CHAPTER VI
POLY(L-LACTIC ACID)-POLY(ETHYLENE GLYCOL)-POLY(L-LACTIC ACID) (PLLA-PEG-PLLA) TRIBLOCK COPOLYMER AND ITS PERFORMANCE IN PLA-BASED FILM

6.1 Abstract

PLLA-PEG-PLLA triblock copolymer was simply prepared through esterification between L-lactic acid (L-LA) and diol PEG. Chain length of PLLA in block copolymer was varied by molar feeding ratios (mole LA/mole PEG). The short PLLA chain in block copolymers influenced on crystallization behavior of block copolymers, it performed completely amorphous phase. The crystallinity of commercial PLA was improved significantly to 40% when 20 %wt and 30 wt% PLLA-PEG-PLLA2 triblock copolymer were blended with PLA. PEG homopolymer as plasticizer was replaced by PLLA-PEG-PLLA block copolymer which demonstrated the miscibility improvement in PLA matrix and noncrystallizable PEG segment, traced by calorimetry technique and temperature dependence of X-ray diffraction. The mechanical properties of PLA blended with PLLA-PEG-PLLA block copolymers were comparable to PLA/PEG homopolymer blend.

6.2 Introduction

At the present, poly(lactic acid) or PLA has played an important role in packaging films since its outstanding performances are high transparency, high mechanical strength, and moderate gas barrier properties.[1-2] Unfortunately, the slow crystallization and its high glass transition (T_g) temperature, leading to the PLA film brittleness, always obstruct the practical uses.

In general, these problems can be overcome simply by adding plasticizer. The acceptable plasticizers for PLA, such as polyethylene glycol (PEG), polypropylene glycol (PPG), triphenyl phosphate (TPP), citrate esters, etc were reported.[3-7] They function in reducing T_g and accelerating crystallization due to a promotion of PLA chains mobility and packing. For instance, the T_g of PLA blended

with PEG shifted to 20 °C with 30 wt% PEG whereas PLA blended with PPG, its T_g was reduced to 30 °C with 12.5 wt% PPG.[4,5] The totally amorphous PPG resulted in no phase separation during PLA crystallization when the PPG molecular weight was less than 1000 g/mol.[4] PEG plasticizer is widely applied with PLA because of its biocompatibility and its low T_g, however, simple blending of PLA and PEG has a major drawback, i.e. PEG migration. This occurred by the differences of crystallization behavior because two-component systems containing high-molecular-weight materials generally exhibit unfavorable thermodynamics of mixing, leading to macrophase separation, poor interfacial adhesion, and inferior mechanical properties.[4,5,8,9] The 20 wt% PEG having a molecular weight of 1,000 g/mol, blended with PLA performed phase segregation in PLA matrix.[10]

Many previous studies explored PLA-b-PEG copolymers (both linear and branched copolymers) to overwhelm the phase separation. Lee *et al.* prepared PLLA-PEG multiblock copolymers with long blocks of PEG (M_n: 2,000-10,000) and PLLA (M_n: 2,000-4,500), as a compatiblizer in PLLA/PEG blends.[11] In addition, Luo *et al.* also adjusted the block lengths of both PLA and PEG segments to control the crystallinity and hydrophilicity while their main objective was the material for drug delivery system.[12]

Mostly, PLA-PEG block copolymer was developed for only biomedical applications[12-15] while few reports about the use of PLA-PEG block copolymer for ductilable packaging. It comes to our viewpoint to clarify the possibility of the use of PLA-PEG block copolymer as a component in PLA blend under the concept of block copolymer in order to avoid phase separation. In addition, the mechanism of PLA-PEG block copolymer in PLA blend during crystallization have not been elucidated enough.

Herein, PLLA-PEG-PLLA block copolymer was simply synthesized by esterification between L-lactic acid (L-LA) and PEG with satisfying structure clarification in order to illustrate the concept of applying block copolymer in polymer matrix in order to improve miscibility. The effect of different PLLA chain length in block copolymer on PLA crystallinity and miscibility was also studied systematically. Furthermore, the mechanical properties of PLLA-PEG-PLLA block

copolymer as plasticizer were investigated and compared to PLA/PEG homopolymer blend.

6.3 Experimental

6.3.1 Materials

Poly(lactic acid) (PLA2002D, M_w 140,000 Da) was the product of Nature-Works LLC, USA. L-Lactic acid (L-LA) (88 wt% aqueous solution) and polyethylene glycol (PEG) (M_n 6,000 Da) are the gifts from PURAC Thailand Ltd., and Thai Polyacetal Co.,Ltd., Thailand, respectively. Stannous octoate (Sn(Oct)$_2$) was purchased from Sigma-Aldrich, Germany.

6.3.2 Synthesis of Poly(L-lactic acid)-poly(ethylene glycol)-poly(L-lactic acid) (PLLA-PEG-PLLA) Triblock Copolymers

L-LA and PEG at a certain molar ratio (i.e. L-LA/PEG molar feeding ratio : 300/1 and 100/1) was added into a three-necked round bottom flask and purged with nitrogen gas thoroughly. The reaction was carried out under vacuum with continuous stirring at 100 °C for 2 h, before adding Sn(Oct)$_2$ as catalyst into the system (only for 300/1 molar ratio). The temperature was raised up to 140 °C to proceed the polymerization of PLLA for 24 h. The crude product obtained was dissolved in chloroform at room temperature before precipitating in cold methanol. The purification was carried out for three times followed by drying in vacuum at 50 °C for a day to obtain PLLA-PEG-PLLA 1 and PLLA-PEG-PLLA 2 which were the products from LA/PEG molar feeding ratio : 300/1 and 100/1, respectively.

