World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:6, No:6, 2012

Open Science Index, Materials and Metallurgical Engineering Vol:6, No:6, 2012 publications.waset.org/9996926.pdf

Preparation and Properties of Biopolymer from L-Lactide (LL) and ε-Caprolactone (CL)

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***Abstract*—**Biopolymers have gained much attention as ecofriendly alternatives to petrochemical-based plastics because they are biodegradable and can be produced from renewable feedstocks. One class of biopolyester with many potential environmentally friendly applications is polylactic acid (PLA) and polycaprolactone (PCL). The PLA/PCL biodegradable copolyesters were synthesized by bulk ring-opening copolymerization of successively added L-lactide (LL) and ε-caprolactone (CL) in the presence of toluene, using 1-hexanol as initiator and stannous octoate ($Sn(Oct)_2$) as catalyst. Reaction temperature, reaction time and amount of catalyst were evaluated to obtain optimum reaction conditions. The results showed that the %conversion increased with increases in reaction temperature and reaction time, but after a critical amount of catalyst was reached the %conversion decreased. The yield of PLA/PCL biopolymer achieved 98.02% at the reaction temperature 160 °C, amount of catalyst 0.3 mol% and reaction time of 48 h. In addition, the thermal properties of the product were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

***Keywords*—**Biopolymer, Polylactic Acid (PLA), Polycaprolactone (PCL), L-Lactide (LL), ε-Caprolactone (CL)

I. INTRODUCTION

SINCE many years, biodegradable polymers have become of interest as substitution materials to polluting petrochemical ones. These compounds have been classified into two groups that are agro-polymers and biopolyesters [1]-[2]. Polyesters play a predominant role as biodegradable plastics due to their potentially hydrolysable ester bonds [3]. The polyester family is made of two major groups aliphatic (linear) polyesters and aromatic (aromatic rings) polyesters. Biodegradable polyesters which have been developed commercially and are in commercial development are polyhydroxyalkanoates (PHA), polyhydroxyhexanoate (PHH), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polylactic acid (PLA), polycaprolactone (PCL), polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), polybutylene adipate/terephthalate (PBAT) and polymethylene adipate /terephthalate (PTMAT).

PLA is promising biomaterials in the field of temporary therapeutic applications in surgery, pharmacology and tissue engineering due to their biocompatibility and degradability. Recently, low cost PLA products are finding uses in many applications including packaging, paper coating, fibers and films. The degradation has been extensively investigated and it was concluded that degradation by products can be assimilated by microorganisms, PLA can be considered as environmental friendly materials [4]-[7].

PCL is an aliphatic polyester well known for its demonstrated biodegradability and biocompatibility. It is of great interest due to its favorable permeability to drugs and thermal properties. Over the last two decades, PCL had received increased attention for applications that span the range from environmentally friendly thermoplastics to medicine. However, the lack of functional groups along the PCL backbone is the main drawback to broaden potential applications. The introduction of pendant functional groups along the polyester chain is highly desirable to tailor and modulate physico-chemical properties. As a result, numerous examples of PCL bearing pendant functional groups, especially PCL-based graft polyesters, have been reported in the literature [8]-[10].

Synthetic aliphatic polyester derived from L-lactide (LL) and ε-caprolactone (CL) is regarded as profitable in the field of temporary therapeutic applications in surgery, sustained drug delivery and tissue engineering. Copolymerization and stereocopolymerization provide worthwhile means to adjust the degradation rate, as well as physical and mechanical properties [11]-[16]. The present article focuses on the preparation and characterization of PLA/PCL biodegradable copolyesters. Biopolymers were synthesized by the bulk ring-opening copolymerization of LL with CL. The polymerization was optimized by varying reaction temperature, reaction time and amount of catalyst.

II. EXPERIMENTAL METHODS

A. Materials

L-lactide (LL) and ε-caprolactone (CL) were purchased from Aldrich Chemistry. Stannous octoate ($Sn(Oct)_2$) was purchased from Aldrich Chemistry, is used as catalyst for bulk ring-opening copolymerization of PLA/PCL biopolymer. 1-Hexanol was supplied from Sigma-Aldrich, is used as

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initiator. All chemicals and reagents were of analytical reagent grade.

