พลาสติกชีวภาพผสมของพอลิแอล-แล็กติกไทด์และพอลิเอทิลีนไกลคอลมอนอเมธิลอีเทอร์ : อิทธิพลของการยืดสายโซ่ที่มีต่อสมบัติเชิงความร้อน

Bioplastic blends of poly(L-lactic acid) and Poly(ethylene glycol) monomethyl ether : Effect of chain extension on their thermal properties

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บทคัดย่อ

ความยืดหยุ่นและความหนืดหลอมของพลาสติกชีวภาพพอลิแอล-แล็กไทด์ (PLLA) นั้นปกติปรับปรุงได้ด้วยการเสริมสภาพพลาสติกและการยืดสายโซ่ ตามลำดับ โดยทั่วไปในเชิงการค้าทำการยืดสายโซ่ PLLA ก่อนทำการผสมสารเสริมสภาพพลาสติก ในงานวิจัยนี้ทั้ง PLLA และสารเสริมสภาพพลาสติกถูกหลอมผสมด้วยการทำปฏิกิริยาพร้อมกันกับสารช่วยยืดสายโซ่ โดยใช้พอลิเอทิลีนไกลคอลมอนอเมธิลอีเทอร์ (mPEG) และ Joncryl® ADR 4368 เป็นสารเสริมสภาพพลาสติกและสารช่วยยืดสายโซ่ ตามลำดับ ได้ศึกษาถึงอิทธิพลของอัตราส่วนผสม mPEG และปริมาณ Joncryl® ADR 4368 ที่มีต่อสมบัติเชิงความร้อนของ PLLA ผลการทดลองพบว่าอุณหภูมิเปลี่ยนสภาพคล้ายแก้วของ PLLA ลดลงอย่างมากเมื่อมีการเพิ่มอัตราส่วนผสม mPEG และอุณหภูมิเปลี่ยนสภาพคล้ายแก้วของ PLLA ลดลงเล็กน้อยเมื่อปริมาณ Joncryl® ADR 4368 เพิ่มขึ้น การผสม mPEG เหนี่ยวนำการเกิดผลึกของ PLLA ขณะที่การเกิดผลึกของ PLLA ลดลงจากการยืดสายโซ่ ทั้งการเสริมสภาพพลาสติกและการยืดสายโซ่ทำให้ความเสถียรเชิงความร้อนของ PLLA ลดลง จากการศึกษาความเสถียรเชิงความร้อนบ่งชี้ได้ว่า PLLA และ mPEG มีการผสมแบบเกิดปฏิกิริยากับ Joncryl® ADR 4368 สรุปได้ว่าสมบัติเชิงความร้อนของ PLLA ที่มีการเสริมสภาพพลาสติกและการยืดสายโซ่ซึ่งเตรียมด้วยการผสมแบบเกิดปฏิกิริยานั้นขึ้นอยู่กับอัตราส่วนผสม mPEG และปริมาณ Joncryl® ADR 4368 เป็นอย่างมาก

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Abstract

The flexibility and melt strength of poly(L-lactide) (PLLA) bioplastic are usually improved by plasticization and chain extension, respectively. In commercial processes, the PLLA is usually chain-extended by reactive blending before plasticizer blending. In this research, both the PLLA and the plasticizer were reactive melt

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blended with the chain extender at the same time. Poly(ethylene glycol) monomethyl ether (mPEG) and the Joncryl® ADR 4368 were used as the plasticizer and the chain extender, respectively. The effects of the blend ratio of MPEG and Joncryl® ADR 4368 on the thermal properties of the PLLA were investigated. The glass transition temperatures (T_g) of the PLLA matrices largely decreased as the mPEG blend ratio increased. The T_g values slightly increased with the Joncryl® ADR 4368 content. The mPEG blending induced the crystallization of the PLLA, whereas, the PLLA crystallization was depressed by the chain extension. Both plasticization and chain extension reduced the thermal stability of the PLLA matrices. The thermal stability results suggested that the PLLA and the mPEG were reactive blended with the Joncryl® ADR 4368. In conclusion, the thermal properties of plasticized and chain-extended PLLAs prepared by reactive blending strongly depended on the mPEG blend ratio and Joncryl® ADR 4368 content.

