Asian Journal of Scientific Research

ISSN 1992-1454

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OPEN ACCESS Asian Journal of Scientific Research

ISSN 1992-1454
DOI: 10.3923/ajsr.2019.508.515

Research Article

Influence of Chain Extension on Thermal and Mechanical Properties of Injection-molded Poly(L-lactide)-*b*-poly(ethylene Glycol)-*b*-poly(L-lactide) Bioplastic

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Abstract

Background and Objective: Poly (L-lactide) (PLLA) is a biodegradable bioplastic that has attracted much attention for use in biomedical and packaging applications. In this work, effect of chain extender on thermal and mechanical properties of injection-molded PLLA-*b*-poly (ethylene glycol)-*b*-PLLA triblock copolymer (PLLA-PEG-PLLA) and their comparison with the injection-molded PLLA were investigated. **Materials and Methods:** A flexible PLLA-PEG-PLLA was adjusted by changing its Melt Flow Index (MFI) by chain-extension reaction before injection molding. Differential scanning calorimeter was used to investigate the thermal properties. The mechanical properties of injection-molded PLLA and PLLA-PEG-PLLA were determined by universal testing machine for tensile and flexural properties, impact tester and hardness testers. One-way analysis of variance and Duncan's multiple test ($p<0.05$) were used to assess data. **Results:** The addition of chain extender decreased the MFI of PLLA-PEG-PLLA. The chain-extended PLLA-PEG-PLLA exhibited faster crystallization and more hydrophilicity than the PLLA. Hydrophilicity of PLLA-PEG-PLLA increased with the chain-extender content. From tensile curves, the chain-extended PLLA-PEG-PLLA had a yield effect indicating they were flexible. Strain at break and impact strength of chain-extended PLLA-PEG-PLLA were higher than the PLLA while their flexural stress and hardness were lower. The crystallization behaviors and mechanical properties of PLLA-PEG-PLLA did not change with the chain-extender content. **Conclusion:** The injection-molded bioplastics with high flexibility and toughness could be fabricated from chain-extended PLLA-PEG-PLLA.

Key words: Bioplastic, poly(L-lactide), triblock copolymer, chain-extender, melt flow index, injection molding, mechanical properties

Citation: Yodthong Baimark, Supasin Pasee, Wuttipong Rungseesantivanon and Natcha Prakymoramas, 2019. Influence of chain extension on thermal and mechanical properties of injection-molded poly(L-lactide)-*b*-poly(ethylene glycol)-*b*-poly(L-lactide) bioplastic. Asian J. Sci. Res., 12: 508-515.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Poly(L-lactide) or poly(L-lactic acid) (PLLA) is an important biodegradable bioplastic that has been widely investigated for use in several different applications. Its biodegradability, biocompatibility, bio-renewability good processability[1,2] and low cost have made it especially interesting to the biomedical and packaging industries. However, some applications of PLLA are limited due to its poor flexibility and toughness[3-5].

The flexibility of PLLA has been improved by block copolymerization[6,7] and blending with plasticizers[4,8-12]. Leaching risk and phase separation of the plasticizers from PLLA matrix to reduce plasticization efficiency with time has been reported previously[8,9,12,13]. High molecular-weight (MW) PLLA-*b*-poly(ethylene glycol)-*b*-PLLA triblock copolymers (PLLA-PEG-PLLA) synthesized by ring-opening polymerization of L-lactide monomer with PEG macro-initiators were more flexible than the PLLA due to plasticization effect of the PEG middle-blocks that decrease glass transition temperature (T_g) of the PLLA end-blocks[6,7]. While the toughness of PLLA has been improved by blending with flexible biodegradable polymers such as poly(ε-caprolactone)[14], poly(butylene succinate)[15], poly(ε-caprolactone-co-δ-valerolactone)[16], poly (ε-caprolactone-co-D,L-lactide)[17], poly(ε-caprolactone-co-L-lactide)[18] and natural rubber[5]. Phase compatibility and interfacial adhesion between PLLA matrix and flexible polymer dispersed-phases were important factors for improving the PLLA toughness.

