-diol was successfully synthesized via microwave-assisted synthesis.

Figure 4. FTIR spectra for PLA-diol synthesized via microwave-assisted synthesis method.

4. Conclusion

PLA-diol from reaction between 1-lactide, 1,4-butanediol and stannous octoate was successfully synthesized via microwave-assisted synthesis method. From the optimization process, it was found that to achieve maximum amount of PLA-diol synthesized, the reaction should take place at 900W for 90 minutes reaction time, compared to 6 hours of reaction time of synthesis via conventional method. This showed a great reaction time reduction. GPC chromatogram showed the produced PLA-diol was able to
separate and showing peaks at 28 minutes retention time. On the other hands, FTIR spectra confirmed the formation of PLA-diol by showing broad hydroxyl group at 3500 cm⁻¹. In conclusion, PLA-diol was able to be synthesized via newly studied method, known as microwave-assisted synthesis. This also concluded that, even with modified domestic microwave oven, synthesis process could be carried out when appropriate safety measures were taken into consideration.

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