



## Improvement of Properties of Poly(L-lactic acid) through Solution Blending of Biodegradable Polymers

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**Abstract.** This study concerns the improvement and enhancement of the properties of poly(L-lactic acid) (PLLA) through simple solution blending of pure PLLA with different kinds of biodegradable polymers. Synthesized PLLA was blended with synthesized poly(D,L-lactic acid) (PDLLA) or poly(ethylene glycol) (PEG) at various composition ratios in a solvent mixture of dichloromethane/ethanol at room temperature to produce dipolymer. The polymer-blend properties were analyzed using FTIR, DSC, UTM data and an enzymatic degradation test was conducted. It was found that PLLA blend films were obtained with limitation of the second polymer content up to 20% (w) through solvent casting. From the DSC data, two different melting temperature peaks showed that stereocomplex formation occurred during polymer precipitation for all PLLA/PDLLA blends, while only one single melting temperature peak appeared in the PLLA/PEG blend. Regarding the mechanical properties, the PLLA/PEG blend showed better performance with an improvement of the mechanical strength by around 11.18% and an improvement of the elongation at break by around 89% compared to pure PLLA. Furthermore, after the 48-hour enzymatic biodegradability test, the PLLA/PEG blends showed improvement of biodegradability with 21.88% of sample weight-loss compared to 2.53% for pure PLLA.

**Keywords:** *biodegradability; mechanical properties; polylactic acid; PLLA/PDLLA; PLLA/PEG; solution blending; stereo-complex.*

### 1 Introduction

Consumption of conventional plastics as raw materials is increasing considerably from year to year along with the growing human population. Conventional plastic production contributes to petroleum consumption, CO<sub>2</sub> emission and non-degradable plastic waste. In the present millennium, demand and development of biomass-based polymers has increased significantly to substitute conventional plastics. Polymers made from biomass can reduce global warming by diminishing carbon emissions, reduce our carbon footprint and further improve carbon life-cycle assessment. This can occur because the synthesis process and raw materials of biomass-based polymers do not require

any fossil-fuel resources. Other environmental problems, such as air pollution and earth pollution, caused by conventional petroleum-based polymers can also be reduced with biomass-based polymers. The use of biodegradable polymers as an alternative conventional polymer material for replacing conventional polymer in the near future has been studied in [1,2].

Poly(lactic acid) (PLA) is a kind of biodegradable polymer from the polyester group that has excellent characteristics. PLA has a high tensile modulus, which leads to high thermal stability. Poly(L-lactic acid) (PLLA) has been known since 1960 as a biodegradable polymer for many biomaterial and biomedical applications such as implant materials, surgical sutures and controlled drug delivery systems due to its good biocompatibility and biodegradability [3,4]. It is the most promising bio-based polymer as a substitute for petro-based polymers as well as for other industrial fields because PLA has comparable properties, including mechanical properties, thermo-plasticity and fabricability [5]. However, PLA has drawbacks that limit its use in certain applications. In commercial applications for large-scale industrial production of packaging materials such as film and sheet casting, stretch blow molding, injection molding, bio-based PLA causes problems with its brittle mechanical properties and low crystallization rate [6]. Although its tensile strength and elastic modulus are comparable to those of petro-based polymer, its poor toughness limits its use in applications that need plastic deformation at higher stress levels [7].

Poly(lactic acid) has two enantiomers based on its monomer configuration, i.e. poly(L-lactic acid) and poly(D-lactic acid) (PDLA). A poly(lactic acid) with a monomer mixture. L- and D-lactyl units in unequal amounts is called poly(D,L-lactic acid) (PDLLA). Generally, PDLLA has a low molecular weight and crystallinity, showing weaker mechanical properties and a faster degradation rate, making it possible to be applied as a drug delivery vehicle or a scaffolding material for tissue generation [5].