The high molecular-weight PLLA-PEG-PLLA films have been fabricated by compression molding for mechanical test[6,7]. However, these PLLA-PEG-PLLA exhibited too low melt viscosity (high melt flow index, MFI)[7] which is not appropriate for injection molding. Plastic products with complex shapes should be prepared using the injection molding technique. The MFI of PLLA-PEG-PLLA can be reduced by melt reacting with a chain extender form as long-chain branching structures[7]. The chain-extended PLLA-PEG-PLLA could process by injection molding. However, the flexible PLLA-PEG-PLLA has not been processed by injection molding and properties of injection-molded PLLA-PEG-PLLA have not been reported so far. The objective of this work was to investigate thermal and mechanical properties of injection-molded PLLA-PEG-PLLA by chain extension with different chain-extender contents.

MATERIALS AND METHODS

Laboratory experiments: Study duration was 12 months from October, 2017-September, 2018. This experimental research was done in the Biodegradable Polymers Research Unit, Faculty of Science, Mahasarakham University, Thailand and the National Metal and Materials Technology Centre (MTEC), Thailand.

Materials: The PLLA and PLLA-PEG-PLLA were synthesized by ring-opening polymerization of L-lactide monomers at 165°C under nitrogen atmosphere for 2.5 and 6.0 h, respectively with 0.01 and 0.075 mol% stannous octoate, respectively, as a catalyst. About 1-Dodecanol and PEG with a molecular weight of 20,000 g mol^{-1} were used as initiators for synthesizing the PLLA and PLLA-PEG-PLLA, respectively. Number-average molecular weights (M_n) of the PLLA and PLLA-PEG-PLLA obtained from Gel Permeation Chromatography (GPC) were 88,400 and 89,900 g mol^{-1}, respectively, as well as dispersity indices were 2.3 and 2.8, respectively. As measured by Differential Scanning Calorimetry (DSC), glass transition temperatures (T_g) of the PLLA and PLLA-PEG-PLLA were 59 and 34°C, respectively. Their melting temperatures (T_m) were 174 and 172°C, respectively. A Joncryl® chain-extender (ADR 4368, BASF, Thailand) was used as supplied.

Preparation of chain-extended PLLA-PEG-PLLA: Chain-extended PLLA-PEG-PLLA was prepared in a molten state with Joncryl® contents of 4.0 and 8.0 parts per hundred of resin (phr). The PLLA-PEG-PLLA contained 4.0 and 8.0 phr Joncryl® were assigned as 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA, respectively. The blending was performed by an internal batch mixer (HakkeRheomex) at 190°C for 4 min with a rotor speed of 100 rpm. The PLLA-PEG-PLLA and Joncryl® were dried at 50°C overnight under high vacuum before melt blending.

Injection-molded specimens (ASTM D638 and D790) of PLLA and chain-extended PLLA-PEG-PLLA were prepared at 170°C using a PS40E5ASE type injection-molding machine (Nissei Plastic Industrial Co., Ltd., Japan). Mold temperature and cooling time were 25°C and 35 sec, respectively.

Characterization of PLLA and PLLA-PEG-PLLA

Differential scanning calorimetry: Thermal transition properties of the PLLA and chain-extended PLLA-PEG-PLLA pellets were measured on a Perkin-Elmer Pyris Diamond DSC under a nitrogen flow. The sample (3-5 mg) was firstly melted at 200°C for 2 min to erase its thermal history. It was then quenched to 0°C and re-heated to 200°C again at 10°C min^{-1} to observe their T_g, T_m and cold-crystallization temperature (T_{cc}). Enthalpies of melting (ΔH_m) and of cold crystallization (ΔH_{cc}) were used to calculate the degree of crystallinity from DSC ($X_{c,DSC}$) of the samples as Eq. 1:

$$X_{c,DSC}\ (\%) = \frac{\Delta H_m - \Delta H_{cc}}{93 \times W_{PLLA}} \times 100 \qquad (1)$$

where, 93 J g^{-1} is 100% ΔH_m for PLLA[19]. The PLLA weight-fractions (W_{PLLA}) of the PLLA and PLLA-PEG-PLLA obtained from ^{1}H-NMR were 1.00 and 0.83, respectively.

For half-time on crystallization ($t_{1/2}$) measurement, the sample (3-5 mg) was melted at 200°C for 2 min to remove its thermal history. It was then quenched to desired crystallization temperature (T_c) and hold at each desired T_c until exothermic peak of crystallization was complete.

