CHAPTER VIII
PC/PLA BLENDS WITH LYSINE TRIISOCYANATE (LTI)

8.1 Abstract

PC blended with PLA exhibited the low impact strength which is the drawback of neat PLA because of the immiscibility of the PC/PLA blends. In order to improve the mechanical properties especially impact strength of PC/PLA blends, Lysine triisocyanate (LTI) as a coupling agent was chosen to add into PC/PLA blends. The PC/PLA blends was studied at 70/30 %by weight and then vary the LTI content at 0.1 to 3 phr. The morphology, physical and thermal properties of blends were presented in this chapter. By the mechanical properties, all compositions of PC/PLA/EAA/DBTO demonstrated the low tensile modulus compared to PC70. The flexural modulus of all compositions of PC/PLA/LTI were significantly increased. LTI is not the suitable compatibilizer to improve the impact strength of PC/PLA blends.

8.2 Introduction

All composition of PC/PLA blends without the compatibilizers are generally immiscible, which cause low mechanical properties especially impact strength. To improve the mechanical properties of the PC/PLA blend, additional compatibilizers are used to improve mechanical properties of the blend. Poly(styrene-co-acrylonitrile)-g-maleic anhydride (SAN-g-MAH), Poly(ethylene-co-octene) rubber-maleic anhydride (EOR-MAH) and poly(ethylene-co-glycidyl methacrylate) (EGMA) (Lee, J. K., 2011) were the examples of additional compatibilizers in PC/PLA blend. Khowanit, M. *et al.*, (2012) found that ethylene methyl acrylate copolymers (EMA) can dramatically improve the impact strength of PLA/PC blends but HDT were not significant improved compared to PC70.

PC70 has the highest mechanical properties such as tensile strength and flexural strength in the all ratio of the PC/PLA blends. Furthermore, the composition

of the PC/PLA blend from the commercial grade is approximately PC70. Therefore, PC70 is the optimum composition of the PC/PLA blends to do further experiment.

Lysine triisocyanate (LTI) has three isocyanate groups which can react with hydroxyl groups at the chains end of both PC and PLA. Copolymer of PC/PLA are expected to generate in order to improve the mechanical properties of PC/PLA blends.

The purpose of this study was to observe the effect of LTI on the physical, thermal and mechanical properties of PC70.

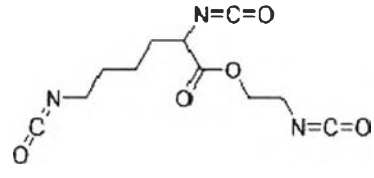


Figure 8.1 Chemical structure of LTI.

8.3 Experimental

8.3.1 Extrusion

PC and PLA were dried in oven at 60°C for 5 hours before mixing in twin screw extruder. Three kilograms of blends were prepared per each blends ratio. The blend ratios was 70/30 by weight with respected to PC/PLA. LTI was added in PC/PLA blends by varying ratio from 0.1 to 3 phr. The amount of materials prepared of each blend ratio is shown in table 8.1

Table 8.1 Amount of polymers prepared of each blends ratio for PC/PLA/LTI

Formula	PC (kg)	PLA (kg)	LTI (phr)
PC70L0.1	2.1	0.9	0.1
PC70L0.5	2.1	0.9	0.5
PC70L1	2.1	0.9	1
PC70L3	2.1	0.9	3

PC/PLA/LTI blends were mixed by the twin screw extruder. The processing condition and the operating temperature are shown in table 8.2. The processing factors of the PC/PLA/LTI are fixed as same as those of PC70.

Table 8.2 The processing condition of twin screw extruder for PC/PLA/LTI blend

Formula	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PC70L0.1	220	225	230	235	235	235	235	235	235	235	25
PC70L0.5	220	225	230	235	235	235	235	235	235	235	25
PC70L1	220	225	230	235	235	235	235	235	235	235	25
PC70L3	220	225	230	235	235	235	235	235	235	235	25

All PC/PLA/LTI blends show opaque and off-white as same as PC70 which is shown in Figure 8.2.

