CHAPTER VII
PC/PLA BLENDS WITH THE POLY (ETHYLENE-CO-ACRYLIC ACID) (EAA) AND DIBUTHYLTIN OXIDE (DBTO)

7.1 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) (EAA) as an impact modifier incorporated with Dibuthyltin oxide (DBTO) as a transesterification catalyst was chosen to add into PC/PLA blends. The PC/PLA/EAA blends was studied at 70/30/1 %by weight and then vary the DBTO content at 0.01 to 0.1 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 lower tensile properties than those of PC/PLA/EAA because of the effect of adding DBTO. The flexural properties of all compositions of PC/PLA/EAA/DBTO slightly dropped compared to PC70. Therefore, adding only EAA is more efficiently than adding EAA incorporated with DBTO for improving the mechanical properties of PC/PLA blends.

7.2 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.

PC70E1 has the higher young's modulus and impact strength than those of PC70 and other compositions of PC/PLA/EAA. Therefore, adding 1 phr EAA into PC/PLA blends is the optimum content to do further experiment which is adding optimum EAA content incorporated with DBTO to improve the mechanical properties of PC/PLA blends.

The purpose of this study was to observe the effect of EAA incorporated with DBTO on the physical, thermal and mechanical properties of PC70.

(a) (b)

Figure 7.1 Chemical structure of (a) EAA and (b) DBTO.

7.3 Experimental

7.3.1 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 70/30/1 by weight with respected to PC/PLA/EAA. DBTO was added in PC/PLA blends by varying ratio from 0.01 to 0.1 phr. The amount of materials prepared of each blend ratio is shown in table 7.1

Table 7.1 Amount of polymers prepared of each blends ratio for PC/PLA/EAA/DBTO

Formula	PC (kg)	PLA (kg)	EAA (phr)	DBTO (phr)
PC70E1D0.01	2.1	0.9	1	0.01
PC70E1D0.05	2.1	0.9	1	0.05
PC70E1D0.1	2.1	0.9	1	0.1

PC/PLA/EAA/DBTO blends were mixed by the twin screw extruder. The processing condition and the operating temperature are shown in table 7.2. The processing factors of the PC/PLA/EAA/DBTO are fixed as same as those of PC70.

Table 7.2 The processing condition of twin screw extruder for PC/PLA/EAA/DBTO blend

Formula	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PC70E1D0.01	220	225	230	235	235	235	235	235	235	235	25
PC70E1D0.05	220	225	230	235	235	235	235	235	235	235	25
PC70E1D0.1	220	225	230	235	235	235	235	235	235	235	25

All PC/PLA/EAA/DBTO blends show opaque and off-white as same as PC70 which is shown in Figure 7.2.

Figure 7.2 Pellets of PC, PLA and PC/PLA/EAA/DBTO blends.

7.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 7.3.

Table 7.3 The processing condition of injection molding for PC, PLA, and PC/PLA/EAA/DBTO blends

Formulations	Temperature (°C)					Injection Pressure (kg/cm^2)	T_{mold} (°C)
	Z1	Z2	Z3	Z4	Nozzle		
PC70E1D0.01	210	215	220	225	1200	40	70
PC70E1D0.05	210	215	220	225	1200	40	70
PC70E1D0.1	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 7.3.

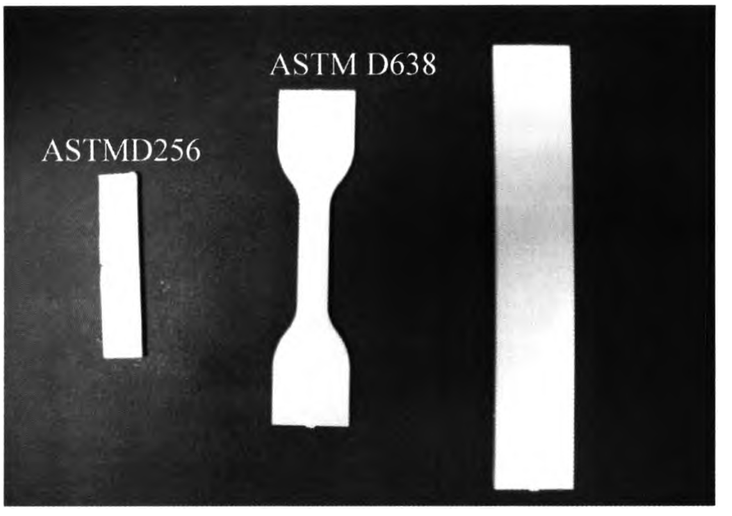


Figure 7.3 The specimens for mechanical testing.