Melt flow index: Determination of Melt Flow Index (MFI) of the PLLA and chain-extended PLLA-PEG-PLLA pellets was performed at 190°C under 2.16 kg load with a Tinius Olsen MP1200 melt flow indexer according to the ASTM D1238.

Density: Density of the PLLA and chain-extended PLLA-PEG-PLLA pellets was determined at 25°C with an Ohaus Adventurer AX224E analytical balance.

X-ray diffraction: Crystalline structure of the injection-molded PLLA and chain-extended PLLA-PEG-PLLA specimens was analysed on a Bruker D8 Advance wide-angle X-ray diffractometer (XRD) at 25°C using Cu Ka radiation at 40 kV and 40 mA. The sample was recorded from 2θ = 5-30° at the scanning rate of 3°C min^{-1}. The degree of crystallinity from XRD ($X_{c,XRD}$) was calculated as below.

$$X_{c,XRD}\,(\%) = \frac{S_c}{S_c+S_a}\times 100 \tag{2}$$

where, S_c and S_a are the integrated intensity of the crystalline peaks and of the amorphous halo, respectively.

Water contact angle: Measurement of water contact angle of injection-molded specimens was conducted in a ramé-hart Contact Angle Goniometers. The 5 µL droplet volume was used to neglect the gravity flattening effect. Measurements were repeated at least 5 times on different areas of each sample.

Tensile test: Tensile properties, i.e., stress at yield, strain at yield, stress at break, strain at break and Young's modulus of injection-molded specimens were obtained in an Instron 55R4502 Universal Testing Machine, following the guidelines of ASTM D638 with dumbbells type I at 25°C under a relative humidity of 50%. A crosshead speed was set to 50 mm min^{-1}. At least five specimens of each sample were tested and the average values were calculated. Tensile toughness of the specimens was the resistance to fracture under tensile force that was calculated by integrating the strain-stress curve in a unit of kJ m^{-3}.

Flexural test: Flexural properties including flexural stress at 5% strain and flexural modulus of the injection-molded specimens were measured with an Instron 55R4502 Universal Testing Machine, according to the ASTM D790 at 25°C and a relative humidity of 50%. The specimen size was 80×12×3 mm. A crosshead speed of flexural test was 1.25 mm min^{-1} with a support span length of 50 mm. At least five specimens of each sample were tested and averaged.

Impact test: Notched Izod impact strength of the injection-molded specimens with a size of 65×12×3 mm was carried out on a Resil Impactor, S/N 21130 pendulum impact tester with the pendulum at 2.16 J, according to the ASTM D256. An average value of at least five specimens was determined for each sample.

Hardness test: Rockwell Hardness (HR) of the injection-molded specimens (30×19×3 mm) was performed according to ASTM D785, procedure A, using a hardness tester (Wilson Rockwell 574 twin, S/N R574-00-1464) with 10 kg of preloading, 60 kg of loading, drift of 1/8 inch and loading time of 15 sec. Hardness shore D was performed according to ASTM D2240 using a Shore Type D hardness tester (Instron-Shore Instruments). At least five experiments were used to average each sample.

Statistical analysis: The data were expressed as means and Standard Deviation (SD). Statistical analysis was performed using a one-way analysis of variance (ANOVA, SPSS version 17.0 Institute Inc., Cary, NC). Data were assessed with Duncan's multiple test (p<0.05).

RESULTS

Thermal transition properties: The DSC heating curves of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA are presented in Fig. 1. The T_g, T_{cc} and T_m peaks were observed. The DSC results from Fig. 1 are summarized in Table 1. The T_g, T_{cc} and ΔH_{cc} of PLLA were 50, 97°C and 23.6 J g^{-1}, respectively. These values of both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were less than the PLLA suggested that they were faster crystallization than the PLLA. The T_m of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were nearly values. The $X_{c,DSC}$ results of the 4-PLLA-PEG-PLLA (30.3%) and 8-PLLA-PEG-PLLA (27.7%) calculated from Eq. 1 were higher than that of the PLLA (11.2%).

