CHAPTER V
PC/PLA BLENDS WITH DIBUTHYLTIN OXIDE (DBTO) AS A TRANSESTERIFICATION CATALYST

5.1 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 impact strength and miscibility of PC/PLA blends, Dibuthyltin oxide (DBTO) was used as a transesterification catalyst to generate the copolymers of PC/PLA. The PC/PLA blends with DBTO was studied at 70/30 ratio 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, PC70D0.1 demonstrated the higher Young's modulus and still maintain the other mechanical properties, compared with PC70. The other compositions of PC/PLA/DBTO show the low mechanical properties because the shortening polymer chains of PC and PLA from the thansesterification catalyst. However, the impact strength of all compositions of PC/PLA/DBTO are low which have to be improvement.

5.2 Introduction

All composition of PC/PLA blends without the compatibilizers are generally immiscible, which cause low impact strength. To improve the miscibility of the PC/PLA blend, additional compatibilizers are used to improve miscibility 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.

Reactive processing is a cost-effective way to improve miscibility of polymer blends. Chemical bonding between polymer blends in the extruding process during melt reactions to block or graft copolymer by using a transesterification catalyst. Pesneau, I. *et al.*,(1996) reported that Dibutyltin oxide (DBTO) as a transesterification catalyst efficiently improved the morphology of PE/PBT blend.

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.

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

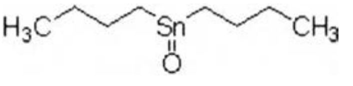

Figure 5.1 Chemical structure of DBTO.

5.3 Experimental

5.3.1 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 DBTO as a transesterification catalyst 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 5.1

Table 5.1 Amount of polymers prepared of each blends ratio for PC/PLA/DBTO

Formula	PC (kg)	PLA (kg)	DBTO (phr)
PC70D0.01	2.1	0.9	0.01
PC70D0.05	2.1	0.9	0.05
PC70D0.1	2.1	0.9	0.1

PC/PLA/DBTO blends were mixed by the twin screw extruder. The processing condition and the operating temperature are shown in table 5.2. The processing factors of the PC/PLA/DBTO are fixed as same as those of PC70.

Table 5.2 The processing condition of twin screw extruder for PC/PLA/DBTO blend

Formula	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PC70D0.01	220	225	230	235	235	235	235	235	235	235	25
PC70D0.05	220	225	230	235	235	235	235	235	235	235	25
PC70D0.1	220	225	230	235	235	235	235	235	235	235	25

All PC/PLA/DBTO blends show opaque and off-white as same as PC70 which is shown in Figure 5.2.

PC PC70 PC70D0.01 PC70D0.05 PC70D0.1 PLA

Figure 5.2 Pellets of PC, PLA and uncompatibilized PC/PLA/DBTO blends.

5.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 5.3.

Table 5.3 The processing condition of injection molding for PC, PLA, and PC/PLA/DBTO blends

Formulations	Temperature (°C)					Injection Pressure (kg/cm^2)	T_{mold} (°C)
	Z1	Z2	Z3	Z4	Nozzle		
PC70D0.01	210	215	220	225	1200	40	70
PC70D0.05	210	215	220	225	1200	40	70
PC70D0.1	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 5.3.

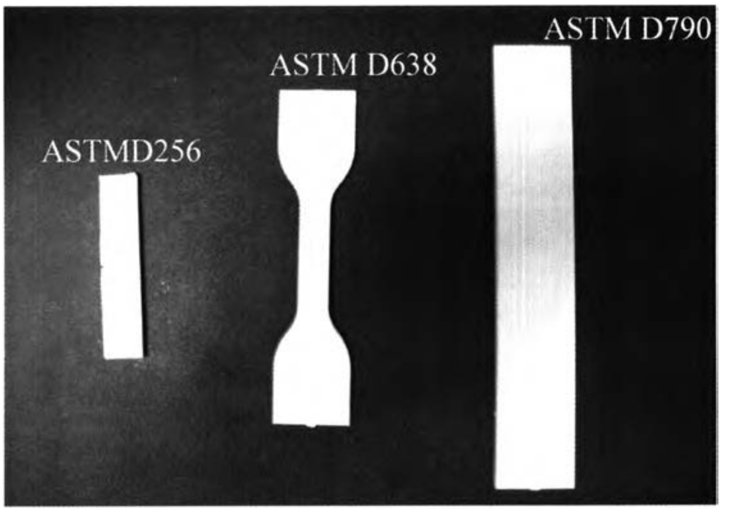

Figure 5.3 The specimens for mechanical testing.

