การปรับปรุงความยืดหยุ่นของพลาสติกชีวภาพพอลิ(แอล-แล็กติกแอซิด)ด้วยการผสมแบบเกิดปฏิกิริยากับพอลิโพรพิลีนไกลคอล

Improvement of flexibility of poly(L-lactic acid) bioplastics by reactive blending with poly(propylene glycol)

กชพร คาคำดวน,[1] ยอดธง ใบมาก[2*]

Kotchaporn Kakomduan,[1] Yodthong Baimark[2*]

บทคัดย่อ

พลาสติกชีวภาพชนิดพอลิ(แอล-แล็กติกแอซิด) (PLLA) ได้รับความสนใจอย่างมากในการใช้เป็นบรรจุภัณฑ์อาหาร เพราะว่า PLLA สามารถแตกสลายทางชีวภาพได้และผลิตได้จากวัตถุดิบหมุนเวียน แต่ PLLA มีลักษณะแข็งเปราะจึงต้องมีการเสริมสภาพพลาสติกเพื่อให้ได้ผลิตภัณฑ์ PLLA ที่มีความยืดหยุ่น ในงานวิจัยนี้ได้ใช้พอลิโพรพิลีนไกลคอลมอนอบิวทิลอีเทอร์ (mPPG) เป็นสารเสริมสภาพพลาสติกด้วยการหลอมผสมกับ PLLA โดยได้วิจัยถึงอิทธิพลของการผสมเกิดปฏิกิริยาแบบ อิน สิทู ของสารช่วยยืดสายโซ่ที่มีต่อสมบัติเชิงความร้อน สมบัติเชิงกลและสัณฐานวิทยาของ PLLA ผสม mPPG ซึ่งใช้ Joncryl® ADR 4368 เป็นสารช่วยยืดสายโซ่ พบว่าอุณหภูมิเปลี่ยนสภาพคล้ายแก้วของ PLLA ลดลงต่อเนื่องและการยืดตัว ณ จุดขาดเพิ่มขึ้นเมื่ออัตราส่วน mPPG เพิ่มขึ้น การยืดสายโซ่ลดความเป็นผลึกและปรับปรุงความยืดหยุ่นของ PLLA ผสม mPPG มีการแยกเฟสเกิดขึ้นโดยมีช่องว่างภายในเนื้อ PLLA ขนาดช่องว่างลดลงเมื่อมีการยืดสายโซ่ และการยืดสายโซ่ทำให้ PLLA และ mPPG มีความเข้ากันได้มากขึ้นด้วย กล่าวโดยสรุปการเสริมสภาพพลาสติกและการยืดสายโซ่เป็นการเสริมกันในการปรับปรุงความยืดหยุ่นของ PLLA

คำสำคัญ: พลาสติกชีวภาพ พอลิ(แอล-แล็กติกแอซิด) สารเสริมสภาพพลาสติก สารช่วยยืดสายโซ่ สมบัติเชิงกล

Abstract

Poly(L-lactic acid) (PLLA) bioplastic has received much attention in food packaging because of its biodegradability and that it is produced from renewable resources. The rigid PLLAs need to be plasticized for use as flexible PLLA products. In this research, poly(propylene glycol) monobutyl ether (mPPG) was used as a plasticizer for melt blending with the PLLA. The influence of the *in situ* reactive blending of the chain extender on the thermal properties, mechanical properties and morphology of the PLLA/mPPG blends was investigated. Joncryl® ADR 4368 was used as the chain extender. It was found that the glass transition

---

[1] นิสิตปริญญาโท, [2] รองศาสตราจารย์, หน่วยวิจัยพอลิเมอร์แตกสลายได้ทางชีวภาพ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม อำเภอกันทรวิชัย จังหวัดมหาสารคาม 44150

[1] Master degree student, [2] Assoc. Prof., Biodegradable Polymers Research Unit, Department of Chemistry, Faculty of Science, Mahasarakham University, Mueang District, Mahasarakham 44150, Thailand.