6.3.3 PLA/PLLA-PEG-PLLA Blends Preparation

PLA (PLA 2002D) was blended with a PLLA-PEG-PLLA obtained from 6.3.2 by using a LABTECH ENGINEERING LTE-20-40 counter-rotating twin screw extruder (L/D 40/1, screw speed 25-30 rpm at 155-165 °C). The blend ratios between PLA and those of PLLA-PEG-PLLA were 90:10, 80:20 and 70:30

6.3.4 Characterization of PLLA-PEG-PLLA Triblock Copolymers and Their Blends

Chemical structure of PLLA-PEG-PLLA triblock copolymers was clarified by a Bruker Ultrashield Plus 500 MHz AVANCE III nuclear magnetic resonance (NMR) spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent.

Molecular weights of PLLA-PEG-PLLA block copolymers were determined by a LC-10ADvp Shimadzu gel permeation chromatography (GPC). Chloroform was used as the mobile phase at a flow rate of 1 mL/min. Standard polystyrene was used to develop calibration curve to calculate molecular weight of the polymers.

Thermal properties and crystallinity were determined by using a Netzch DSC 200 F3 Maia differential scanning calorimetry (DSC). All types of PLLA-PEG-PLLA and their blends with PLA were sealed in aluminium pan (about 5-10 mg) and were heated from -20 to 200 °C (heat-cool-heat) at a scanning temperature rate 5 °C/min under nitrogen flow (50 ml/min).

Crystallization behavior of both PLLA-PEG-PLLA block copolymers and PLA/PLLA-PEG-PLLA blends were investigated by temperature dependence of X-ray diffraction with a Rigaku TTR-III X-ray diffractometer where the Cu-Kα line was used as incident X-ray beam.

Machanical property was characterized by a Lloyd LRX tensile test, all samples were performed on rectangular 1 cm wide x 10 cm long strips. They were extended with 50 mm/min and 0.5 kN load capacities according to ASTM D-638 at room temperature.

6.4 Results and Discussion

6.4.1 PLLA-PEG-PLLA Structure Characterization

In this work, PEG was used as a diol functional molecule for esterification with L-LA. Two different molecular weights of block copolymer can be obtained by varied feeding molar ratios. The structural characterization by using Fourier transform infrared spectroscopy (FTIR) confirmed an increase of C=O ester

peak (1760 cm⁻¹) and a decrease of C=O carboxyl group (1690 cm⁻¹). The hydroxyl group band (3350 cm⁻¹) was also declined obviously which could confirm indirectly the success of esterification between L-LA and diol PEG. It has an agreement with ¹H NMR spectrum of PLLA-PEG-PLLA block copolymer, it showed the chemical shifts at 1.47-1.60 (methyl (-CH₃)) and 5.10-5.20 ppm (methine (-CH-)) of PLA chain units and at 3.66 ppm (methylene (-CH₂-CH₂-O-)) of PEG segment that can confirm the successful block copolymerization between PEG and PLLA. The terminal PLA chains connected PEG segment together with -CH₂-CH₂-O- protons of PEG shows which appear in the range of 4.10-4.37 ppm (Figure 6.1).[12]
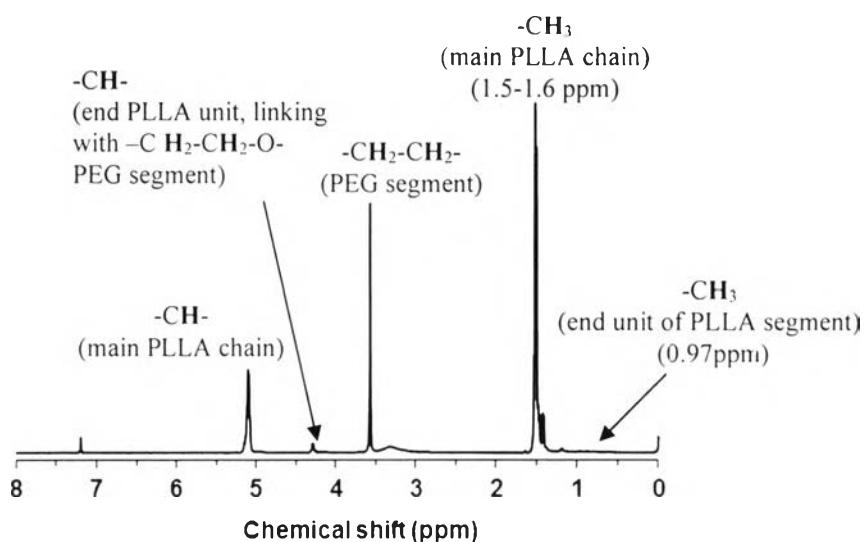

Figure 6.1 ¹H NMR spectrum of PLLA-PEG-PLLA 1 triblock copolymer obtained from L-LA/PEG molar feeding ratio 100/1.