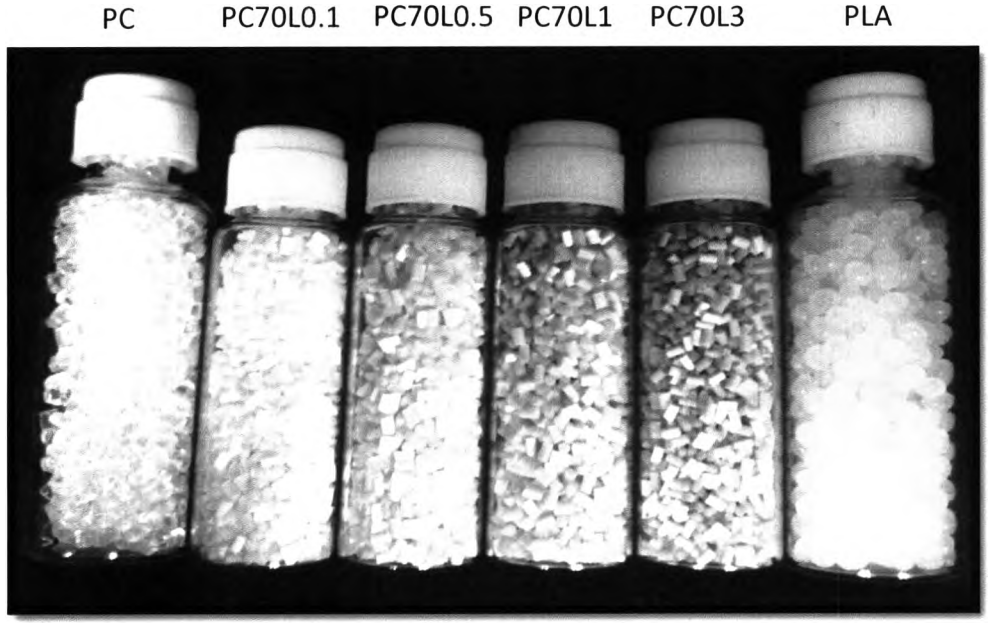


Figure 8.2 Pellets of PC, PLA and PC/PLA/LTI blends.

8.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 8.3.

Table 8.3 The processing condition of injection molding for PC, PLA, and PC/PLA/LTI blends

Formulations	Temperature (°C)					Injection Pressure (kg/cm^2)	T_{mold} (°C)
	Z1	Z2	Z3	Z4	Nozzle		
PC70L0.1	210	215	220	225	1200	40	70
PC70L0.5	210	215	220	225	1200	40	70
PC70L1	210	215	220	225	1200	40	70
PC70L3	210	215	220	225	1200	40	70

All specimens were injected in dumbbell and bar shape for tensile (ASTM D638), flexural (ASTM D790) and notched izod impact (ASTM D256) testing as shown in Figure 8.3.

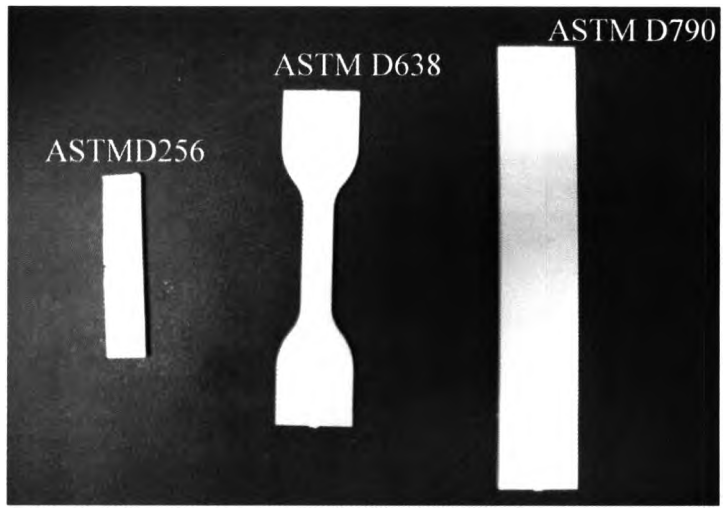


Figure 8.3 The specimens for mechanical testing.

8.4 Results and Discussion

8.4.1 Physical Properties

8.4.1.1 Rheological properties

In this study, the rheological properties have been investigated in term of melt flow index (MFI) described in the standard ASTM D1238. MFI is a measurement of the ease of flow of the molten thermoplastic polymer. MFI It is defined as the mass of polymer, in grams, flowing in 10 min through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. Figure 8.4 shows MFI of PC, PLA, PC70 and PC/PLA/LTI blends at the condition of 250°C/2.16 kg. MFI of PC/PLA/LTI blends are decreased when increasing the content of LTI compared to PC70E1. This result implies that the longer PC and PLA chains are generated during melt process. Additional LTI into PC/PLA blends dramatically reduce the MFI due to longer PC and PLA chains obstructed the polymer chains slip and disentanglement.

