

CHAPTER IV

PC/PLA BLENDS WITHOUT THE COMPATIBILIZERS

4.1 Abstract

Polycarbonate/poly(lactic acid) blends were expected to provide an excellent balance of the properties of neat PC and PLA which are impact resistance and tensile strength. The PC/PLA blends were studied at 90/10, 80/20, 70/30, 60/40 and 50/50 %by weight prepared by a twin screw extruder. The PC/PLA blends without compatibilizer exhibit the low impact strength due to the immiscibility of PC and PLA. That led to the poor interfacial adhesion, resulting low impact properties. SEM micrographs showed the support of this assumption. The fractural surface of the blends showed phase separation and the dispersive spherical PLA in the PC matrix, corresponding to the brittleness behavior. Furthermore, the physical, thermal and mechanical properties of PC/PLA blends were reported in this chapter.

4.2 Introduction

The growth of petroleum-based engineering plastic has rapidly been increased in recent year. The use of engineering plastic provided several advantages including lower cost of fabrication, lower weight and ease of processing step. Many types of products such as electronic gadgets, automotive part were mainly fabricated from petroleum-based engineering plastic. However, the environmental concern of the fracbrication of the petroluem-based plastic still remains a hot issue.

In order to prevent this concern as well as to encourage the policy of environmental preservation, the “Green concept” was widely used. The use of hazardous materials and their processing step should be preferably avoided for obtaining sustainable aspect in engineering industry. Futhermore, in order to fulfill this requirement, the bio-based materials has been recently developed for replacing any traditional engineering plastic.

Polycarbonate (PC) is one of an important engineering plastic which has excellence in mechanical, optical and heat resistance properties. Nevertheless, PC still exhibited some disadvantages including high processing temperature.

From the fundamental point of view, blending PC with other bio-based polymer is the efficient way to solve the environmental concern.

Therefore, in this research work, we wish to study the ability of PC and its blended properties such as rheological, mechanical, thermal and morphological with polylactic acid (PLA) in order to find the optimum ratio of PC/PLA blends to do the further experiment. The reactive compatibilizers is going to be added into the optimum ratio of PC/PLA blends to generate the copolymer of PC/PLA. The details about the PC/PLA blends with the reactive compatibilizers will be described in the next chapter.

4.3 Experimental

4.3.1 Extrusion

PC and PLA pellets were dried in oven at 60°C for 12 hours before mixing in twin screw extruder. 3 kg of blends were prepared per each blends ratio. The blend ratios were 90/10, 80/20, 70/30, 60/40, and 50/50 by weight with respected to PC/PLA. The amount of materials prepared of each blend ratio was shown in table 4.1.

Table 4.1 Amount of polymers prepared of each blends ratio

Formula	PC (kg)	PLA (kg)
PC90	2.7	0.3
PC80	2.4	0.6
PC70	2.1	0.9
PC60	1.8	1.2
PC50	1.5	1.5

PC/PLA blends were mixed by twin screw extruder. The processing condition and the operating temperature are shown in table 4.2.

Table 4.2 The processing condition of twin screw extruder for uncompatibilized PC/PLA blends

Formula	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PC90	240	245	250	255	260	260	260	260	260	260	25
PC80	230	235	240	245	245	245	245	245	245	245	25
PC70	220	225	230	235	235	235	235	235	235	235	25
PC60	210	215	220	225	225	225	225	225	225	225	25
PC50	205	210	215	220	220	220	220	220	220	220	25

Appearances of PC pellets are transparent, PLA pellets are translucent. All PC/PLA blends show opaque and off-white as shown in Figure 4.1.

