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Preparation of Biodegradable Polymer Copolyesteramides from L-Lactic Acid Oligomers and Polyamide Monomers

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Abstract

Biodegradable copolyesteramide was synthesized from L-lactic acid oligomers and polyamide monomers to improve the properties of poly(lactic acid). The oligomer was synthesized from L-lactic acid using direct polycondensation process at 170 °C, 30 torr for 7 h. *p*-Toluenesulfonic acid used as a catalyst. From ¹H NMR analysis the oligomers have degree of polymerization of *ca.* 5. The L-lactic acid oligomer (OLLA) was subjected to reacted with ϵ -caprolactam (CLM) with different ratios: 90:10, 80:20, 70:30 and 60:40 using SnCl₂·2H₂O as a catalyst at 130, 150 and 170 °C pressure 30 torr for 3 h. The synthesized polymers were subjected to thermal property analysis using DSC technique and analyzed the functional groups with FT-IR. It was found that the melting temperature of the polymers increased with increasing amounts of CLM but decreased when the amount of CLM exceeded 30 percent. FT-IR analysis confirmed structure of copolyesteramide comprised of amide ide units and lactate unit.

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1. Introduction

Poly(lactic acid) (PLA) is thermoplastic polyester which is obtained from renewable resources. PLA is a crystalline thermoplastic with clear and transparent appearance. In addition, PLA has relatively high strength and modulus, biocompatibility, and biodegradability. Therefore, PLA is a good candidate in both of the industrial packaging field and the biocompatible/bioabsorbable medical device market. Limitations of PLA are brittleness, insufficient impact

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strength and low thermal stability. In order to improve its properties, various studies have been conducted by blending with non-biodegradable resins [1], preparing as copolymers, or as functionalized polymers [2]. Chemical modification of polymer by preparing as copolymer can attract much interest due to the controllability of the structural architecture, its properties, and molecular weight which depend on the molecular composition of copolymer [3]. Copolymerization and stereocopolymerization provide worthwhile means to adjust the degradation rate, as well as physical and mechanical properties [4–7]. Poly(l-lactide)-poly(ethylene glycol) multiblock copolymers (Multi-PLE) with high molecular weight were synthesized and successfully used to fabricate three-dimensional scaffolds [8]. Feng et al. [9] and Ye et al. [10, 11] reported block copolymerization of DL-lactide and 3-caprolactone with the aim of taking advantage of the degradability of PLA and the permeability to drugs of PCL. Poly(ϵ -caprolactone) /poly(L-lactic acid) (PCL/PLA) biodegradable poly(ester-urethane)s, was synthesized and characterized. The first step of the synthesis consisted of the ring opening polymerization of L-lactide, initiated by the hydroxyl terminal groups of the PCL chain, followed by the chain extension of these PLA-PCL-PLA triblocks, using hexamethylene diisocyanate (HDI) [12]. This research emphasize to study the preparation of biodegradable copolymer regarding copolyesteramides by oligomer of L-lactic acid with polyamide monomers (ϵ -caprolactam, ϵ -CLM). The chemical characterizations of copolyesteramides were performed by FT-IR, $^1\text{H-NMR}$, and XRD. Their thermal properties were evaluated by DSC technique. Productivity of the research can be applied to packaging industry.

2. Experimental

2.1 Materials

In this research, 2 type of initial substance as L-lactic acid and ϵ -caprolactam monomers were obtained from Archer Daniels Midland Ltd. and Fluka chemical Ltd., respectively. While *p*-toluene sulfonic acid and Tin (II) chloride were used as catalyst, supplied from Fluka Chemical Ltd. and Ajax Finechem Ltd.

2.2 Synthesis of Oligomer of L-lactic acid (OLLA)

Oligomer of L-lactic acid is synthesized from L-lactic acid by using Melt polycondensation process at 170 °C under pressure of 30 torr for 7 h. using *p*-Toluenesulfonic acid as a catalyst at 0.5 wt%. Procedure for melt polycondensation process show in fig.1.