To enlarge the application area of PLA, considerable research has been done by modifying and improving PLA properties through several common methods, such as blending, copolymerization and compositing [8-10]. Blending between two or more kinds of polymers is the most common and economical method of modifying PLA properties because it only utilizes physical interactions between the combined polymer chains. Blending of equimolarly fraction composition between PLLA and PDLA has been proven to produce a stereocomplex polymer blend of PLLA/PDLA with outstanding tensile strength, elastic modulus and elongation at break better than individual PLLA and PDLA homopolymers [11]. Further, poly(ethylene glycol) (PEG), known as a biodegradable plasticizer, is water soluble and has a low molecular weight,

ranging from 100-20,000 g/mol. PEG can enhance PLLA mechanical properties because PEG phase separation can be obtained at a certain composition [12,13].

The objective of this study was to modify and improve synthesized PLLA with PDLLA and study the effects of polymer blending with regard to the composition ratio of PDLLA or PEG. Synthesized PLLA was modified by solution blending with other biodegradable polymers such as PDLLA and PEG. The PLLA polymer blend was compared with PLLA as reference for improvement. Furthermore, detailed characterizations of the structural, thermal, mechanical and biodegradable properties of the polymer blends are reported and analyzed.

## **2 Experimental Method**

### **2.1 Material**

L-Lactide and lactic acid were purchased from Purac Biochem. Stannous Octoate [Sn(Oct)<sub>2</sub>: stannous 2-ethylhexanoate] catalyst and another catalyst, zinc oxide (ZnO) of 99.9% purity, were purchased from Sigma-Aldrich. Ethyl benzene, chloroform and methanol were supplied from Merck. Poly(ethylene glycol) (PEG) with average molecular number 400 as plasticizer was obtained from Sigma Aldrich. Dichloromethane and ethanol 96% were supplied from Merck. Enzyme proteinase K (lipophilic) was purchased from Sigma-Aldrich. Carbonate buffer (NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>), with pH 8.5, aqua bidestilation and sodium azide were purchased from Merck.

### **2.2 Synthesis of PLLA and PDLLA**

PLLA was synthesized through ring-opening polymerization using 755 g L-lactide monomer, 0.07 g Sn-(Oct)<sub>2</sub> catalyst and 45 g ethyl benzene in a 2-liter polymerization reactor. Polymerization was performed under stirring at 180 °C for 300 minutes at a speed of 100 rpm. PDLLA was synthesized through direct melt-polycondensation using 200 g lactic acid monomer and 0.1 g ZnO catalyst. PDLLA production was conducted in a 1-liter four-necked flask equipped with a mechanical stirrer and a reflux condenser connected to a vacuum system through a cold trap. The reaction was performed under stirring at 180 °C for 30 hours in reduced pressure of 10 torr.

The synthesized PDLLA had an average molecular weight (*M<sub>v</sub>*) of 79,000 gram/mol and the average molecular weight (*M<sub>v</sub>*) of the synthesized PLLA was 148,000 gram/mol. The related experimental conditions and results have been reported in our previous research paper [14].

### 2.3 Production of PLA Polymer Blends

For the polymer blend production, PLLA and PDLLA resin were placed into a drying oven at 40°C for 24 hours to remove their moisture. PLLA and PDLLA or PLLA and PEG were dissolved in dichloromethane-ethanol and stirred for two hours. Different amounts of PDLLA or PEG were added to the PLLA. Blended polymer solutions (PLLA/PDLLA and PLLA/PEG) were cast manually onto a 20 cm × 20 cm glass plate to produce PLLA/PDLLA or PLLA/PEG polymer blend films. The cast films were then air dried at room temperature (25°C) for 24 hours.

### 2.4 Characterization of PLA Polymer Blends

Functional group analysis of the synthesized PLLA and its polymer blend films was conducted with an FTIR instrument (IR Prestige-21 Shimadzu). The infrared spectrum of each sample was recorded from wavenumber 500 to 4000 cm<sup>-1</sup>.