Table 1: Thermal properties of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA

Sample	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	$X_{c,DSC}$ (%)
PLLA	50	97	23.6	171	34.0	11.2
4-PLLA-PEG-PLLA	31	74	13.6	166	37.0	30.3
8-PLLA-PEG-PLLA	30	75	14.1	166	35.5	27.7

PLLA: Poly (L-lactide), PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Table 2: Half-time on crystallization ($t_{1/2}$) at various crystallization temperatures (T_c) of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA

	$t_{1/2}$ (min)		
T_c (°C)	PLLA	4-PLLA-PEG-PLLA	8-PLLA-PEG-PLLA
70	-	2.4	2.5
80	-	1.5	1.6
90	18.1	0.9	0.9
100	11.8	1.1	1.2
110	10.4	2.1	2.3
120	16.4	-	-

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Table 3: Melt Flow Index (MFI) and density of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA

Sample	MFI (g/10 min)	Density (g cm^{-3})
PLLA	20±2	1.25±0.01
4-PLLA-PEG-PLLA	47±2	1.23±0.02
8-PLLA-PEG-PLLA	16±3	1.24±0.01

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

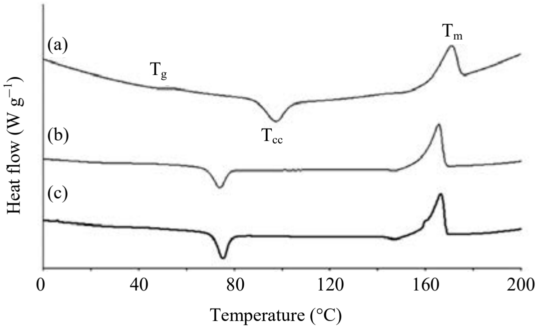

Fig. 1: DSC heating curves of (a) PLLA, (b) 4-PLLA-PEG-PLLA and (c) 8-PLLA-PEG-PLLA

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

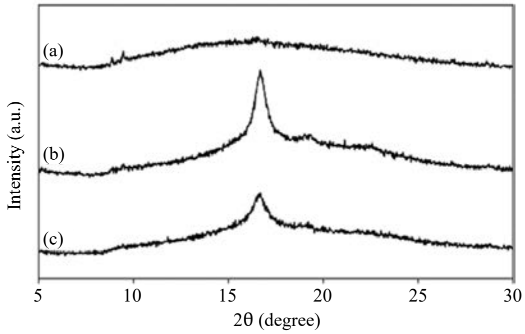

Fig. 2: XRD profiles of injection-molded specimens of (a) PLLA, (b) 4-PLLA-PEG-PLLA and (c) 8-PLLA-PEG-PLLA

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Half-times on crystallization ($t_{1/2}$) at various crystallization temperatures (T_c) of the samples are reported in Table 2. The 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA showed shorter $t_{1/2}$ than the PLLA for the same T_c. The lowest $t_{1/2}$ of PLLA was 10.4 min at 110°C while the lowest $t_{1/2}$ of both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA was 0.9 min at 90°C. The results of $t_{1/2}$ confirmed that both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited faster crystallization than the PLLA. However, the $t_{1/2}$ of the PLLA-PEG-PLLA did not significantly change when the Joncryl® content increased from 4.0-8.0 phr.

Melt flow index and density: The data in Table 3 reported the MFI and density of the samples. The MFI of PLLA was 20 g/10 min. Joncryl®-free PLLA-PEG-PLLA had too low melt strength at 190°C. Its MFI could not be determined. The MFI of PLLA-PEG-PLLA decreased from 47-16 g/10 min as the Joncryl® contents increased from 4.0-8.0 phr suggested that the melt strength of PLLA-PEG-PLLA increased with the Joncryl® content. The densities of PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA pellets were in the range of 1.23-1.25.

Crystalline structures: The XRD profile was used to determine the crystalline structure of the injection-molded specimens at room temperature as shown in Fig. 2. The PLLA had no diffraction peaks indicating mostly amorphous. Both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited only one peak at 16°. The $X_{c,XRD}$ results calculated from Eq. 2 were 8.9 and 5.8% for the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA, respectively. The $X_{c,XRD}$ of PLLA-PEG-PLLA slightly decreased as the Joncryl® content increased from 4.0-8.0 phr.

Hydrophilicity: The hydrophilicity of the injection-molded specimens was determined from water contact angle at room temperature as shown in Fig. 3. Larger water contact angle of the sample was assigned to its lower hydrophilicity. The water contact angle of PLLA was 79.0° that higher than both the 4-PLLA-PEG-PLLA (67.0°) and 8-PLLA-PEG-PLLA (62.6°). In addition, higher Joncryl® content exhibited lower water contact angle. The results of water contact angle suggested the PLLA-PEG-PLLA exhibited more hydrophilicity than the PLLA.