7.4 Results and Discussion

7.4.1 Physical Properties

7.4.1.1 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 7.4 shows MFI of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends at the condition of 250°C/2.16 kg. MFI of PC/PLA/EAA/DBTO blends are increased when increasing the content of DBTO compared to PC70E1. This result implies that the shortening PC and PLA chains are generated during melt process. Additional EAA into PC/PLA/DBTO blends dramatically reduce the MFI due to EAA acts as a chain extender obstructed the polymer chains slip and disentanglement.

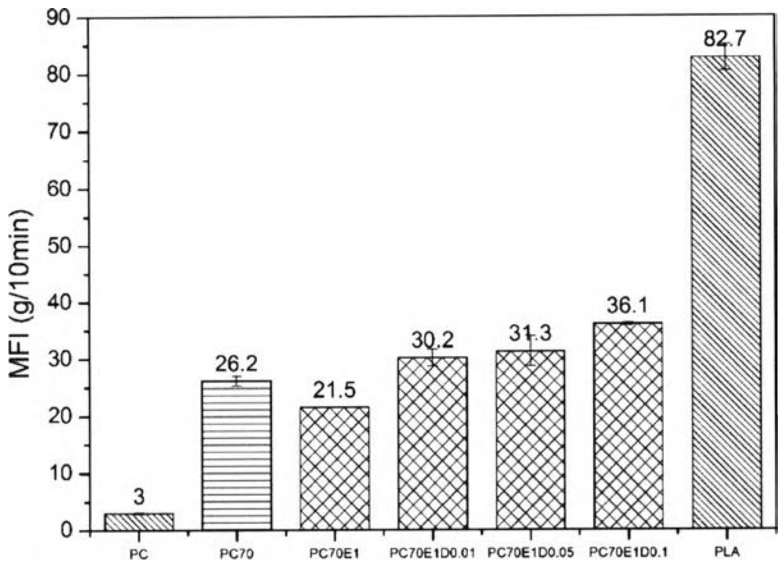


Figure 7.4 Melt Flow Index of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. Figure 7.5 reports apparent density of PC/PLA/EAA blends. The apparent density of all formulas of PC/PLA/EAA/DBTO are lower than PC70.

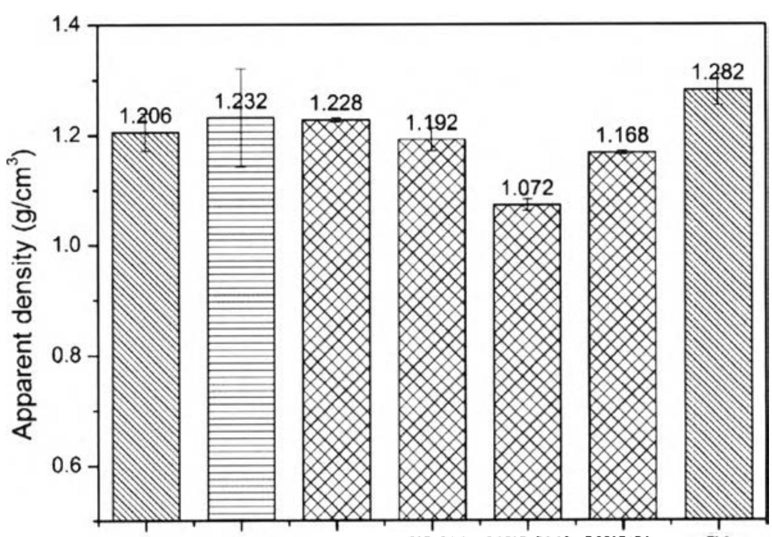


Figure 7.5 Specific gravity of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.4.2 Thermal Properties

7.4.2.1 Differential Scanning Calorimeter: DSC

The glass transition temperature (T_g) of PC/PLA/EAA/DBTO blends were investigated by DSC. Figure 7.6 shows the Tg of PC/PLA/EAA/DBTO blends. The glass transition temperatures of PLA in PC/PLA/EAA/DBTO blends are not detected. Tg of PC in the blends are decreased when increasing the content of DBTO due to the shortening PC chains are generated during the melt processing. The result indicates that all ratios of PC/PLA/EAA/DBTO blends are incompatible. Therefore, additional EAA incorporated with DBTO does not improve the miscibility of PC/PLA blends.