5.4 Results and Discussion

5.4.1 Physical Properties

5.4.1.1 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 5.4 shows MFI of PC, PLA, PC70 and PC/PLA/DBTO blends at the condition of 250°C/2.16 kg. When adding DBTO into PC/PLA blends, MFI is significantly increased. MFI of PC/PLA/DBTO is dramatically increased when increasing amount of DBTO. The results implies that the polymer chains were cut by transesterification reaction, led to the shorter polymer chains of PC/PLA blends.

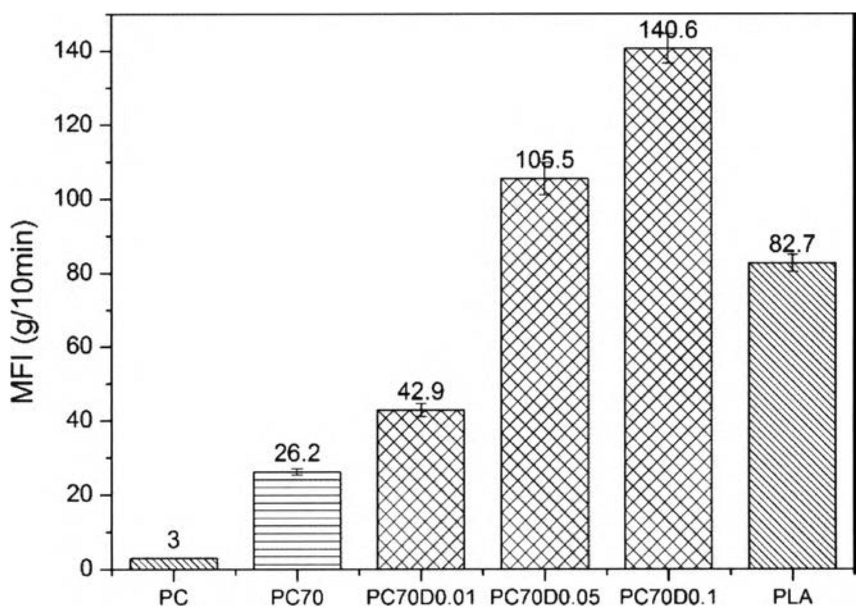

Figure 5.4 Melt Flow Index of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. The apparent density of PC/PLA/DBTO is slightly increased with inceasing the content of DBTO as shown in Figure 5.5. Thus, weight of PC/PLA/DBTO blends with higher DBTO contents were lower. From D=M/V (D= density, M = mass and V = volume), at the same volume, mass decrease yielding the lower apparent density.

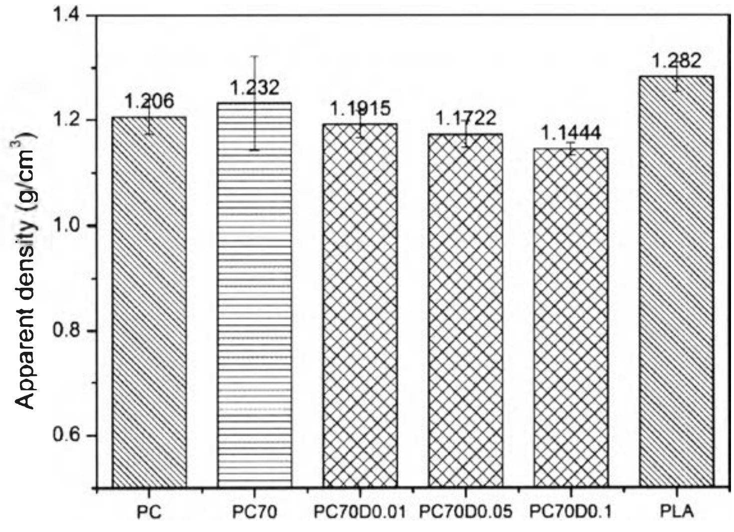

Figure 5.5 Specific gravity of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.4.2 Thermal Properties

5.4.2.1 Differential Scanning Calorimeter: DSC

The glass transition temperature (T_g) and % crystallinity PC/PLA/DBTO blends were investigated by DSC. Figure 5.6 shows the second heating of PC, PLA, PC70 and PC/PLA/DBTO blends. The DSC graphs of PC70D0.01 and PC70D0.05 showed the extraordinary exothermic peak which may refer to the occerence of the copolymer of PC/PLA while PC70D0.1 showed extraordinary endothermic peak which may refer to the degradation of the shorten polymer chains of PLA because of the tranesterification reaction. However, the PC70D0.01 and PC70D0.05 two T_g. Each T_g does not shift in of T_g of pure materials. It indicate that additional DBTO does not improve the miscibility of PC/PLA blends.