* Corresponding author: Assoc. Prof. Yodthong Baimark, Biodegradable Polymers Research Unit, Department of Chemistry, Faculty of Science, Mahasarakham University, Kantarawichai District, Mahasarakham 44150, Thailand.

temperature of the PLLA decreased steadily and the elongation at break increased significantly as the mPPG ratio increased. The chain extension reduced the crystallinity and improved the flexibility of the PLLA/mPPG blends. The phase separation occurred as void structures on the PLLA matrices. The void sizes were decreased by the chain extension. The chain extension enhanced the compatibility of the PLLA and mPPG. In conclusion, the plasticization and the chain extension showed a synergistic effect to improve the flexibility of the PLLA.

Keywords: Bioplastics, poly(L-lactic acid), plasticizer, chain extender, mechanical properties

Introduction

Poly(L-lactic acid) (PLLA) has been widely investigated for use as a substitute for commodity plastics due to its biodegradability, renewability, good processing ability and good mechanical properties.[1-3] However PLLA has a high glass transition temperature ($T_g \approx 55$ °C) that leads to low flexibility in PLLA products,[4] which limits its practical applications. The flexibility of PLLA can be improved either by copolymerization[5] or by blending PLLA with other substances and polymers.[6-10] The blending method is a fast, convention and less expensive for plasticization of the PLLA.

The best plasticizers for PLLA were poly(ethylene glycol) (PEG)[10-12] [10-12] and poly(propylene glycol) (PPG),[10,13,14] etc. It has been reported that the phase separation of PLLA/PEG blends increased when the molecular weight and blend ratio of PEG were increased, which reduced the plasticization effect.[15] The PEG crystallization also induced immiscibility with the PLLA.[16] PPG is a viscous liquid that does not crystallize as it has a low T_g in the range -60 to -75 °C. PPG influenced the crystallization behavior via the phase separation of PLLA and the plasticizer less than that PEG did. The PPG has also been shown to give efficient plasticization to improve the flexibility of the PLLA.[13,14]

The reactive blending of the linear PLLA with a styrene-acrylic multifunctional oligomeric agent, under the trade name Joncryl®, is the usually method to improve the melt strength of PLLA by chain extension for use in melt processing.[17] The chain extension produces long-chain branching structures of the PLLA.[18] The hydroxyl and/or carboxyl end-groups of linear PLLA chains react with the epoxy rings of Joncryl®. It has been reported that Joncryl® ADR 4368 is the most efficient chain extender to restore the molecular weight of PLLA during melt processing.[19,20]

However, to the best of our knowledge, the *in situ* reactive blending of PLLA and PPG with Joncryl® ADR 4368 has not been reported so far. The aim of this research was to study the effect of the plasticization and the chain extension obtained from the *in situ* reactive blending on the thermal properties, mechanical properties and phase morphology of PLLA bioplastic. For this purpose, poly(propylene glycol) monobutyl ether (mPPG) containing one hydroxyl end-group was chosen as the plasticizer. The un-reacted monobuthyl ether end-chains of mPPG were easily mobile for the plasticization in the PLLA matrix. In addition, the obtained results were compared with those of the neat PLLAs.

Materials and Methods

Materials

The linear poly(L-lactic acid) (PLLA) was synthesized in our research unit at Mahasarakham University by the ring-opening polymerization of a L-lactide monomer in bulk at 165 °C for 2.5 h under a nitrogen atmosphere using 0.01 mol% stannous octoate (95%, Sigma) and 0.14 mol% 1-dodecanol (98%, Fluka) as the initiating system. The obtained PLLA was granulated before drying in a vacuum at 110 °C for 2 h to remove any un-reacted lactides. The intrinsic viscosity ($[\eta]$) and viscosity-average molecular weight (M_v) of the PLLA were determined in chloroform at 25 °C, and they were 2.53 dL/g and 104,700 g/mol, respectively.

Poly(propylene glycol) monobutyl ether (mPPG) with a molecular weight of 2,500 g/mol (Sigma-Aldrich) was chosen as a plasticizer. A styrene-acrylic multi-functional-epoxide oligomeric agent, under the trade name of Joncryl® ADR 4368 in flake form with a molecular weight of 6,800 g/mol (an epoxy equivalent weight of 285 g/mol) was used as a chain extender (supplied by BASF, Thailand). All reagents used were analytical grade.