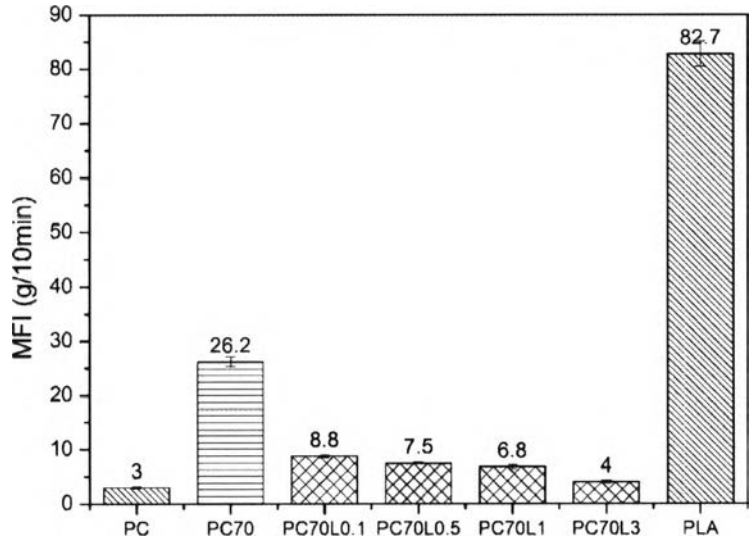


Figure 8.4 Melt Flow Index of PC, PLA, PC70 and PC/PLA/LTI blends.

8.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. Figure 8.5 reports apparent density of

PC/PLA/EAA blends. The apparent density of all formulas of PC/PLA/LTI are indifferent compared to PC70.

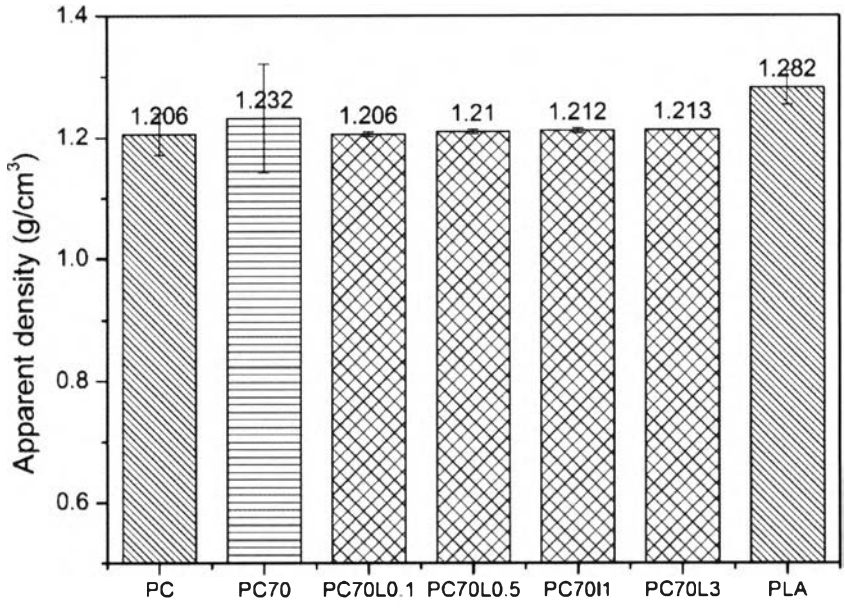


Figure 8.5 Specific gravity of PC, PLA, PC70 and PC/PLA/LTI blends.

8.4.2 Thermal Properties

8.4.2.1 Differential Scanning Calorimeter: DSC

The glass transition temperature (T_g) of PC/PLA/LTI blends were investigated by DSC. Figure 8.6 shows the Tg of PC/PLA/LTI blends. The glass transition temperatures of PLA in all compositions of PC/PLA/LTI blends are slightly shifted closed to that of neat PC because longer PLA chains obstruct the mobility of polymer chains. Each Tg insinificantly shift in of Tg of pure materials. It indicates that all ratios of PC/PLA/LTI blends are incompatible.