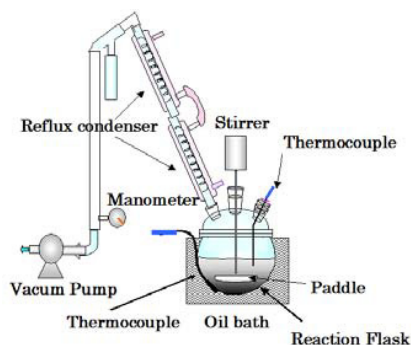


Fig.1. Melt polycondensation

2.3 Synthesis of copolyesteramides.

Copolyesteramides were synthesized from copolymerization of oligomers of L-lactic acid (OLLA) and ϵ -caprolactam (CLM) using Tin (II) chloride as catalyst. The copolymers were precipitated in methanol. The synthesis had been carried out using two procedures.

- (1) Copolymerization process under atmospheric pressure. The copolyesteramide was prepared from OLLA

and ϵ -caprolactam ratio 50:50 by weight using Tin (II) chloride as catalyst at 120°C and 180 °C for 5 h.

(2) Copolymerization process under reduced pressure. The copolymerization were carried out using OLLA and ϵ -caprolactam ratios 90:10, 80:20, 70:30, 60:40 and 50:50 at 130 °C, 150 °C and 180°C, under 30 torr for 3 h. The process is shown in Fig.2.

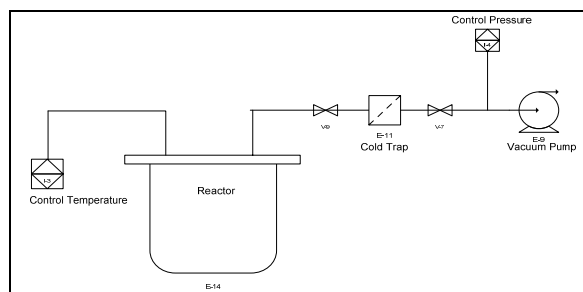


Fig. 2 Copolymerization process

2.4 Thermal property

Thermal property of copolyesteramides was determined using Differential Scanning Calorimetry (PerkinElmer DSC 8000). Samples were heated from 20 °C to 250 °C, heating rate 20 °C/min under nitrogen.

2.5 Chemical structure characterization

The ^1H NMR analysis was carried out using CDCl_3 as solvent. The FT-IR was performed on a FT-IR spectrometer (PerkinElmer Spectrometer Frontier). The ^1H NMR spectra was recorded in solution of CDCl_3 and TMS as internal standard. The wide angle X-ray scattering of copolyesteramide was carried out by PAN analytical (X'Pert Pro Sci Spec Co., Ltd).

3. Results and Discussion

3.1 Synthesis of L-lactic acid oligomers

L-lactic acid oligomers (OLLA) were synthesized by direct polycondensation. Fig. 3 shows the synthesized OLLA was transparency but white powder was obtained after grinding. The OLLA powder was subjected to thermal and chemical properties analysis.



Fig. 3. Oligomers of L-lactic acid

3.1.1. Thermal property analysis

Thermal property of polymers was characterized using DSC technique. Fig. 4 shows a DSC thermogram of OLLA. Melting temperature (T_m) of OLLA synthesized by melt polycondensation at 170 °C, 30 torr for 7 h was found at 133.8 °C. The crystallization temperature of OLLA was 72.6 °C.