Tensile properties: The results in Fig. 4 shows selected stress-strain curves of injection-molded specimens. Both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited a yield point but the PLLA did not. The results indicated the PLLA was brittle while the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were flexible. The averaged tensile results of injection-molded specimens are summarized in Table 4. Both the 4-PLLA-PEG- PLLA and 8-PLLA-PEG-PLLA specimens exhibited lower stress at break, higher strain at break and lower Young's modulus than the PLLA specimens. The tensile results indicated the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were highly flexible. In addition, tensile toughness of the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA also were very high compared with the PLLA.

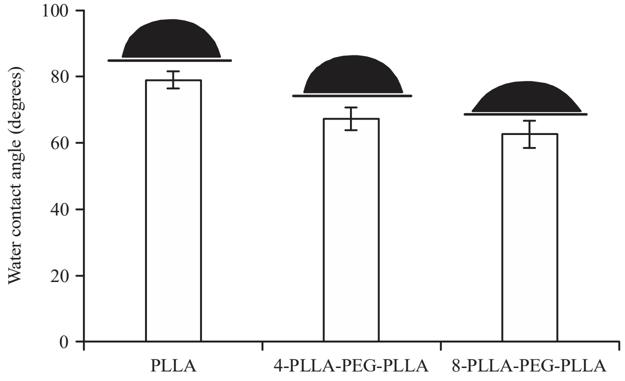

Fig. 3: Water contact angles of injection-molded PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Flexural properties, impact strength and hardness: Flexural properties including flexural stress at 5% strain and flexural moduli of injection-molded specimens are summarized in Table 5. Both the flexural stress and moduli of samples were in order PLLA>4-PLLA-PEG-PLLA>8-PLLA-PEG-PLLA. The PLLA exhibited lower impact strength and higher the Rockwell and shore D hardness than those of the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA. However, the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA had almost similar values of impact strength and hardness.