Thermal properties were characterized using differential scanning calorimetry (DSC/TA Instruments, DSC 2010). The melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ) of each sample were measured. Specimens weighing 1-2 mg were heated at 250°C for 2 min and then quenched to 25°C at a cooling rate of 10°C/min. The samples were then reheated at a rate of 10°C/min from 25 to 250°C with constant nitrogen flow throughout. These second heating data were recorded to determine the melting point and crystallinity of the samples. The percentage of crystallinity ( $X_c$ ) of each sample was calculated according to Eq. (1):

$$X_c (\%) = \frac{\Delta H_m}{\omega_{PLLA} \times \Delta H_m^o} \times 100 \quad (1)$$

where  $\Delta H_m$  and  $\omega_{PLLA}$  are the melting enthalpy of the sample polymer blends and the weight fraction of the PLLA, respectively.  $\Delta H_m^o$  is the melting enthalpy for a pure component [5,6].

Stress at break ( $\sigma_B$ ), elongation at break ( $\epsilon_B$ ) and Young's modulus (E) of the PLLA and its polymer blend films were measured using a universal testing machine (TESTONE, TO-101). Specimen samples, 28 mm × 100 mm, were cut from the films. The samples were tensile tested at a crosshead speed of 12.5 mm/min. The values presented here are the averages of quadruple measurements.

Biodegradability testing was conducted out with an enzymatic method using proteinase K at pH 8.5. The films were cut to a size of 20 mm × 10 mm and weighed to give the initial weight before the degradation test ( $W_o$ ) and placed in

a 20-ml vial bottle containing 5 ml of carbonate buffer (pH 8.5), 0.25 mg of proteinase K and 1 mg of sodium azide. The enzymatic degradation test was carried out at 37°C in a shaking incubator at 140 rpm for 48 hours. Samples were taken periodically, washed with distilled water and then dried in a vacuum oven at 30°C for 24 hours. The dried samples were weighed to give the final weight after the degradation test ( $W_f$ ) in order to calculate the weight loss ( $\Delta W$ ).

### 3 Results and Discussion

#### 3.1 Structure Properties of PLA Polymer Blend

Table 1 shows the specific IR absorption peaks of the functional groups in the PLLA and its PLLA/PDLLA and PLLA/PEG polymer blends. In the PLLA/PDLLA polymer blend samples there was a slight absorption peak shift of the carbonyl functional group (C = O) from 1757  $\text{cm}^{-1}$  to 1755  $\text{cm}^{-1}$ . This suggests that weak interactions between PLLA and PDLLA chains occurred in the ester carbonyl functional group. The absorption peak of hydroxyl group vibration (3504  $\text{cm}^{-1}$ ) had not changed, indicating that the interaction between PLLA and PDLLA chains did not occur in the terminal-OH group of the PLLA. Note that the spectra of the methyl functional group (C-H) absorption peak that were found are similar to those from literature, in the range 2850–3000  $\text{cm}^{-1}$  [11].

On the other hand, the PLLA/PEG sample showed different interaction behavior compared to the PLLA/PDLLA sample. Interaction between PLLA and PEG chains occurred at the hydroxyl group and ether group vibrations, represented by a large shift of the hydroxyl absorption and ether peak from 3504 to 3429  $\text{cm}^{-1}$ , from 1097 to 1103  $\text{cm}^{-1}$ , respectively, while IR absorption from carbonyl and methyl vibration were observed relatively without any change. This proves that there is a strong OH group interaction at the end of the PLLA chains in the hydroxyl group of the PEG as hydrogen bond interaction.

In this research, it was found that a stereocomplex structure was formed in the polymer blend that contained PDLLA components only. In the PLLA/PDLLA polymer blend samples there was a slight absorption peak shift of carbonyl group vibration from 1757 to 1755  $\text{cm}^{-1}$  and symmetric  $\text{CH}_3$  vibration from 1381 (PLLA) to 1382  $\text{cm}^{-1}$  and ester group vibration from 1091 to 1097  $\text{cm}^{-1}$  (PLLA/PDLLA 20%-wt). This proves that there was interaction between the symmetric methyl and carbonyl functional groups as hydrogen bonds, which allows the formation of a stereocomplex structure [11].

