CHAPTER VI
PC/PLA BLENDS WITH THE POLY(ETHYLENE-CO-ACRYLIC ACID) (EAA)

6.1 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, poly (ethylene-co-acrylic acid) as an impact modifier was chosen to add into PC/PLA blends. The PC/PLA blends with EAA was studied at 70/30 ratio and then vary the EAA content at 1 to 5 phr. The morphology, physical and thermal properties of blends were presented in this chapter. By the mechanical properties, PC70E1 demonstrated the higher Young's modulus and impact strength compared to PC70. However, the flexural properties of PC70E1 slightly dropped. The other compositions of PC/PLA/EAA show the low mechanical properties because of the aggregation of EAA.

6.2 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.

Poly(ethylene-co-acrylic acid) (EAA) is a copolymer which has an ethylene chain as a chain extender and acrylic acid as a reactive site which has a potential to react with hydroxyl groups at the chain end of polycarbonate and polylactic acid. Therefore, EAA has a potential compatibilizer to improve the mechanical properties of PC/PLA blends.

The purpose of this study was to observe the effect of EAA on the physical, thermal and mechanical properties of PC70 blends and to verify the miscibility between PC and PLA by EAA compatibilizer.

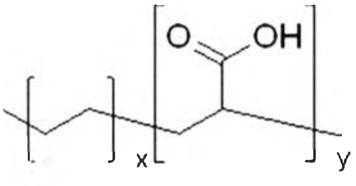

Figure 6.1 Chemical structure of EAA.

6.3 Experimental

6.3.1 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. The EAA was added in PC/PLA blends by varying ratio from 1 to 5 phr. The amount of materials prepared of each blend ratio is shown in table 6.1

Table 6.1 Amount of polymers prepared of each blends ratio for PC/PLA/EAA

Formula	PC (kg)	PLA (kg)	EAA (phr)
PC70E1	2.1	0.9	1
PC70E3	2.1	0.9	3
PC70E5	2.1	0.9	5

PC/PLA/EAA blends were mixed by the twin screw extruder. The processing condition and the operating temperature are shown in table 6.2. The processing factors of the PC/PLA/EAA are fixed as same as those of PC70.

Table 6.2 The processing condition of twin screw extruder for PC/PLA/EAA blend

Formula	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PC70E1	220	225	230	235	235	235	235	235	235	235	25
PC70E3	220	225	230	235	235	235	235	235	235	235	25
PC70E5	220	225	230	235	235	235	235	235	235	235	25

All PC/PLA/EAA blends show opaque and off-white as same as PC70 which is shown in Figure 6.2.

PC PC70 PC70E1 PC70E3 PC70E5 PLA

Figure 6.2 Pellets of PC, PLA and PC/PLA/EAA blends.

6.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 6.3.

Table 6.3 The processing condition of injection molding for PC, PLA, and PC/PLA/EAA blends

Formulations	Temperature (°C)					Injection Pressure (kg/cm^2)	T_{mold} (°C)
	Z1	Z2	Z3	Z4	Nozzle		
PC70E1	210	215	220	225	1200	40	70
PC70E3	210	215	220	225	1200	40	70
PC70E5	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 6.3.