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

Introduction

In the past few decades, poly(L-lactide) (PLLA) has been widely investigated for use in commodity plastic applications due to its unique advantages, such as biodegradability, renewability, good processing ability and good mechanical properties.[1-3] However, PLLA products have low flexibility due to its a high glass transition temperature ($T_g \approx 55$ °C).[4] This limits its practical applications. The flexibility of PLLA can be improved either by copolymerization[5] or by blending methods.[6-9] However, the blending method is more convenient, less expensive and faster compared to copolymerization.

Polyethylene glycol (PEG) has been widely investigated for plasticization of PLLA due to its biodegradability and food contactable applications.[10,11] The resulting PLLA/PEG blends showed a lower glass transition temperature, higher elongation and lower tensile strength.[10] The influence of PEG with various blend ratios and molecular weights has been extensively reported.

It is well known that linear PLLA has a low melt strength.[12] This is not appropriate for melt processing. Reactive blending with a styrene-acrylic multifunctional oligomeric agent, under the trade name Joncryl®, has been widely used to improve the melt strength of PLLA by introducing a long-chain branching structure.[13] The hydroxyl and/or carboxyl end-groups of linear PLLA chains reacted 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.[14,15]

However, to the best of our knowledge, the effects of the plasticizer and the chain extender on the thermal properties of PLLA prepared by reactive blending have not been reported so far. Thus, the aim of this research was to investigate the effect of the plasticizer and the chain extender reactive blending on the thermal transition

properties and thermal stability of PLLA bioplastic. The PLLA, plasticizer and chain extender were blended in various ratios *via* a reactive blending method. For this purpose, poly(ethylene glycol) monomethyl ether (mPEG) containing one hydroxyl end-group was chosen as the plasticizer. The un-reacted monomethyl ether end-chains of mPEG could easily rotate to plasticization the PLLA matrix. In addition, the obtained results were compared with those of the plasticizer-free and chain extender-free PLLA.

Materials and Methods

Materials

The linear poly(L-lactide) (PLLA) was synthesized in our research unit at Mahasarakham University by 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 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(ethylene glycol) monomethyl ether (mPEG) with a molecular weight of 2,000 g/mol (Fluka) 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/mPEG blends

The PLLA, mPEG 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, mPEG 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 mPEG ratios of 10% and 20% wt. and Joncryl® ADR 4368 contents of 0.5 and 1.0 phr were investigated. 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/mPEG blends

The thermal transition properties of the PLLA blends were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow to detect their glass transition temperature (T_g), crystallization 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 at 10 °C/min under a nitrogen atmosphere over the temperature range 0 to 200 °C for the 1st

heating scan to eliminate the thermal history. Then, the samples were quenched to 0 °C according to the DSC instrument's own default cooling mode before heating from 0 to 200 °C for the 2nd heating scan. The thermal transition properties were investigated from the 2nd heating scan. The degree of crystallinity (X_c) of the PLLA phase was calculated from equation (1).

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

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.[16]

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 thermal stability (or thermal decomposition) of the PLLA blends was investigated with a TA-Instrument SDT Q600 thermogravimetric analyzer (TGA) in a non-isothermal mode. For TGA analysis, samples of 5 – 10 mg in weight were heated at 20 °C/min under a nitrogen atmosphere over the temperature range 50 to 800 °C. The TG thermogram was obtained as a weight loss profile. The temperature of the maximum decomposition rate ($T_{d,\ max}$) was derived from a derivative TG (DTG) thermogram.

Results and Discussion

Thermal transition properties of chain-extended PLLA/mPEG blends

The thermal transition properties of the PLLA/mPEG blends with and without Joncryl®ADR 4368 chain extension were determined from DSC thermograms as illustrated in Figure 1. The T_g, T_c and T_m of the PLLA matrices were detected and are reported in Table 1.