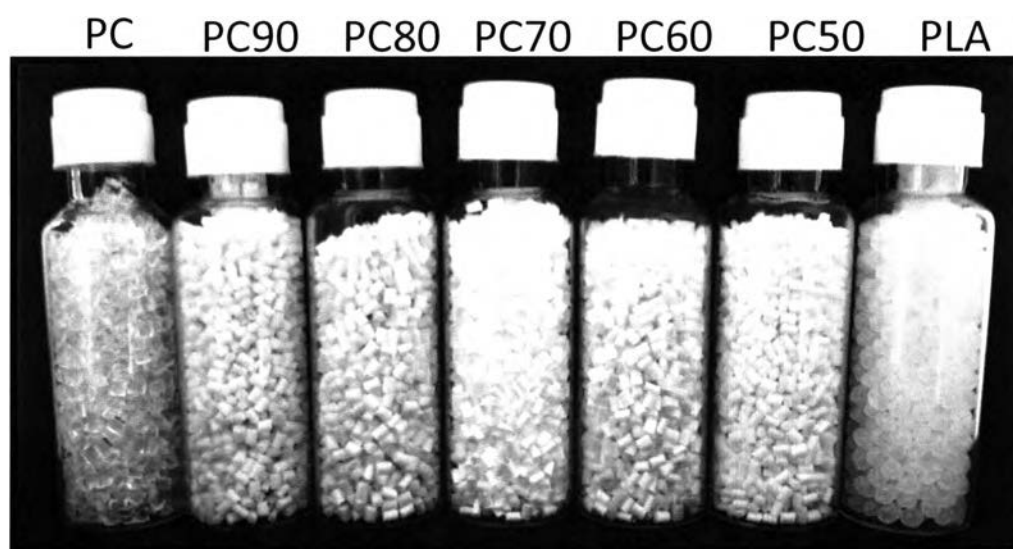


Figure 4.1 Pellets of PC, PLA and uncompatibilized PC/PLA blends.

4.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 4.3.

Table 4.3 The processing condition of injection molding for PC, PLA, and uncompatibilized PC/PLA blends

Formulations	Temperature (°C)				Nozzle	Injection	
	Z1	Z2	Z3	Z4		Pressure (kg/cm ²)	T _{mold} (°C)
PC	245	250	255	260	1200	40	70
PC90	220	225	230	235	1200	40	70
PC80	215	220	225	230	1200	40	70
PC70	210	215	220	225	1200	40	70
PC60	210	215	220	225	1200	40	70
PC50	210	215	220	225	1200	40	70
PLA	195	200	205	210	1200	40	30

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 4.2.

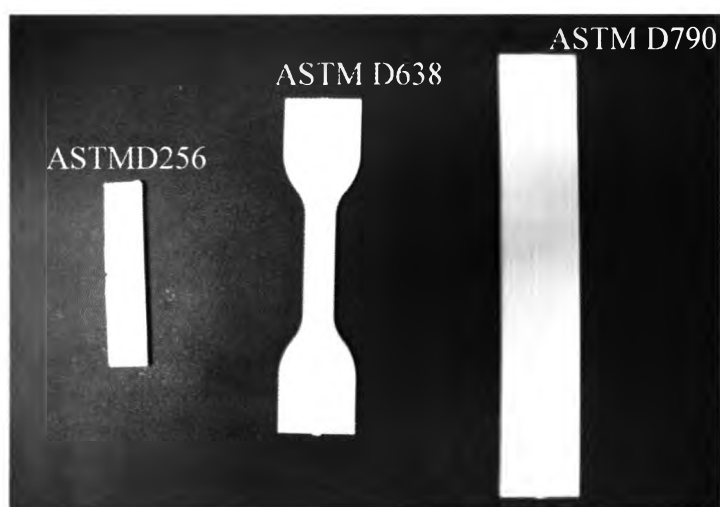


Figure 4.2 The specimens for mechanical testing.

4.4 Results and Discussion

4.4.1 Physical Properties

4.4.1.1 *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 4.3 shows MFI of PC, PLA and uncompatibilized PC/PLA blends at the same 250°C/2.16 kg. MFI of PC is less than that of PLA. This results indicate that the processing temperature of PLA is lower than that of PC. MFI of blends significantly increase with increasing PLA contents. It indicates that addition of PLA in PC can improve the processability of this polymer blends.