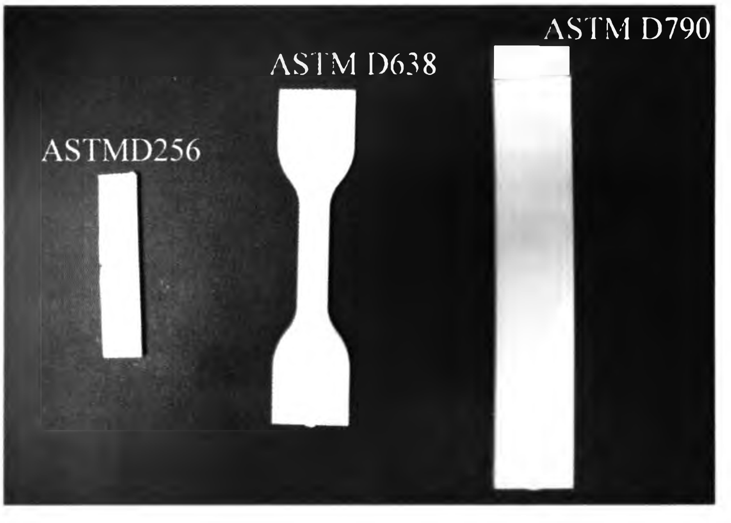

Figure 6.3 The specimens for mechanical testing.

6.4 Results and Discussion

6.4.1 Physical Properties

6.4.1.1 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 6.4 shows MFI of PC, PLA, PC70 and PC/PLA/EAA blends at the condition of 250°C/2.16 kg. MFI of PC/PLA/EAA blends were increasing when increasing the content of EAA. This result indicates that the processing temperature of EAA is lower than that of PC70 due to EAA is a copolymer with low molecular weight. However, MFI of PC70E1 is lower than that of PC70 implied that the ethylene chain in EAA act as a chain entanglement obstructed the PC/PLA chain slide to each other.

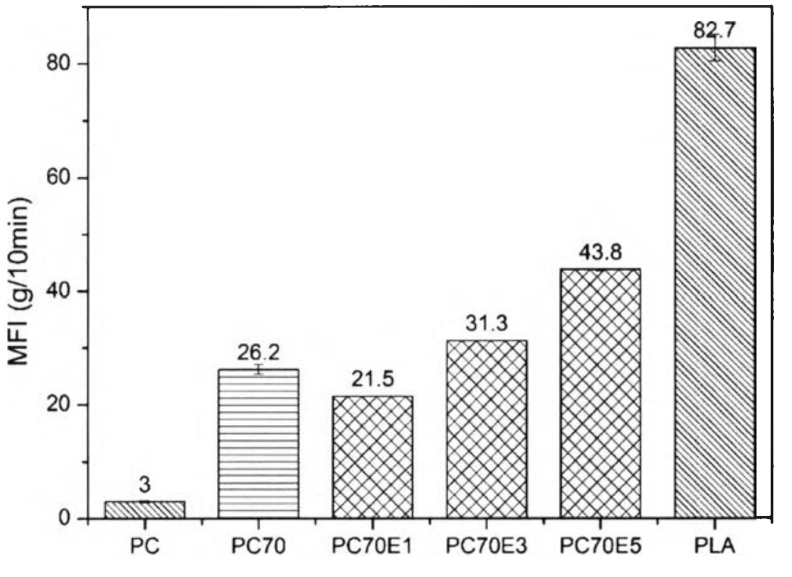

Figure 6.4 Melt Flow Index of PC, PLA, PC70 and PC/PLA/EAA blends.

6.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. Figure 6.5 reports apparent density of PC/PLA/EAA blends. PC70E5 is the lowest apparent density.

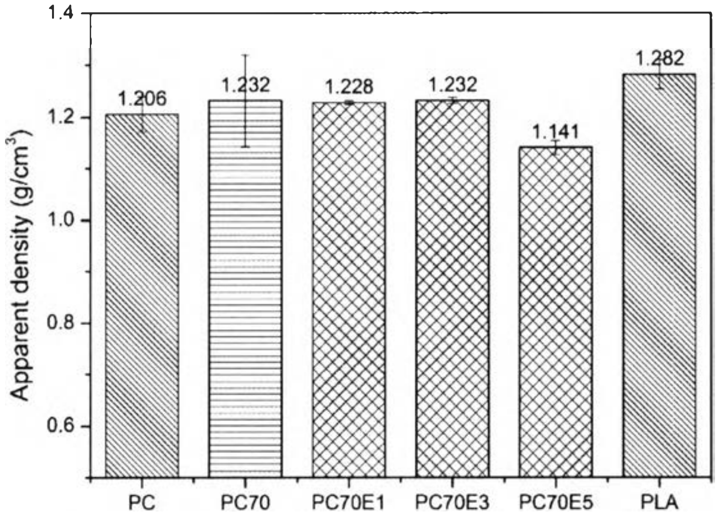

Figure 6.5 Specific gravity of PC, PLA, PC70 and PC/PLA/EAA blends.