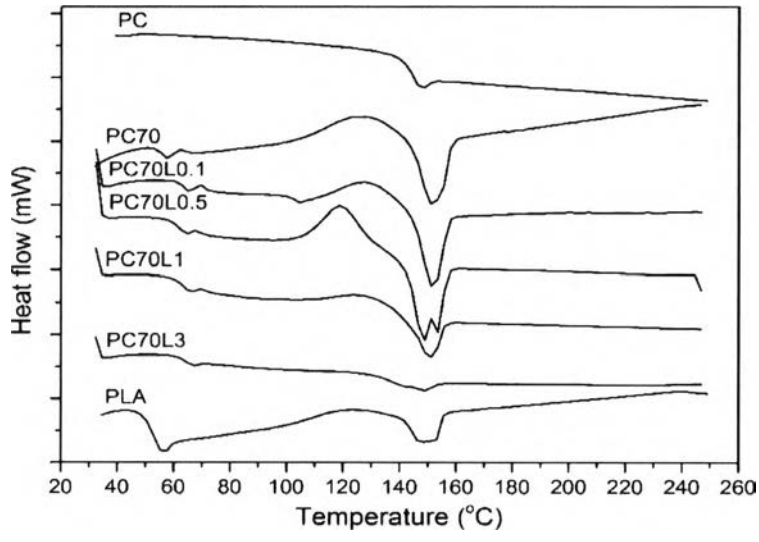


Figure 8.6 DSC plots (second heating) of PC, PLA, PC70 and PC/PLA/LTI blends.

8.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC/PLA/LTI blends were evaluated by TGA. Figure 8.7 and Table 8.4 shows the TGA results of PC, PLA, PC70 and PC/PLA/LTI blends. The degradation temperature (T_d) of PC/PLA/LTI blends was slightly decreased when increasing the content of LTI.

Table 8.4 The T_d and % weight loss of PC/PLA/EAA/LTI

Composition	T_d (°C)	% weight loss
PC70	348, 451	38.5, 51.6
PC70L0.1	352, 470	46.9, 39.7
PC70L0.5	340	93.8
PC70L1	343	90.7
PC70L3	346	92.2

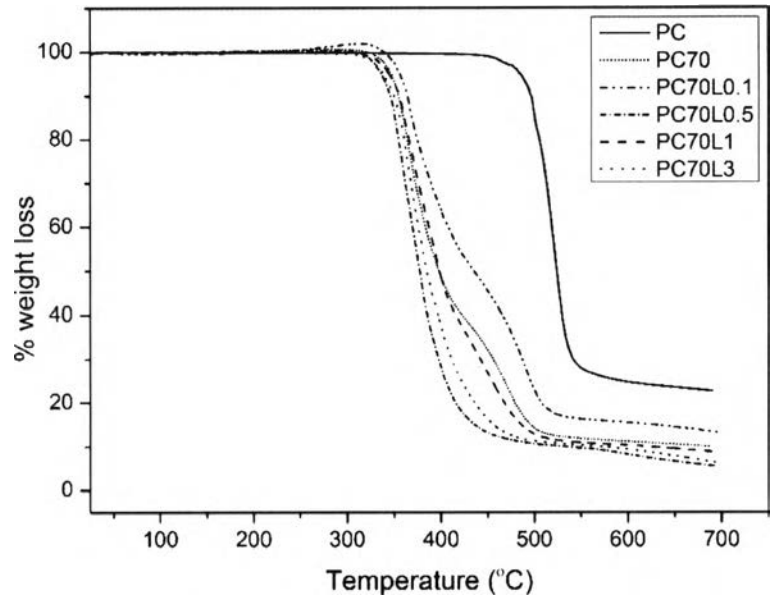


Figure 8.7 TGA plots of PC, PLA, PC70 and PC/PLA/LTI blends.

8.4.2.3 Dynamic Mechanical Analysis: DMA

DMA measures the physical and mechanical changes in a material, this technique is inherently more sensitive to the glass transition temperature but DSC can be used to examine the material from a sub ambient starting temperature into the glass transition event and finally through the crystalline melting region. Thus the glass transition temperature (Tg) from DMA was correctly than Tg from DSC. The tan δ as a function of temperature which obviously exhibited Tg than storage modulus (E') and loss modulus (E''). The neat PC and PLA exhibit a single peak at Tg in the temperature range studied as shown in Figure 8.8, while the blends show two peaks indicating a two-phase morphology and each Tg slightly shifts to higher Tg of neat PC due to the higher molecular weight of PC and PLA are generated during the melt processing. All formulas of PC/PLA/EAA/LTI blends show two Tg around 62 – 64.5 °C and 156.6-161.3 °C. The glass transition peaks of the blends are slightly different from those of the neat components which indicate that the blends are completely immiscible.

