Chemical Recycling of Post-consumer Polylactide Products by Microwave-Assisted Aminolysis with Ethylenediamine

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Abstract: The demand for bioplastics has recently increased as a promising alternative to conventional plastics. Although these materials are degradable, recycling their post-consumer products is considered effective and sustainable, especially by converting them into value-added feedstocks. In this work, a chemical recycling process for polylactide (PLA) by microwave-assisted aminolysis has been developed, employing ethylenediamine (EDA) as a nucleophile to cleave the ester bonds of PLA. The effects of the PLA: EDA feed ratio on the chemical structures and compositions of the aminolyzed PLA oligomers are investigated by ATR-FTIR and ^{1}H-NMR spectroscopy. The product mixture consists of amino-capped lactate sequences of different lengths, *i.e.*, mono-lactate, di-lactate, and poly-lactate. These are classified into two structures: *Structure A* is generated when a single -NH_2 of EDA reacts and attaches to lactate sequences, while *Structure B* is formed when both amine groups react. At a feed content of 5:1, the aminolyzed products consist of 91% *Structure A* content with the shortest length of lactate, as the high EDA effectively enables its -NH_2 groups to compete with each other to convert the ester bonds of PLA. When the feed ratio was increased to 30:1, *Structure B* became a major product at 85%, with a longer length of lactate, due to the deficit of -NH_2 groups in the system. The variation in these reaction parameters enables the synthesis of products with tunable structures for use in specific applications. The developed process is promising for converting PLA waste, with a short reaction time, into starting materials for other value-added products, especially lactide-based polyurethanes.

Keywords: Chemical recycling, PLA, Aminolysis, Microwave-assisted, Circular economy

1. Introduction

Sustainable and eco-friendly plastic products are of interest in various fields or industries. Plastics are used in many products, ranging from general items to high-performance products [1, 2]. The materials' high versatility, excellent properties, lightweight, and high durability have sharply increased their consumption rate [3]. However, the high volume of consumption and mismanagement of the products after use lead to serious environmental problems.

A large amount of plastic waste remains in the ecosystem, causing hazards to creatures and polluting the environment, as they are difficult to digest or degrade [4]. Degradable bioplastics are promising alternatives as they are derived from natural resources, such as starch and sugar, and can be degraded after use. Additionally, carbon emissions are reduced from their production and degradation, compared to conventional plastics derived from fossil resources [5, 6].

Polylactide (PLA) is a widely used degradable and biocompatible thermoplastic because of its good mechanical properties, high transparency, and renewability. This aliphatic polyester is derived from a lactic acid monomer or lactide dimer, in which the monomer is produced from the fermentation of corn, sugarcane, cassava, or other biomass [7]. Although PLA is degradable, it requires industrial compost conditions with degradation times longer than its consumption rate. This may also lead to environmental concerns. Therefore, recycling is an alternative to reducing this waste. Among practical recycling processes, chemical recycling is of interest in converting low-grade, heterogeneous, or unpurified plastic waste to recycled feedstocks with high quality and value comparable to virgin materials [8, 9]. In the chemical recycling reaction, the heating factor is important for depolymerization and affects the chemical structures and yield of the products. Microwave irradiation is a heating technique that shows a high potential for depolymerizing various plastics in chemical recycling processes, providing high production yield within a short reaction time compared to conventional heating methods [10, 11].

In this work, a chemical recycling of PLA is developed *via* aminolysis using ethylenediamine (EDA). A microwave-assisted reaction is employed. The effect of the reaction parameters, such as PLA/EDA feed ratios, temperature, and time, on the chemical structures of the products and the conversion yield is examined. The products are qualitatively and quantitatively characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The efficiency of the aminolysis reactions is described by the lactate sequence's average length and the chemical structures of the product mixture. The hydroxyl and amino-terminated lactate oligomeric products have a high potential for use as starting materials for various value-added polymeric materials, especially bio-based polyurethanes.

