CHAPTER IX
PC/PLA BLENDS WITH POLY(STYRENE-G-GLYCIDYL METHACRYLATE) (PS-G-GMA)

9.1 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(styrene-g-glycidyl methacrylate) (PS-g-GMA) as a compatibilizer was chosen to add into PC/PLA blends. The PC/PLA blends was studied at 70/30 %by weight and then vary the PS-g-GMA content at 0.25 to 1 phr. The morphology, physical and thermal properties of blends were presented in this chapter. By the mechanical properties, all compositions of PC/PLA demonstrated the high impact strength compared to neat PC. PC70G0.5 had the highest impact strength. The flexural properties of all compositions of PC/PLA/PS-g-GMA were significantly increased. PS-g-GMA is the suitable compatibilizer to improve the impact strength and flexural properties of PC/PLA blends.

9.2 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(styrene-g-glycidyl methacrylate) (PS-g-GMA) is the graft copolymer of Polystyrene (PS) and Poly(glycidyl methacrylate) (PGMA). The structure of PS can be compatible with that of PC and Epoxide ring in PGMA can react with hydroxyl and carbonyl groups at the chains end of PC and PLA. Therefore, PS-g-GMA are expected to improve the mechanical properties of PC/PLA blends.

The purpose of this study was to observe the effect of PS-g-GMA on the physical, thermal and mechanical properties of PC70.

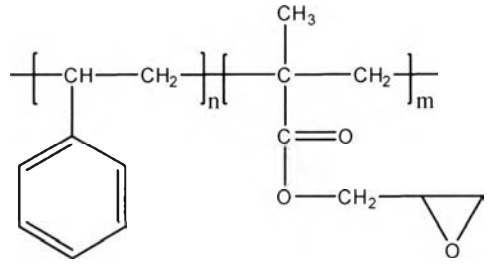

Figure 9.1 Chemical structure of PS-g-GMA.

9.3 Experimental

9.3.1 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. PS-g-GMA was added in PC/PLA blends by varying ratio from 0.25 to 1 phr. The amount of materials prepared of each blend ratio is shown in table 9.1

Table 9.1 Amount of polymers prepared of each blends ratio for PC/PLA/PS-g-GMA

Formula	PC (kg)	PLA (kg)	PS-g-GMA (phr)
PC70G0.25	2.1	0.9	0.25
PC70G0.5	2.1	0.9	0.5
PC70G0.75	2.1	0.9	0.75
PC70G1	2.1	0.9	1

PC/PLA/PS-g-GMA blends were mixed by the twin screw extruder. The processing condition and the operating temperature are shown in table 9.2. The processing factors of the PC/PLA/PS-g-GMA are fixed as same as those of PC70 expect the first zone. The temperature of first zone is 40 °C in order to prevent the undesired reaction

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	
PC70G0.25	40	225	230	235	235	235	235	235	235	235	25
PC70G0.5	40	225	230	235	235	235	235	235	235	235	25
PC70G0.75	40	225	230	235	235	235	235	235	235	235	25
PC70G1	40	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 9.2.

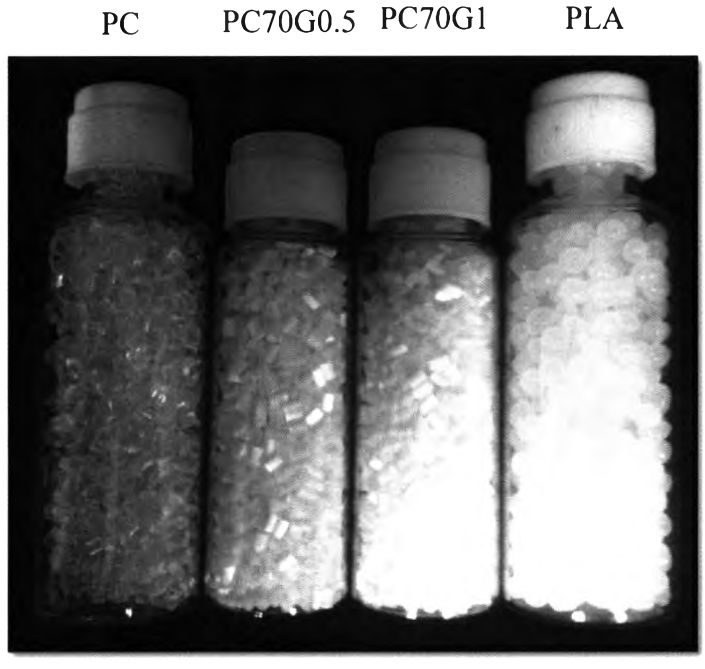

Figure 9.2 Pellets of PC, PLA and PC/PLA/PS-g-GMA blends.