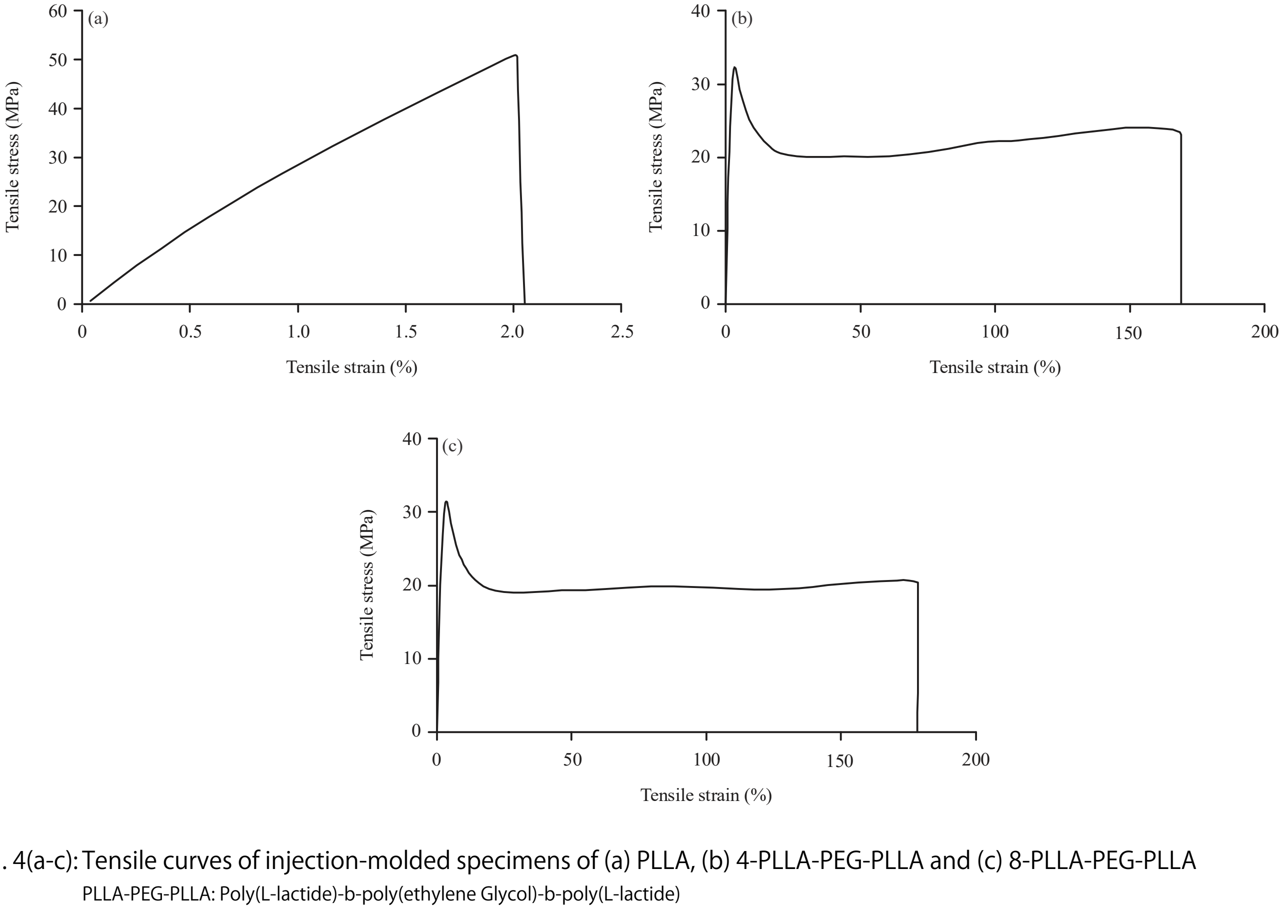

Fig. 4(a-c): Tensile curves of injection-molded specimens of (a) PLLA, (b) 4-PLLA-PEG-PLLA and (c) 8-PLLA-PEG-PLLA

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Table 4: Tensile properties of injection-molded PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA specimens

Injection-molded specimens	Stress at yield (MPa)	Strain at yield (%)	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)	Tensile toughness (kJ m^{-3})×10^6
PLLA	-	-	51±6	1.9±0.3	3399±101	1.2
4-PLLA-PEG-PLLA	32±2	4.2±0.4	24±1	163.0±9.7	1661±35	86.2
8-PLLA-PEG-PLLA	31±3	4.6±0.3	22±1	180.4±17.2	1576±40	84.4

PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

Table 5: Flexural, impact and hardness properties of injection-molded PLLA, 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA specimens

Injection-molded specimens	Flexural stress at 5% strain (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})	Rockwell hardness (HRR)	Hardness shore D
PLLA	91.6±13.4	4286±110	25.0±1.9	119.2±0.2	72.6±1.1
4-PLLA-PEG-PLLA[a]	44.5±0.9	1468±40	37.5±7.6	96.0±1.9	66.6±1.1
8-PLLA-PEG-PLLA[a]	41.7±3.2	1399±69	37.0±4.2	95.5±0.7	66.4±0.6

[a]The sample specimens did not broke before stopping of flexural test. PLLA-PEG-PLLA: Poly(L-lactide)-b-poly(ethylene Glycol)-b-poly(L-lactide)

DISCUSSION

The lower T_g, T_{cc} and ΔH_{cc} of both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA assigned to higher mobility of the PLLA end-blocks for glassy-to-rubbery transition and for cold crystallization during DSC heating scan. This is due to plasticization effect of the flexible PEG middle-blocks[6,20]. The $X_{c,DSC}$ of PLLA was lower than both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA. This can be explained by the growth rate of PLLA spherulites being improved by increasing its chain mobility for cold crystallization due to the plasticization effect[6,20]. The $X_{c,DSC}$ of 8-PLLA-PEG-PLLA slightly smaller than the 4-PLLA-PEG-PLLA. This may be due to more branching structures of 8-PLLA-PEG-PLLA disrupting chain packaging for crystallization of the PLLA end-blocks[21]. However, the $t_{1/2}$ values of 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA for the same T_c were similar. The Joncryl® contents in range 4.0-8.0 phr did not significantly affect the $t_{1/2}$ values of the PLLA-PEG-PLLA.