2. Methodology

2.1 Materials

Polylactide (PLA 4043D) was purchased from NatureWorks. Ethylenediamine (EDA) (98%), tetrahydrofuran (THF) (≥ 99.9%, AR grade), and D-chloroform ($CDCl_3$) (99.8%, AR grade) were supplied by Sigma Aldrich. All chemicals were used without further purification.

2.2 Aminolysis of PLA

PLA pellets were dried at 60 °C for 24 h in an air oven to eliminate the moisture and prevent hydrolysis side reactions before undergoing all aminolysis reactions. The depolymerization of PLA by aminolysis was conducted on a microwave reactor (Discover SP series, CEM Matthews NC, USA.) using a 2455 MHz frequency and a power of 200 watts. The PLA: EDA feed ratios varied at 30:1, 25:1, 20:1, 10:1, and 5:1 wt/wt. The reaction was performed in an 80 mL tube, heated at a fixed temperature of 180 °C for 10 min and a pressure of 200 psi. The products were then purified by dissolving in THF, precipitating in DI water by gradually dropping, filtering with paper filters under vacuum, and drying in an air oven at 60 °C for 24 h.

2.3 Characterization

The product mixture's average lactate length and chemical structures were determined by ^{1}H-NMR spectroscopy. The spectra were recorded on a 500 MHz ^{1}H NMR spectrometer (Bruker). $CDCl_3$ was used as a solvent. The aminolysis by EDA leads to ester bond breaking, generating one or two hydroxyl end groups. The length of the lactate sequence depends on the degree of the aminolysis reaction, which can be classified as one, two, or more than two repeat units, referred to as mono-lactate, di-lactate, and poly-lactate, respectively, according to their unique

methine proton signals. The average degree of polymerization (DP_{PLA}) value of the lactate sequence was calculated using an end-group analysis through the following equation:

$$DP_{PLA}, unit = \frac{(I_{5.20})}{(I_{4.38}+I_{4.22}+I_{4.42})} \qquad (1)$$

where $I_{5.20}$ represents the integral value of the signal at 5.20 ppm, corresponding to the methine protons in lactate's repeat unit. $I_{4.38}$, $I_{4.22}$, and $I_{4.42}$ represent the integral values of the signals of mono-lactate, di-lactate, and poly-lactate end groups, respectively.
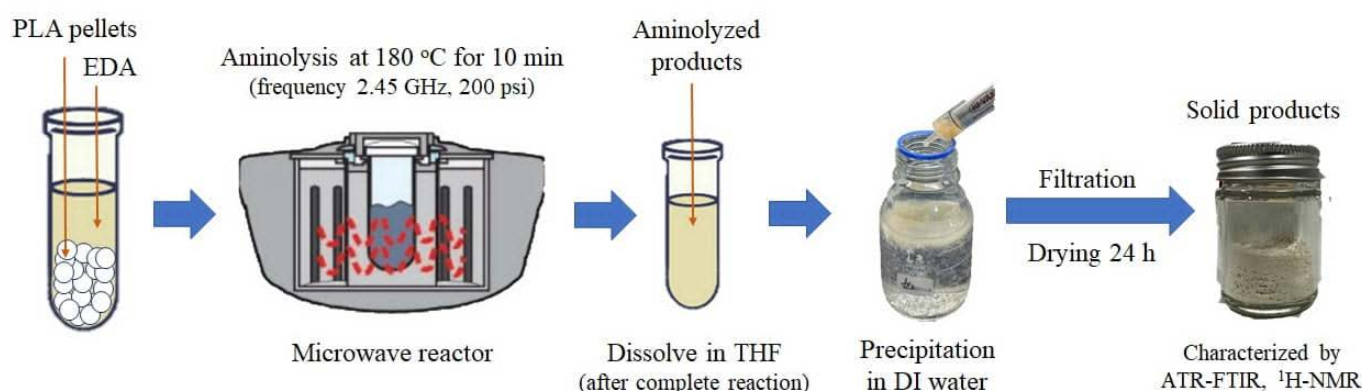
Figure 1 The overall process of the aminolysis of PLA.