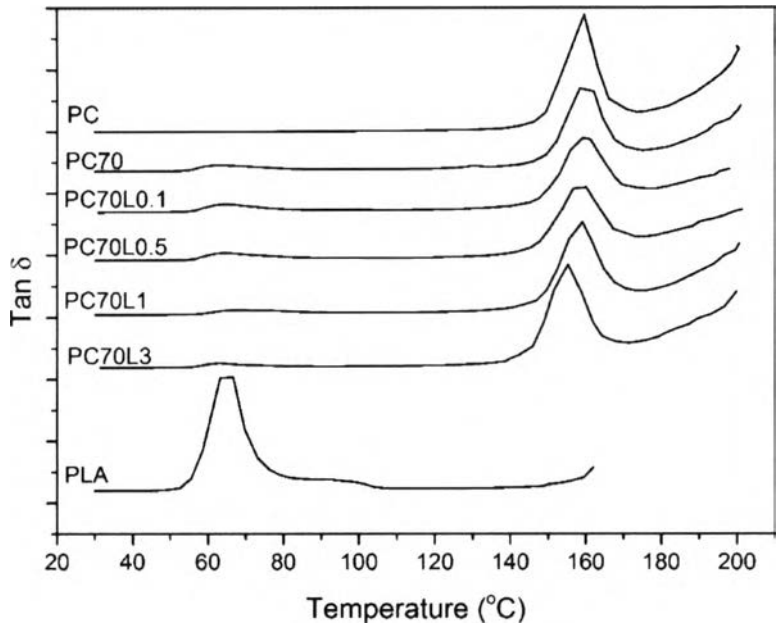


Figure 8.8 Tan δ plots of neat PC, PLA, PC70 and PC/PLA/LTI blends.

8.4.3 Molecular weight distribution

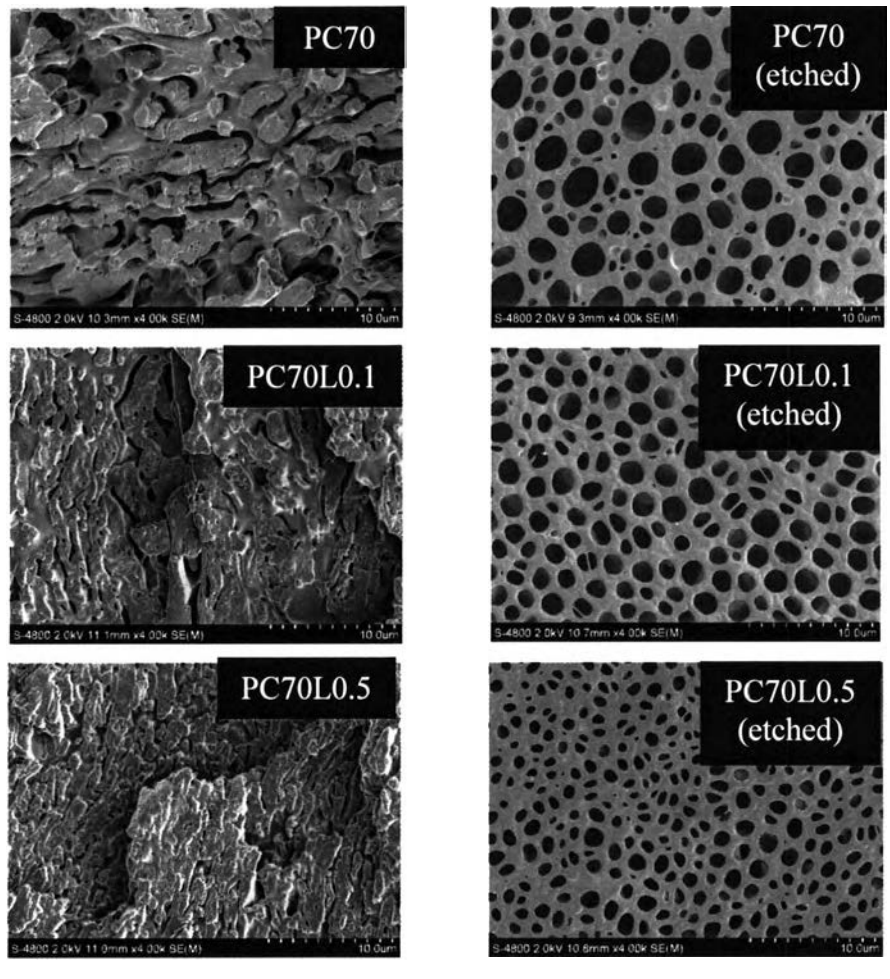
Table 8.5 $\overline{M}_w$, $\overline{M}_n$ and PDI of PC/PLA/LTI blends