Due to simple esterification reaction of PEG and LA monomer, ¹H-NMR integral ratio of PLLA and PEG segments implied that chain scission of PEG could occur, especially in high molar feeding ratio. To answer the question that the success of PLLA-PEG-PLLA block copolymer formation was obtainable through simple synthesis, 2D HMBC NMR spectra are evident with the appearance of the correlation between protons of PEG segment (3.6-3.8 ppm) and carbon of carbonyl group in PLLA segment (around 170 ppm) (Figure 6.2). PLLA-PEG-PLLA1 shows

the correlation at 3.65 ppm and 172 ppm whereas PLLA-PEG-PLLA2 correlation was presented at 3.69 ppm and 169.5 ppm, respectively. It is worth noticing that this simply synthesized PLLA-PEG-PLLA block copolymer can be achievable.
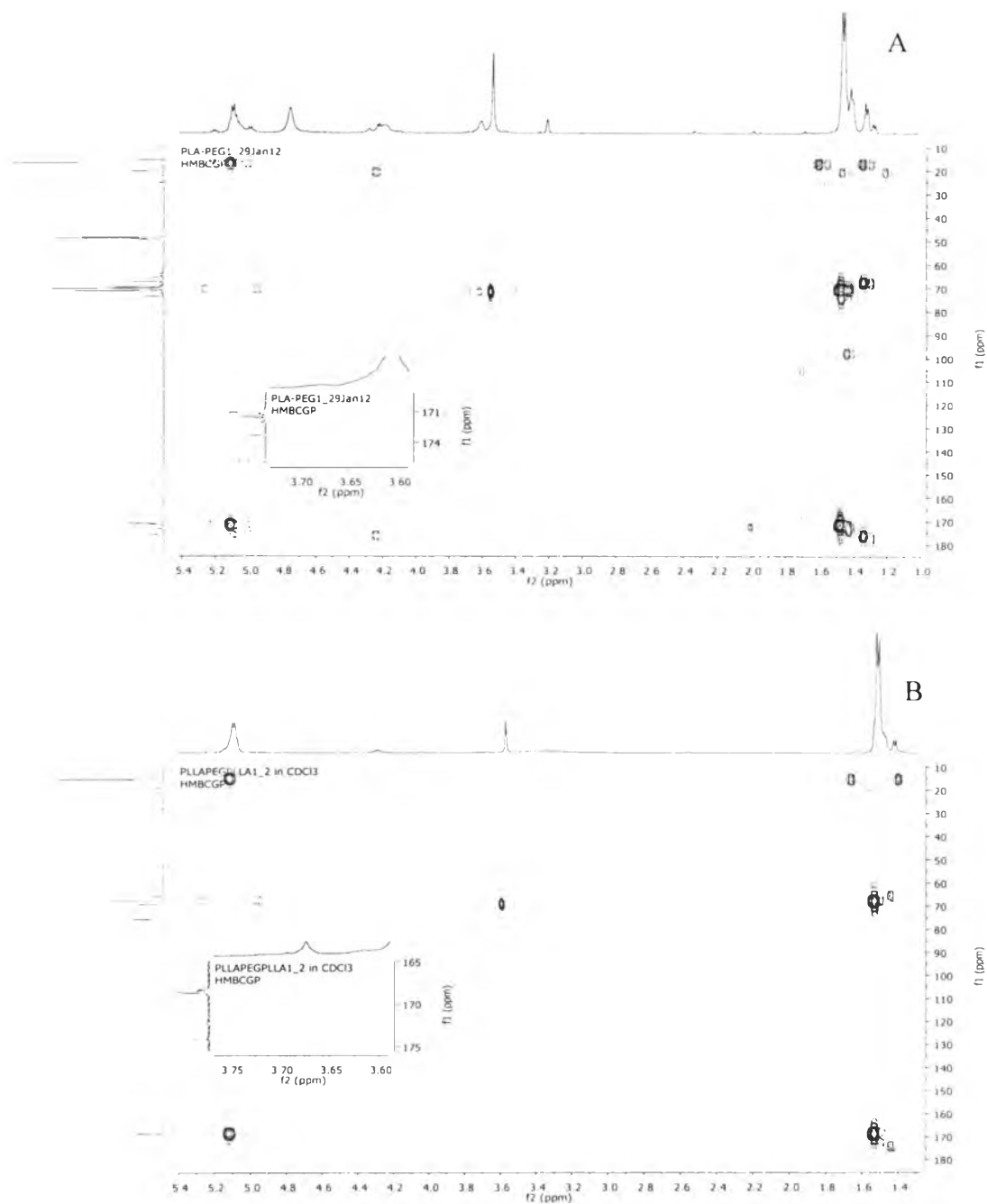

Figure 6.2 2D HMBC NMR spectra of (A) PLLA-PEG-PLLA1 and (B) PLLA-PEG-PLLA2.

The molecular weights of each PLLA-PEG-PLLA copolymers were determined by GPC (Table 6.1). In case of high molar feeding ratio, bimodal distribution of molecular weight was found which are around M_w 11,140 and 1,280 Da with low PDI whilst low molar feeding ratio provided M_w ~4,000 Da. Regarding to synthetic condition, PEG chain scission might occur in this system, the molecular weight of PEG was reduced to around 1,500-2,000 Da consisting in block copolymer, approximately caluculated from ^{1}H NMR spectrum integral ratio.