The product composition, *i.e.*, the percentages of mono-lactate, di-lactate, and poly-lactate, were calculated using their respective integral values. The signals of methylene protons from EDA units were used to calculate the products' structural compositions. In addition, the chemical structures and functional groups of the aminolyzed PLA products were characterized by Fourier transform infrared (FTIR) spectroscopy in an attenuated total reflectance (ATR) mode on a Nicolet iS5 spectrometer.

3. Results and discussion

Structural Analysis by ^{1}H-NMR Spectroscopy

The chemical structures of the resulting aminolyzed PLA products were characterized by ^{1}H-NMR and FTIR spectroscopy. The aminolysis mechanism of PLA involves the $-NH_2$ group of the diamine reagent (EDA) attacking the ester bonds of PLA by the microwave-assisted reaction, leading to amide linkages. This generates shorter lactate oligomers. The lengths of the lactate sequences vary, and they are classified as mono-lactate, di-lactate, and poly-lactate, depending on the PLA/EDA feed ratio and the reaction time. The products possess a hydroxyl and an amine terminal when only one amine of the diamine reacts. In contrast, the products with two hydroxyl-capped are generated when both amines react and link two lactate sequences. ^{1}H-NMR spectra of the aminolyzed PLA products obtained from the PLA: EDA feed ratios of 30:1, 25:1, 20:1, 10:1, and 5:1 were investigated, as shown in Figure. 2. The signal assignments were adopted from previous studies [12, 13]. The major signals associated with the depolymerization of ester cleavages are the methine signals at hydroxyl terminal units of the aminolyzed PLA products.