Formulations	M_w	M_n	PDI
PC70	45720	23231	1.97
PC70L0.1	55176	25115	2.20
PC70L0.5	55871	25760	2.17
PC70L1	55763	24272	2.30
PC70L3	54573	23777	2.18

Table 8.5 shows molecular weight and molecular weight distribution of PC/PLA/LTI. Both $\overline{M}_w$ and $\overline{M}_n$ of PC/PLA/LTI blends are significantly increased when increasing the content of LTI suggesting that the longer PC and PLA chains are generated during the melting process. High PDI of PC/PLA/LTI implied that the reaction are randomly occurred. The molecular weight and molecular weight distribution can explain the results of mechanical properties.

8.4.4 Morphology

After impact test, the fracture surfaces of PC/PLA/LTI blends were etched by dichloromethane for 45 second to remove the PLA phase. The SEM observation of etched and unetched PC/PLA/LTI blends are shown in Fig. 8.9. The micrograph of all formulas of PC/PLA/EAA/LTI blends show phase separation between PC phase and PLA phase and distribution of uniformly shaped PLA particles dispersed in PC main phase. The etched micrographs of PC70L3 shows the smallest average size of PLA suggesting PLA phase is harder to dissolve by DCM because longer PLA chains are generated.



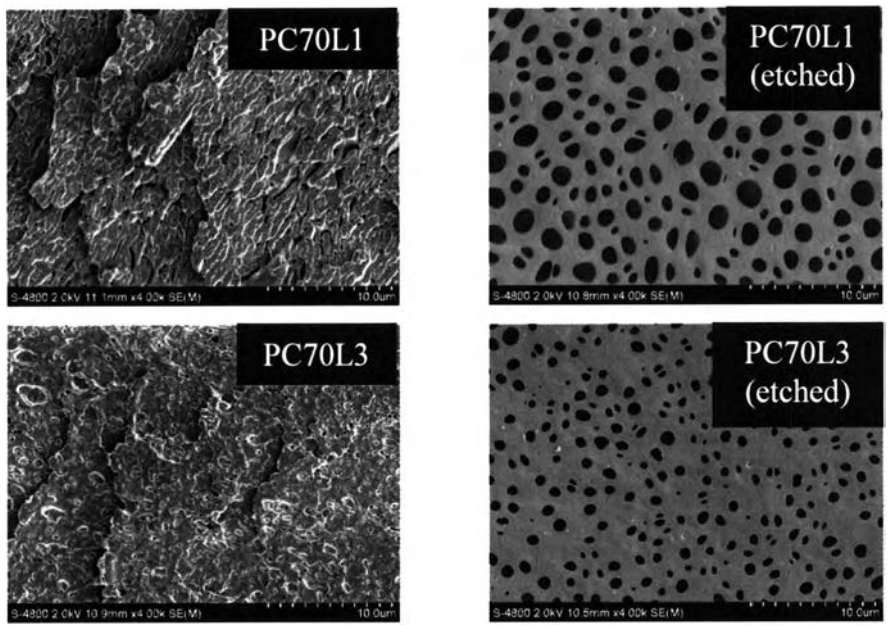


Figure 8.9 SEM micrographs of fractural impact surface of PC/PLA/LTI blends.

8.4.5 Mechanical Properties

8.4.5.1 Tensile and Flexural testing

All specimens were injected in dumbbell and bar shape followed by (ASTM D638) for tensile and (ASTM D790) for flexural. The tensile strength at yield, Young's modulus, flexural strength and flexural modulus of PC, PLA, PC70 and PC/PLA/EAA blends are shown in Figure 8.10-8.13, respectively. The overview of results show that additional LTI into the PC/PLA blends significantly influence the mechanical properties. By tensile strength, PC70L1 has highest tensile strength while the young's modulus of all compositions of PC/PLA/LTI are low compared to PC70 because longer PC and PLA chains may generate the more free volume that led the polymer chains are easy to slip.