Table 6.1 Molecular weights of PLLA-PEG-PLLA triblock copolymers obtained from varied molar feeding ratios.

L-LA/PEG (Molar feeding ratio)	M_n^b (x 10^3 g/mol)	M_u^b (x 10^3 g/mol)	PDI
100/1 (PLLA-PEG-PLLA1)	2.97	3.94	1.33
300/1 (PLLA-PEG-PLLA2)	10.96, 1.10	11.14, 1.28	1.02, 1.34

^{a} calculated from ^{1}H NMR ^{b} determined by GPC

6.4.2 Thermal Properties of PLLA-PEG-PLLA

Melting temperature (T_m) of PEG homopolymer was changed drastically when PLLA-PEG-PLLA block copolymer formed. In case of high moleculare weight PLLA-PEG-PLLA2, T_m of PEG was observed around 30.5 °C while low molecular weight PLLA-PEG-PLLA1 shows fully amorphous phase with glass transition temperature (T_g) ~2.7 °C. PLLA T_g in PLLA-PEG-PLLA2 decreased from 55 °C to 25.6 °C which overlapped with PEG T_m.
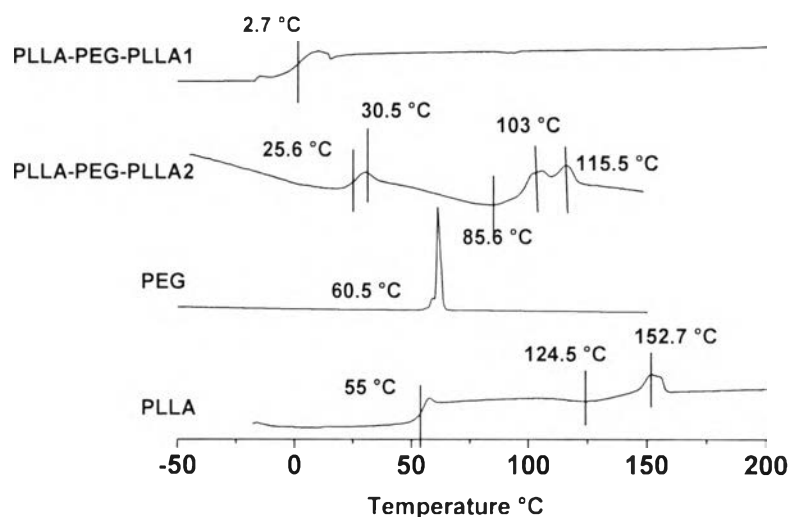
Figure 6.3 DSC thermogram of pure PLLA, PEG and PLLA-PEG-PLLA1 and 2.

It could be noted that the chain length of PLLA segment of block copolymer has an effect on PLLA and PEG crystallization, short PLLA chain can retard PEG to crystallize itself which is an important factor in phase separation reduction between PLA and PEG.

6.4.3 Thermal Properties of PLA/PLLA-PEG-PLLA Blends

In order to observe how PLLA-PEG-PLLA block copolymer plays the role as plasticizer for brittle PLA, crystallization temperature (T_c), T_g and T_m of PLA after blending, compared to PLA/PEG homopolymers blend were investigated. In addition, the crystallinity of each blend was studied by focusing on the enthalpy of diffusion (ΔH_m) as compared to the ΔH_m of the completed crystalline PLA for 93.1 J/mol.[16] In the case of our PLA, the crystallinity as about 3.7% whereas those of the blends were about 30-50%. At 10 wt% PEG and PLLA-PEG-PLLA, PEG T_m cannot be observed which indicated that there was no phase separation of PEG in PLA matrix, as tabulated in Table 6.2.

Table 6.2 Thermal properties of neat PLA, PEG, and PLLA-PEG-PLLA block copolymers.

Sample	Temperature (°C)				PLA X_c[a]
	T_g	T_c	PEG T_m	PLA T_m	(%)
PLA	58.2	124.5		152.2/ 156.2	3.7
PEG (M_w 6000 g/mol)	-	36.3	60.5	60.5	89.6[b]
PLLA-PEG-PLLA 1	2.7	-	-	-	-
PLLA-PEG-PLLA 2	25.6	85.6	30.5	103/115.5	-
PLA/PEG6000 90/10	36.6	80.2	-	153.2	38.5
PLA/PLLA-PEG-PLLA 1 90/10	5.6	59.3	-	104.1/130.1	34.4
PLA/PLLA-PEG-PLLA 2 90/10	42.7	96.0		134.7/146.3	45.8
PLA/PEG6000 80/20	32.6	-	51.7	136.8/ 149.5	49.4
PLA/PLLA-PEG-PLLA 1 80/20	-5.9	63.0	-	109.1/119.5	24.32
PLA/PLLA-PEG-PLLA 2 80/20	36.3	85.2	-	126.3/138.8/146.2	48.6
PLA/PEG6000 70/30	-	-	**56.0**	**138.6/150.9**	**36.2**
PLA/PLLA-PEG-PLLA 1 70/30	**-13.6**	**65.0**	-	**103.6/107.9**	**29.4**
PLA/PLLA-PEG-PLLA 2 70/30	**16.9**	**66.1**	-	**130.3/145.7/148.2**	**49.5**