B. Synthesis of PLA/PCL Biopolymer

LL 50 mol% and CL 50 mol% were reacted in the bulk in the presence of $Sn(Oct)_2$ (0.1-0.5 mol%) and 1-hexanol (0.2 mol%). The reaction mixture was placed in a three-necked round bottom flask (reactor), under a dry nitrogen atmosphere and mechanical stirring (100 rpm) and immersed in an oil bath at 120-160 ^{o}C for 24-72 h. The resulting copolyesters were dissolved in chloroform, precipitated in methanol, filtered and dried at 60 ^{o}C. The syntheses of the PLA/PCL biopolymers were conducted following a single stage method, as schematically described in Fig. 1.

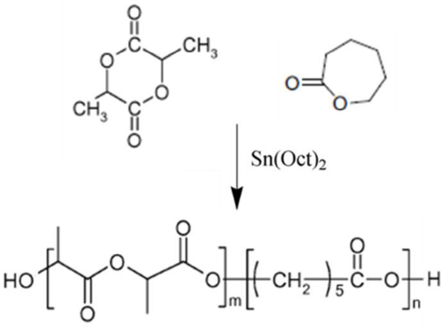

Fig. 1 Synthesis and structure of PLA/PCL biopolymers

III. RESULTS AND DISCUSSION

A. Effect of Reaction Temperature

Fig. 2 shows the relationship between the copolymerization temperature and %conversion of PLA/PCL biodegradable copolyesters. In this study, the polymerization time was fixed at 48 h and amount of catalyst at 0.3 mol%. It was found that the %conversion was almost 0% at reaction temperature below 130 ^{o}C. The %conversion slowly increased after 150 ^{o}C and was about 93% at 150 ^{o}C and was 98% at 160 ^{o}C. The monomer conversion at 160 ^{o}C were higher than other reaction temperatures. Compared with the reaction temperature at 150-160 ^{o}C, the monomer was completely consumed [17]-[18].

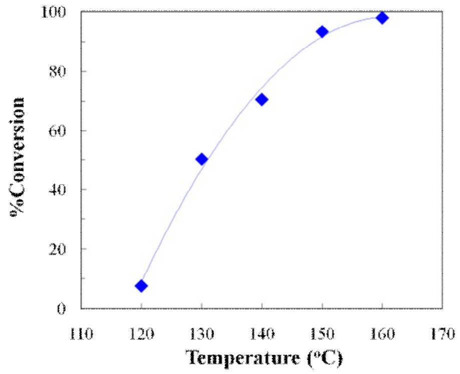

Fig. 2 Effect of reaction temperature on %conversion of PLA/PCL biopolymer (reaction time = 48 h and amount of catalyst = 0.3 mol%)

B. Effect of Reaction Time

The influence of the variation of reaction time on %conversion of PLA/PCL biopolymer was studied by fixing the temperature at 160 ^{o}C and the amount of catalyst as 0.3 mol%. The polymerization time was varied from 24 to 72 h. It was observed that the %conversion increased with an increase in the polymerization time and approached a steady state at about 48 h, it was 90% at 60 h and about 98% beyond 72 h (Fig. 3). As can be seen from the curve even at the verry initial stage polymerization proceed at a high rate. Longer reaction time leads to further but quite moderate increase of yield of PLA/PCL. It reaches the highest yield at 72 h of reaction. It seems that equilibrium state is reached at 48-72 h of reaction [19].

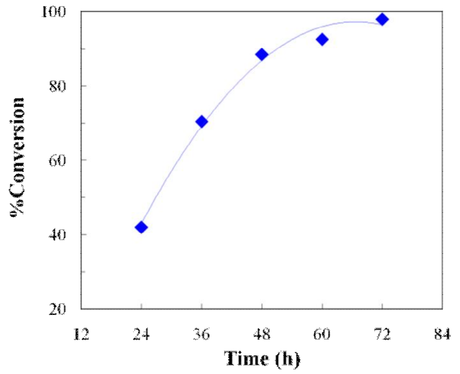

Fig. 3 Effect of reaction time on %conversion of PLA/PCL biopolymer (reaction temperature = 160 ^{o}C and amount of catalyst = 0.3 mol%)