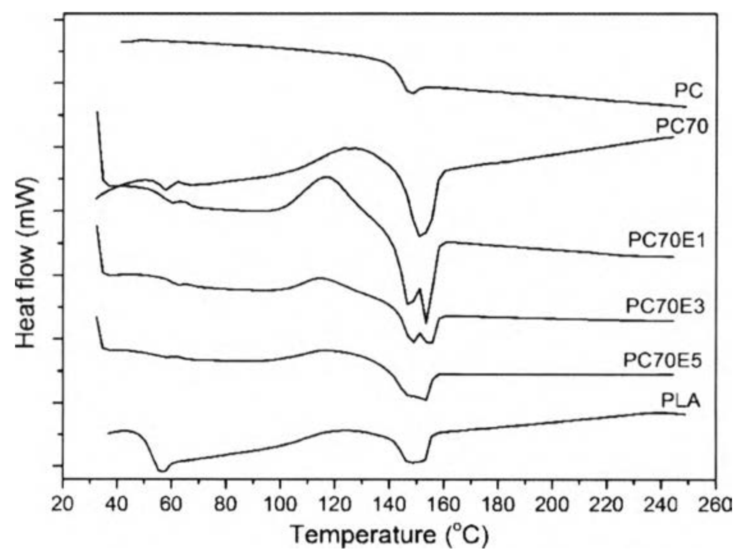


Figure 7.6 DSC plots (second heating) of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC/PLA/DBTO blends were evaluated by TGA. Figure 7.7 and Table 7.4 shows the TGA results of PC, PLA, PC70 and PC/PLA/EAA blends. All formulas of PC/PLA/EAA/DBTO blends have two steps of the degradation same as PC70. The degradation temperature (Td) of PC/PLA/EAA/DBTO blends was significantly decreased when increasing the content of DBTO. This phenomena implies that the shortening PC and PLA chains start to degrade at lower temperature. Therefore, the effect of additional DBTO is more than that of additional EAA.

Table 7.4 The T_d and % weight loss of PC/PLA/EAA/DBTO

Composition	T_d (°C)	% weight loss
PC70	348, 451	38.5, 51.6
PC70E1	350, 553	85.1, 13.5
PC70E1D0.01	340, 540	84.9, 15.0
PC70E1D0.05	323, 533	48.9, 50.2
PC70E1D0.1	310, 522	83.9, 15.5

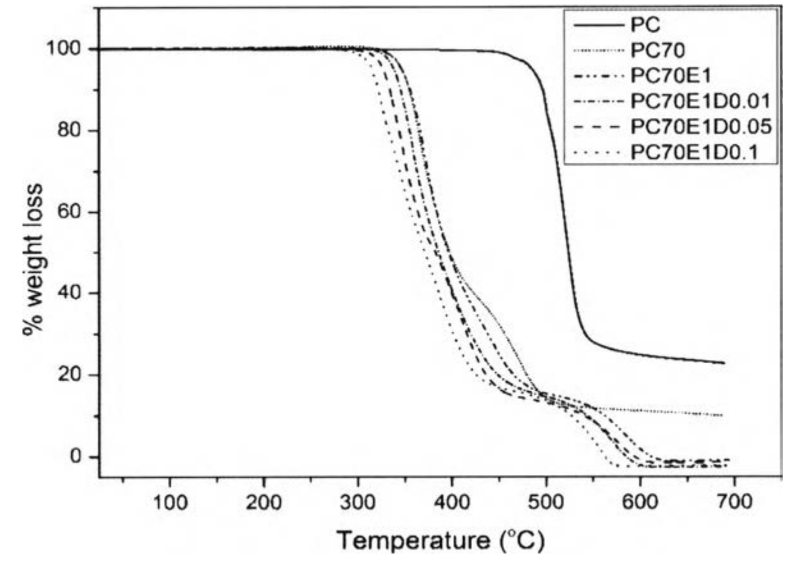


Figure 7.7 TGA plots of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.4.2.3 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 7.8, while the blends show two peaks indicating a two-phase morphology and each Tg slightly shifts to lower Tg of pure materials due to the lower molecular weight of PC and PLA are generated during the melt processing. All formulas of PC/PLA/EAA/DBTO blends show two Tg around 58.6 – 61.5 °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.