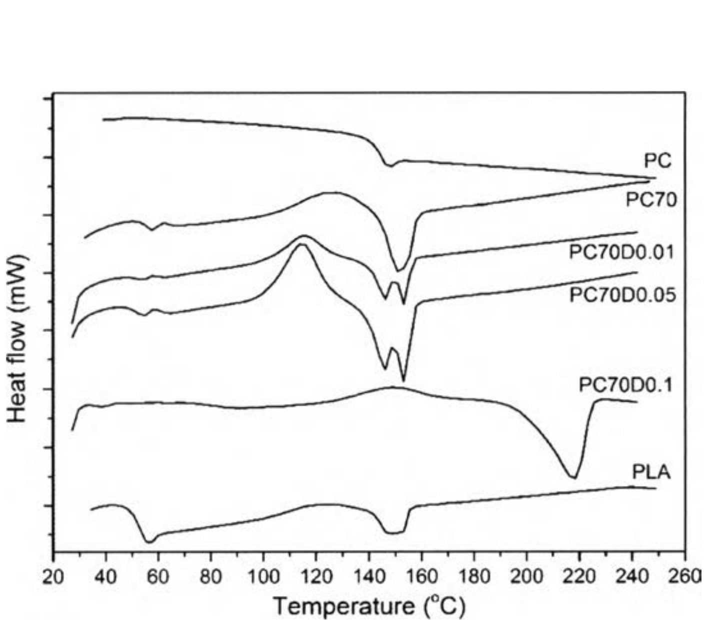

Figure 5.6 DSC plots (second heating) of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC/PLA/DBTO blends were evaluated by TGA. Figure 5.7 and Table 5.4 shows the TGA results of PC, PLA, PC70 and PC/PLA/DBTO blends. The degradation temperature (T_d) of all compositions of PC/PLA/DBTO blends have two steps of the degradation which generate two degradation temperature (T_d). The weight loss of first step of degradation around 300 °C corresponded to PLA and the second step of degradation around 450 °C corresponded to PC. The results show that both of the T_d of the first and second steps of the PC/PLA/DBTO is lower with increasing the DBTO content. This phenomena implies that the shortening polymer chains of PLA and PC are occurred during the melting processing.

Table 5.4 The T_d and % weight loss of PC/PLA/DBTO

Composition	T_d (°C)	% weight loss
PC70	348, 451.3	38.5, 51.6
PC70D0.01	321.2, 445.6	41.5, 45.6
PC70D0.05	316, 440	39.4, 48.6
PC70D0.1	290, 430	36.1, 49.5

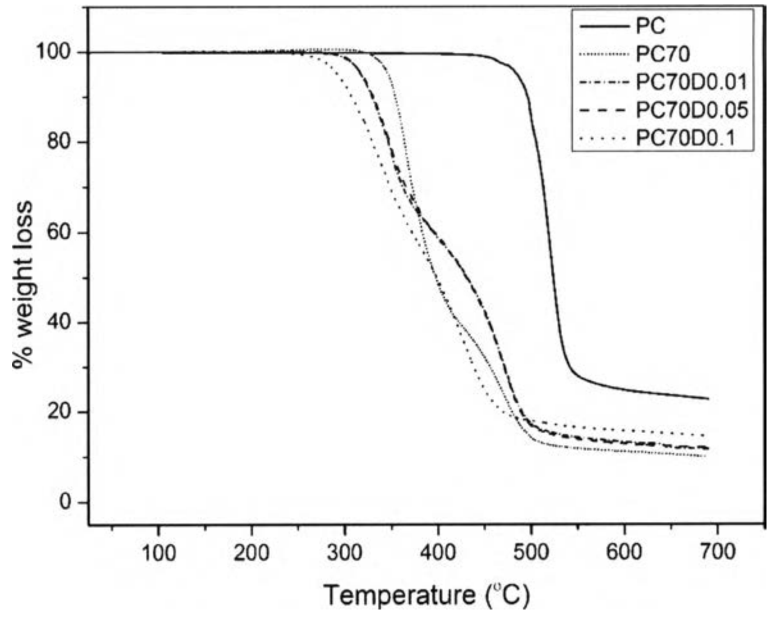

Figure 5.7 TGA plots of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.4.2.3 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''). In figure 5.8, all compositions of PC/PLA/DBTO show two peaks indicating a two-phase morphology and each T_g slightly shifts of T_g of pure materials, indicating that the blends are completely immiscible. Moreover, There is no trace of the occurrence of copolymer of PC/PLA.