6.4.2 Thermal Properties

6.4.2.1 Differential Scanning Calorimeter: DSC

The glass transition temperature (T_g) of PC/PLA/EAA blends were investigated by DSC. Figure 6.6 shows the second heating of PC, PLA, PC70 and PC/PLA/EAA blends. The glass transition temperatures of PLA in PC/PLA/EAA blends are slightly shifted closed to that of neat PC. The PC/PLA/EAA blends show two Tg. Each Tg insinificantly shift in of Tg of pure materials. It indicates that all ratios of PC/PLA/EAA blends are incompatible.

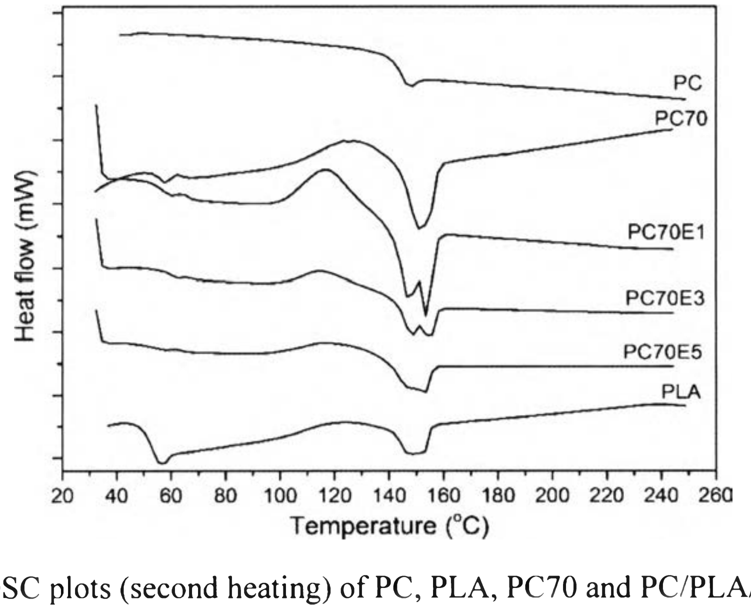

Figure 6.6 DSC plots (second heating) of PC, PLA, PC70 and PC/PLA/EAA blends.

6.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC/PLA/DBTO blends were evaluated by TGA. Figure 6.7 and Table 6.4 shows the TGA results of PC, PLA, PC70 and PC/PLA/EAA blends. The degradation temperature (Td) of neat EAA (421.2 °C) was higher than that of PC/PLA/EAA blends. Thus, PC is much more stable than PC/PLA/EAA blends at the same operating temperature because the structure of EAA has acrylic acid which have highly heat resistance. In addition, all formulas of PC/PLA/EAA blends have two steps of the degradation same as the degradation of PC70.The Td of PC/PLA/EAA are dropped when increasing the content of EAA. This phenomena implies that the excess EAA obstruct the packing of PC and PLA chains suggesting PC and PLA chain are easy to degrade.