**Table 1** Specific IR absorption peaks of PLLA and polymer blends.

Functional Group	PLLA	PLLA	
		80%/PDLLA 20 %	PLLA 80%/PEG 20%
Hydroxyl (-OH)	3504 cm <sup>-1</sup>	3504 cm <sup>-1</sup>	3429 cm <sup>-1</sup>
Carbonyl (-C=O)	1757 cm <sup>-1</sup>	1755 cm <sup>-1</sup>	1757 cm <sup>-1</sup>
Methyl (C-H)	2995 cm <sup>-1</sup>	2995 cm <sup>-1</sup>	2995 cm <sup>-1</sup>
	2945 cm <sup>-1</sup>	2945 cm <sup>-1</sup>	2943 cm <sup>-1</sup>
	2881 cm <sup>-1</sup>	2881 cm <sup>-1</sup>	2879 cm <sup>-1</sup>
Methyl Symmetric (-CH <sub>3</sub> sym)	1381 cm <sup>-1</sup>	1382 cm <sup>-1</sup>	1381 cm <sup>-1</sup>
Carbonyl (-C=O)	1757 cm <sup>-1</sup>	1755 cm <sup>-1</sup>	1757 cm <sup>-1</sup>
Ether (C-O-C)	1186 cm <sup>-1</sup>	1184 cm <sup>-1</sup>	1184 cm <sup>-1</sup>
	1091 cm <sup>-1</sup>	1097 cm <sup>-1</sup>	1103 cm <sup>-1</sup>

### 3.2 Thermal Properties of PLLA Polymer Blend

From the DSC data in Table 2, the PLLA had a melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ) of 176.9°C and 64.6 J/g, respectively, which are quite similar to data in the literature [5], as shown in the Table 2. Crystallinity of the PLLA polymer films was obtained at 42.6%. For all PLLA polymer blends, there was a melting temperature depression compared to pure PLLA. This phenomenon naturally occurs in polymer blend systems that are miscible and compatible [6]. Note that even though the synthesized PDLLA showed a lower melting temperature, it still produced increasing crystallinity ( $X_{HC}$ ) compared with the PLLA and its value was close to data reported in the literature.

**Table 2** Thermal properties of PLA and polymer blends.

Sample	Temperature (°C)		Enthalpy (J/g)		Crystallinity (%)	
	$T_{m1}$	$T_{m2}$	$\Delta H_{m1}$	$\Delta H_{m2}$	$X_{HC}$	$X_{SC}$
PLLA	176.9	-	64.6	-	42.6	-
PDLLA	112.9	-	62.1	-	66.7	-
PLLA 90%/PDLLA 10%	172.8	206.4	25.5	23.7	30.5	16.7
PLLA 80%/PDLLA 20%	173.2	207.0	20.2	25.0	27.2	17.6
PLLA 90%/PEG 10%	171.8	-	55.3	-	66.1	-
PLLA 80%/PEG 20%	170.0	-	51.7	-	69.5	-

In PLLA/PDLLA, two peaks of the melting temperature can be seen, where  $T_{m2}$  (206.4°C) was higher than  $T_{m1}$  (172.8°C) and  $T_m$  of the PLLA (176.7°C). The values of  $T_{m2}$  increased with the increase of PDLLA components from 10 to 20%-wt. The first melting temperature ( $T_{m1}$ ) is PLLA crystallite while the second melting temperature ( $T_{m2}$ ) is stereocomplex crystallite. The increase of PDLLA composition causes a higher melting temperature of the stereocomplex, which indicates that the stereocomplex structure is easier to be formed with a maximum value at an equimolar ratio of PLLA and PDLA [11]. Because of the melting point behavior, the crystallinity of the PLLA/PDLLA sample is divided into two types, i.e. crystallinity of homo-crystallite ( $X_{HC}$ ) and crystallinity

stereocomplex-crystallite ( $X_{SC}$ ). The calculations show a decrease in  $X_{HC}$  to 27.2%, whereas its  $X_{SC}$  increased with a maximum value of 17.6% for the composition of PDLLA 20%-wt.