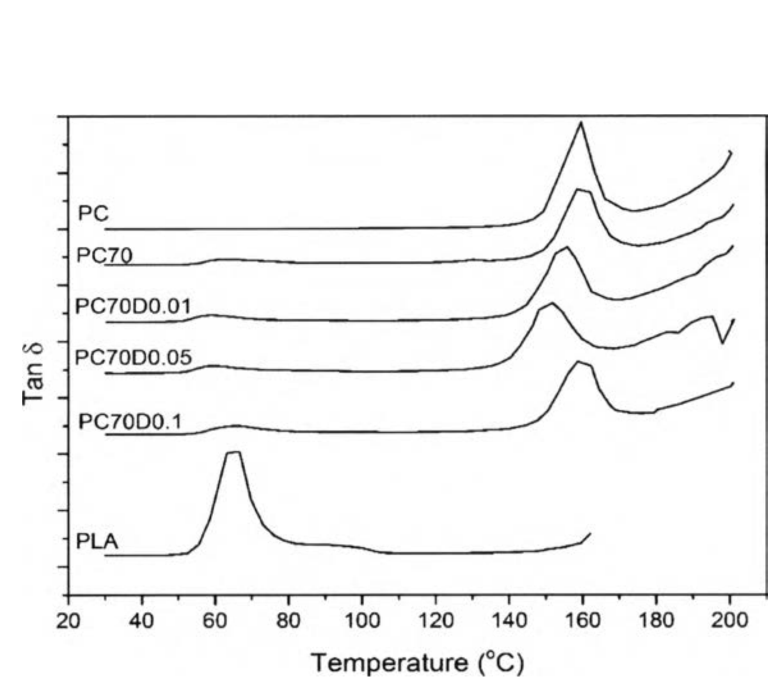

Figure 5.8 Tan δ plots of neat PC, PLA, PC70 and PC/PLA/DBTO blends.

5.4.3 Molecular weight distribution

Table 5.5 $\overline{M}_w$, $\overline{M}_n$ and PDI of PC/PLA/EAA blends

Formulations	$\overline{M}_w$	$\overline{M}_n$	PDI
PC70	45720	23231	1.97
PC70D0.01	52077	24354	2.14
PC70D0.05	44621	21014	2.12
PC70D0.1	42644	20073	2.12

Table 5.5 shows molecular weight and molecular weight distribution of PC/PLA/DBTO. Both $\overline{M}_w$ and $\overline{M}_n$ of PC/PLA/DBTO blends are 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 transesterification reaction are randomly occurred. The molecular weight and molecular weight distribution can explain the results of mechanical properties.

5.4.4 The occurrence of PC/PLA copolymer

The occurrence of the copolymer was confirmed by ^{1}H NMR spectrum. Based on theory, the chemical shifts values corresponding to a hydrogen around functional group are slightly shifted if the surrounding hydrogen of that hydrogen is changed due to the occurrence of transesterification reaction between carbonate linkage of PC and ester linkage of PLA. Fig. 5.9 shows the comparison of ^{1}H NMR spectrum between PC70 and PC70D0.1. There are no trace of change of chemical shift values of PC7D0.1 compared to PC70 implied that ^{1}H NMR spectrum does not confirm the occurrence of PC/PLA copolymer. PC70D0.1 generates new chemical shift values at 4.35 ppm corresponding to hydrogen at the end group of PLA suggesting many end groups of PLA are generated. The result confirms that the shortening PLA chains are generated by applying DBTO into PC/PLA blends during the extruder process.