Preparation of chain-extended PLLA/mPPG blends

The PLLA, mPPG plasticizer and Joncryl® ADR 4368 chain extender were dried in a vacuum at 50 °C for 24 h before melt blending. The mixtures of PLLA, mPPG and Joncryl® ADR 4368 were melt blended in an internal mixer (HAAKE Polylab OS system) at 190 °C for 4 min. A rotor speed of 100 rpm was used. The PLLA blends with mPPG ratios of 10% and 20% wt. were investigated. The Joncryl® ADR 4368 content was kept constant at 1.0 phr. The neat PLLAs (PLLA/mPEG = 100/0 w/w) with and without Joncryl® ADR 4368 were also prepared by the same method for comparison.

Characterization of chain-extended PLLA/mPPG blends

The thermal transition properties of the PLLA blends were measured with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) to detect their glass transition temperature (T_g), crystallizing temperature (T_c), heat of crystallization (ΔH_c), melting temperature (T_m) and heat of melting (ΔH_m).

For DSC, samples (3 – 5 mg) were heated to 200 °C at 10 °C/min under a nitrogen flow to eliminate the thermal history. Then, the samples were quenched to 0 °C using the DSC instrument's own default cooling mode before heating from 0 to 200 °C to observe the thermal transition properties. The degree of crystallinity (X_c) of the PLLA phase was calculated from equation (1).

$$X_c\ (\%) = [(\Delta H_m - \Delta H_c)/(f_{PLLA} \times 93.7)] \times 100 \qquad (1)$$

where f_{PLLA} was the weight fraction of PLLA in the PLLA/mPPG blends. ΔH_m and ΔH_c were the heat of melting and heat of crystallization, respectively, that were obtained from the DSC method. The 93.7 J/g was the heat of melting for 100% crystallinity of PLLA.[21]

The T_g was taken as the midpoint of the heat capacity increment associated with the glass-to-rubber transition. The T_c and T_m were measured as the peak value of the endothermal and exothermal phenomena in the DSC curve, respectively. The ΔH_c and ΔH_m were calculated from the total areas of the T_c and T_m peaks, respectively.

The mechanical properties, including stress at break and elongation at break, of the PLLA blends were determined at 25 °C and 50% relative humidity with a Narin Instrument NRI-TS501 Universal Mechanical Testing Machine. For this purpose, the specimens of the PLLA blend were prepared by compression molding at 190 °C following the ASTM D638 standard. The specimen samples were tested with a crosshead speed of 10 mm/min. The mechanical properties were determined from the average of at least five measurements for each sample.

The phase morphology of the PLLA blends was determined from the fracture surfaces of the specimens using a JEOL JSM-6460LV scanning electron microscope (SEM). For the SEM observation, samples were sputter coated with gold to enhance the conductivity before scanning.

Results and Discussion

Thermal transition properties

The thermal transition properties of the PLLA blends were investigated from the heating scan DSC thermograms, and examples of these are shown in Figure 1 for the PLLA blends without Joncryl® ADR 4368. They exhibited T_g, T_c and T_m points of the PLLA matrices. The DSC results are summarized in Table 1, including the X_c values. The mPPG decreased the T_g of the PLLA matrices from about 59 °C for neat PLLA without Joncryl® ADR 4368 to 53 °C and 51 °C for the PLLA blends plasticized with 10 and 20 wt% of mPPG, respectively, as reported in Table 1. For the Joncryl® ADR 4368 addition, the T_g values of the PLLA also decreased as the mPPG ratio increased. The decreasing T_g results may be explained by the mPPG enhanced segmental mobility of the PLLA chains for plasticizing effect.[13] The T_c slightly decreased when the mPPG ratio was increased. This may be due to the mPPG chains penetrating into the PLLA matrices that increase the mobility of the PLLA chains to crystallize. The T_m values of the PLLA matrices were similar in the range of 172 – 175 °C. The chain extension of PLLA with 1.0 phr Joncryl® ADR 4368 did not significantly affect the T_g, T_c and T_m of the PLLA matrices.