The melting point properties ( $T_m$  and  $\Delta H_m$ ) of the PLLA/PEG samples behave as single point. There was a melting temperature depression and an increase of  $X_{HC}$  with an increase of PEG components from 10 to 20%-wt. There was no new melting peak ( $T_{m2}$  and  $\Delta H_{m2}$ ) at a temperature of around 200 °C because no new stereocomplex interaction was formed. This finding is supported by the FTIR spectrum that did not show any absorption peak shift at 1757  $\text{cm}^{-1}$  or 1381  $\text{cm}^{-1}$ . The increase in crystallinity of PLLA homocrystallite ( $X_{HC}$ ) can be explained by the FTIR spectra that exhibit interaction between the PLLA and the PEG at the hydroxyl group of the PLLA terminal chains as hydrogen bonds, which can induce the PLLA crystallization process and produce a higher degree of PLA crystallinity [15]. Maximum crystallinity was obtained of 69.5% with a composition of PEG 20%-wt.

### 3.3 Mechanical Properties of PLA Polymer Blend

Table 3 shows the results of the mechanical tests of the PLLA and its PLLA/PDLLA and PLLA/PEG polymer blends. PLLA has a brittle property, which is represented by its high Young's modulus ( $E$ ) and low elongation at break ( $\epsilon_B$ ) [11,15,16]. In this research, the results of the mechanical tests of the PLLA film showed similar behavior, i.e. high stress at break ( $\sigma_B$ ) (6.56 Mpa) and modulus of elasticity ( $E$ ) (314.60 Mpa), while the value of its elongation at break ( $\epsilon_B$ ) was very low (1%). Modification of PLLA with other biodegradable polymers can apparently decrease the value of the Young's modulus ( $E$ ), accompanied by an increase in the value of elongation at break ( $\epsilon_B$ ).

In the PLLA/PDLLA polymer-blend samples, an increase of PDLLA weight in the PLLA matrix affected the mechanical properties of the PLLA matrix. The mechanical test results showed that the addition of PDLLA 10%-wt resulted in a greater value of all mechanical property terms compared with the pure PLLA, which were:  $\sigma_B = 7.61$  MPa,  $\epsilon_B = 2.75$  %, and  $E = 349.77$  MPa. It can be concluded that the overall terms of mechanical strength of PLLA/PDLLA 10%-wt was slightly stronger than that of pure PLLA, an improvement of around 11.18%. This may be due to the presence of PDLLA components that contribute to stereocomplex formation [11,17].

The mechanical results of the polymer blends supported other results that PEG can improve the mechanical properties PLLA up to 20%-wt because PEG phase separation can occur at higher composition [13]. The different composition may be due to the difference in PLLA molecular weight used.

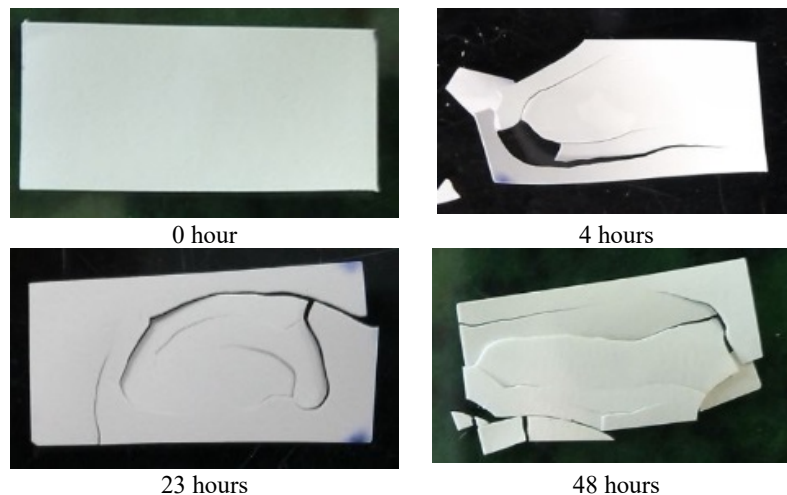
**Table 3** Mechanical properties of PLA and polymer blends.