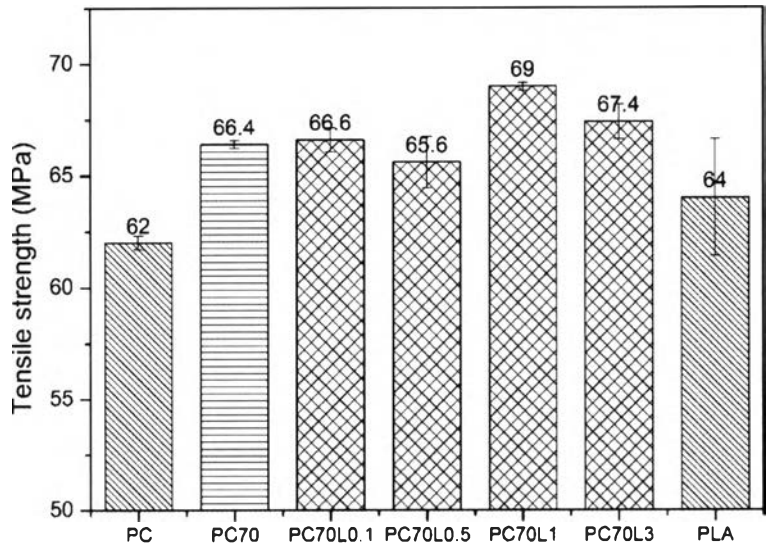


Figure 8.10 Tensile strength at yield of PC, PLA, PC70 and PC/PLA/LTI blends.

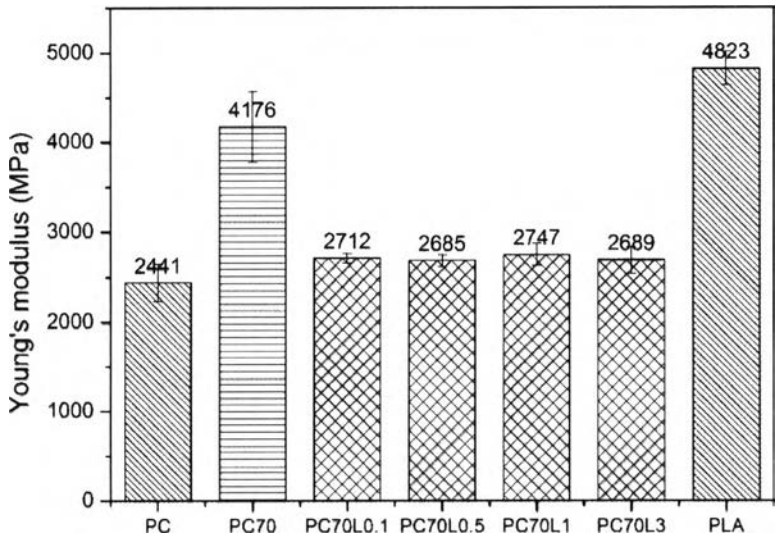


Figure 8.11 Modulus of PC, PLA, PC70 and PC/PLA/LTI blends.

For the flexural strength, From fig. 8.12 - 8.13, flexural strength of all compositions of PC/PLA/EAA/DBTO blends are significantly dropped compared to PC70 because the longer PC and PLA chains may increase the boundaries with weak interaction. The flexural modulus of all compositions of PC/PLA/LTI are insignificantly increased.

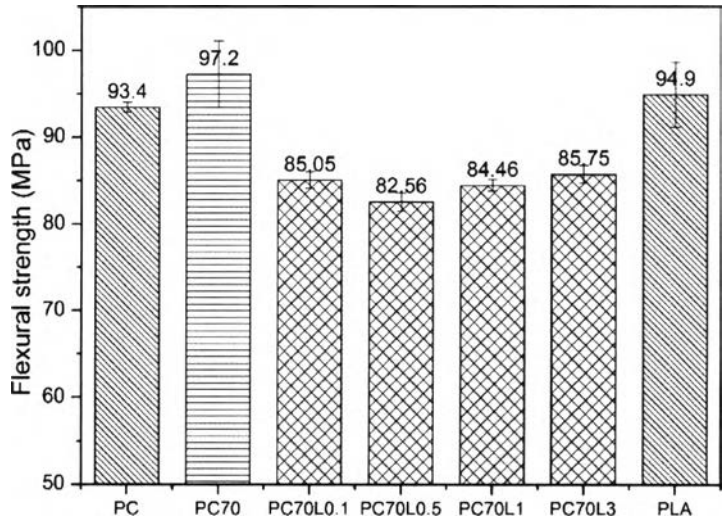


Figure 8.12 Flexural strength of PC, PLA, PC70 and PC/PLA/LTI blends.