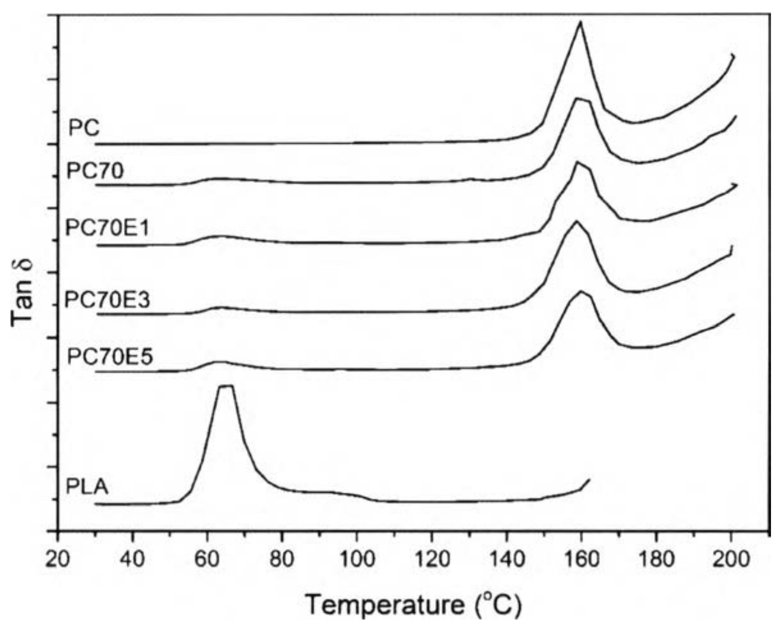


Figure 7.8 Tan δ plots of neat PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.4.3 Molecular weight distribution

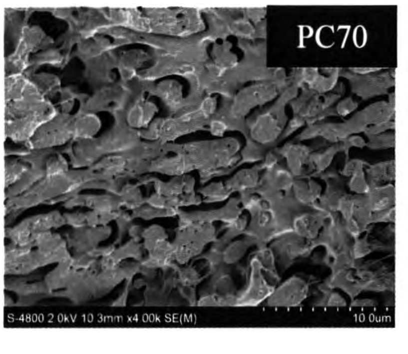
Table 6.5 $\overline{M}_w$, $\overline{M}_n$ and PDI of PC/PLA/EAA blends

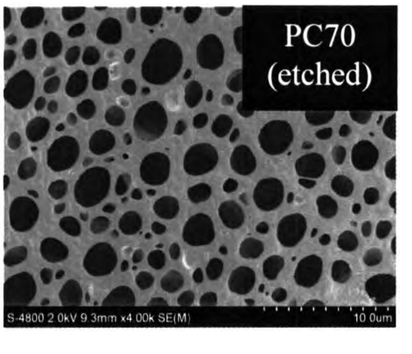
Formulations	M_w	M_n	PDI
PC70	45720	23231	1.97
PC70E1	57255	27956	1.66
PC70E1D0.01	57095	25546	2.24
PC70E1D0.05	50556	23409	2.16
PC70E1D0.1	51918	25770	2.01

Table 7.5 shows molecular weight and molecular weight distribution of PC/PLA/EAA/DBTO. Both $\overline{M_w}$ and $\overline{M_n}$ of PC/PLA/EAA/DBTO blends are significantly deceased when increasing the content of DBTO suggesting the shortening PC and PLA chains are occurred during the melting process. High PDI of PC/PLA/DBTO confirms that the tranesterification reaction are randomly occurred. The molecular weight and molecular weight distribution can explain the results of mechanical properties.

7.4.4 Morphology

After impact test, the fracture surfaces of PC/PLA/EAA/DBTO blends were etched by dichloromethane for 45 second to remove the PLA phase. The SEM observation of etched and unetched PC/PLA/EAA/DBTO blends are shown in Fig. 7.9. The micrograph of all formulas of PC/PLA/EAA/DBTO 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 PC70E1D0.01 show the slightly ductile failure suggesting impact strength of PC70E1D0.01 should be relatively improved same as PC70E1. The etched micrographs of PC70E1D0.05 and PC70E1D0.1 show the smaller average size of PLA compared to PC70.