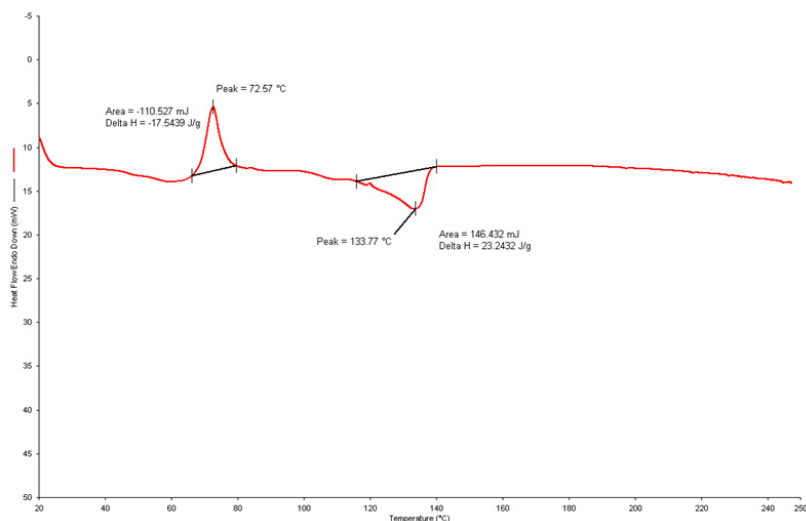


Fig. 4. DSC thermogram of Oligomer of L-lactic acid

3.1.2 Chemical property characterization

Fig. 5 shows FT-IR spectra of oligomers of L-lactic acid. The peak at 1752 cm^{-1} indicated carbonyl aliphatic peak. The characterization of $-\text{CH}_3$ asymmetric bending was found at 1447 cm^{-1} , C-H in plane bending at $1182, 1129, 1087, 1043\text{ cm}^{-1}$ and C-H out-of-plane bending at $871, 686, 755\text{ cm}^{-1}$.

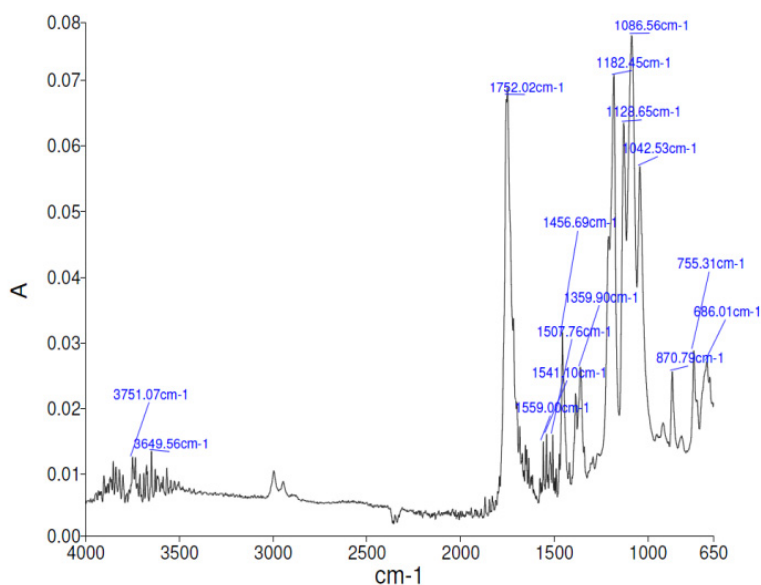


Fig.5. FT-IR spectrum of oligomer of L-lactic acid

Oligomer of L-lactic acid synthesized by direct polycondensation was subjected to ^1H NMR analysis to confirm the chemical structure using CDCl_3 as solvent and TMS as internal standard. From Fig. 7 it can be confirmed the chemical shift at 1.5 ppm (CH_3 of OH terminal of 2-hydroxypropionate), 1.6 ppm (CH_3 of lactate

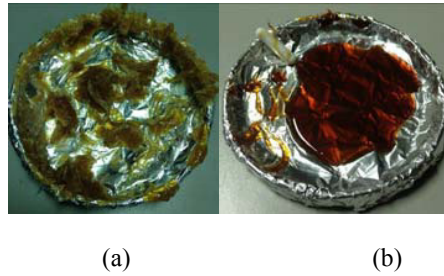


Fig. 8. Copolymer products synthesized under atmospheric pressure at (a) 120 °C and (b) 180 °C

3.2.2 Synthesis process under reduced pressure

Fig. 9 shows the polymer products synthesized by copolymerization at 130 °C with different ratios of OLLA and ϵ -caprolactam. The OLLA does not melt at 130 °C due to its higher T_m (133.77 °C) than the reaction temperature while ϵ -caprolactam melts (T_m 73.92 °C) but OLLA does not dissolve in ϵ -caprolactam. Therefore, the reaction temperature was increased to 150 °C and 170 °C as shown in Fig. 10 and Fig. 11.

