Uncatalysed Polycondensation of Lactic Acid to Polylactic Acid Under Microwave Irradiation: Effect of Microwave Power

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Abstract. In this study, polycondensation of 88wt% lactic acid (LA) was performed by irradiating LA with microwave at different powers (P=250, 440, 715 and 900W) for 5 min, in the absence of a catalyst. The recovered products were analysed by attenuated total reflectance-infrared (ATR-IR) and thermogravimetric analysis (TGA). It was found that raising microwave power resulted in a significant increase in mass loss, even much higher than the water content of the fresh LA (12wt%). Such an observation was likely to be caused by two occurrences. The first is associated with the evaporation of 12wt% of water molecules in the fresh LA that escalated upon increasing microwave power. This is supported by ATR-IR analysis illustrating a decreasing trend in the intensity of O-H stretching band. The second is linked to the intensified polycondensation of LA to polylactic acid (PLA) when elevating microwave power, forming more ester bonds and consequently eliminating more water molecules. The increased formation ester bonds was evidenced by the shift in T_onset values towards higher temperatures, as exhibited by TGA profiles. As overall, the outcomes of this study could lead to a cost effective and energy saving production of biodegradable plastics, substituting the time-consuming conventional heating.

1. Introduction

Despite their current uses in a wide range of applications, petroleum-derived plastics are known to pose several environmental threats. This had led to the emergence of biodegradable plastics that are more environmental friendly, and the most frequently cited amongst them is polylactic acid (PLA). PLA offers several benefits, including biodegradability, biocompatibility, and high mechanical strength [1]. An emerging application utilising PLA is in 3D-printing, where the polymer is used as the filament for prototyping.

Interestingly, PLA can be synthesized from biomass, a renewable feedstock, through four subsequence steps [2]. The first is the isolation of cellulose biopolymer from biomass via deconstruction.
process [3-5]. The second deals with converting the cellulose biopolymer to glucose via either enzymatic hydrolysis or dilute acid hydrolysis [3, 6]. Production of lactic acid (LC), the monomer of PLA, from glucose is the third step conducted prior to converting of LA to PLA in the final step.

A number of synthesis pathways for converting LA to PLA have been reported in the chemical literature, and one of them is the direct polycondensation [7]. The direct polycondensation is a step-growth polymerization reaction that removes water as the by-product; a proposed mechanism of the reaction can be found elsewhere [8]. The reaction can be accomplished using conventional heating; however, it is a time-consuming process [1, 9]. Unlike the conventional heating, the direct polycondensation assisted by microwave allows the reaction to complete quickly. This is because materials that are susceptible to microwave absorb the resultant electromagnetic energy, causing molecules to vibrate (at 2450 million times per second) and collide. The vibration and collision creates heat for evaporating the molecules [8].

This paper investigates the impact of varying microwave powers on the uncatalysed polycondensation of LA (containing 12wt% of water) to PLA. The reaction was performed in a microwave oven, and the resultant products were analysed by thermogravimetric analysis (TGA) and attenuated total reflectance-infrared (ATR-IR).

2. Methodology

Polycondensation Reaction. In a microwave induction oven, 88wt% lactic acid (LA) (0.048 mole) was irradiated with microwave at a desired power (P = 250, 440, 715 or 900 W) for 5 min. Each reaction was conducted in triplicate. When the period had elapsed, the polycondensation product was dried in an oven at 80°C overnight and then weighed. Equation 1 was applied for determining the percentage of mass recovery.

\[
\% \text{ Mass recovery} = \frac{m_a}{m_b} \times 100\%
\]

Here, \(m_a\): mass of product following the reaction (g), and; \(m_b\): mass of fresh LA used in the reaction (g).

Thermogravimetric Analysis (TGA). Polycondensation products were analysed on a thermogravimetric analyser (Mettler Toledo) under the following conditions: \(\text{N}_2\) gas at a flow rate of 10 mLmin\(^{-1}\), and temperature from 70 to 800°C at a heating rate of 10°Cmin\(^{-1}\).

Attenuated total reflectance-Infrared (ATR-IR). A Perkin Elmer spectrophotometer (p/n Q0315) was employed to characterise polycondensation products. The instrument equipped with a universal ATR sampling accessory with diamond crystals.

3. Results

Mass Recovery/Loss. Masses of polycondensation products, recovered through irradiating the fresh LA with microwave at different powers for 5 min, are shown in Figure 1.
Figure 1. Products recovered following the polycondensation of the fresh LA assisted by microwave at different powers for 5 min. Mass recovery/loss (%) was calculated relative to the initial quantity of the fresh LA used. Error bars are standard deviations of triplicate samples.

The fresh LA contained 12wt% of water, and the reagent was used as received without further purification. Thus, any mass loss up to 12wt% strongly indicates the evaporation of water in the fresh LA. Interestingly, when applied P=400W and above, the mass loss further increased, even much higher than the water content of the fresh LA (Figure 1, dotted line).

**ATR-IR Analysis.** The resultant spectra recorded on the polycondensation products are shown in Figure 2. A broad peak at 3400 cm$^{-1}$, assignable to O-H stretching of water molecules, was pronounced in the fresh LA (Figure 2 (a)). Its intensity decreased in all products (Figure 2 (b)-(e)). Interestingly, the peak attributed to C=O stretching shifted towards higher frequencies in the spectra of the products obtained at P=400W and above (Figure 2 (b)-(e)).
Figure 2. ATR-IR spectra of (a) fresh LA, and the polycondensation products obtained at (b) 250W, (c) 440W, (d) 715W and (e) 900W. The products were obtained through irradiating LA with microwave at desired powers for 5 min.