Sample	$\sigma_B$ (MPa)	$\epsilon_B$ (%)	E (MPa)
PLLA	6.56	1.00	314.60
PLLA 90%/PDLLA 10%	7.61	2.75	349.77
PLLA 80%/PDLLA 20%	5.48	6.25	237.77
PLLA 90%/PEG 10%	6.01	29.50	280.77
PLLA 80%/PEG 20%	3.37	89.00	228.35

The behavior of the mechanical properties of the PLLA/PEG polymer blend showed better performance of elongation at break, decrease of stress at break, and Young's modulus (E). This is because PEG has a lower tensile strength than pure PLLA [15,18]. Improved composition of the PEG resulted in an increased value of  $\epsilon_B$ , maybe due to the addition of PEG, which plays a role as a nucleating agent improving crystallinity of the PLLA as well acting as a plasticizer.

### 3.4 Biodegradable Properties of PLA Polymer Blend

The addition of PDLLA or PEG to the PLLA matrix through solution-blending improved the biodegradability of the PLLA. Figure 1 shows a visual representation of typical enzymatic degradation of the polymer blend samples during the course of a biodegradability experiment from 0 to 48 hours. The polymer blend was degraded significantly by the enzyme compared with after 4 and 23 hours, respectively.



**Figure 1** Visual representation of enzymatic degradation of polymer blend samples.



Furthermore, Table 4 and Figure 2 show the dynamic weight of selected samples during enzymatic degradation. It supports the visual representation: significant loss of weight from the initial weight of the samples after 48 hours of enzymatic degradation. The PLLA sample had the lowest weight loss during the degradation test from 0 to 48 hours, while its polymer blend samples showed higher weight loss compared to the pure PLLA. This may be due to pure PLLA having higher crystallinity than PLLA/PDLLA [17].

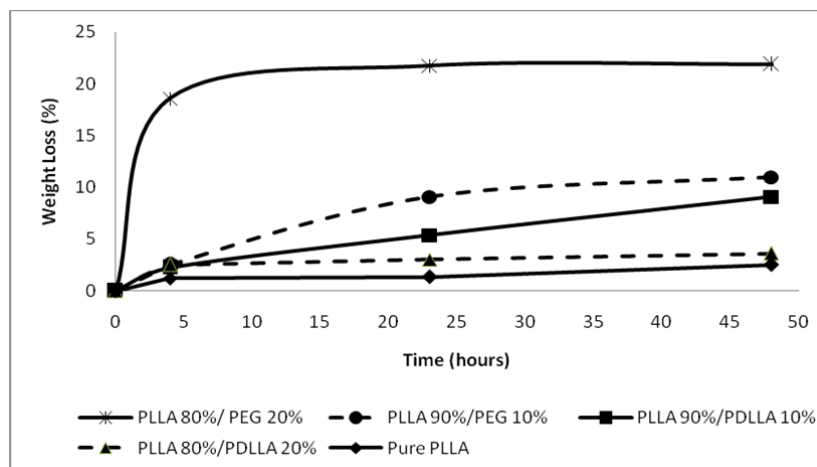
In the PLLA/PDLLA sample, the increase of PDLLA content showed a decrease of weight loss percentage along the degradation test. This can be explained by the increase of PDLLA content in the PLLA matrix producing an increase of stereocomplex crystallinity ( $X_{SC}$ ) among chains of PLLA/PDLLA. Stereocomplex crystallinity could affect the degree of degradability of the polymer by the enzyme proteinase K [11]. Moreover, the addition of PDLLA can increase the fraction of D-unit ( $X_D$ ) in a polymer blend, which can be more difficult to be hydrolyzed by the enzyme proteinase K due to differences between the catalytic site (binding site) of the enzyme structure and the substrate structure [19].