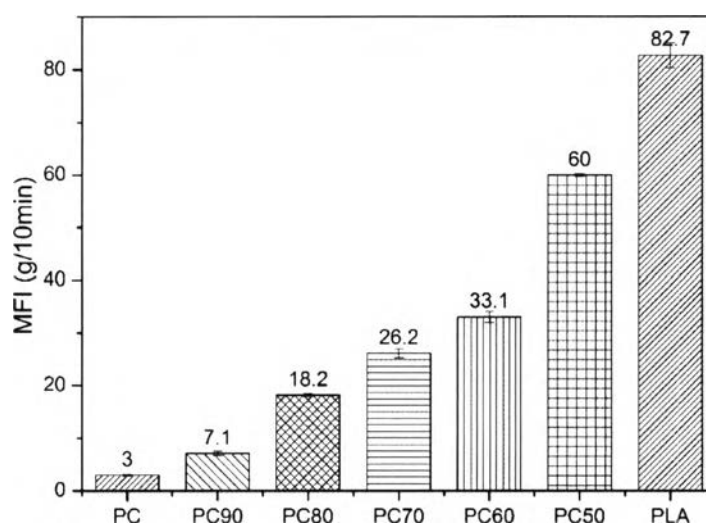


Figure 4.3 Melt Flow Index of PC, PLA, and uncompatibilized PC/PLA blends.

4.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. According to the equation $D=M/V$ (D = density, M = mass and V = volume), at the same volume, mass increases yielding the higher density. Table 4.5 reports apparent density of PC, PC/PLA blends and PLA. PC is the lowest (1.205 ± 0.033 g/cc) and specific gravity of PLA is the highest (1.282 ± 0.028 g/cc). Apparent density of PC/ PLA blends increase with PLA contents (Figure 4.4) due to PLA has higher apparent density.

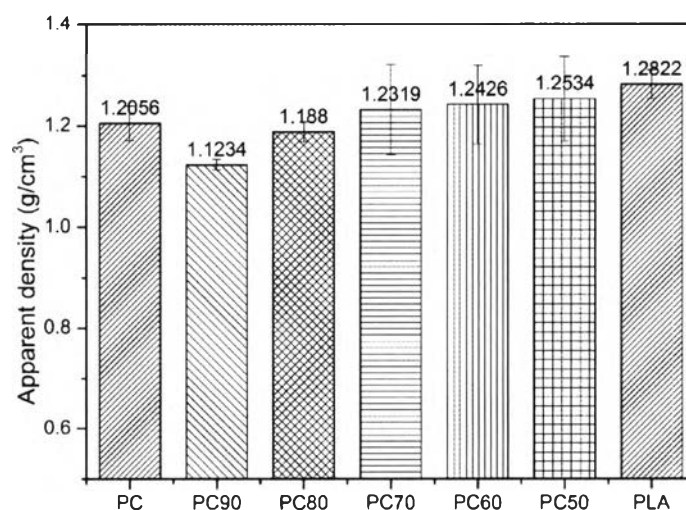


Figure 4.4 Specific gravity of PC, PLA, and uncompatibilized PC/PLA blends.

4.4.2 Thermal Properties

4.4.2.1 *Differential Scanning Calorimeter: DSC*

The glass transition temperature (T_g) and % crystallinity of PC, PLA and uncompatibilized PC/PLA blends were investigated by DSC. Figure 4.5 shows the second heating of PC, PLA and uncompatibilized PC/PLA blends. PC is an amorphous which shows the glass transition temperatures (T_g) around 145.4 °C and the glass transition temperatures of PLA is around 61.2 °C. PC/PLA blends without compatibilizer show two T_g . Each T_g does not shift in of T_g of pure materials. It indicate that all ratio of PC/PLA blends are incompatible. Amorphous PC is definitely non crystalline while the crystallinity of PLA is 1.41 %.

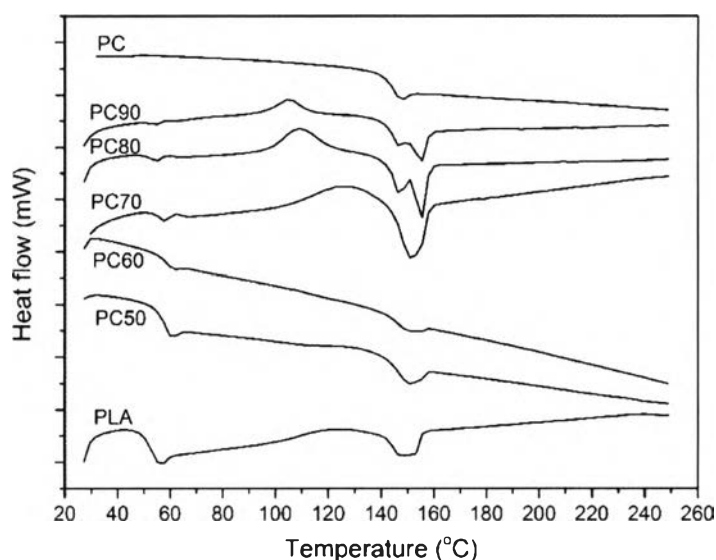


Figure 4.5 DSC plots (second heating) of PC, PLA, and uncompatibilized PC/PLA blends.