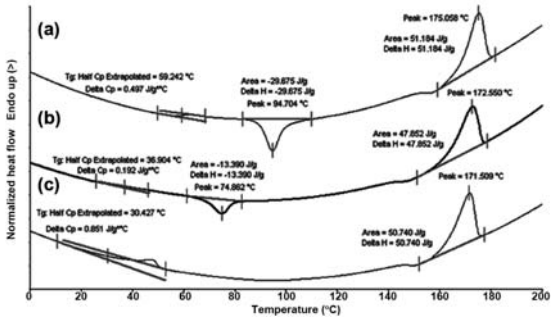

Figure 1 DSC thermograms of PLLA blends prepared with PLA/mPEG ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) without Joncryl® ADR 4368.

Table 1 Thermal transition properties of PLLA blends obtained from DSC thermograms.

PLLA/mPEG ratio (w/w)	Joncryl® content (phr)	T_g (°C)	T_c (°C)	T_m (°C)	X_c (%)
100/0	-	59	95	175	23
90/10	-	37	75	173	41
80/20	-	30	-	172	68
100/0	0.5	58	95	175	18
90/10	0.5	40	76	173	32

80/20	0.5	38	-	171	68
100/0	1.0	59	98	175	5
90/10	1.0	44	80	174	26
80/20	1.0	42	-	172	57

As it can be seen, the T_g and T_c values of the PLLA matrices decreased significantly as the mPEG was incorporated and the MPEG blend ratio was increased. This may be explained by the penetration of the mPEG chains between the PLLA chains that increases the free volume of the PLLA matrices. The T_g values of the PLLA matrices then decreased, which suggests the plasticization action had occurred.[17,18] It is well known that polymer flexibility increases when the T_g is depressed. Therefore, a plasticizing effect improves the polymer flexibility. A slight increase of MPEG from 10 to 20% slightly decreased T_g. The mPEG-plasticized PLLA with higher free volume easily rearranged for crystallization. The T_cs of the PLLA matrices were then decreased. It should be noted that the T_c exothermic peaks completely disappeared when the mPEG blend ratio was increased up to 20% for all Joncryl® ADR 4368 contents. This suggests that the 20% MPEG induced easier chain mobility of PLA. The complete crystallization of PLA was then obtained. In addition, the T_g and T_c values of the PLLA matrices slightly increased with the Joncryl® ADR 4368 content for the same mPEG blend ratio. This may be due to the PLLA molecules with long-branched structures that were formed by the chain extending with the Joncryl® ADR 4368. These chain-extended PLLAs were then difficult to rotate for the glass-to-rubber transition. The T_m of the PLLA matrices also decreased slightly when the mPEG blend ratio was increased.

The X_c values of the PLLA matrices calculated from equation (1) are also summarized in Table 1. The X_c changes are compared in Figure 2. It can be seen that the X_c increased steadily with the mPEG blend ratio. This may be explained that the mPEG blending enhanced mobility of PLA chains to crystallization. The PLLA plasticized with mPEG enhanced the PLLA crystallization as previous described. However, the X_c values decreased when the Joncryl® ADR 4368 content was increased. This suggests that the long-branched PLLA structures prevented the rearrangement of the PLLA chains for crystallization. The DSC results indicated that the mPEG and the Joncryl® ADR 4368 blending mainly affected the thermal transition properties of the PLLA matrices.

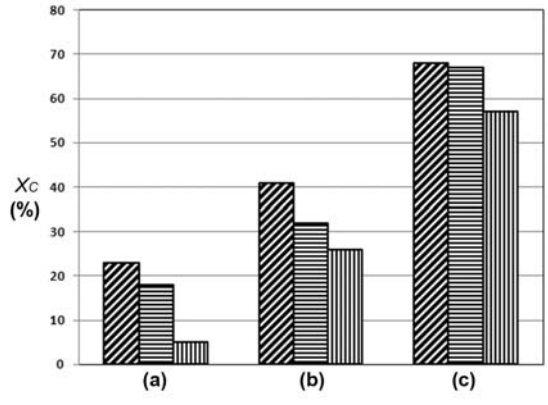

Figure 2 Degree of crystallinity (X_c) of PLLA blends prepared with PLA/mPEG ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) and with Joncryl® ADR 4368 contents of (▨) 0, (▤) 0.5 and (▥) 1.0 phr.