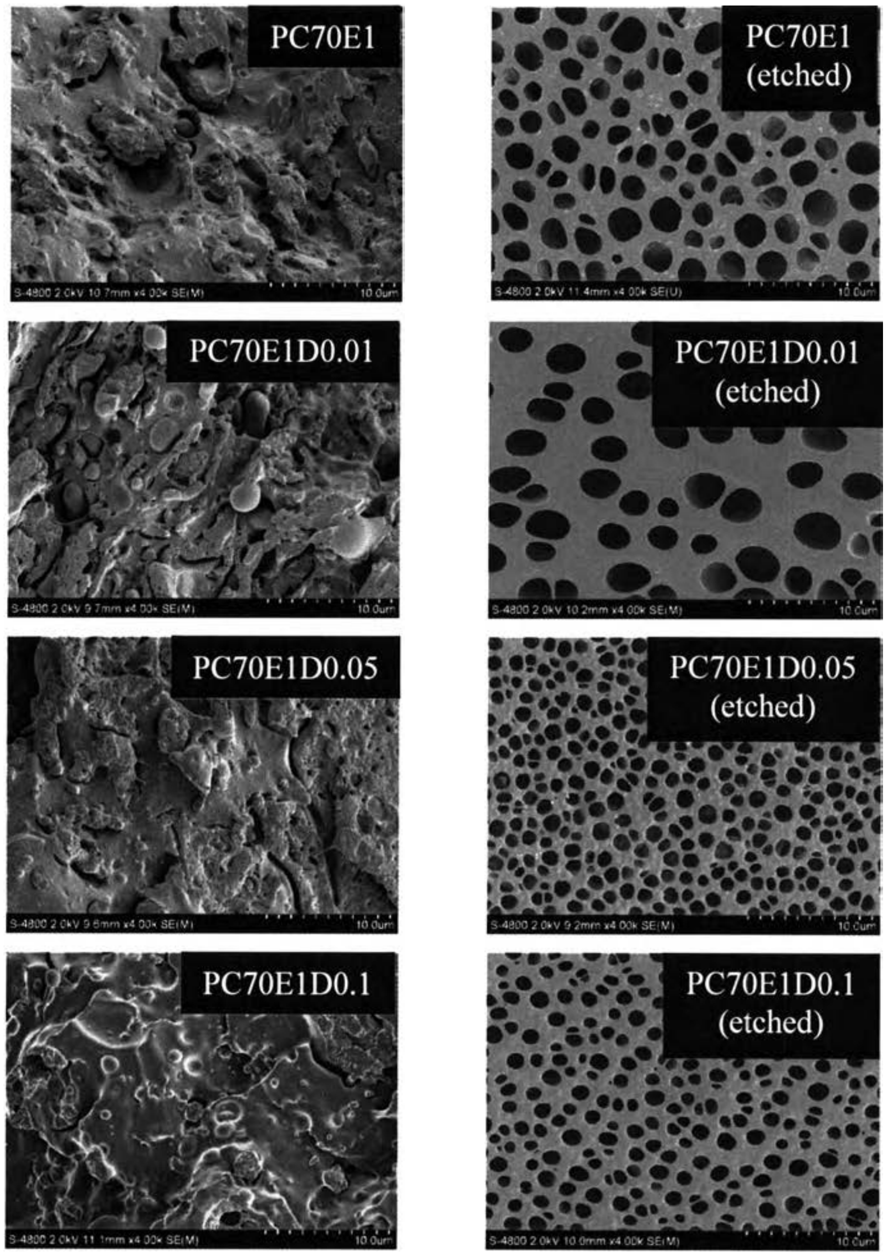


Figure 7.9 SEM micrographs of fractural impact surface of PC/PLA/EAA/DBTO blends.

7.4.5 Mechanical Properties

7.4.5.1 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 7.10-7.13, respectively. The overview of results show that additional EAA into the PC/PLA blends significantly influence the mechanical properties. By tensile strength, Fig. 7.10 shows decline of tensile strength at yield of PC/PLA/EAA/DBTO because of the effect of DBTO. The Young's modulus of PC/PLA/EAA/DBTO are insignificantly increased when increasing the content of DBTO because of high molecular weight distribution (PDI). The shortening PLA chains may obstruct the PC chains slip that why the Young's modulus of PC/EAA/DBTO are improved compared to PC70. Therefore, additional DBTO into PC/PLA/EAA blends decrease the tensile properties compared to PC70E1.