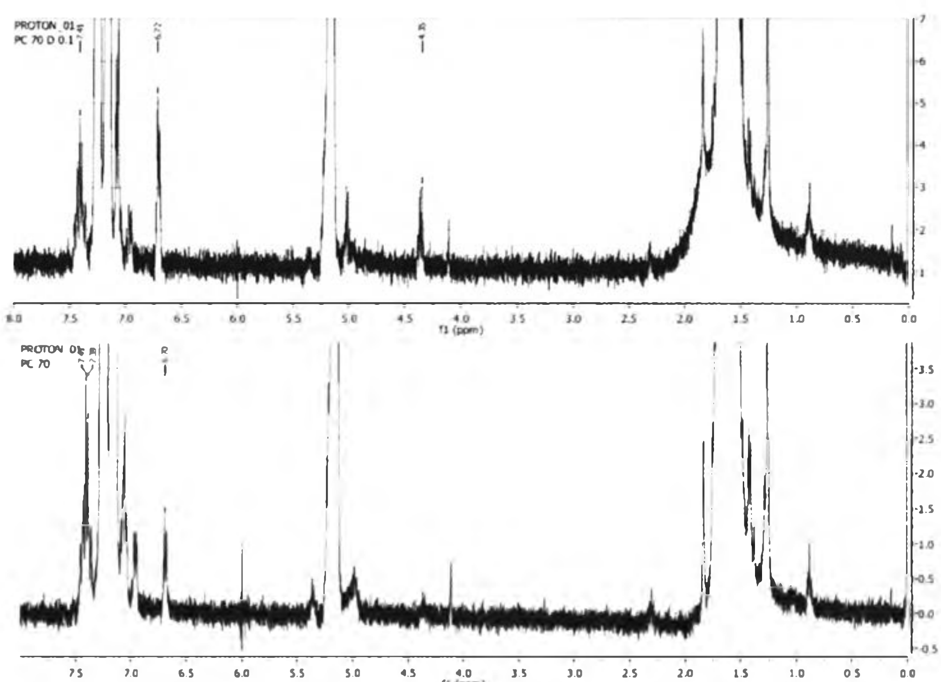

Figure 5.9 ^{1}H NMR spectrum of PC70 and PC70D0.1.

5.4.5 Morphology

After impact test, the fracture surfaces of PC/PLA/DBTO blends were etched by dichloromethane for 45 second to remove the PLA phase. The SEM observation of etched and unetched PC/PLA/DBTO blends are shown in Fig. 5.10. The micrograph of all formulas of PC/PLA/DBTO 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 PC/PLA/DBTO show the smaller average size of PLA compared to PC70.