C. Effect of Amount of Catalyst

In the study of copolymerization of PLA/PCL, catalyst concentration had a profound effect on the monomer conversion and product molecular weight [18], [20]. Effect of catalyst concentration was investigated using different amounts of $Sn(Oct)_2$, temperature was set at 160 ^{o}C, reaction time was 48 h and the amount of catalyst was varied from 0.1 to 0.5 mol%. Monomer conversion as a function of amount of catalyst was shown in Fig. 4. It was observed that the

%conversion increased with an increase in the amount of catalyst. But after a critical amount of catalyst was reached the %conversion decreased, because of equilibrium among the chemicals in system [19], [21]. The %conversion was found maximum when the $Sn(Oct)_2$ was 0.3 mol%. Therefore, amount of catalyst 0.3 mol% was the optimal catalyst concentration in the reaction system, and employed in the subsequent research.

D. Thermal Properties of PLA/PCL Biopolymer

The thermal properties of pure PLA and PLA/PCL copolyesters such as crystallization temperature (T_c), melting temperature (T_m), the degree of crystallinity (X_c), initial degradation temperatures (T_d) and char residue obtained from the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies are summarized in Table I.

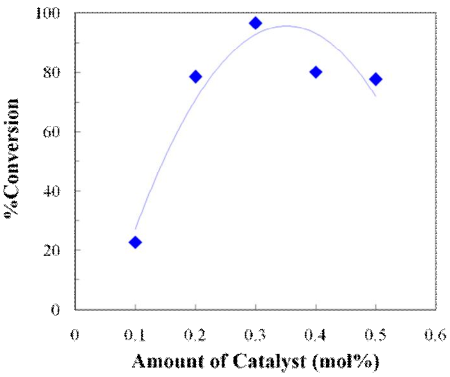

Fig. 4 Effect of amount of catalyst on %conversion of PLA/PCL biopolymer (reaction temperature = 160 °C and reaction time = 48 h)

TABLE I
THERMAL PROPERTIES OF PURE PLA AND PLA/PCL BIOPOLYMER COPOLYESTERS.

Material	T_c [°C]	T_m [°C]	X_c [%]	T_d [°C]	Char Residue [%]
PLA	115.37	147.71	20.50	292.93	1.43
PLA/PCL	114.76	132.55	14.10	280.01	1.70

IV. CONCLUSION

Biodegradability, biocompatibility and permeable properties of aliphatic polyesters such as PLA, PCL and their copolymers show their potential applications in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs. Therefore, there has been increasing interest in the development of efficient catalytic systems for the preparation of PLA and PCL. In this paper, the PLA/PCL biodegradable copolyesters were successfully synthesized by bulk ring-opening copolymerization method under a dry nitrogen atmosphere. The conditions for the polymerization of LL and CL were observed at reaction temperature 120-160 °C, 24-72 h of reaction time and amount of catalyst 0.1-0.5 mol%. The optimum conditions for the copolymerization of PLA/PCL biopolymer were synthesized by the bulk polymerization at 160 °C of monomers. The optimum of reaction time and amount of catalyst for synthesis copolyester were 48 h of and catalyst 0.3 mol%.

ACKNOWLEDGMENT

The authors acknowledge sincerely the Department of Materials Science and Engineering (MSE), Faculty of Engineering and Industrial Technology, Silpakorn University (SU) and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials (PPAM), Chulalongkorn University (CU) for supporting and encouraging this investigation.