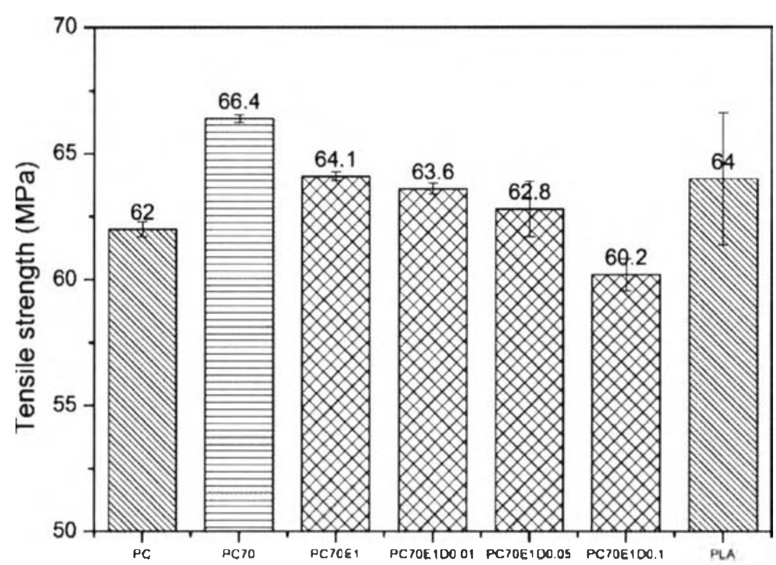


Figure 7.10 Tensile strength at yield of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

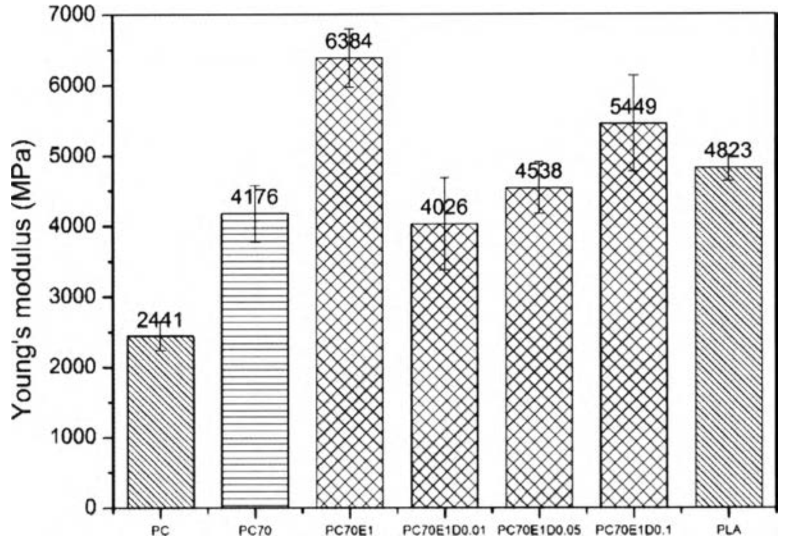


Figure 7.11 Modulus of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

For the flexural strength, From fig. 7.12 - 7.13, flexural strength and modulus of all PC/PLA/EAA/DBTO blends are insignificantly dropped compared to PC70 because of the high randomly shortening PC and PLA chains. PC70E1D0.1 has the flexural strength same as PC70. Therefore, additional EAA incorporated with DBTO into PC/PLA blends does not improve the flexural properties.

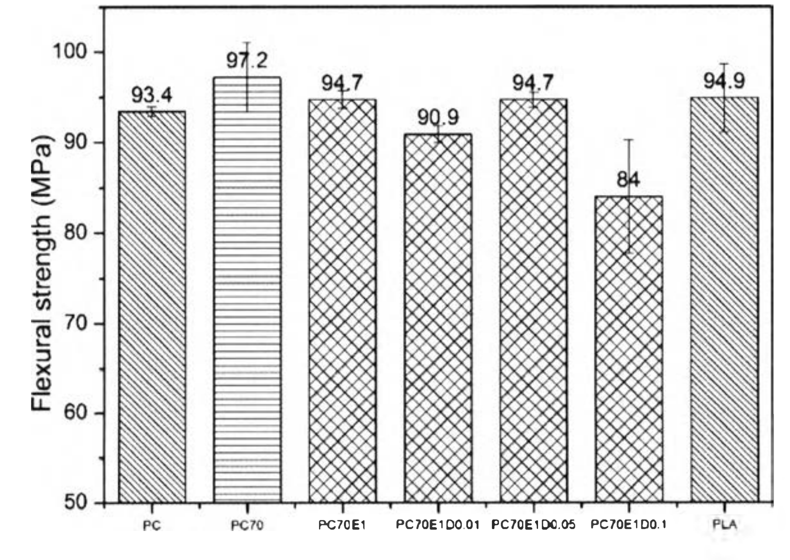


Figure 7.12 Flexural strength of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