The methine proton signals of the aminolyzed PLA products were used to determine their structures and compositions. The signal at 5.20 ppm is due to methine protons in the lactate's in-chain repeat unit. In contrast, the signals at 4.38, 4.22, and 4.42 ppm are assigned to the methine protons of mono-lactate, di-lactate, and poly-lactate end groups, respectively. The increase in the $I_{4.38}/(I_{4.38} + I_{4.22} + I_{4.42})$ relative integrals indicate ester cleavage due to the aminolysis of PLA chains. The average degree of polymerization (DP), calculated by Equation 1 [11, 12], is summarized in Figure 3. The average lactate length (DP) decreased from 11.1 to 0.9, with a decrease in the PLA: EDA feed contents from 30:1 to 5:1, reflecting a higher degree of chain scission. The compositions of mono-lactate, di-lactate, and poly-lactate in the product mixtures are summarized in Figure 4.
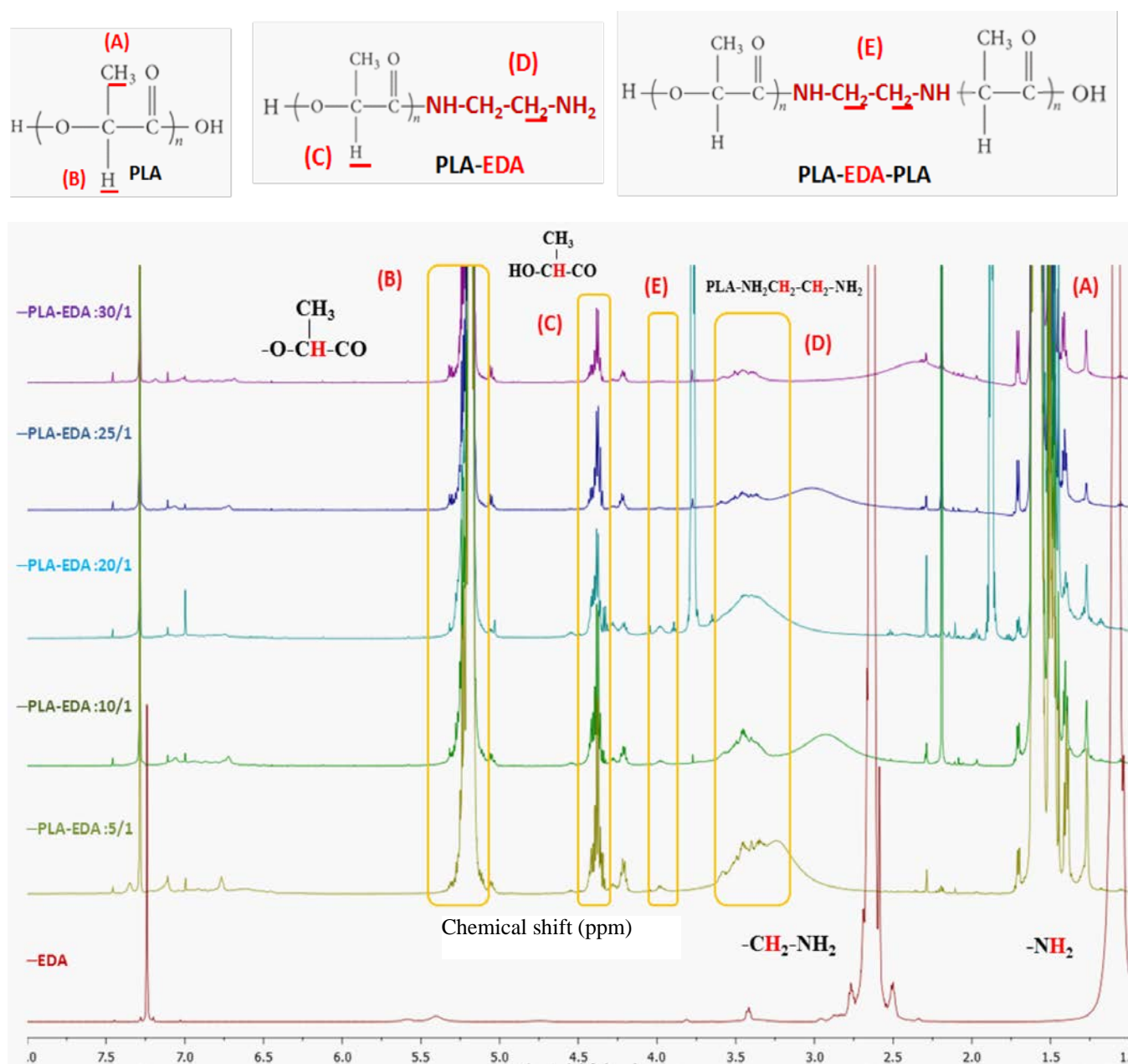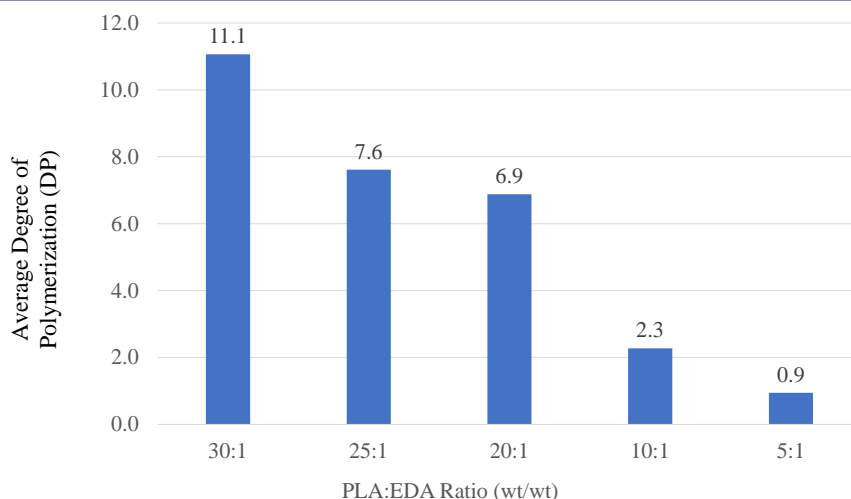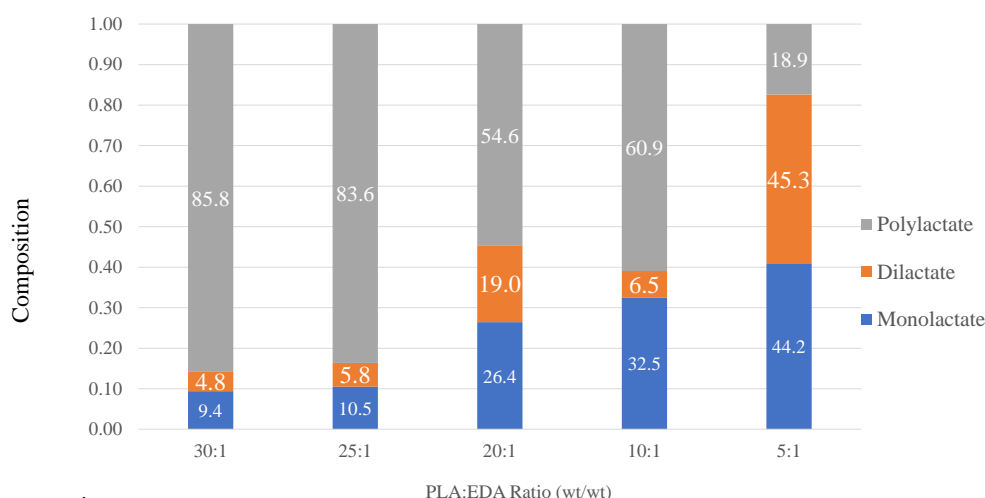