TGA Analysis. Decomposition profiles of polycondensation products are illustrated in Figure 3.

Figure 3. TGA profiles of polycondensation products obtained through irradiating LA with microwave at different powers for 5 min.
For the fresh LA, its profile exhibited no plateau; the evaporation begun at 70°C and intensified rapidly with elevating the analysis temperature (Figure 3, black line). This is in agreement with that observed by Komesu et al. Surprisingly, raising microwave power enhanced the stability of the products, as evidenced by the increased T\text{onset} values. The stability of the products could thus be ranked as follows: 250W (T\text{onset}=N/A) < 440W = 714W (T\text{onset}=90°C) < 900W (T\text{onset}=100°C).

4. Discussion

In theory, microwave heating mainly relies on two aspects. The first is associated with the susceptibility of the tested sample absorbing electromagnetic energy that is determined by its dielectric constant (\(\varepsilon'\)). The second deals with the strength of electromagnetic energy generated by microwave power. When a liquid sample, possessing a relatively high \(\varepsilon'\), absorbs sufficient strength of electromagnetic energy, intermolecular interactions between the sample’s molecules are disrupted. This in turn forces the molecules to move around and rotate until their dipoles are balanced by electrostatic interactions. The movement and rotation triggers collision, creating friction that generates heat for evaporating the molecules. Water has \(\varepsilon'=80\); the theory, therefore, justifies the success of removing water from the fresh LA irrespective of microwave powers, as observed in Figure 1 and Figure 2.

**Microwave Power of 250W.** From Figure 1 and Figure 2 (b), it can be seen that P=250W removed water the least, far lesser than the water content of the fresh LA (12wt%). Referring to the theory of microwave heating (the explanations described above), it is very likely that the generated electromagnetic energy by P=250W might not be strong enough to disrupt intermolecular H-bonding between water molecules to a maximum level. This in turn generated less heat, abating evaporation of water. Interestingly, despite being the least stable, TGA curve of P=250W (Figure 3, orange line) slightly shifted towards higher temperatures compared to the fresh LA (Figure 3, black line). The shift was believed to be due to the formation of ester bonds via the polycondensation reaction (mechanism shown in Figure 4), yielding PLA oligomers but at a relatively lower concentration. This is further supported by the fact that LA has a \(\varepsilon'\) value of ca. 20; such a moderate value was believed to enable LA to absorb electromagnetic energy generated by P=250W and later initiated the polycondensation reaction.

![Figure 4](image)

**Figure 4.** A likely mechanism of polycondensation of LA to PLA oligomer.

**Microwave Powers of 400W to 900W.** Unlike P=250W, applying P=400W and above removed water from the fresh LA the most (Figures 1 and 2 (b)-(e)). This was believed to be correlated with the aforementioned theory of microwave heating: the higher the microwave power applied (increase in the strength of electromagnetic energy), the more the intermolecular H-bonding between water molecules are disrupted. As a result, heat generation increases that in turn intensifies the removal of water. The most striking finding to emerge from the mass recovery (shown in Figure 1) is that the applied powers also caused further mass loss, even far exceeding the water content in the fresh LA (12wt%) (Figure 1). This is very likely to be due to the intensified polycondensation reaction of LA to PLA oligomers that removed a substantial quantity of water (mechanism is shown Figure 4). It is very unlikely that marked reduction in mass recovery (Figure 1) was due to the degradation of PLA oligomers. This is because PLA has a very low \(\varepsilon'\) value (\(\varepsilon'=3.5\)), like other plastics, such as polypropylene (\(\varepsilon'= 2.1\)) and polyvinylchloride (\(\varepsilon'= 4.0\)). The polymer, therefore, does not susceptible to electromagnetic energy.
The intensified polycondensation was corroborated by ATR-IR and TGA results (Figure 2 and Figure 3, respectively). In ATR-IR, the peak of C=O stretching moved to higher frequencies upon raising microwave power from P=400W to P=900W (Figure 2 (c)-(e)) compared to the fresh LA (Figure 2 (a)). The peak shift is an indicator of the formation of ester bonds. This is justified by normal base values for C=O stretching vibrations for both carboxylic acids and esters, which are 1710 cm\(^{-1}\) and 1735 cm\(^{-1}\), respectively\(^\text{11}\). LA in a concentrated solution, like other carboxylic acids, tends to dimerise with its neighbouring molecules via H-bonding through the carboxyl groups. The dimerization weakens the C=O bond. Meanwhile, in an ester, oxygen bonded to C=O (\(\text{O-C=O}\)) affords electron-withdrawing effect, strengthening the C=O bond. As a result, the frequency of C=O experiencing the inductive effect is slightly higher than that experiencing the dimerization effect. As for TGA profiles, the increased number of ester bonds upon elevating microwave power might have escalated the stability of PLA oligomers; a plausible explanation to the trend observed in TGA results (Figure 3).

5. Conclusion

This study has demonstrated the ability of performing polycondensation of LA to PLA assisted by microwave in the absence of a catalyst. The increase of microwave power was found to result in a higher mass loss mostly likely due to the extensive evaporation of water molecules and the intensified polycondensation reaction. This is confirmed through the analysis of recovered products with ATR-IR and TGA analyses. The former exhibited gradual disappearance O-H stretching bond, while the latter showed the shift in \(T_{\text{onset}}\) values towards higher temperature indicating the increased number of ester bonds.

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