9.3.2 Injection Molding

All specimens were injected by AP 90 Injection molding at PONTEX (Thailand) Co., Ltd. The processing condition was shown in table 9.3.

Table 9.3 The processing condition of injection molding for PC, PLA, and PC/PLA/PS-g-GMA blends

Formulations	Temperature (°C)					Injection Pressure (kg/cm^2)	T_{mold} (°C)
	Z1	Z2	Z3	Z4	Nozzle		
PC70G0.25	210	215	220	225	1200	40	70
PC70G0.5	210	215	220	225	1200	40	70
PC70G0.75	210	215	220	225	1200	40	70
PC70G1	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 9.3.

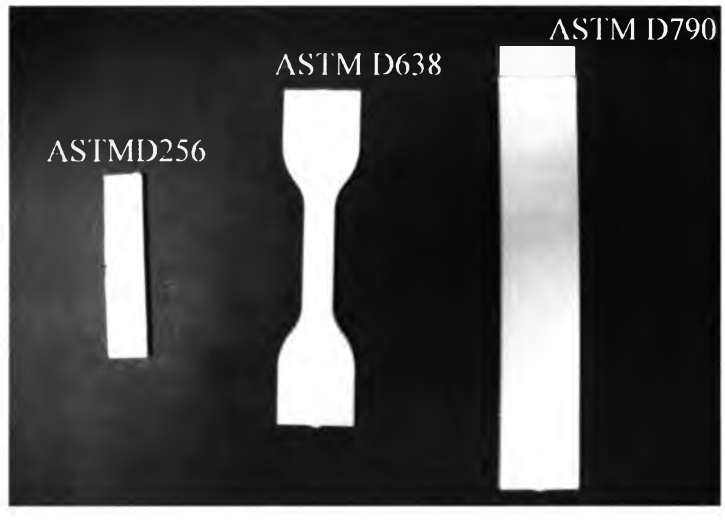

Figure 9.3 The specimens for mechanical testing.

9.4 Results and Discussion

9.4.1 Physical Properties

9.4.1.1 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 9.4 shows MFI of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends at the condition of 250°C/2.16 kg. MFI of PC/PLA/PS-g-GMA blends are drastically decreased when adding PS-g-GMA closed to neat PC. This result implies that PC and PLA chains are hareder to slip and disentanglement in melt state.

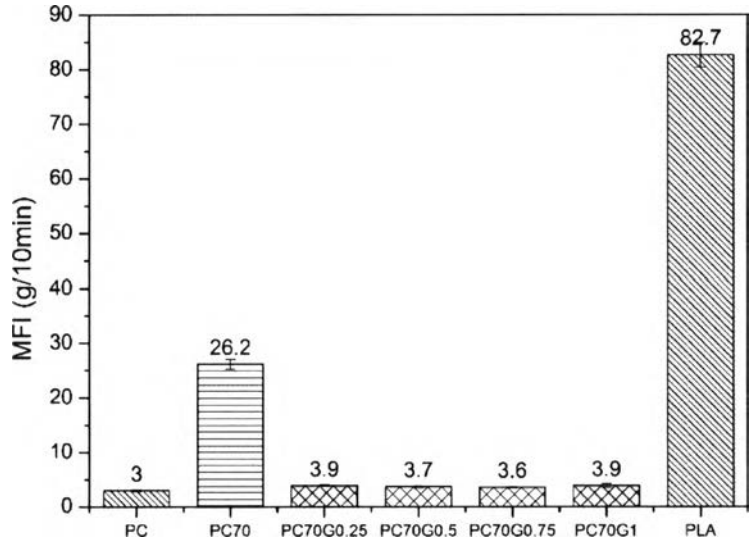

Figure 9.4 Melt Flow Index of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

9.4.1.2 Specific gravity properties

The specific gravity of the polymer pellet was examined by using a micro balance with density kit. Figure 9.5 reports apparent density of PC/PLA/PS-g-GMA blends. The apparent density of all formulas of PC/PLA/PS-g-GMA are indifferent compared to PC70.