[a] $X_c = \Delta H_m * 100/(93.1 * \text{weight fraction of PLA})$

[b] $X_c = \Delta H_m * 100/196.8$

Considering to PEG content in blend, T_m of PEG appears significantly with increasing of PEG weight fraction in blend whereas PLA crystallintiy was improved drastically from 4% to 38% with 10 wt% PEG. The PLA crystallinity was enriched by PEG until its content reached 30 wt%, the PLA crystallinity was dropped for 15%. It is an evidence of PEG segregation from PLA matrix (Figure 6.4). In case of block copolymer blends, amorphous PLLA-PEG-PLLA1 contributed to decrease PLA T_g remarkablely whilst its PLA crystallinity was decreased with PLLA-PEG-PLLA1 content increase, related to short PLLA chain obstructing crystallization as evidence in Huang *et al.* study.[17] Additionally, PLLA-PEG-PLLA2 also gradually reduced PLA T_g with preserved high crystallinity, as shown in Table 6.2. PLLA-PEG-PLLA2 with long PLLA segment demonstrates significantly in high crystallinity maintenance even in 70/30 weight ratio without PEG T_m presence. Furthermore, T_m of low molecular weight PLLA homopolymer, contaminant in block copolymer, can be observed in all weight ratio which was lower than that of commercial PLA. It is worth noticing that both PLLA-PEG-PLLA block copolymers can perform as effective plasticizer for PLA without PEG phase segregation.
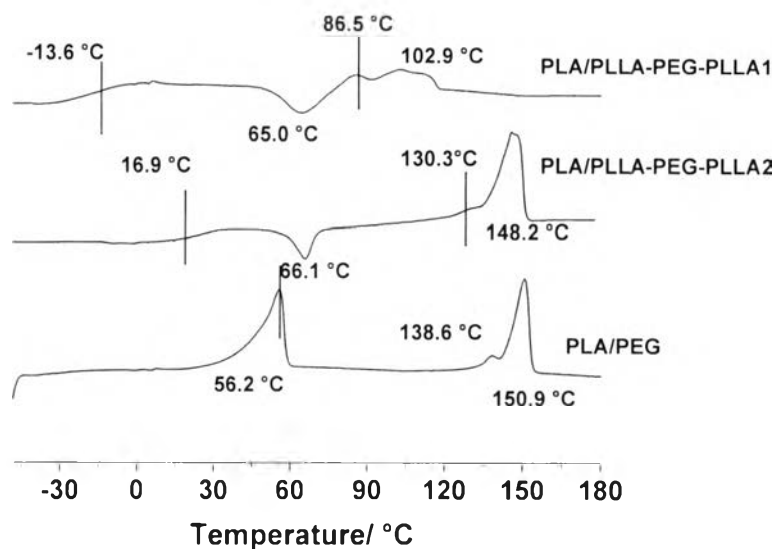
Figure 6.4 DSC thermogram of 70/30 PLA/PEG and PLA/PLLA-PEG-PLLA blends.

6.4.4 Crystallization Behavior of PLA/PLLA-PEG-PLLA Blends

In order to clarify more precisely in noncrystallizable PEG of block copolymer, temperature dependence X-ray diffraction technique was applied. At room temperature, PEG homopolymer presents highly crystalline state, the main diffraction at 23.3° appears strongly whereas PLA homopolymer presents the main diffraction at 16.4° after annealing at 110 °C for 1 hour. When 30 wt% PEG was blended with PLA, the board peak at 23.3° was observed clearly that was disappeared in PLA/PLLA-PEG-PLLA blends even annealing at 20 °C for 1 h (Figure 6.5). It should be noted that miscibility was improved through PLLA-PEG-PLLA block copolymer.
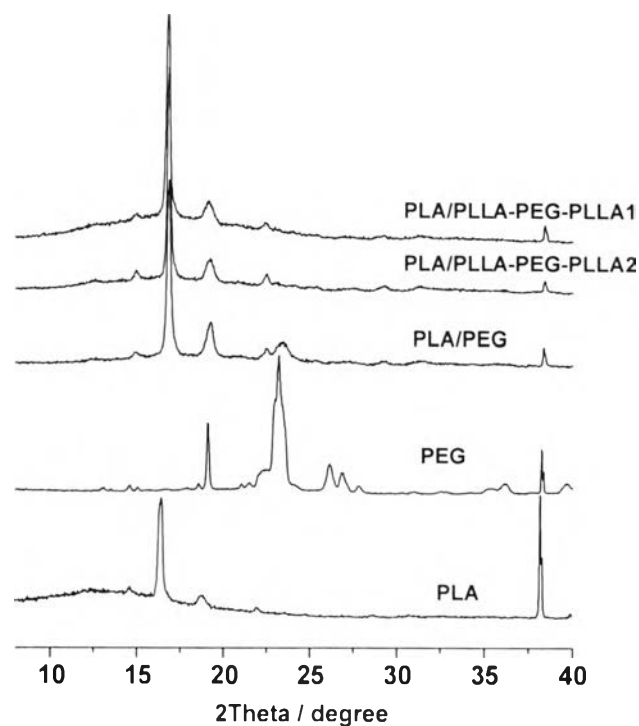
Figure 6.5 WAXD profiles of PLA, PEG and PLA/PEG and PLLA-PEG-PLLA 70/30 blend.