4.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC, PLA and uncompatibilized PC/PLA blends were evaluated by TGA. Figure 4.6 shows the TGA results of PC, PLA and uncompatibilized PC/PLA blends. The degradation temperature (T_d) of PC (498.6°C) was higher than that of PLA (343.8°C) and %weight loss of PC was lower. Thus, PC is much more stable than PLA at the same operating temperature because the structure of PC has aromatic ring which have highly heat resistance. In addition, PC90, PC80 and PC70 have two steps of the degradation which generate two degradation temperature (T_d). The weight loss of first step of degradation around 350°C corresponded to PLA and the second step of degradation around 450°C corresponded to PC. This phenomena implies that the incompatibility of PC/PLA blends. The PC60 and PC50 generate one steps of the degradation because PLA has lower degradation temperature (T_d) and PLA phase induced the degradation. Percentage of weight loss of PC/PLA blends was increased with increasing PLA content because the char yield of the PC/PLA blend is corresponded to PC.

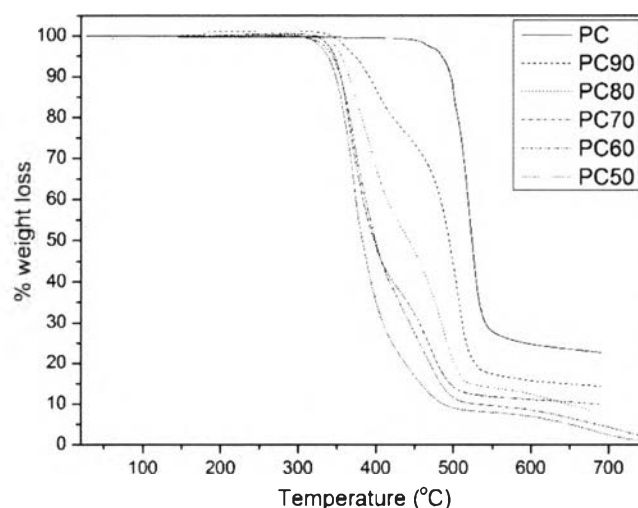


Figure 4.6 TGA plots of PC, PLA, and uncompatibilized PC/PLA blends.

4.4.2.3 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 $\tan \delta$ 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 T_g in the temperature range studied as shown in Figure 4.7, while the blends show two peaks indicating a two-phase morphology and each T_g slightly shifts out of T_g of pure materials. The glass transition temperature (T_g) of PC and PLA at 159.5°C and 64.8°C, respectively. All PC/PLA blends show two T_g around 55.8 – 65.2 °C and 159.5-168.9 °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.

From Fig. 4.8, the initial storage modulus of neat PLA is higher than that of PC indicating PLA is stiffer than PC at room temperature. However, the storage modulus of PLA dramatically decreased after operating temperature above 65 °C while PC is still maintain the storage modulus indicating that PC is stiffer than PLA at high temperature. In case of PC/PLA blends, adding more than 10 % by weight of PLA, the storage modulus dramatically decreased at the operating temperature

above T_g of PLA. This results indicate that the PC/PLA blends are more sensitive to temperature than neat PC.

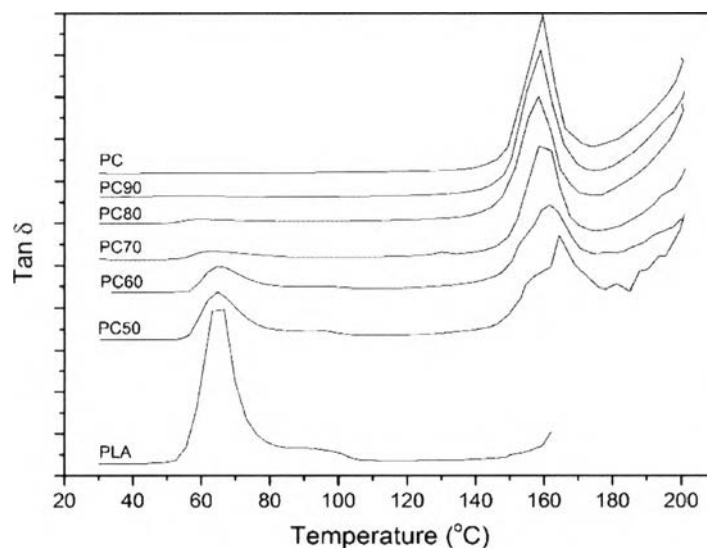


Figure 4.7 $\tan \delta$ plots of neat PC, PLA, and uncompatibilized PC/PLA blends.