The MFI of PLLA-PEG-PLLA decreased as the Joncryl® contents increased. The chain-extension reaction of PLLA-PEG-PLLA with the Joncryl® reduced its MFI by formation of long-chain branching structures[21,22]. From the MFI results, both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA could process by injection molding. From XRD results, the injection-molded PLLA specimens had no XRD peaks suggested that it was completely amorphous. This is due to the PLLA exhibited slow crystallization after melt process[23]. Both the injection-molded 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA specimens exhibited XRD peaks at 16° assigned to the crystallites of PLLA end-blocks[7]. This demonstrated that the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were faster crystallization according to the DSC results as described above. However, the $X_{c,XRD}$ slightly decreased as the Joncryl® content increased from 4.0-8.0 phr. This may be explained by more branching structures of PLLA-PEG-PLLA suppressed crystallization of PLLA end-blocks[7].

The fact that 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited lower water contact angle than the PLLA suggested that both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA had more hydrophilicity than the PLLA. This is due to high hydrophilic nature of the PEG middle-blocks[12,19]. In addition, higher Joncryl® content also decreased water contact angle. This could be due to 8-PLLA-PEG-PLLA had lower the $X_{c,XRD}$.

The tensile curves of 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA showed the yield effect and higher stain at break than the PLLA. Both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA had more flexibility than the PLLA. This is due to 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA had lower T_g (30 and 31°C, respectively) than the PLLA (50°C). In this work, the 4.0 and 8.0 phr Joncryl® did not significantly change tensile properties of the injection-molded PLLA-PEG-PLLA. In a previous work, the chain-extension reaction also did not affect tensile properties of the compressed PLLA films[7].

The PLLA specimens were broken during flexural test but both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA specimens did not. The results indicated that the PLLA was brittle while the PLLA-PEG-PLLA was ductile[5]. The flexural properties, impact strength and hardness of the injection-molded specimens depended on its T_g value. The lower T_g specimens resulted in lower flexural stress, flexural modulus and hardness as well as higher impact strength because of its greater flexiblity[6]. The 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited smaller flexural stress and modulus than the PLLA suggested the PLLA-PEG-PLLA were more flexible than the PLLA due to their lower T_g.

The reduction in flexural stress and modulus of the PLLA-PEG-PLLA when Joncryl® contents increased from 4.0-8.0 phr was explained by the decrease in $X_{c,XRD}$ of the PLLA-PEG-PLLA with increasing the Joncryl® content. From the results of impact strength and hardness suggested that both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA were tougher and softener than the PLLA. This is due to highly flexible PEG middle-blocks[6]. So this study developed a novel bioplastic resins by chain extension of PLLA-PEG-PLLA. These bioplastic resins can be applied to polymer laboratories and companies for fabricating flexible and toughened bioplastic products through the injection molding process.

CONCLUSION

Both the 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA exhibited faster crystallization and a higher degree of crystallinity than that of the PLLA. From the results of mechanical tests, it was clearly shown that the injection-molded PLLA-PEG-PLLA specimens showed flexibility, toughness, soft and hydrophilicity greater than the injection-molded PLLA specimens. By increasing Joncryl® content in the PLLA-PEG-PLLA, the degree of crystallinity and MFI decreased as well as hydrophilicity increased but tensile properties, toughness and hardness did not change significantly. It can be concluded that these 4-PLLA-PEG-PLLA and 8-PLLA-PEG-PLLA might be of interest as highly flexible and toughened bioplastics for the production of injection-molded items in biomedical and packaging applications.

SIGNIFICANCE STATEMENT

This study discovered the chain-extension reaction can improve melt strength of PLLA-PEG-PLLA to decrease its MFI; that can be beneficial for injection molding application. The injection-molded PLLA-PEG-PLLA specimens exhibited crystallizability, hydrophilicity, flexibility, toughness and softness better than the injection-molded PLLA. The Joncryl® content in range 4.0-8.0 phr did not affect the mechanical properties of PLLA-PEG-PLLA. This study will help researchers uncover previously unexplored critical areas of melt processing of PLLA-PEG-PLLA by injection molding technique. Thus a new theory on injection molding of highly flexible and toughened PLLA-based bioplastics may have arrived.

ACKNOWLEDGMENTS

This research was funded by Mahasarakham University with grant number: 6105029. The National Research Council of Thailand (NRCT) and the Biodiversity-based Economy Development Office (BEDO) grant year 2017, Thailand are also acknowledged.

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