Figure 2 ¹H-NMR spectra and signal assignments of aminolyzed PLA products obtained at different PLA: EDA feed ratios.

Figure 3 The average degree of polymerization (DP) of lactate sequences of aminolyzed PLA products as a function of PLA: EDA feed ratios.


Figure 4 The mono-lactate, di-lactate, and poly-lactate compositions in the product mixtures as a function of PLA: EDA feed ratios.

The aminolysis mechanism of PLA involves $-NH_2$ groups of EDA attacking the ester bonds of PLA, generating amide linkages with shorter lactate sequences containing hydroxyl and amine terminals (OH-PLA-EDA-NH_2), called *Structure A*. When the amine terminal of PLA-EDA competes with EDA to react with the ester of lactate sequences, EDA-cored lactate with two hydroxyl terminals is generated (HO-PLA-EDA-PLA-OH), called *Structure B*. The compositions of these two structures were calculated from ^{1}H-NMR spectra using the methylene proton signals from the EDA structures, as summarized in Figure 5. The signal at 3.98 ppm (D) is associated with *Structure B*, while that at 3.44 ppm (C1) represents *Structure A* [13]. Unreacted EDA showed a methylene signal at 2.60 ppm. All samples exhibited a very weak signal at 2.60 ppm, implying a highly reactive nature of EDA toward PLA's ester bonds. The calculated compositions of *Structure A* and *Structure B* as a function of the PLA: EDA feed ratios are summarized in Figure 6. *Structure A* was a major product (91/9) when a low PLA: EDA feed ratio was employed (5:1). However, when the ratio was increased to 20:1 and 30:1, the content of *Structure B* increased and became higher than *Structure A* (31/69 and 15/85). This is because, at low PLA: EDA ratios, the excess $-NH_2$ in the EDA structure competes with each other in reacting with ester bonds, leading to most single functional reactions and forming products with hydroxyl and amine terminals. When the ratio increases, however, the lower content of $-NH_2$ groups from free EDA enables the EDA-capped terminal to compete with a similar probability to attack ester bonds, forming *Structure B*.
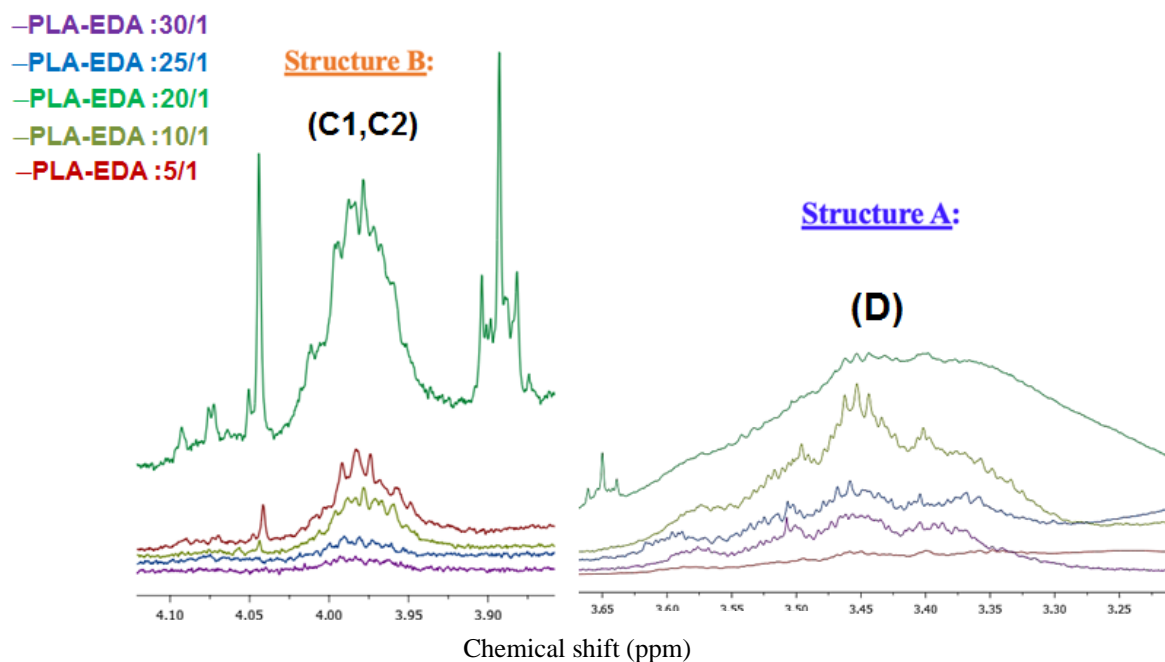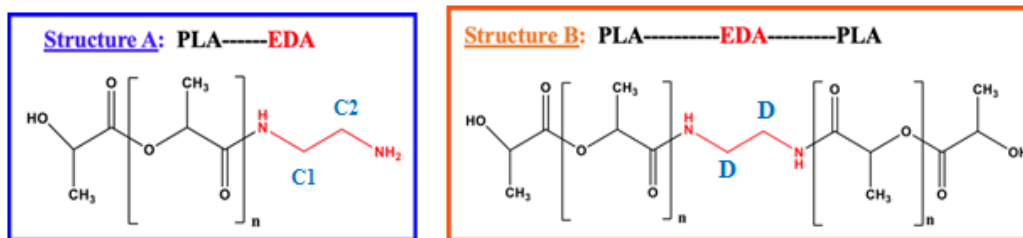
Figure 5 The determination of *Structure A* and *Structure B* compositions of aminolyzed PLA products using ^{1}H-NMR spectra in the region of the methylene signals of EDA.
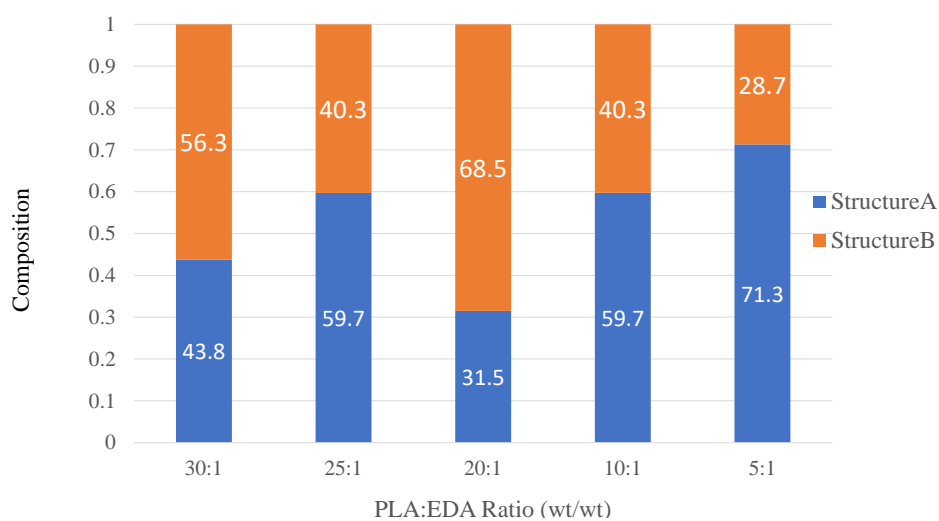