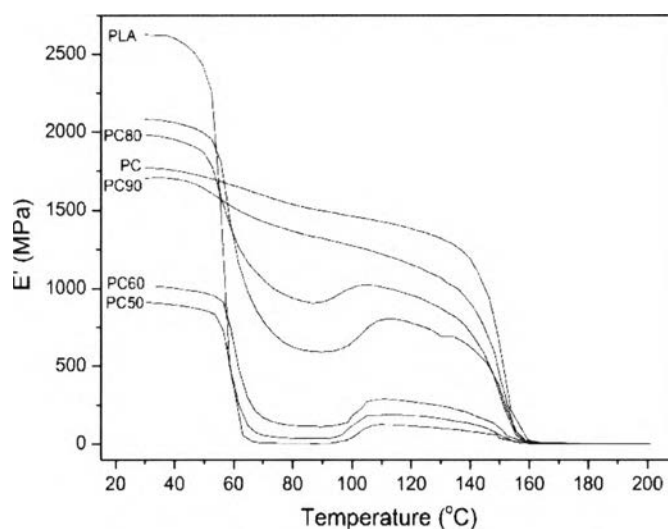


Figure 4.8 E' plots of neat PC, PLA, and uncompatibilized PC/PLA blends.

4.4.3 Mechanical Properties

4.4.3.1 *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

and uncompatibilized PC/PLA blends are shown in Figure 4.9-4.12, respectively. The overview of results show that blending of PLA into PC significantly influence the mechanical properties. By tensile strength, Fig. 4.9 shows slightly changed of tensile strength at yield of PC/PLA blends at various PLA contents. PC70 shows the highest tensile strength at yield. By Young's modulus, PLA shows higher stiffness than PC and PC/PLA blends. The Young's modulus of PC/PLA blends were increased with increasing PLA content because the matrix phase is PLA which align itself in helix shape.

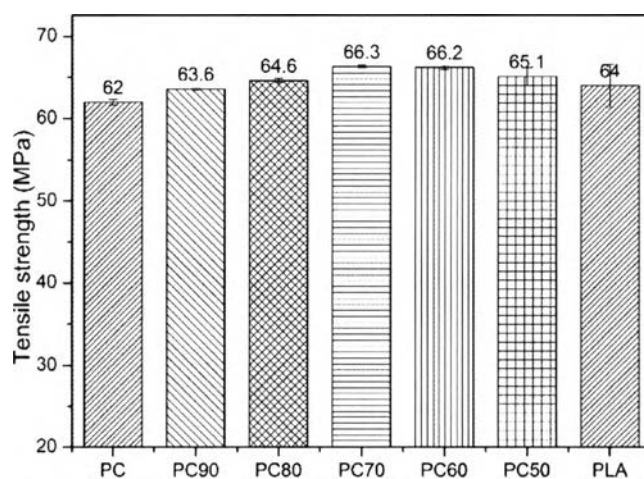


Figure 4.9 Tensile strength at yield of PC, PLA, and uncompatibilized PC/PLA blends.