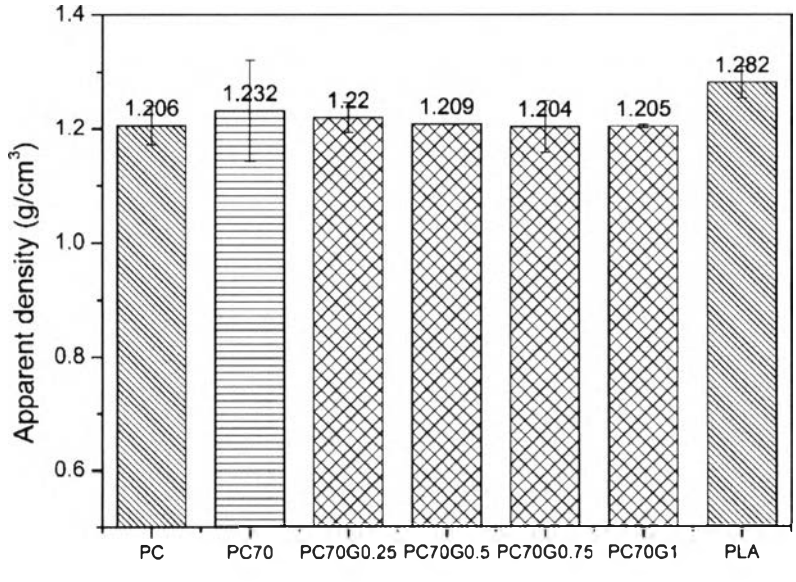

Figure 9.5 Specific gravity of PC, PLA, PC70 and PC/PLA/ PS-g-GMA blends.

9.4.2 Thermal Properties

9.4.2.1 Differential Scanning Calorimeter: DSC

The glass transition temperature (T_g) of PC/PLA/PS-g-GMA blends were investigated by DSC. Figure 9.6 shows the Tg of PC/PLA/PS-g-GMA blends. The glass transition temperatures of PLA in all compositions of PC/PLA/ PS-g-GMA 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/PS-g-GMA blends are incompatible.

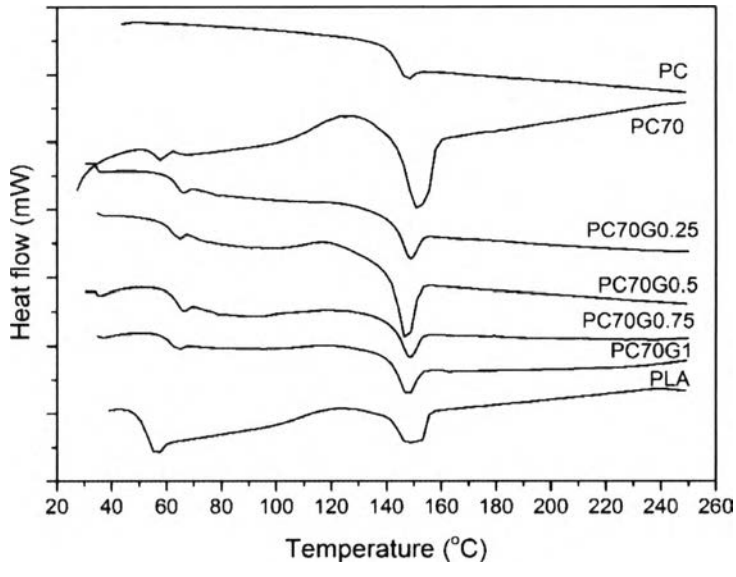

Figure 9.6 DSC plots (second heating) of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

9.2.2.2 Thermogravimetric Analysis: TGA

Thermal stability of PC/PLA/PS-g-GMA blends were evaluated by TGA. Figure 9.7 and Table 9.4 shows the TGA results of PC, PLA, PC70 and PC/PLA/ PS-g-GMA blends. The degradation temperature (T_d) of all compositions of PC/PLA/PS-g-GMA blends were indifferent compared to PC70. The results confirmed that adding PS-g-GMA did not improve T_d of PC/PLA blends.