Thermal stability of chain-extended PLLA/mPEG blends

The thermal stability of the PLLA/mPEG blends with and without Joncryl®ADR 4368 was investigated under a nitrogen atmosphere from TG thermograms, and examples of these are shown in Figure 3 for the PLLA/mPEG blends without Joncryl®ADR 4368. The neat PLLA exhibited a single thermal decomposition stage in the range of 300 – 400 °C [see Figure 3(a)]. Meanwhile, the PLLA/mPEG blends showed two thermal decomposition stages: major and minor thermal decomposition stages in the ranges of 250 – 350 °C and 350 – 450 °C, respectively [see Figures 3(b) and 3(c)]. It can be seen that the weight loss on the minor thermal decomposition stage increased with the mPEG blend ratio. This suggests that the major and minor thermal decomposition stages were the decomposition of the PLLA and the mPEG phases, respectively. The PLLA/mPEG blends reacted with 0.5 and 1.0 phr Joncryl®ADR 4368 also showed similar decomposition profiles (TG thermograms not shown).

The thermal decomposition behaviors of the PLLA/mPEG blends were investigated from the DTG thermograms as shown in Figure 4. The $T_{d,\ max}$ assignment of the PLLA/mPEG blends is also shown.

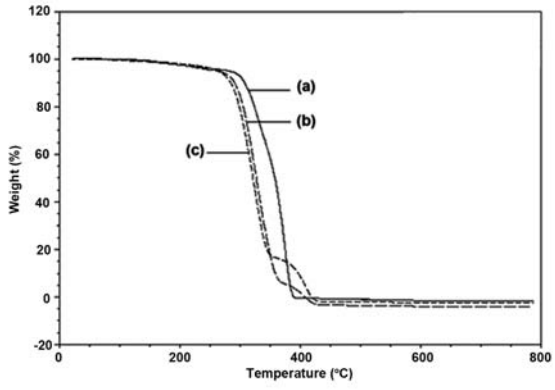

Figure 3 TG thermograms of PLLA blends prepared with PLA/mPEG ratios of (a) 100/0, (b) 90/10 and (c) 80/20 (w/w) without Joncryl® ADR 4368.

The higher and lower $T_{d,\ max}$ values of the neat PLLA without Joncryl® ADR 4368 at 374 °C and 328 °C in Figure 4(a) may be attributed to the thermal decomposition of the longer and shorter linear PLLA chains, respectively. The higher $T_{d,\ max}$ was the main thermal decomposition stage. The neat PLLA chain-extended with Joncryl® ADR 4368 [Figures 4(b) and 4(c)] also shows two $T_{d,\ max}$ values. However, for the neat PLLA chain-extended with 1.0 phr Joncryl® ADR 4368, the main decomposition stage was shifted to a lower $T_{d,\ max}$. This may be explained by the chain-extended PLLA molecules with long-branched structures inhibiting the intra- and intermolecular forces of the PLLA molecules. Thus, the chain extension decreases the thermal stability of the PLLA matrices.[19]

When the mPEG was blended, their lower and higher $T_{d,\ max}$ values were detected in the ranges of 313 – 328 °C and 398 – 407 °C, respectively. The intensities of the higher $T_{d,\ max}$

peaks increased with the mPEG blend ratio. Therefore, the lower and higher $T_{d, max}$ values may be attributed to the thermal decompositions of the PLLA and mPEG phases, respectively.

The $T_{d, max}$ values of the PLLA decomposition shifted to a lower temperature when the mPEG blend ratio and Joncryl® ADR 4368 content were increased. The results indicated that the thermal decompositions of the PLLA matrices were increased by mPEG and Joncryl® ADR 4368 blending. Therefore, both plasticization and chain extension effects decrease the thermal stability of the PLLA matrices.