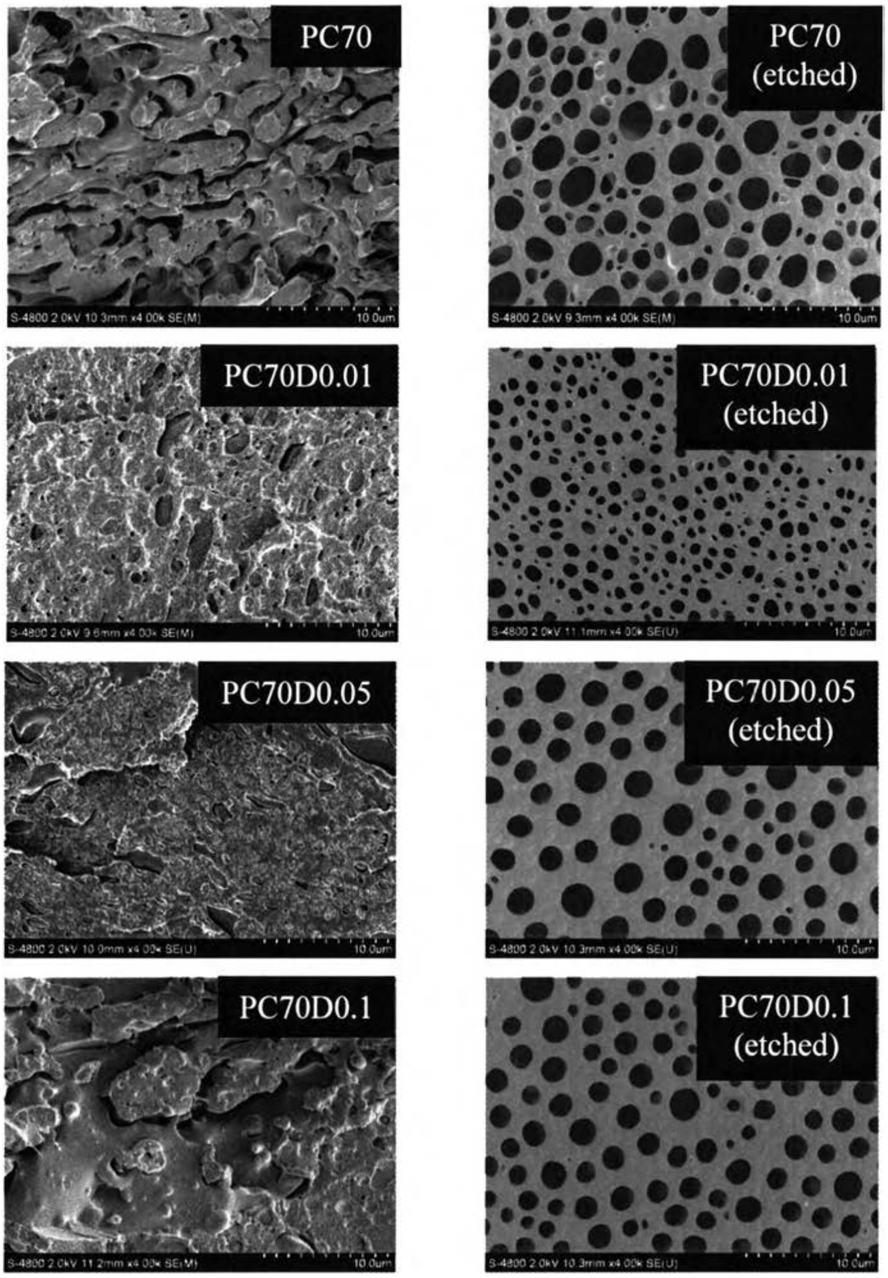

Figure 5.10 SEM micrographs of fractural impact surface of PC/PLA/DBTO blends

5.4.6 Mechanical Properties

5.4.6.1 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/DBTO blends are shown in Figure 5.11-5.14, respectively. The overview of results show that additional DBTO into the PC/PLA blends significantly influence the mechanical properties. By tensile strength, Fig. 5.11 shows dramatically decrease of tensile strength at yield of PC70D0.01 and PC70D0.05 while the tensile strength at yield of PC70D0.1 is slightly dropped, compared with that of PC70. By Young's modulus, Young's modulus of PC70D0.01 and PC70D0.05 are lower than that of PC70 while PC70D0.1 has the highest Young's modulus. Both of PC70D0.01 and PC70D0.05 have the lower tensile strength and modulus because the shorten polymer chains of PC and PLA are easy to slip from each other. On the other hand, PC70 has the highest both of tensile strength and modulus because the optimum length of polymer chains of PC and PLA can act as a reinforcement filler. Therefore, the tensile properties of PC70D0.1 is slightly improved.

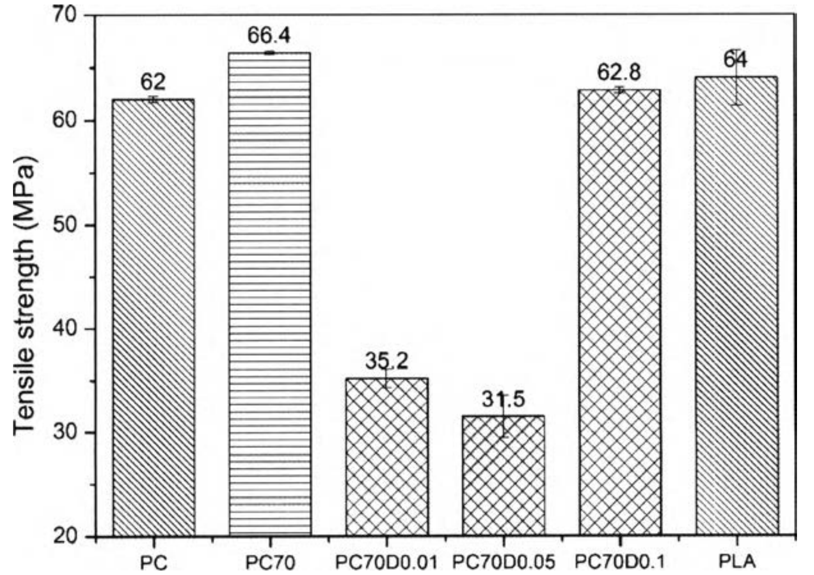

Figure 5.11 Tensile strength at yield of PC, PLA, PC70 and PC/PLA/DBTO blends.