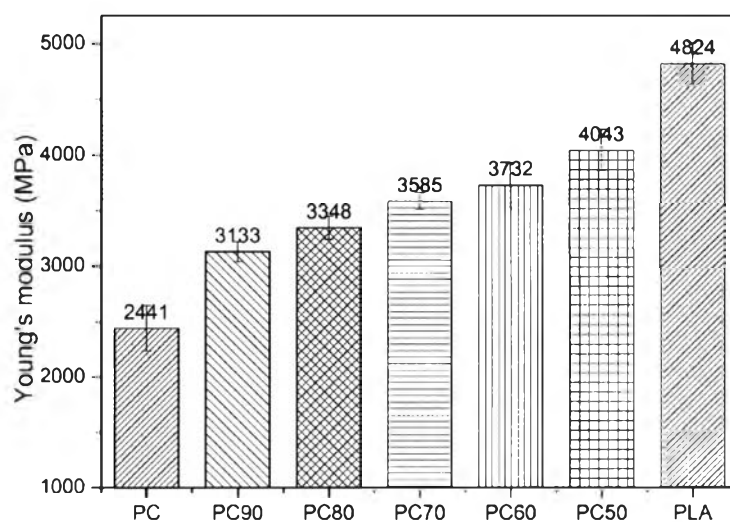


Figure 4.10 Modulus of PC, PLA, and uncompatibilized PC/PLA blends.

Flexural strength and flexural modulus of neat PC were less than those of neat PLA. These results from tensile and flexural properties confirm that neat PLA is stiffer than that of PC in all directions. For the the PC/PLA blends, Flexural strength of the various ratio of PC/PLA blends are insignificantly different except PC60 and PC50. The Flexural strength of these two formulas are dramatically declined. The phenomena may occur due to large phase separation between PC and PLA and crack propagation occurred along with boundaries of two phases which is weak interaction. On the other hand, blending PLA into PC can improve the flexural modulus. The explanation of this phenomena is similar as adding a reinforcement into a polymer. The initial force of the flexural test would be applied to the stiffer phase which is PLA as a stress concentration. Therefore, when increased the ratio of PLA in the PC/PLA blends, the flexural and tensile modulus will be significantly increased.

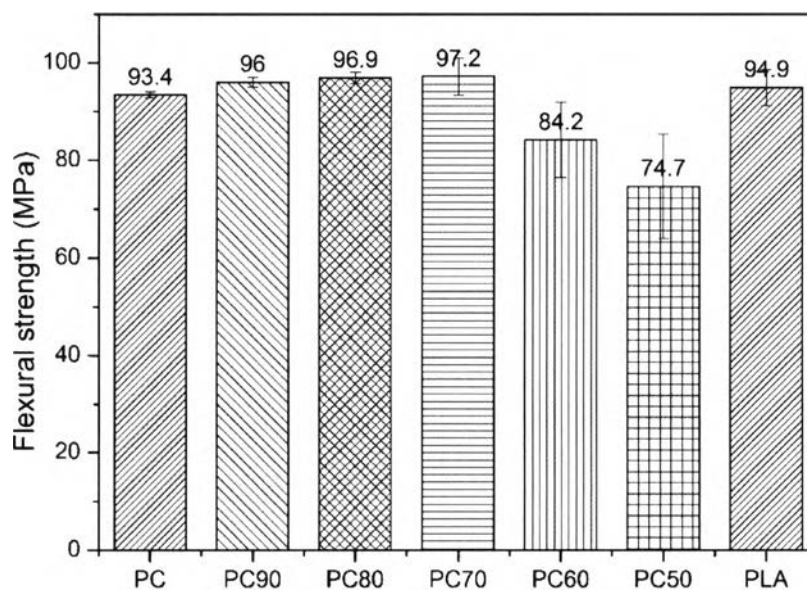


Figure 4.11 Flexural strength of PC, PLA, and uncompatibilized PC/PLA blends.

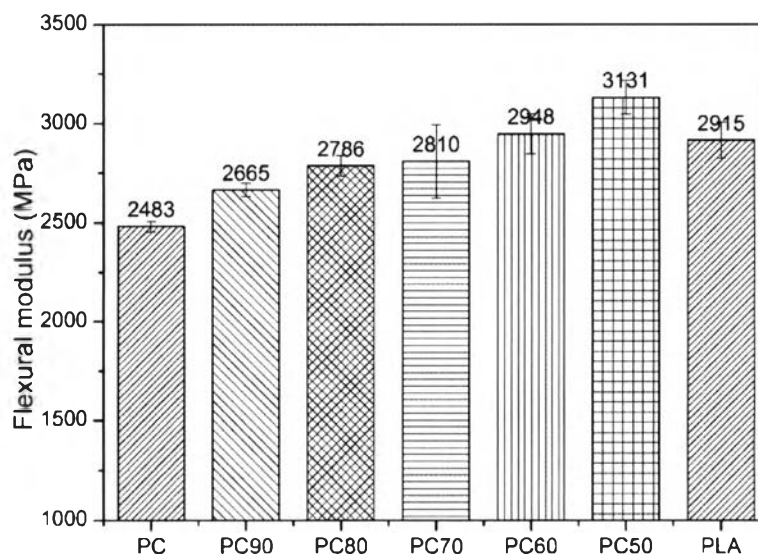


Figure 4.12 Flexural modulus of PC, PLA, and uncompatibilized PC/PLA blends.