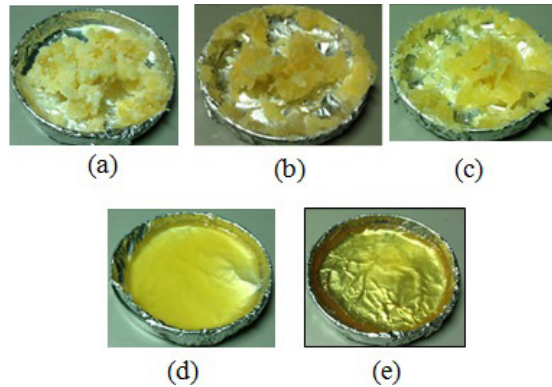


Fig. 9. Copolyesteramides at 130°C, 30 torr with ratios of OLLA:CLM (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40 (e) 50:50

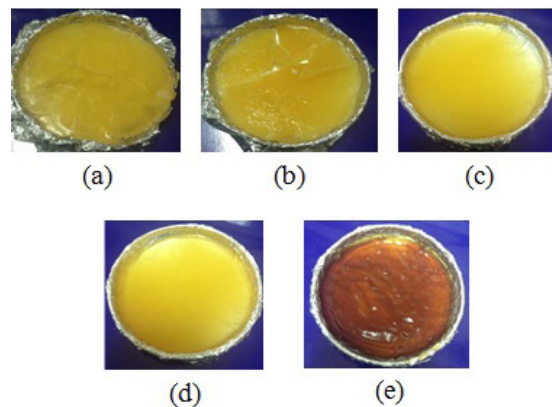


Fig.10. Copolyesteramides at 150 °C, 30 torr with ratio of OLLA:CLM (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40 (e) 50:50

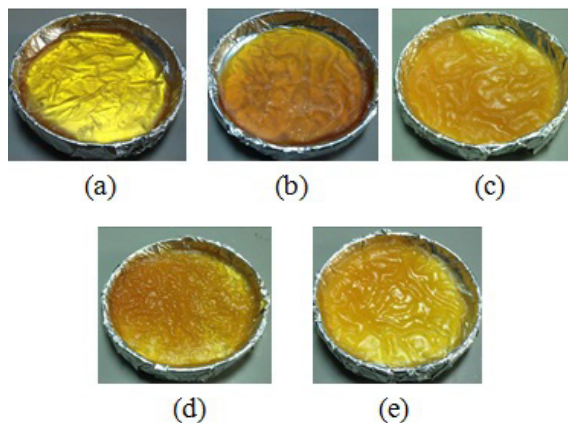


Fig. 11. Copolyesteramides at 170°C, 30 torr with ratio of OLLA:CLM (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40 (e) 50:50

The copolymer products synthesized at 150 °C and 170 °C were reprecipitated in methanol and dried at 50 °C for 8 h to remove the monomer and oligomers.

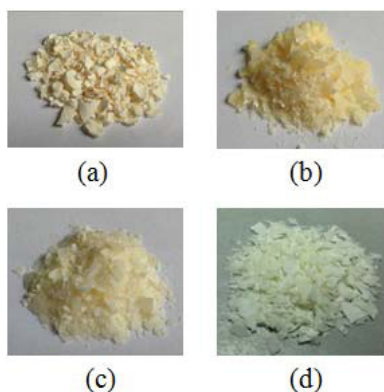


Fig.12. Copolyesteramides synthesized at 150 °C (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40

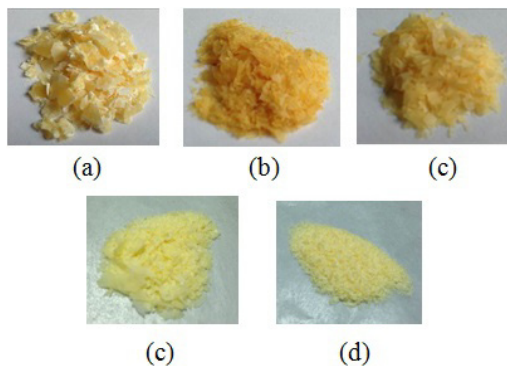


Fig. 13. Copolyesteramides synthesized at 170 °C (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40 (e) 50:50

Fig.12 and Fig. 13 show the copolymers synthesized at 150 °C and 170 °C after precipitation in methanol. The polymers were subjected to physical and chemical property analysis.