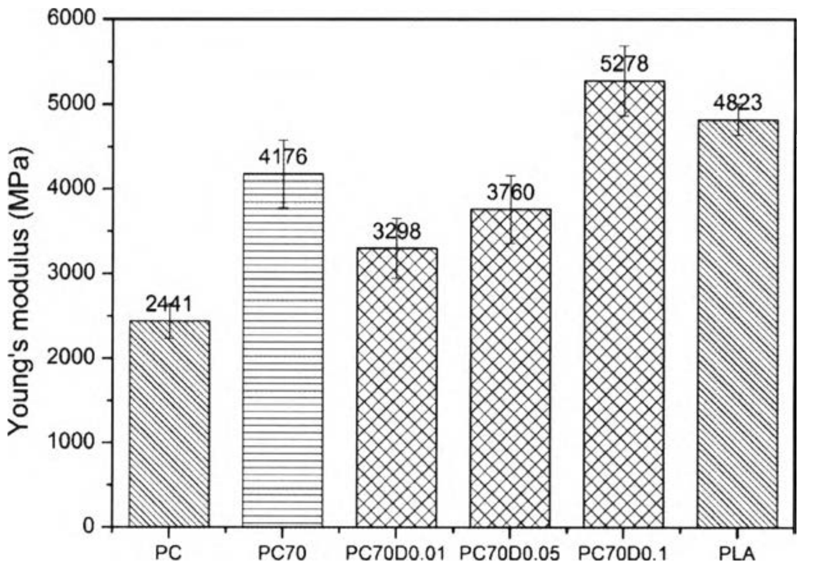

Figure 5.12 Modulus of PC, PLA, PC70 and PC/PLA/DBTO blends.

For the flexural strength, fig. 5.13 shows dramatically decrease of flexural strength at yield of PC70D0.01 and PC70D0.05 while the flexural strength at yield of PC70D0.1 is insignificantly decreased, compared with that of PC70. By the flexural modulus, The flexural modulus of all compositions of PC/PLA/DBTO are slightly changed but not a trend. These results from tensile and flexural properties confirm that addition of inappropriate amount of DBTO in the PC/PLA blends significantly decrease the mechanical properties. The phenomena may occur due to the shortening polymer chains of PC and PLA from transesterification reaction and stress concentration occurred at the shortening polymer chains. On the other hand, addition of 0.1 phr of DBTO can improve Young's modulus and maintain the other mechanical properties of the PC/PLA blends because the optimum length of shortening polymer chains of PC and PLA can act as a reinforcement filler of the PC/PLA blends.

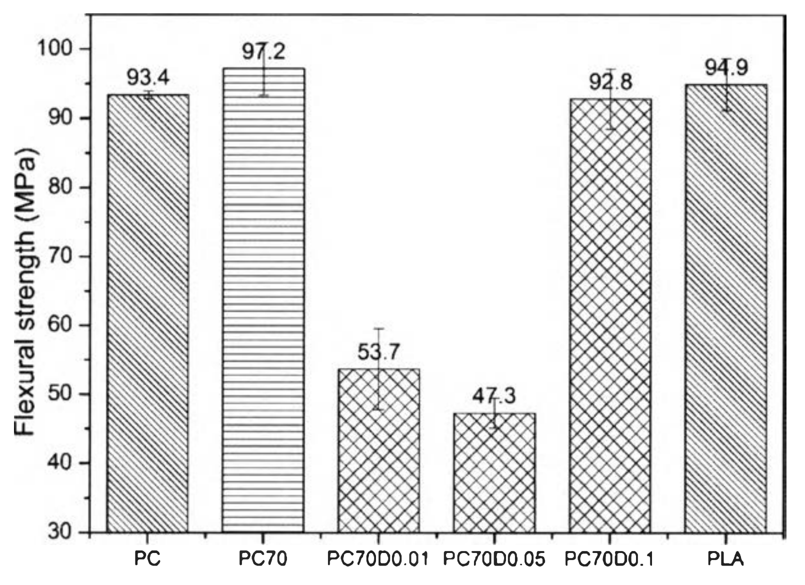

Figure 5.13 Flexural strength of PC, PLA, PC70 and PC/PLA/DBTO blends.