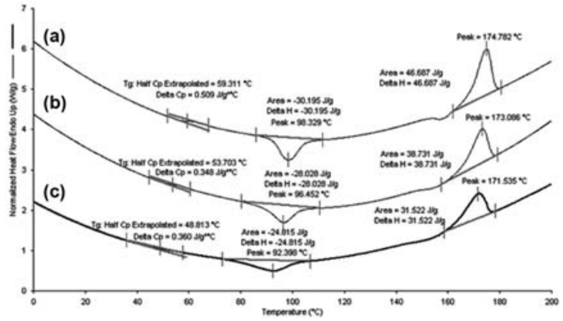

Figure 1 DSC thermograms of PLLA blends prepared with PLLA/mPPG blend ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) containing 1.0 phr Joncryl® ADR 4368.

Table 1 Thermal transition properties of PLLA/mPPG blends.

PLLA/mPPG ratio (w/w)	Joncryl® content (phr)	T_g (°C)	T_c (°C)	T_m (°C)	χ_c (%)
100/0	-	59	95	175	22.4
90/10	-	53	96	174	23.2
80/20	-	51	92	173	25.0
100/0	1.0	59	98	175	17.6
90/10	1.0	54	96	173	12.7
80/20	1.0	49	92	172	8.9

The X_c of the PLLA matrices without Joncryl® ADR 4368 calculated from equation (1) increased slightly when the mPPG ratio was increased. However, the X_c of the chain-extended PLLA blends was lower than the non-chain-extended PLLA for the same mPPG ratio. This suggests that the long-branched PLLA structures of the chain-extended PLLA produced from the chain extension inhibited the rearrangement of the PLLA chains for crystallization. In addition, the X_c of the chain-extended PLLA blends significantly decreased as the mPPG ratio increased. Thus, the chain extension of the plasticized PLLA blends reduced the crystallization of the PLLA. The mPPG chains extended with the Joncryl® ADR 4368 were branching structures as it could prevent the crystallization of the PLLA. This is an advantage of the mPPG plasticization because the thermal crystallization has a negative effect on the drawability of the plasticized PLLA.[14]

Mechanical properties

The mechanical properties of the PLLA blends were investigated by tensile testing. Figure 2 shows the broken tensile bars of the PLLA blends after testing. The broken tensile bars of the neat PLLA [PLLA/mPPG = 100/0 (w/w)] showed brittle fractures for both the non-chain-extended and the chain-extended PLLA blends. While, a ductile fracture was observed for the PLLA blends plasticized with 10% and 20% wt. mPPG. This indicates the flexibility of the PLLA was improved by blending with mPPG. In addition, the extensions of the tensile bars before breaking of the chain-extended PLLA blends were longer than those of the non-chain-extended PLLA blends for the same mPPG ratio. Therefore, it can be concluded that the chain extension also improved the flexibility of the PLLA.

The tensile curves of the chain-extended PLLA blends are illustrated in Figure 3. The load at break decreased and the extension at break increased when the mPPG ratio was increased. The neat PLLA yield at the extension was about 3.5% and the load was about 750 N [see Figure 3(a)]. The yield effects of the PLLA blends were more observed in Figures 3(b) and 3(c). The PLLA blends showed a little strain hardening after the yield point that indicates a plasticizing effect of the mPPG to increase the load at break before the breaking of the PLLA specimens. The mPPG increased the segmental mobility of the PLLA chains during the strain hardening to improve the strain crystallization of the PLLA.[13] The tensile curve changes of the non-chain-extended PLLA blends prepared with different mPPG ratios were similar.