Table 6.4 The T_d and % weight loss of PC/PLA/EAA

Composition	T_d (°C)	% weight loss
EAA	421	96.2
PC70	348. 451	38.5, 51.6
PC70E1	350, 553	85, 15
PC70E3	346, 553	83, 17
PC70E5	336, 538	76, 24

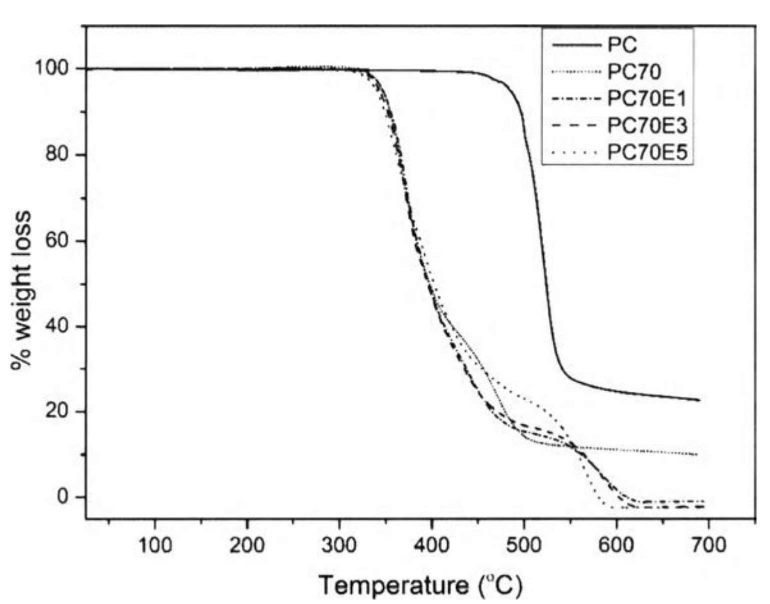

Figure 6.7 TGA plots of PC, PLA, PC70 and PC/PLA/EAA blends.

6.4.2.3 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 (T_g) from DMA was correctly than T_g from DSC. The tan δ as a function of temperature which obviously exhibited T_g 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 6.8, while the blends show two peaks indicating a two-phase morphology and each Tg insinificantly shifts in of Tg of pure materials. Table 3.8 show the glass transition temperature (Tg) of PC/PLA/EAA blends. All formulas of PC/PLA blends show two Tg around 58.6 – 61.7 °C and 158.5-161.3 °C. The glass transition peaks of the blends are insignificantly different from those of the neat components which indicate that the blends are completely immiscible.

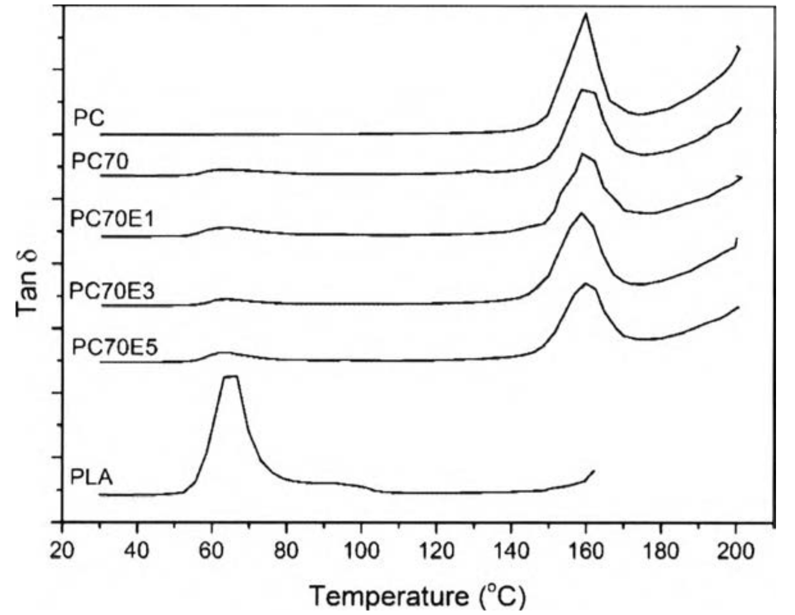

Figure 6.8 Tan δ plots of neat PC, PLA, PC70 and PC/PLA/EAA blends.