Figure 6 Structural compositions of aminolyzed PLA products obtained at different PLA: EDA feed ratios.

Structural Analysis by ATR-FTIR Spectroscopy

The chemical structures and reaction mechanisms were investigated using ATR-FTIR spectroscopy, as shown in Figure 7. All spectra were normalized to a reference band at 1453 cm^{-1}, corresponding to the asymmetric deformation of the -CH$_3$ group of PLA for comparison across different samples [14]. After the aminolysis, all products show a broad band of N-H and O-H stretching modes covering the 3350 to 3250 cm^{-1} region, indicating shorter lactate sequences with hydroxyl and amine terminals [15]. The bands at 3000-2880 cm^{-1} are associated with the C-H stretching modes of PLA. The band at 1750-1730 cm^{-1} is due to the C=O stretching mode of the ester groups of PLA. The normalized intensity of this band decreased when EDA reacted and attached to the lactate sequences due to the conversion of ester to amide groups [16]. This is also confirmed by the decrease in the normalized intensity of the 1085 cm^{-1} band associated with the C-O-C stretching mode of ester groups. The increase in the degree of ester conversion due to the rise in the EDA feed content led to a decrease in the band intensity. The bands at 1685 and 1541 cm^{-1} correspond to the stretching vibration (amide I) and the N-H deformation (amide II) bands, indicating the formation of amide bonds after the transesterification of PLA by EDA [17]. The intensities of these bands also vary with the PLA: EDA feed ratios.
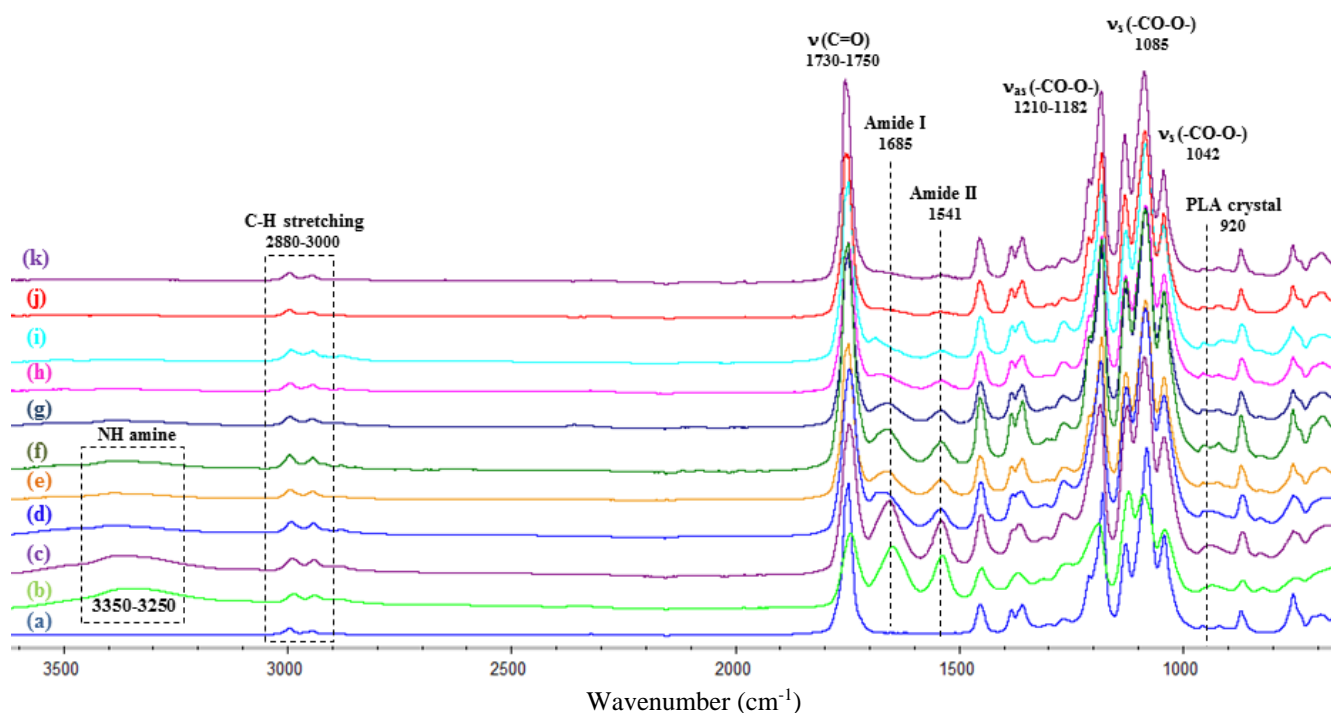
Figure 7 ATR-FTIR spectra of (a) neat PLA and aminolyzed PLA products obtained from various PLA: EDA ratios: (b-f) non-purified products (b) 5:1, (c) 10:1, (d) 20:1, (e) 25:1, (f) 30:1, compared with (g-k) purified products: (g) 5:1, (h) 10:1, (i) 20:1, (j) 25:1, and (k) 30:1.

4. Conclusions

A process for the chemical recycling of PLA *via* aminolysis by ethylenediamine (EDA) using microwave-assisted heating has been successfully developed. This is achieved by transesterifying ester bonds of PLA with amine groups of EDA, leading to a shorter lactate chain length. The product mixtures consist of two structures. *Structure A* is generated when a single -NH$_2$ of EDA reacts and attaches to lactate sequences, while *Structure B* is formed when both amine groups react. The average lactate length and chemical structures of the aminolyzed products can be controlled by varying the PLA: EDA feed ratios, which can be qualitatively and quantitatively characterized by ^{1}H-NMR and ATR-FTIR spectroscopy. At a low PLA: EDA feed content, the aminolyzed products consist of high *Structure A* content with a short average lactate length, as the high EDA feed content effectively enables its -NH$_2$ groups to compete with each

other to convert the ester bonds of PLA. When the feed ratio is increased, *Structure B* becomes a major product, with a higher average lactate length, due to the deficit of -NH$_2$ groups in the system. The reaction parameters can be used to design the structures and compositions of the product mixtures for use in specific applications. The developed process is promising for converting post-consumer PLA products, with a short reaction time, into feedstocks or starting materials for other value-added products, especially lactide-based polyurethanes.

Acknowledgments

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