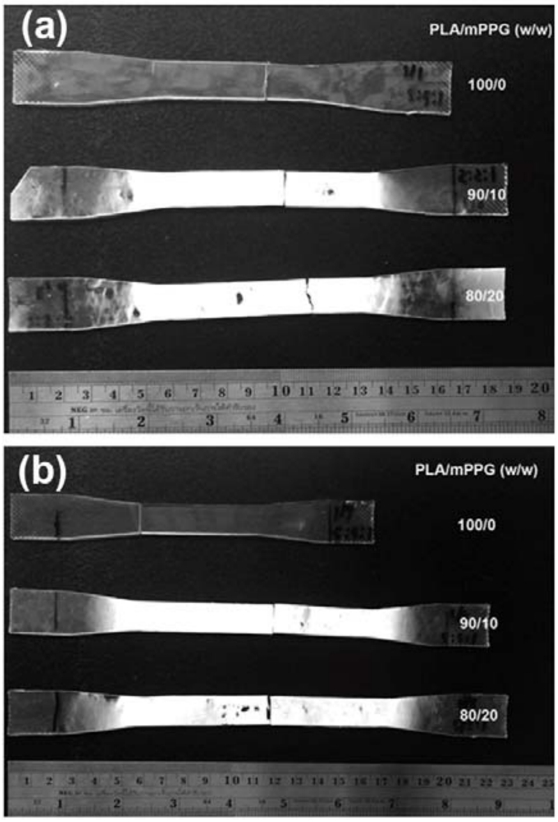

Figure 2 Tensile bars after tensile testing of (a) non-chain-extended and (b) chain-extended PLLA/mPPG blends.

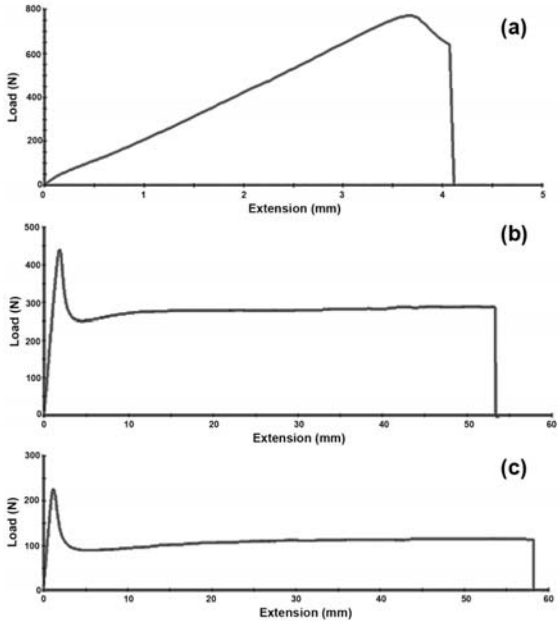

Figure 3 Tensile curves of PLLA blends prepared with PLLA/mPPG blend ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) containing 1.0 phr Joncryl® ADR 4368.

The tensile stress and elongation at break of the PLLA blends calculated from the load and the extension at break, respectively, are reported in Table 2. The mPPG blending caused a decrease in the stress at break and an increase in the elongation at break. The stress at break decreased steadily and the elongation at break increased significantly as the mPPG ratio increased. It should be noted that the chain extension increased the elongation at break of the PLLA blends for the same mPPG ratio. This may be explained by the long-chain branching structures of the chain-extended PLLA enhancing the chain entanglement network during the extension of the PLLA specimens.

Table 2 Mechanical properties of PLLA/mPPG blends.

PLLA/mPPG blend ratio (w/w)	Joncryl® content (phr)	Stress at break (MPa)	Elongation at break (%)
100/0	-	50.0 ± 10.2	5.6 ± 2.2
90/10	-	16.7 ± 8.3	41.4 ± 9.8
80/20	-	7.5 ± 5.8	57.6 ± 12.7
100/0	1.0	45.1 ± 12.1	7.0 ± 4.2
90/10	1.0	15.9 ± 6.7	82.7 ± 22.6
80/20	1.0	8.6 ± 4.5	98.5 ± 31.6

Phase morphology

The phase morphology of the blends was studied from SEM images. Figure 4 shows the fracture surfaces of the PLLA specimens without chain extension. The neat PLLA showed a smooth fracture surface [Figure 4(a)]. The fracture surfaces of both the 90/10 and 80/20 (w/w) PLLA/mPPG blends contained some emptied voids. The liquid mPPG accumulated in these voids during solidification of the PLLA matrices and indicated that the phase separation between the PLLA and mPPG phases had occurred.[13,14] This may be due to the polarities of the PLLA and the mPPG phases being different. However, emptied voids with uniform distribution were observed, which suggests the mPPG phase was well distributed throughout the PLLA matrices. The sizes of the voids increased with the mPPG ratio, which suggests that more phase separation occurred.