1) Thermal property analysis

ϵ -Caprolactam shows melting point at 73.9 °C. Differential scanning calorimetry (DSC) analysis of OLLA shows the crystallization temperature (T_c) at 72.6 °C and melting temperature (T_m) at 133.8 °C. The thermal behavior of copolymers synthesized at 150 °C and 170 °C under reduced pressure with different ratios of OLLA and CLM is shown in Fig. 14.

The percentage of crystallinity (X_c) of the PLA films was calculated according to the following equation:

$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c} \times 100$$

Where ΔH_m^c is the enthalpy of fusion of pure crystalline PLA (93.1 J/g) [13-15]. The crystallinity of PLA in the polymer blends were between 37-93%. It was found that the crystallinity increased with increasing amounts of amide monomers. The results indicated rigid segment of amide units assisted the crystallization of lactic acid segments.

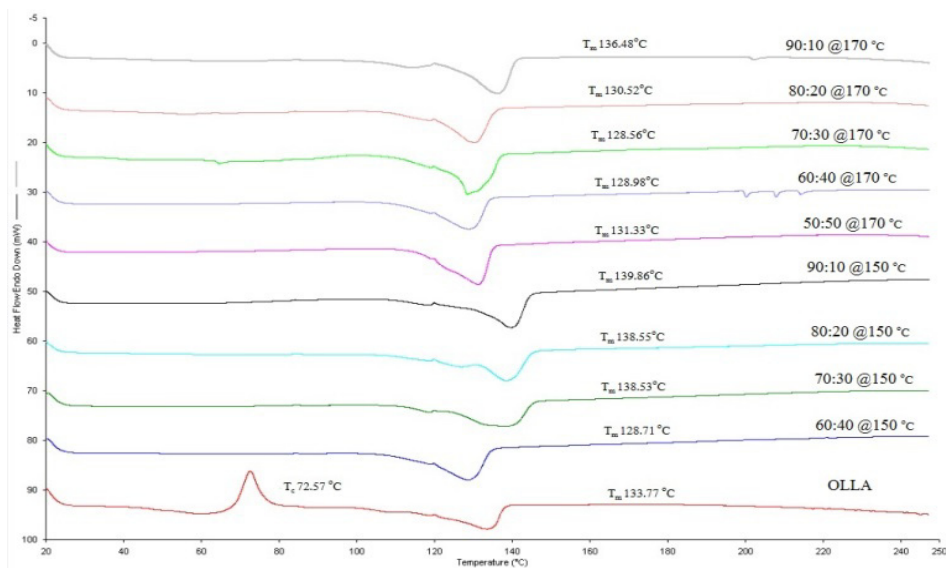


Fig. 14. DSC analysis of polymer blends

2) Chemical property analysis

Copolymers synthesized at 150 °C and 170 °C were characterized by FT-IR spectrometry. The results are shown in Fig. 15 and Fig. 16. The peak at 1634 cm^{-1} indicated the N-H bending which was found to be increased with increasing amounts of ϵ -caprolactam.