6.4.3 Molecular weight distribution

Table 6.5 $\overline{M}_w$, $\overline{M}_n$ and PDI of PC/PLA/EAA blends

Formulations	M_w	M_n	PDI
EAA	8603	5838	1.47
PC70	45720	23231	1.97
PC70E1	57255	27956	1.66
PC70E3	53499	25987	2.06
PC70E5	54482	24502	2.22

Table 6.5 shows molecular weight and molecular weight distribution of EAA and PC/PLA/EAA. Both $\overline{M}_w$ and $\overline{M}_n$ of PC/PLA/EAA blends are higher than PC70 suggesting there are chemical reaction between EAA and PC/PLA. PC70E1 has the highest $\overline{M}_w$ and $\overline{M}_n$ incorporated with the lowest molecular weight distribution (PDI) confirmed that the additional 1 phr EAA into the PC/PLA blends is the optimum ratio.

6.4.4 Morphology

After impact test, the fracture surfaces of PC/PLA/EAA blends were etched by dichloromethane for 45 second to remove the PLA phase. The SEM observation of etched and unetched PC/PLA/EAA blends are shown in Fig. 6.9. The micrograph of all formulas of PC/PLA/EAA blends show phase separation between PC phase and PLA phase and distribution of uniformly shaped PLA particles dispersed in PC main phase. The unetched micrographs of PC70E1 show the slightly ductile failure suggesting impact strength of PC70E1 should be relatively improved. However, the average PLA particle size of all formulas of PC/PLA/EAA are similar to PC70 implied that the additional EAA does not improve the miscibility of PC/PLA blends.