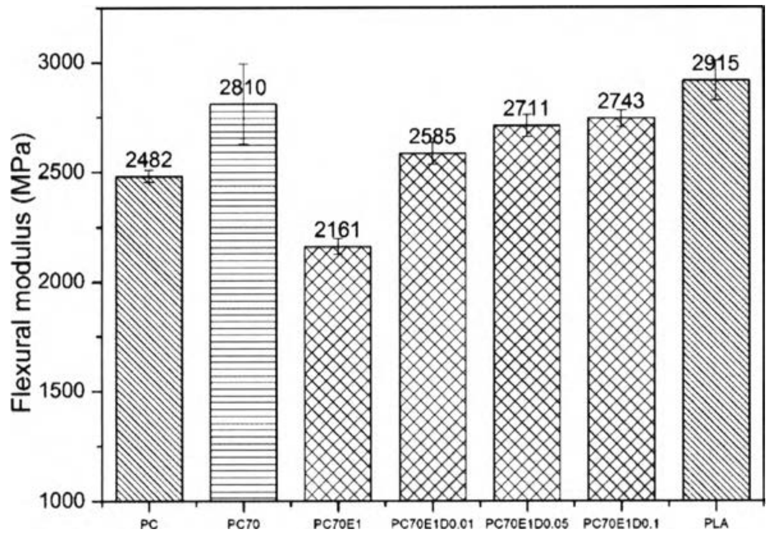


Figure 7.13 Flexural modulus of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.4.5.2 Notched izod impact

Figure 7.14 reported Notched izod impact of PC/PLA/EAA/DBTO blends. All formulas of PC/PLA/DBTO blends are low compared to neat PC. PC70E1D0.01 has higher impact strength than PC70 because of the effect of additional EAA. However, the increasing content of DBTO in PC/PLA/EAA reduce the impact strength due to the shortening PC chains. Therefore, additional DBTO into PC/PLA/EAA decline the impact strength.

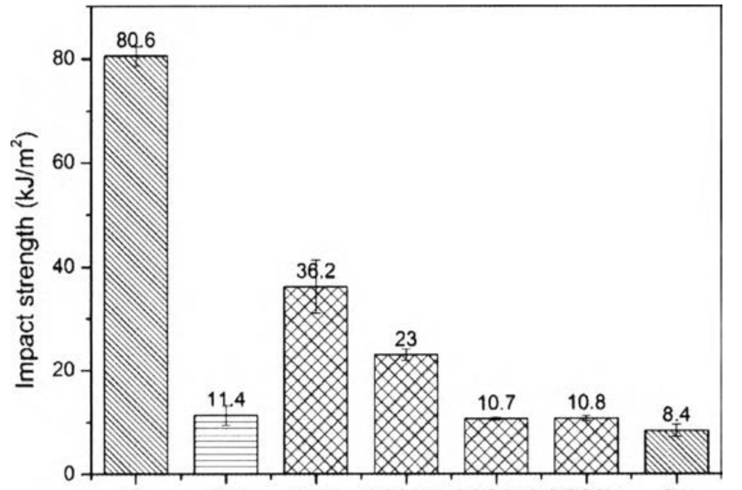


Figure 7.14 The impact strength of PC, PLA, PC70 and PC/PLA/EAA/DBTO blends.

7.5 Conclusions

PC/PLA/EAA/DBTO 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/EAA/DBTO 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/EAA/DBTO blends are immiscible. By the mechanical properties, all compositions of PC/PLA/EAA/DBTO demonstrated the lower tensile properties than those of PC/PLA/EAA because of the effect of adding DBTO. The flexural properties of all compositions of PC/PLA/EAA/DBTO slightly dropped compared to PC70. Therefore, adding only EAA is more efficiently than adding EAA incorporated with DBTO for improving the mechanical properties of PC/PLA blends.

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