4.4.3.2 Notched izod impact

Figure 4.13 shows Notched izod impact of PC, PLA, and uncompatibilized PC/PLA blends. PC shows the highest impact strength which refer to the high toughness and PLA shows low impact strength which refer to brittleness. The impact strength of PC90 was still closed to PC because the main PC phase can absorbs energy. Notched Izod impact strength of the PC/PLA blends was abruptly dropped at more than 20 % PLA because the crack generate around PLA phase which is low impact strength. The results implied that the optimized PLA in PC blends should not exceed 10 % wt. in uncompatibilized system.

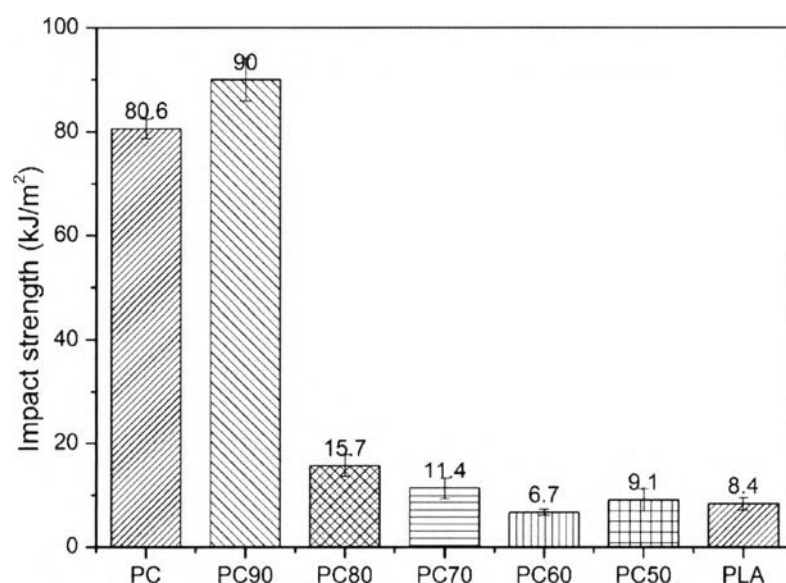


Figure 4.13 Notched izod impact strength of PC, PLA, and uncompatibilized PC/PLA blends.

4.4.4 Morphological property

After impact test, the fracture surfaces of PC/PLA blends were etched by dichloromethane for 45 second to remove the PLA phase as shown in Figure 4.14. The unetched PC90, PC80 and PC70 micrographs 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 PC60 and PC50 show the two large phase separate. On the same way, the etched surfaces of all formulas of PC/PLA blends show the increased PLA particle size with increasing the ratio of PLA in PC/PLA blends. The SEM micrographs confirm that all formulas of PC/PLA blends are incompatibil. The toughness property of PC90 can be confirmed from the unetched micrograph that show the shear yielding and roughness.