In case of PLA blended with PEG and PLLA-PEG-PLLA, the PLA diffrations at 14.9° and 18.8° can be seen explicitly at room temperature. It confirms that PLLA-PEG-PLLA can accelerate PLA crystallization efficiently, comparable to PEG homopolymer.

Figure 6.6 shows diffraction patterns of pure PLA, exhibiting slow crystallization rate with high T_c (~125 °C) as pure PEG can crystallize very fast, its diffraction patterns display sharply at room temperature. In case of block copolymer, PLLA-PEG-PLLA1 cannot be cold-crystallized during heating, it shows amorphous state predominantly. It could be noted that short PLLA segments cannot crystallize itself and also retard PEG crystallization. When PLLA segment length increased, semicrystalline structure can be observed in PLLA-PEG-PLLA2. There was no PEG crystals formation below 60 °C (PEG T_m). Both simply synthesized block copolymers can restrict PEG crystallization, this phenomenon has an agreement with Zhang and coworkers study.[18]
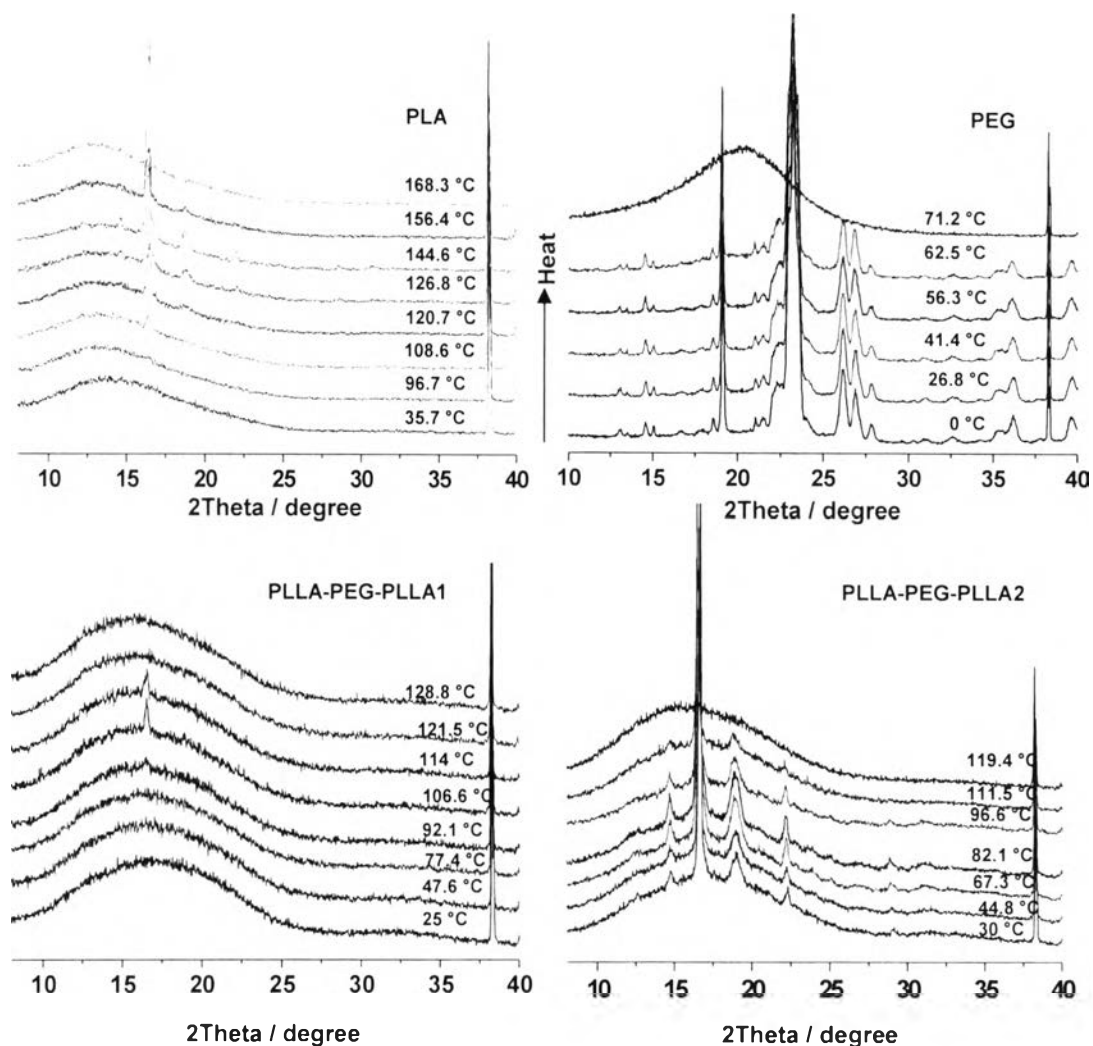
Figure 6.6 Temperature dependence WAXD patterns of PLA, PEG and PLLA-PEG-PLLA block copolymers.