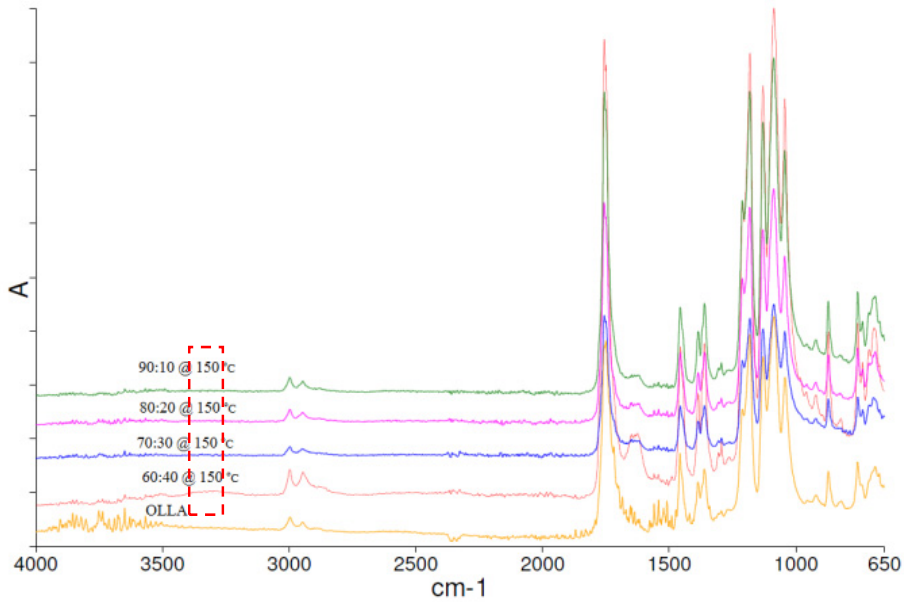


Fig. 15. FT-IR spectra of copolyesteramide with different ratio between OLLA:CLM at 150 °C

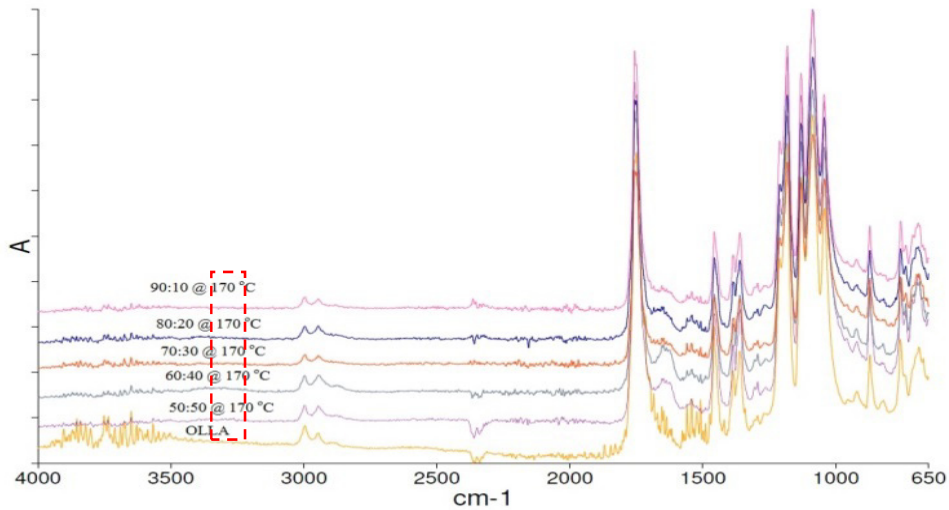


Fig. 16. FT-IR spectra of copolyesteramide with different ratio between OLLA:CLM at 170 °C

The OLLA and copolyesteramide were characterized its crystalline structure using X-ray diffraction technique. The results are shown in Fig. 17-19. Change in sharpness of the peaks indicates crystallinity of the polymers. The XRD peaks confirm structure of copolyesteramides in agreement with linear PLLA at 16.8° (due to diffraction from (200) and/or (110) planes) and 19.2° (due to diffraction from (203) and/or (113) planes).