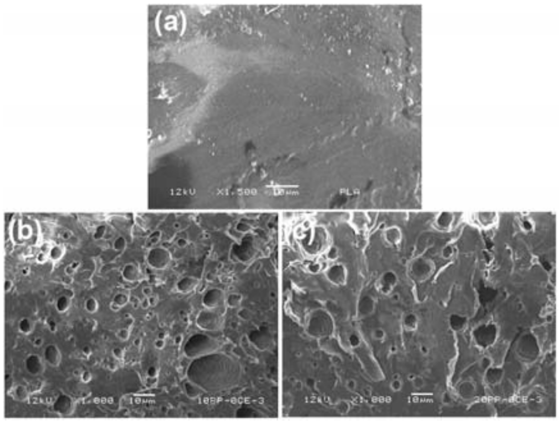

Figure 4 SEM images of PLLA blends prepared with PLLA/mPPG blend ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) without Joncryl® ADR 4368 (all bars = 10 μm).

The SEM images of the fracture surfaces of the chain-extended PLLA blends are shown in Figure 5. The emptied voids of the chain-extended PLLA blends are smaller than those of the non-chain-extended PLLA blends for the same mPPG ratio, and this suggested that the chain extension enhanced the compatibility of PLLA and mPPG. It may be proposed that some mPPG chains could react with the Joncryl® ADR 4368 to produce the long-chain branching molecules of the PLLA and mPPG chains. The latter molecules may act as a compatibilizer for the PLLA/mPPG blending. From the phase morphology study, the liquid mPPG droplets distributed in the PLLA matrices obviously enhance the plastic deformation. The smaller mPPG droplets in the chain-extended PLLA blends induced a higher elongation at break of the PLLA specimens (see Table 2).

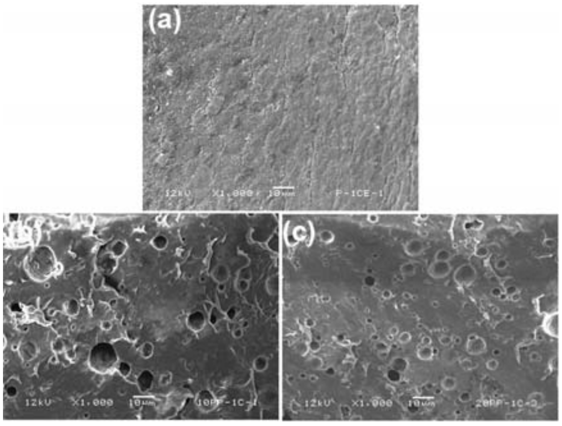

Figure 5 SEM images of PLLA blends prepared with PLLA/mPPG blend ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) containing 1.0 phr Joncryl® ADR 4368 (all bars = 10 μm).

Conclusion

In this research, the *in situ* reactive blending of a liquid plasticizer (mPPG) with a chain extender (Joncryl® ADR 4368) was carried out *via* reactive blending in PLLA/mPPG blends. The DSC analysis revealed the shift of the T_g toward lower temperatures in the case of the PLLA/mPPG blends. The chain extension decreased the X_c values and increased the elongation at break of the PLLA blends compared to the non-chain-extended PLLA/mPPG blends. The introduction of the mPPG by *in situ* reactive blending with Joncryl® ADR 4368 revealed an effective way to presumably depress the crystallinity and improve the flexibility of the PLLA. The above investigations suggest that the reactive blending of the PLLA and the mPPG with Joncryl® ADR 4368 are the most promising to produce novel flexible PLLA bioplastics.

Acknowledgements

The authors gratefully acknowledge the Institute for the Promotion of Teaching Science and Technology (IPST) for providing a scholarship for one of us (K.K.). The Division of Research Facilitation and Dissemination, Mahasarakham University is also acknowledged for financial support. We thank Dr. Jolyon Dodgson, Department of Biology, Faculty of Science, Mahasarakham University for his help improving the English language.