To support our speculation, temperature depencedence WAXD patterns of PLA blended with PEG and PLLA-PEG-PLLA at 70/30 weight ratio were presented in Figure 6.7. The 23.3° diffraction of PEG crystals manifests obviously at 20 °C before it disappears at 70 °C (above PEG T_m). It points out that there were PEG crystals in the system at 20 °C and then they were molten with heating at above 70 °C, as shown in Figure 6.7.
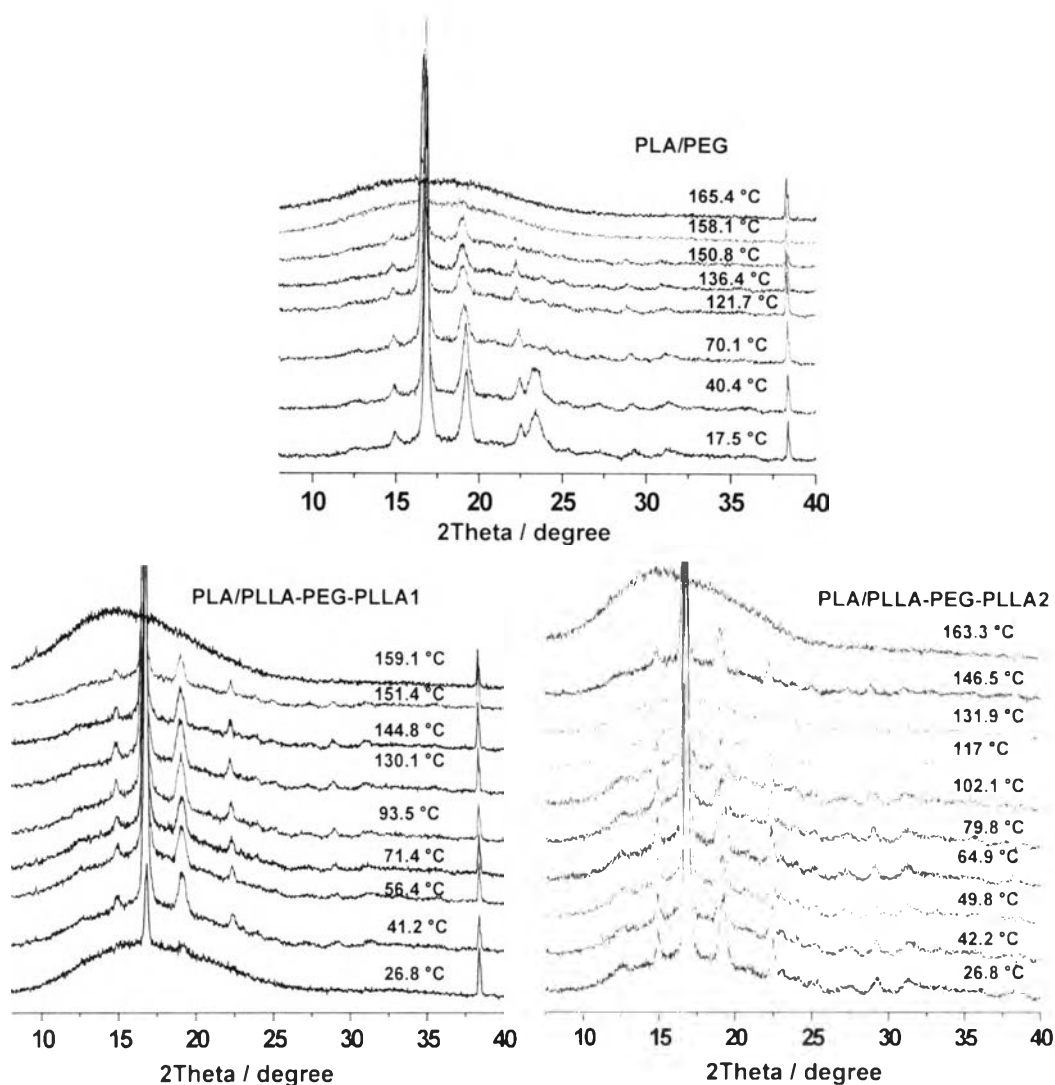
Figure 6.7 Temperature dependence WAXD patterns of PLA/PEG and PLA/PLLA-PEG-PLLA 70/30 blends.

When 30 wt% PLLA-PEG-PLLA blended with PLA, PLA crystallization behavior related to block copolymer structure. Amorphous PLLA-PEG-PLLA1 restricted PLA crystalliation at 26.8 °C, only main diffraction of PLA (16.4°) can be found without 23.3° diffraction of PEG presence. Cold crystallization of PLA blended with PLLA-PEG-PLLA1 has an agreement with DSC data, PLA can crystallize when the system temperature was reached at 40-60 °C. Meanwhile, PLA/PLLA-PEG-PLLA2 70/30 blend presents the crystallized PLA phase without PEG crystals at 26 °C. The intensity of 22.5° was constant even above 70 °C which

confirmed that PLLA-PEG-PLLA2 can prevent PEG recrystallization clearly in the system.