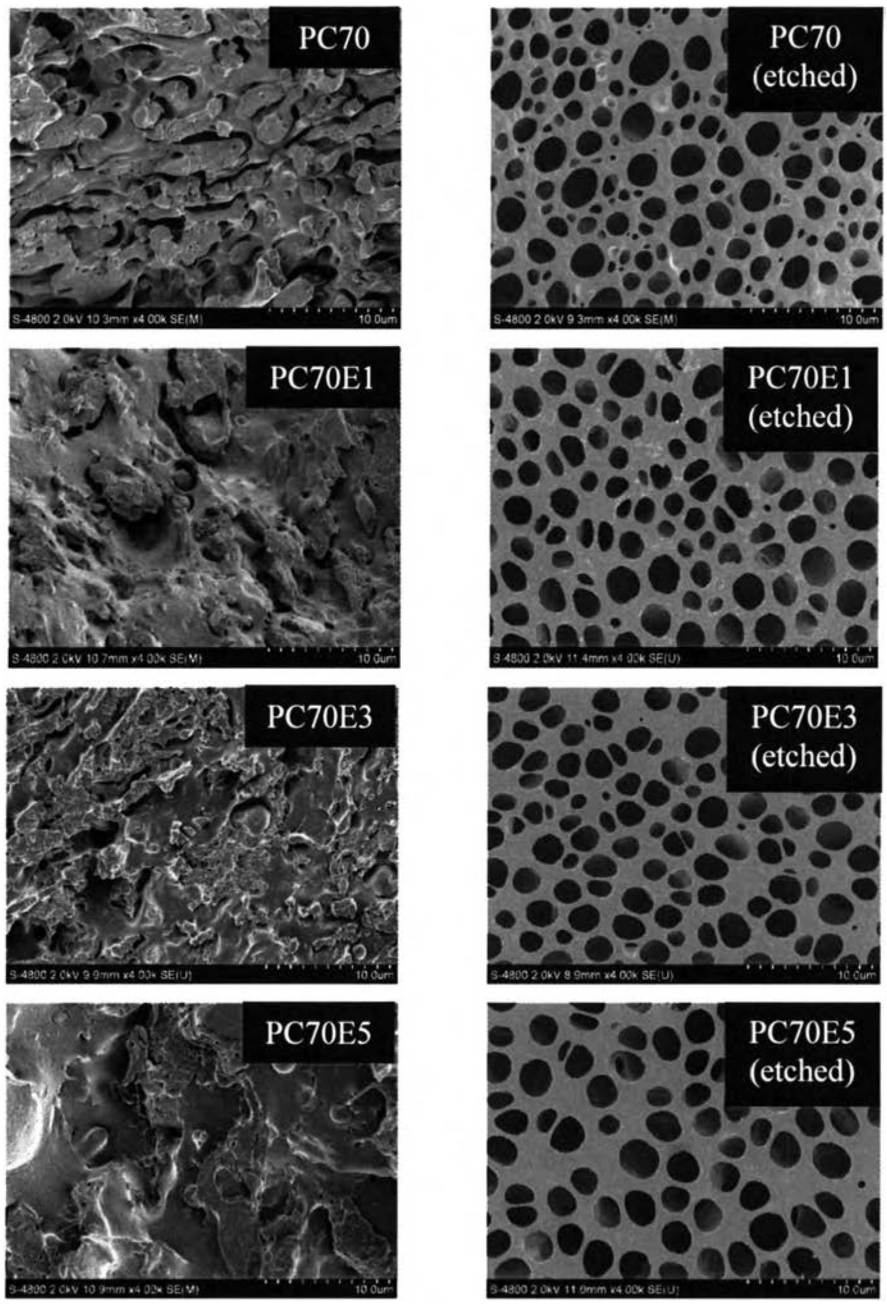

Figure 6.9 SEM micrographs of fractural impact surface of PC/PLA/EAA blends.

6.4.5 Mechanical Properties

6.4.5.1 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 6.10-6.13, respectively. The overview of results show that additional EAA into the PC/PLA blends significantly influence the mechanical properties. By tensile strength, Fig. 6.10 shows significant decrease of tensile strength at yield of PC/PLA/EAA blends at increasing PLA contents especially PC70E5 because of the aggregation of EAA. PC70E1 shows the highest Young's modulus compared to PC70 and other blends as shown in fig. 6.11. The results confirm that additional 1 phr EAA into PC/PLA blends is the optimum ratio.

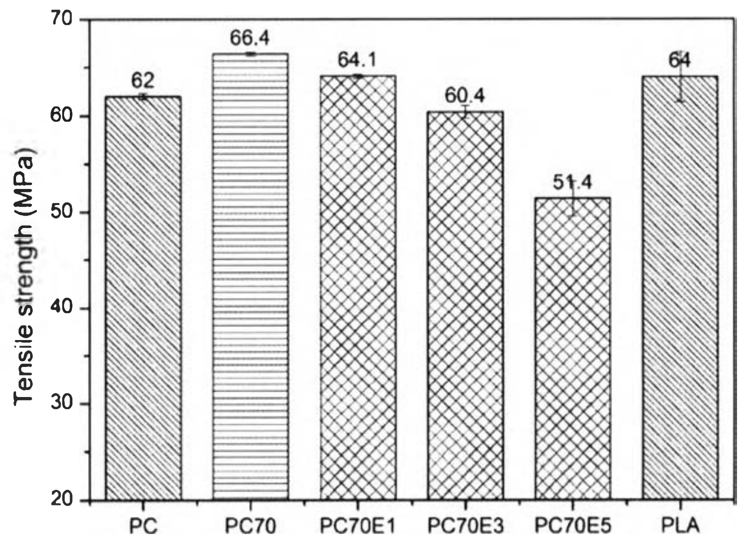

Figure 6.10 Tensile strength at yield of PC, PLA, PC70 and PC/PLA/EAA blends.