REFERENCES

[1] L. Averous, “Biodegradable multiphase systems based on plasticized starch,” *J. Macromol. Sci. Polym. Rev.*, C44, pp. 231–274, 2004.
[2] R. Ouhib, B. Renault, H. Mouaziz, C. Nouvel, E. Dellacherie, J.L. Six, “Biodegradable amylose-g-PLA glycopolymers from renewable resources,” Carbohyd. Polym., 77, pp. 32–40, 2009.
[3] K.M. Nampoothiri, N.R. Nair, R.P. John, “An overview of the recent developments in polylactide (PLA) research,” Bioresour. Technol., 101, pp. 8493–8501, 2010.
[4] V. Langlois, K. Vallee-Rehel, J.J. Peron, A. Borgne, M. Walls, Philippe Guerin, “Synthesis and hydrolytic degradation of graft copolymers containing poly(lactic acid) side chains: in vitro release studies of bioactive molecules,” Polym. Degrad. Stab., 76, pp. 411–417, 2002.
[5] M. Vert, M.S. Li, G. Spenlehauer, P. Guerin, “Bioresorbability and biocompatibility of aliphatic polyesters,” J. Mater. Sci. Mater. Med., 3, pp. 432–446, 1992.
[6] R.E. Drumright, P.R. Gruber, D.E. Henton, “Polylactic Acid Technology,” Adv. Mater., 12, pp. 1841–1846, 2000.
[7] S. Karjomaa, T. Suortti, R. Lempiainen, J.F. Selin, M. Itävaara, “Microbial degradation of poly-(l-lactic acid) oligomers,” Polym. Degrad. Stab., 59, pp. 333–336, 1998.
[8] V. Darcos, H.A. Tabchi, J. Coudane, “Synthesis of PCL–graft–PS by combination of ROP, ATRP, and click chemistry,” Eur. Polymer J., 47, pp. 187–195, 2011.
[9] A.C. Albertsson, I.K. Varma, “Recent developments in ring opening polymerization of lactones for biomedical applications,” Biomacromolecules, 4, pp. 1466–1486, 2003.
[10] P. Lecomte, R. Riva, S. Schmeits, J. Rieger, B.K. Van, C. Jérôme, R. Jérôme, “New prospects for the grafting of functional groups onto aliphatic polyesters. Ring-opening polymerization of alpha- or gamma- substituted epsilon-caprolactone followed by chemical derivatization of the substituents,” Macromol. Symp., 240, pp. 157–165, 2006.
[11] M.H. Huang, S. Li, M. Vert, “Synthesis and degradation of PLA–PCL–PLA triblock copolymer prepared by successive polymerization of ε-caprolactone and DL-lactide,” Polymer, 45, pp. 8675–8681, 2004.
[12] D.W. Hutmacher, “Scaffold design and fabrication technologies for engineering tissues-state of the art and future perspectives,” J. Biomater. Sci. Polym. Ed., 12, pp. 107–124, 2001.
[13] S. Li, H. Garreau, M. Vert, “Structure-property relationships in the case of the degradation of massive aliphatic poly(□-hydroxy acids) in aqueous media, part 1: Poly(D,L-lactic acid),” J. Mater. Sci. Mater. Med., 1, pp. 123–130, 1990.
[14] S. Li, H. Garreau, M. Vert, “Structure-property relationships in the case of the degradation of massive poly(α-hydroxy acids) in aqueous media. Part 3: influence of the morphology of poly(l-lactic acid),” J. Mater. Sci. Mater. Med., 1, pp. 198–206, 1990.
[15] D. Garlotta, “Literature review of poly(lactic acid),” J. Polym. Environ., 9, pp. 63–84, 2001.
[16] X. Pan, A. Liu, L. Yao, L. Wang, J. Zhang, J. Wu, X. Zhao, C.C. Lin, “Synthesis, characterization of hetero-bimetallic complex and application in the polymerization of ε-caprolactone,” Inorg. Chem. Commun., 14, pp. 763–766, 2011.

[17] A. Buasri, N. Chaiyut, T. Jenjaka, S. Weerasunthorn S. Juengrungchaiwattana, “Preparation and characterization of PET-PLA copolyester from waste PET and lactic acid (LA),” Chiang Mai J. Sci., 38, pp. 619–624, 2011.
[18] Q. Li, G. Li, S. Yu, Z. Zhang, F. Ma, Y. Feng, “Ring-opening polymerization of ε-caprolactone catalyzed by a novel thermophilic lipase from Fervidobacterium nodosum,” Process Biochem., 46, pp. 253–257, 2011.
[19] G. Xi, M. Lu, C. Sun, “Study on depolymerization of waste polyethylene terephthalate into monomer of bis(2-hydroxyethyl terephthalate),” Polym. Degrad. Stab., 87, pp. 117–120, 2005.
[20] F. Deng, R.A. Gross, “Ring-opening bulk polymerization of ε-caprolactone and trimethylene carbonate catalyzed by lipase Novozym 435,” Int. J. Biol. Macromol., 25, pp. 153–159, 1999.
[21] F. Mahdi, A.A. Khan, H. Abbas, “Physiochemical properties of polymer mortar composites using resins derived from post-consumer PET bottles,” Cement Concrete Comp., 29, pp. 241–248, 2007.

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