6.4.5 Mechanical Properties of PLA/PLLA-PEG-PLLA Blends

Considering potential of PLLA/PEG/PLLA as plasticizer for PLA comparable to PEG homopolymer, PLA blended with both PEG and PLLA-PEG-PLLA were casted to be film and characterized by tensile test (Figure 6.8).
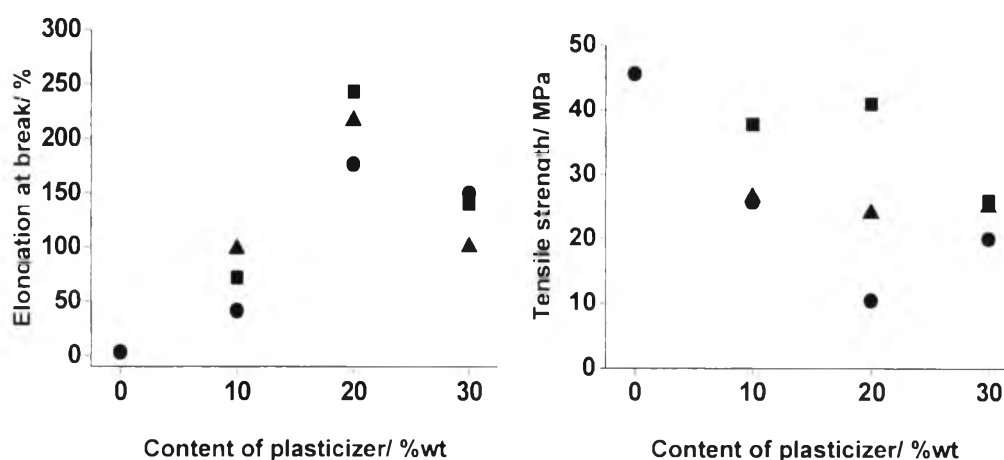

Figure 6.8 %Elongation at break and tensile strength of PLA/PEG and varied PLLA-PEG-PLLA blends as a function of plasticizer content (● PEG, ▲ PLLA-PEG-PLLA1, ■ PLLA-PEG-PLLA2).

PEG can improve %elongation at break of PLA film drastically, especially 20 wt% PEG, while tensile strength was decreased. However, %elongation at break of PLA/PEG film was dropped down at 30 wt% while its tensile strength increased, this phenomenon refers to phase separation of PEG in blend matrix. In case of PLLA-PEG-PLLA blends, the trend of %elongation is similar to of PEG wheras both PLLA-PEG-PLLA block copolymers can preserve tensile strength even at 20 wt% PLLA-PEG-PLLA, higher than that of PEG blend. It is noted that nonrecrystallizable PEG in block copolymer can improve miscibility in PLA blend successfully.

6.5 Conclusions

The polymerization of L-LA on PEG allowed us to obtain PLLA-PEG-PLLA block copolymer. Although the compound obtained might be in various possible block copolymer structures, the structural characterization by GPC and 2D HMBC NMR confirmed PLLA-PEG-PLLA containing PLLA block with short and long PLLA chains. The PLA blend system containing PLLA-PEG-PLLA block copolymer showed a decrease of T_g and a decrease of T_c with two T_m. The enhanced crystallization of PLA blend by PLLA-PEG-PLLA with long PLLA segment can be comparable to PLA/PEG blend. The blend also shows the miscibility between two components. There no PEG crystallization in PLLA-PEG-PLLA and its blend traced from X-ray diffraction patterns, compared to pure PEG. The mechanical properties of PLA blended with PLLA-PEG-PLLA block copolymer was preserved, comparable to PLA/PEG blend.

6.6 Acknowledgements

6.7 References

(1)   Auras, R.; Harte, B.; Selke, S. *Macromolecular Bioscience* **2004**, *4*, 835.

(2)   Garlotta, D. *J Polym Environ* **2002**, *9*, 63.

(3)   Martin, O.; Avérous, L. *Polymer* **2001**, *42*, 6209.

(4) Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. *Biomacromolecules* **2006**, *7*, 2128.

(5) Hu, Y.; Hu, Y. S.; Topolkaraev, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5681.

(6) Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *Journal of Applied Polymer Science* **2003**, *90*, 1731.

(7) Xiao, H.; Lu, W.; Yeh, J.-T. *Journal of Applied Polymer Science* **2009**, *113*, 112.

(8) Kulinski, Z.; Piorkowska, E. *Polymer* **2005**, *46*, 10290.

(9) Bechtold, K.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2001**, *34*, 8641.

(10) Pluta, M.; Paul, M.-A.; Alexandre, M.; Dubois, P. *Journal of Polymer Science Part B: Polymer Physics* **2006**, *44*, 312.

(11) Lee, S.-Y.; Chin, I.-J.; Jung, J.-S. *European Polymer Journal* **1999**, *35*, 2147.

(12) Luo, W.; Li, S.; Bei, J.; Wang, S. *Journal of Applied Polymer Science* **2002**, *84*, 1729.

(13) Kricheldorf, H. R.; Rost, S.; Wutz, C.; Domb, A. *Macromolecules* **2005**, *38*, 7018.

(14) Choi, Y. K.; Bae, Y. H.; Kim, S. W. *Macromolecules* **1998**, *31*, 8766.

(15) Riley, T.; Heald, C. R.; Stolnik, S.; Garnett, M. C.; Illum, L.; Davis, S. S.; King, S. M.; Heenan, R. K.; Purkiss, S. C.; Barlow, R. J.; Gellert, P. R.; Washington, C. *Langmuir* **2003**, *19*, 8428.

(16) Fischer, E. W.; Sterzel, H.; Wegner, G. *Kolloid-Z.u.Z.Polymere* **1973**, *251*, 980.

(17) Huang, J.; Lisowski, M. S.; Runt, J.; Hall, E. S.; Kean, R. T.; Buehler, N.; Lin, J. S. *Macromolecules* **1998**, *31*, 2593.

(18) Zhang, J.; Duan, Y.; Domb, A. J.; Ozaki, Y. *Macromolecules* **2010**, *43*, 4240.