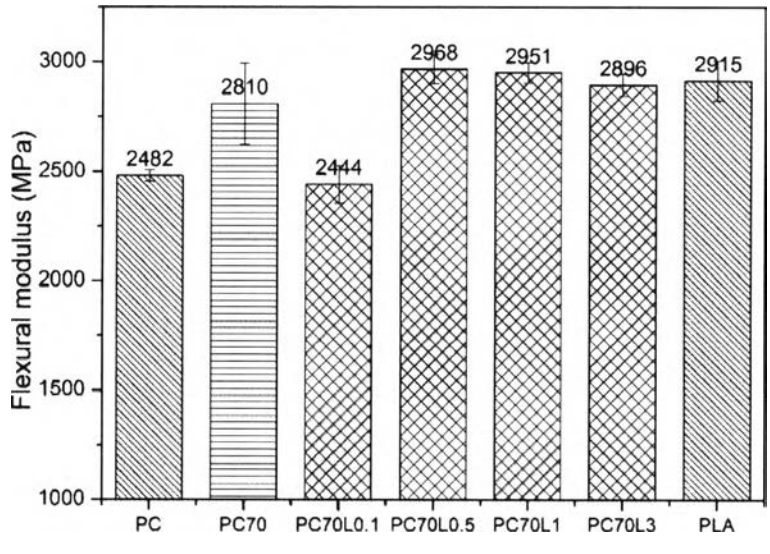


Figure 8.13 Flexural modulus of PC, PLA, PC70 and PC/PLA/LTI blends.

8.4.5.2 Notched izod impact

Figure 8.14 reported Notched izod impact of PC/PLA/LTI blends. The impact strength of all compositions of PC/PLA/LTI blends are very low compared to neat PC. The impact strength of PC70L0.5 and PC70L1 are slightly higher compared to PC70. Therefore, additional LTI into PC/PLA blends do not improve the impact strength of PC/PLA blends.

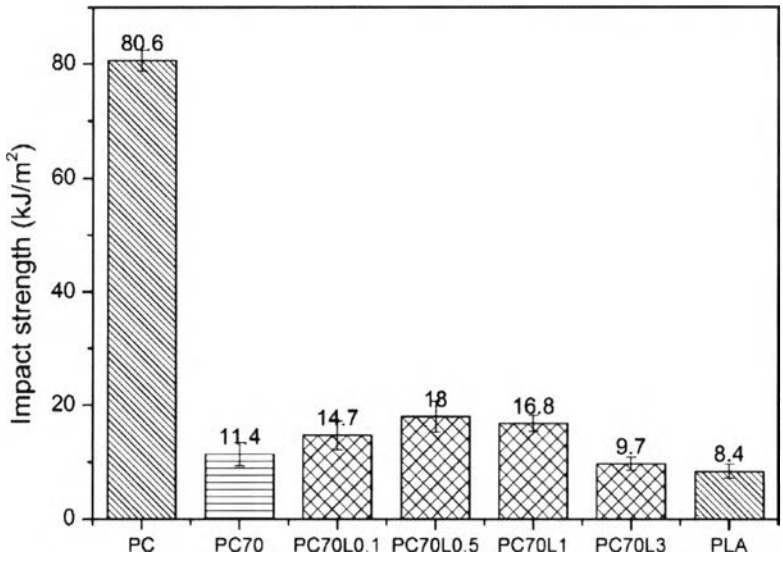


Figure 8.14 The impact strength of PC, PLA, PC70 and PC/PLA/LTI blends.

8.5 Conclusions

PC/PLA/LTI blends were mixed by the twin screw extruder. The processing condition and the operating temperature are fixed as same as those of PC70. The compatibilization of PC/PLA blends were investigated by SEM, DSC and DMA. SEM micrograph observation shows the irrugular PLA particle dispersed in PC as a martrix phase. DSC and DMA results of all compostions of PC/PLA/LTI blends show two T_g which is not closed to Tg of neat PC and PLA. These results confirmed that all compositions of PC/PLA/LTI blends are immiscible. By the mechanical properties, all compositions of PC/PLA/LTI demonstrated the low tensile modulus compared to PC70. The flexural modulus of all compositions of PC/PLA/LTI were significantly increased. LTI is not the suitable compatibilizer to improve the impact strength of PC/PLA blends.

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