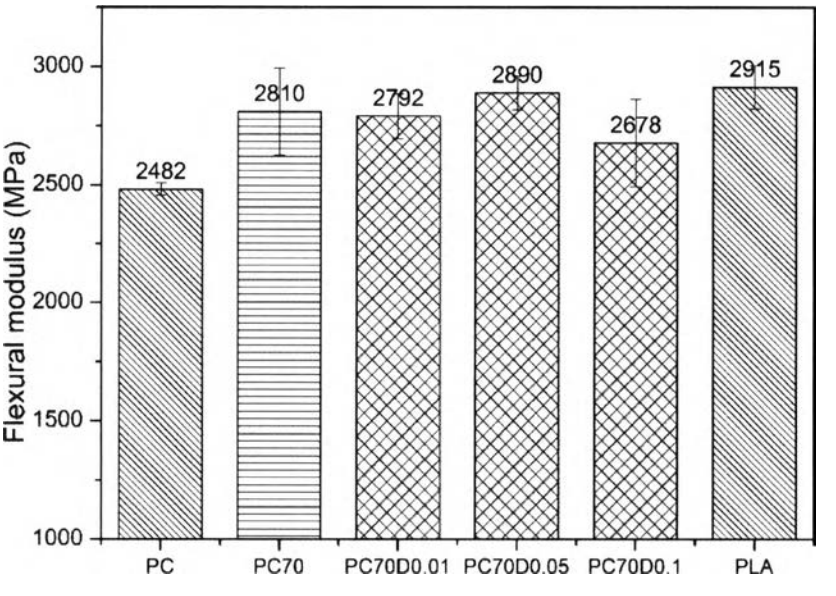

Figure 5.14 Flexural modulus of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.4.6.2 Notched izod impact

Figure 5.15 shows Notched izod impact of PC, PLA, PC70 and PC/PLA/DBTO blends. All composition of PC/PLA/DBTO blends show the significantly low closed to that of neat PLA because the crack propagation generate around PLA phase.

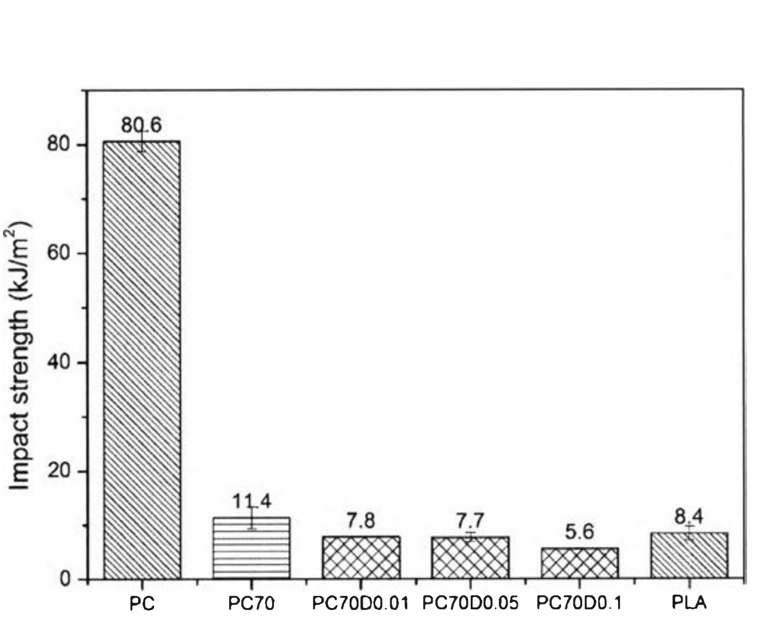

Figure 5.15 The impact strength of PC, PLA, PC70 and PC/PLA/DBTO blends.

5.5 Conclusions

PC/PLA/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 smaller particle size of PLA than those observed in PC70. However, the phase separation between PC and PLA still exist. DSC and DMA results of all compostions of PC/PLA/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 blends are immiscible. DSC results show the extraordinary endothermic peak suggesting the occurrence of copolymer of PC/PLA. By the mechanical properties, addition of inappropriate amount of DBTO in the PC/PLA blends significantly decrease the mechanical properties because the shortening polymer chains of PC and PLA from transesterification reaction are generated. On the other hand, addition of 1 phr DBTO into the PC/PLA blends can improve the Young's modulus and maintain the other mechanical properties, compares with PC70. Nevertheless, the impact strength of all compositions of PC/PLA/DBTO are low because the stress concentration and crack propagation generate around PLA phase.

5.6 Acknowledgements

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