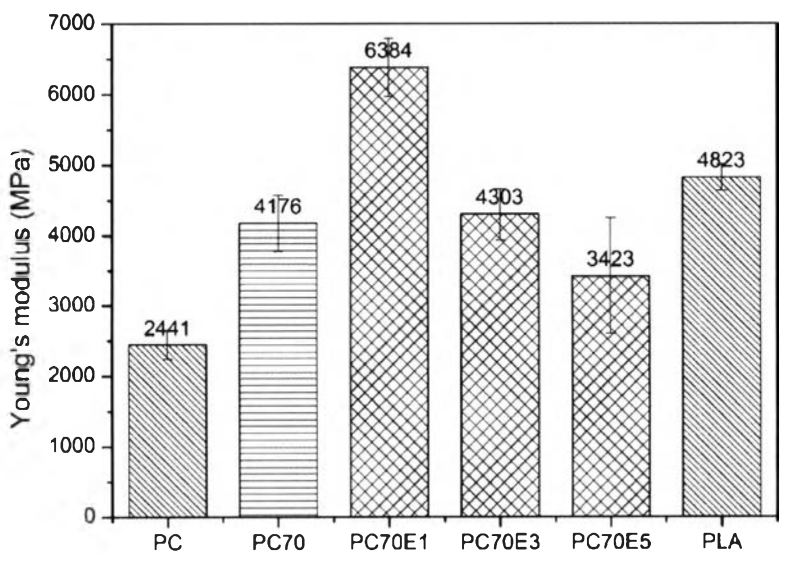

Figure 6.11 Modulus of PC, PLA, PC70 and PC/PLA/EAA blends.

For the flexural strength, From fig. 6.12 - 6.13, Flexural strength and flexural modulus of all PC/PLA/EAA blends are significantly dropped compared to PC70. Additional EAA into PC/PLA generate the third phase with weak interaction between the boundaries and slipped polymer chain occurred along the boundaries. Therefore, additional EAA degenerate the flexural properties of PC/PLA/EAA.

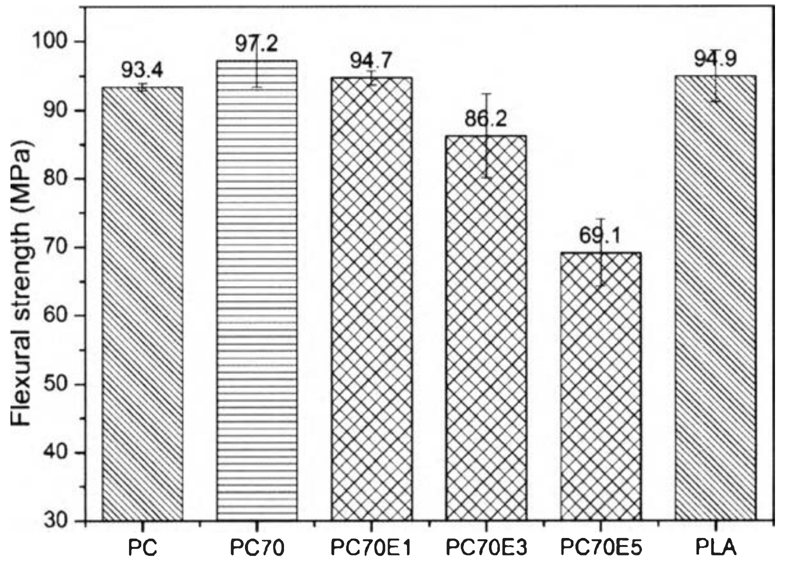

Figure 6.12 Flexural strength of PC, PLA, PC70 and PC/PLA/EAA blends.