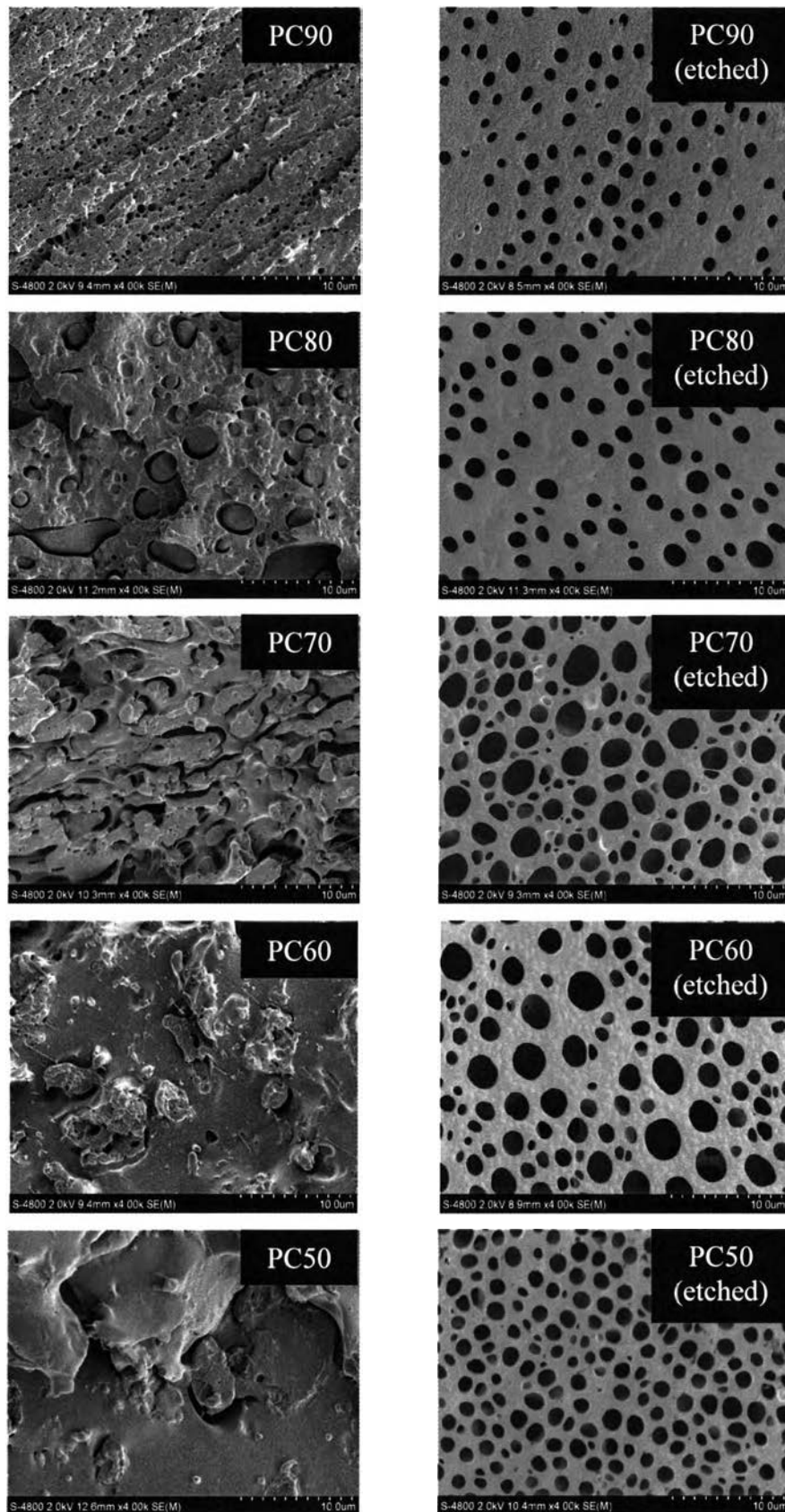


Figure 4.14 SEM micrographs of fractural impact surface of PC/PLA blends.

4.5 Conclusions

Uncompatibilized PC/PLA blends were mixed by twin screw extruder in the range of 230-270 °C and screw speed of 25 rpm. The compatibilization of PC/PLA blends were investigated by SEM, DSC and DMA. SEM observation show the incompatible interphase between PC and PLA and distributed spherical PLA particles uniformly throughout PC. DSC and DMA results of all formulas of PC/PLA blends show two T_g which are closed to T_g of neat PC and PLA. These results confirmed that all formulas of PC/PLA blends are immiscible. Processability was improved with increasing the PLA content. PLA showed higher stiffness than PC and all formulas of PC/PLA blends as presented by higher modulus and tensile strength. The tensile strength at yield of all formulas of PC/PLA blends showed insignificantly change. The Young's modulus of PC/PLA blends were increased with increasing PLA content. Flexural strength and flexural modulus showed the same trend as found in tensile test. The impact strength of PC90 was close to PC because because the main PC phase can absorbs energy. Notched Izod impact strength of the PC/PLA blends was abruptly dropped at the composition of PC80 or higher PLA content. Therefore, the optimized PLA in PC blends should not exceed 10 % wt. in uncompatibilized system.

The properties of the PC/PLA blend with the either DBTO or EAA will be delivered on the next progress report and compared the properties with the PC/PLA blends without the compatibilizers.

4.6 Acknowledgements

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