**Table 4** Dynamic weight of selected samples during enzymatic degradation.

Samples	Time (hours)	Weight ( $\times 10^{-2}$ mg)			Weight Loss (%)
		$W_0$	$W_t$	$\Delta W$	
PLLA	4	0.84	0.83	0.01	1.19
	23	1.52	1.49	0.03	1.97
	48	0.79	0.77	0.02	2.53
PLLA 90%/PDLLA 10%	4	0.90	0.88	0.02	2.22
	23	0.93	0.88	0.05	5.38
	48	0.99	0.90	0.09	9.09
PLLA 80%/PDLLA 20%	4	0.79	0.77	0.02	2.53
	23	1.00	0.97	0.03	3.00
	48	0.83	0.80	0.03	3.61
PLLA 90%/PEG 10%	4	0.80	0.78	0.02	2.50
	23	0.77	0.70	0.07	9.09
	48	0.73	0.65	0.08	10.96
PLLA 80%/PEG 20%	4	0.70	0.57	0.13	18.57
	23	0.69	0.54	0.15	21.74
	48	0.64	0.50	0.14	21.88

Regarding the polymer blend of the PLLA/PEG samples, the increase of PEG content in the PLLA matrix showed the largest weight loss compared to the other blends. This may be because the dissolution of the PEG in the degradation media can increase the porosity of the blend and produce a greater area of the films to be accessed by the enzyme proteinase K. Another possibility is that increasing the PEG content means increasing the hydrophilicity polymer film in the degradation media, so that it accelerates the degradation and increases the

mobility of the molecular chains of the PLA, which facilitates enzymatic degradation.



**Figure 2** Percent weight loss of PLLA and its polymer blends (PLLA/PDLLA and PLLA/PEG).

#### 4 Conclusion

The mechanical and biodegradation properties of poly(L-lactic acid) (PLLA) were successfully modified through solution-blending with a biodegradable polymer, poly(D,L-lactic acid) (PDLLA) or polyethylene glycol (PEG).

The addition of PDLLA in the PLLA matrix produced the formation of stereocomplex structures that could improve the mechanical properties the PLLA, whereas PEG acted as a plasticizer and nucleating agent on the polymer blend. It was found that the polymer blend with PLLA/PDLLA 10%-wt had higher values for all mechanical property terms (around 11.18%) compared with pure PLLA, while the polymer blend with PLLA/PEG 20%-wt had the highest improvement of elongation at break (around 89%).

Furthermore, after a 48-hour enzymatic biodegradability test, the PLLA/PEG blend showed improvement of biodegradability compared with the PLLA. Also, the biodegradability of the homopolymer and the blend polymers was shown visually as well as through the weight loss percentages of the polymers. It was found that the homopolymer PLLA was affected by the other polymers (PDLLA and PEG) added to the PLLA matrix. The polymer blend with PLLA/PEG 20%-wt showed the highest value of weight loss (21.88%) compared with the pure PLLA (2.53%).

### Nomenclature

$\Delta H_m$	Enthalpy of melting (J/g)
$\omega$	Weight fraction (%)
$T_m$	Melting temperature (°C)
$M_v$	Average molecular weight (gr/mol)
$X$	Fraction/composition (%)
$X_c$	Fraction of crystallinity (%)
$X_{HC}$	Fraction of homo-crystalline (%)
$X_{SC}$	Fraction of stereocomplex crystalline (%)
$\epsilon_B$	Elongation at break (%)
$\sigma_B$	Stress at break (MPa)
$E$	Young's modulus (MPa)

### Acknowledgements

We acknowledge the financial support from the research grant (*Grant Sawit*) received through the Indonesia Agency for Oil Palm Estate Fund (BPDP *Kelapa Sawit*), Indonesia, for this work. Dr. Hyung Woo Lee is a distinguished visiting scholar, assigned at the Department of Chemical Engineering, Faculty of Industrial Technology, Bandung Institute of Technology, Indonesia, by National Research Foundation of Korea through TPC program.

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