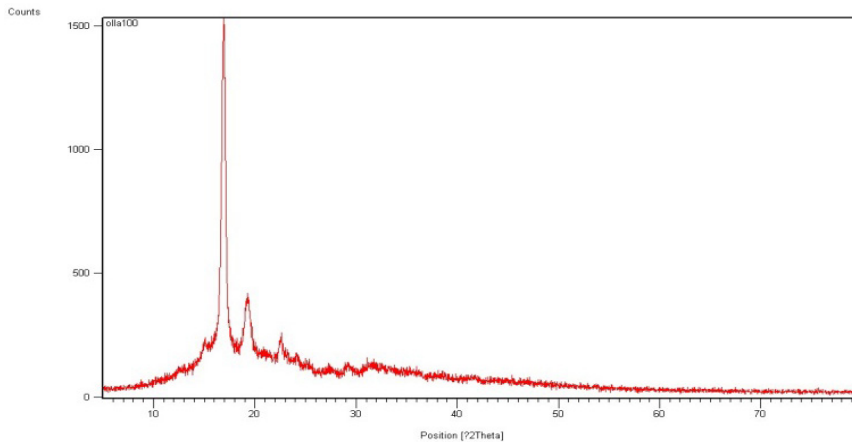


Fig. 17. XRD pattern obtained for OLLA

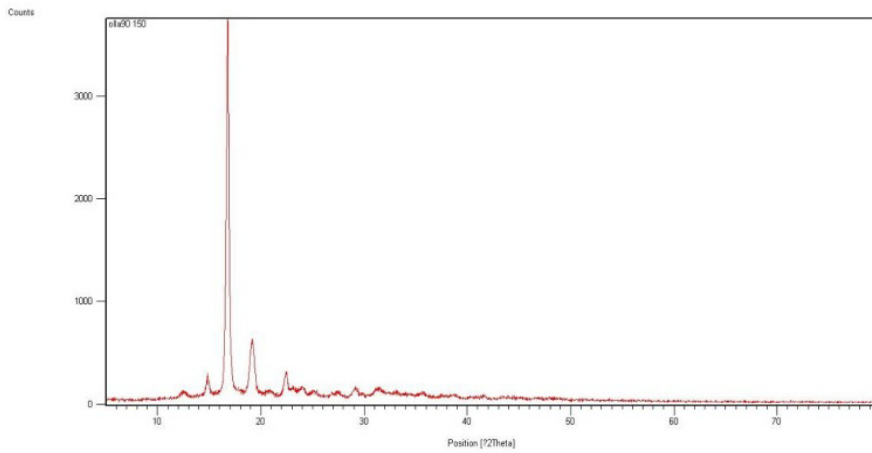


Fig. 18. XRD analysis of copolyesteramide (OLLA:CLM = 90:10) synthesized at 150 °C

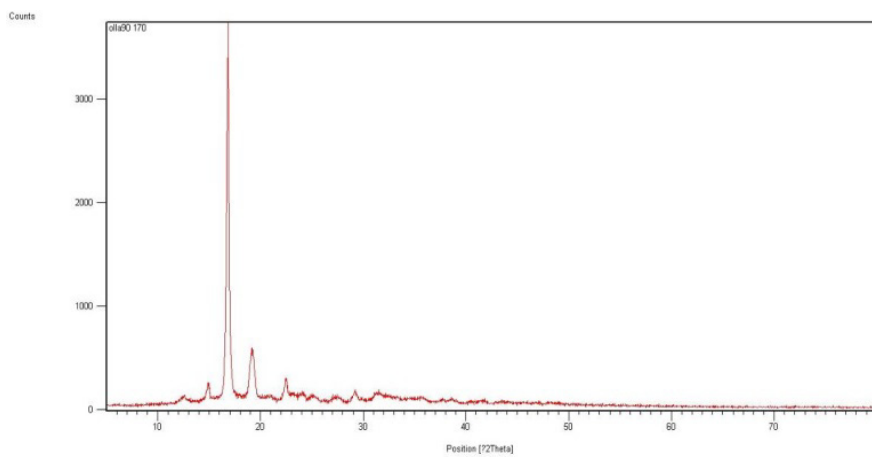


Fig. 19. XRD analysis of copolyesteramide (OLLA:CLM = 90:10) synthesized at 170 °C

The results indicated that crystallinity of lactate units increased in the copolymers. However, the crystallinity of the amide units was not clearly seen due to very small portion of amide parts in the copolymers which confirmed from the ^1H NMR analysis.

4. Conclusion

Oligomer of L-lactic acid (OLLA) was synthesized by melt polycondensation using *p*-Toluenesulfonic acid as catalyst at 170 °C, 30 torr for 7 h. ^1H NMR analysis confirmed the average degree of polymerization of 5. The OLLA was copolymerized with ϵ -caprolactam using Tin (II) chloride as catalyst under reduced pressure. The synthesis temperature at 150 °C and 170 °C produced copolyesteramides having higher crystallinity which were confirmed by XRD and DSC analysis. An amide part in the copolymer was characterized by FI-IR spectrometry which confirmed the N-H bending at 1634 cm^{-1} . DSC analysis of copolymers showed lower T_m than PLLA which resulted from the short amide part in the copolymers. The melting temperature of the polymers increased with increasing amounts of CLM but decreased when the amount of CLM exceeded 30 percent.

Acknowledgements

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