References

1. Gupta AP, Kumar V. New emergimg trends in synthetic biodegradable polymers – polylactide: a critique. Eur Polym J 2007; 43(10): 4053-74.
2. Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). Prog Polym Sci 2008; 33(8): 820-52.
3. Rasal RM, Janorkar AV, Hirt DE. Poly(lactic acid) modifications. Prog Polym Sci 2010; 35(3): 338-56.
4. Saeidlou S, Huneault MA, Li H, Park CB. Poly(lactic acid) crystallization. Prog Polym Sci 2012; 37(12): 1657-77.
5. Fay F, Renard E, Langlois V, Linossier I, Vallee-Rehel K. Development of poly(ε-caprolactone-co-L-lactide) and poly(ε-caprolactone-*co*-δ-valerolactone) as new degradable binder used for antifouling paint. Eur Polym J 2007; 43(11): 4800-13.

6. Kathuria A, Abiad MG, Auras R. Toughening of poly(L-lactic acid) with Cu_3BTC_2 metal organic framework crystals. Polymer 2013; 54(26): 6979-86.

7. Bai H, Huang C, Xiu H, Gao Y, Zhang Q, Fu Q. Toughening of poly(L-lactide) with poly(Ɛ-caprolactone): combined effects of matrix crystallization an impact modifier particle size. Polymer 2013; 54(19): 5257-66.

8. Xue P, Wang K, Jia M. Biodegradation and mechanical property of polylactic acid/thermoplastic starch blends with poly(ethylene glycol). J Wuhan Uni Technol-Mater Sci Ed 2013; 28(1): 157-62.

9. Kang H, Qiao B, Wang R, Wang Z, Zhang L, Ma J, Coates P. Employing a novel bioelastomer to toughen polylactide. Polymer 2013; 54(9): 2450-8.

10. Liu H, Zhang J. Research progress in toughening modification of poly(lactic acid). J Polym Sci Part B: Polym Phys 2011; 49(15): 1051-83.

11. Sungsanit K, Kao N, Bhattacharya SN. Properties of linear poly(lactic acid)/polyethylene glycol blends. Polym Eng Sci 2012; 52(1): 108-16.

12. Sheth M, Kumar RA, Dave V, Gross RA, Mccarthy SP. Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol). J Appl Polym Sci 1997; 66(8): 1495-505.

13. Kulinski Z, Piorkowska E, Gadzinowska K, Stasiak M. Plasticization of poly(L-lactide) with poly(propylene glycol). Biomacromolecules 2006; 7(7): 2128-35.

14. Piorkowska E, Kulinski Z, Galeski A, Masirek R. Plasticization of semicrystalline poly(L-lactide) with poly(propylene glycol). Polymer 2006; 47(20): 7178-88.

15. Baiardo M, Frisoni G, Scandola M, Rimelen M, Lips D, Ruffieux K, Wintermantel E. Thermal and mechanical properties of plasticized poly(L-lactic acid). J Appl Polym Sci 2003; 90(7): 1731-8.

16. Hu Y, Rogunova M, Topolkaraev V, Hiltner A, Baer E. Aging of poly(lactide)/poly(ethylene glycol) blends. Part 1. Poly(lactide) with low stereoregularity. Polymer 2003; 44(19): 5701-10.

17. Dorgan J, Lehermeier RH, Mang M. Thermal and rheological properties of commercial-grade poly(lactic acid). J Polym Environ 2000; 8(1): 1-9.

18. Randal JR, Cink K, Smith JC. Branching polylactide by reacting OH or COOH polylactide with epoxide acrylate (co)polymer. US Patent No. US 7,566,753 B2, 2009.

19. Najafi N, Heuzey MC, Carreau PJ, Wood-Adams M. Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders. Polym Degrad Stab 2012; 97(4): 554-65.

20. Cailloux J, Santona OO, Franco-Urquiza E, Bou JJ, Carrasco F, Gamez-Perez J, Maspoch ML. Sheets of branched poly(lactic acid) obtained by one step reactive extrusion calendering process: melt rheology analysis. Express Polym Lett 2013; 7(3): 304-18.

21. Baimark Y, Srihanam P. Influence of chain extender on thermal properties and melt flow index of stereocomplex PLA. Polym Test 2015; 45: 52-7.