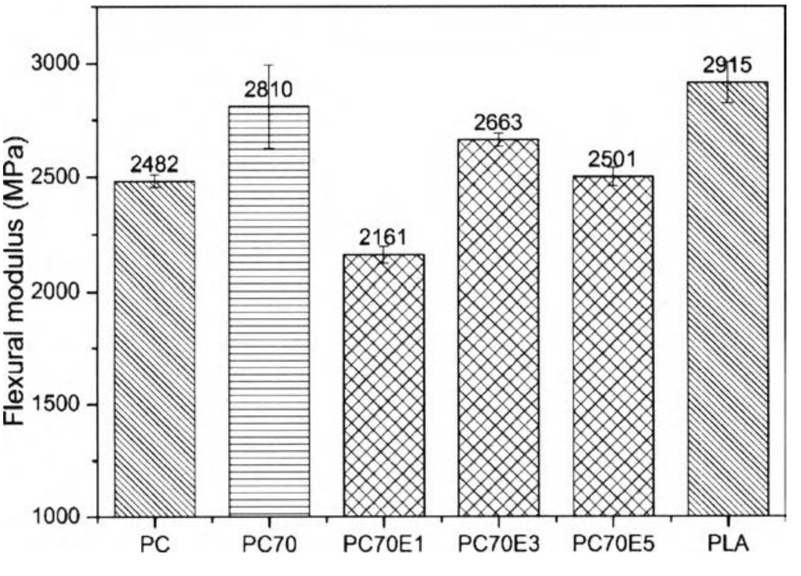

Figure 6.13 Flexural modulus of PC, PLA, PC70 and PC/PLA/EAA blends.

6.4.5.2 Notched izod impact

Figure 6.14 reported Notched izod impact of PC/PLA/EAA blends. PC70E1 shows the higher impact strength compared to PC70 which refer to the high toughness. Corresponding to the SEM observation of PC70E1 showing a little ductile failure. EAA has a ethylene chain act as chain extender. However, the impact strength of PC70E3 and PC70E5 are lower when increasing the content of EAA because of aggregation of exceed EAA that generate a weak interaction between boundaries. The results implied that the optimized EAA in PC/PLA blends should be 1 phr.

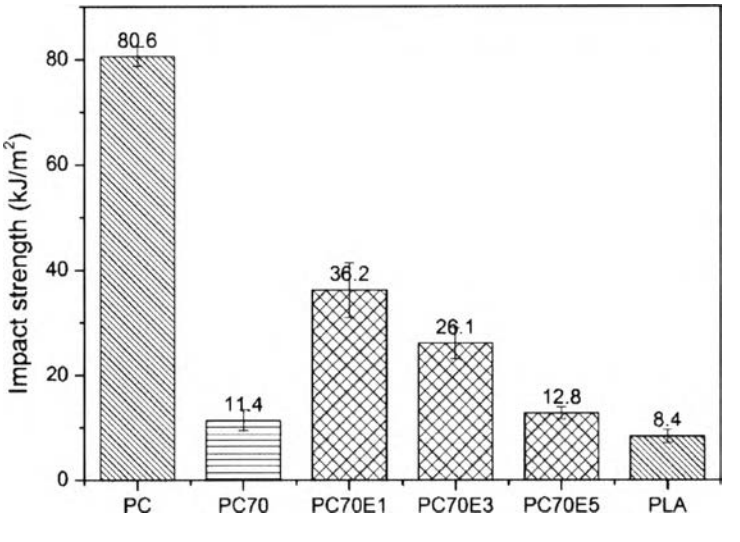

Figure 6.14 The impact strength of PC, PLA, PC70 and PC/PLA/EAA blends.

6.5 Conclusions

PC/PLA/EAA 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 slightly ductile failure of PC70E1. However, the phase separation between PC and PLA still exist. DSC and DMA results of all compostions of PC/PLA/EAA 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 blends are immiscible. By the mechanical properties, adding inappropriate amount of EAA in the

PC/PLA blends significantly decrease the mechanical properties because of the aggregation of EAA. Additional 1 phr EAA into the PC/PLA blends can improve the Young's modulus and impact strength compared to PC70. Therefore, additonal 1 phr EAA is the optimum ratio to improve the mechanical properties of PC/PLA blends.

6.6 Acknowledgements

The author would like to thank PTT Phenol Company Limited for supporting the thesis work.

Finally, The authors are thankful to PTT research and technology institute for analytical support.