It should be noted that the $T_{d, max}$ values of the mPEG phase in the non-chain extended PLLA/mPEG blends were constant at 407 °C [see Figure 4(a)]. The $T_{d, max}$ values of the mPEG phase decreased from 407 °C to 398 °C for the 90/10 (w/w) PLLA/mPEG blends when the Joncryl® ADR 4368 was added [see Figures 4(b) and 4(c)]. This may indicate that the mPEG chains could react with the Joncryl® ADR 4368 molecules to produce branched structures and reduce the thermal stability of the mPEG components. The epoxy rings of the Joncryl® ADR 4368 can reacted with the hydroxyl end-groups of mPEG.[13] However, the $T_{d, max}$ values of the mPEG phase increased slightly from 398 °C to 402 °C when the mPEG blend ratio was increased from 10% to 20%. This may be due to the higher thermal stability of the residue non-chain-extended mPEG for the higher mPEG blend ratio.

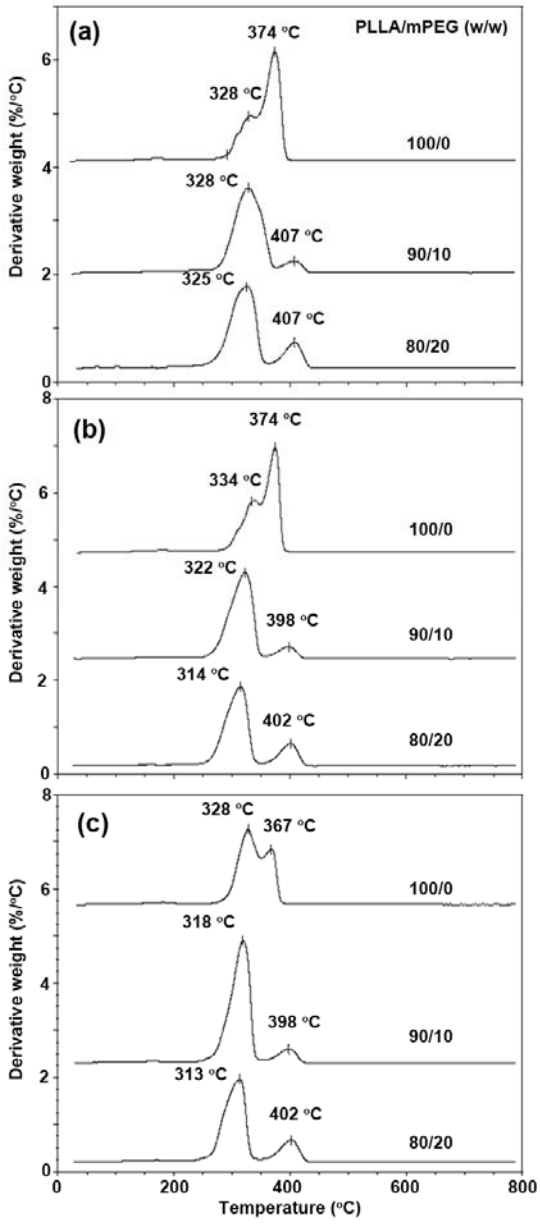

Figure 4 DTG thermograms of PLLA/mPEG blends prepared with Joncryl® ADR 4368 contents of (a) 0, (b) 0.5 and (c) 1.0 phr.

Conclusion

Our research showed that the PLLA plasticized with mPEG and chain-extended with Joncryl® ADR 4368 led to a significant variation in the thermal transition properties and thermal stability. The plasticization and chain extension revealed

an effective way to reduce the glass transition temperature and to increase the degree of crystallinity. The thermal stability study can confirm the chain extension of both PLLA and mPEG molecules with Joncryl® ADR 4368. Therefore, these new plasticized and chain-extended PLLAs prepared by the *in situ* reactive melt blending with the mPEG and the Joncryl® ADR 4368 can be considered promising candidates to fabricate packaging films.

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