Table 9.4 The T_d and % weight loss of PC/PLA/EAA/PS-g-GMA

Composition	T_d (°C)	% weight loss
PC70	348, 451	38.5, 51.6
PC70G0.25	352, 456	66.0, 29.8
PC70G0.5	347, 461	59.2, 30.2
PC70G0.75	351, 442	74.1, 14.2
PC70G1	349, 453	65.1, 26.1

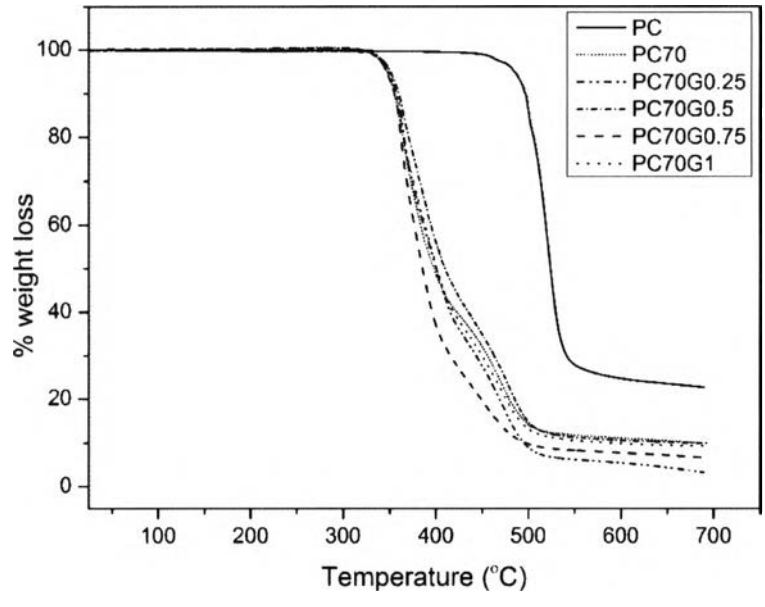

Figure 9.7 TGA plots of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

9.4.2.3 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 9.8, while the blends show two peaks indicating a two-phase morphology. The glass transition peaks of the blends are

slightly different from those of the neat components which indicate that the blends are completely immiscible.

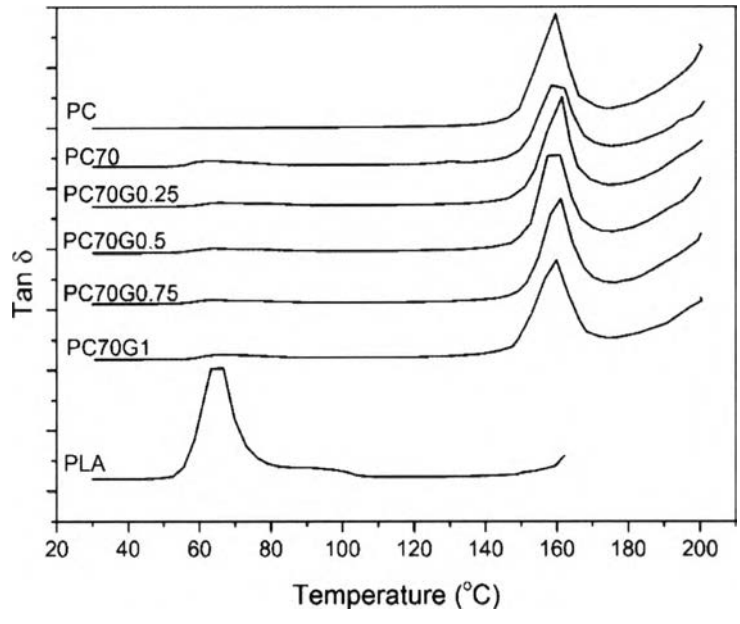

Figure 9.8 Tan δ plots of neat PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

9.4.3 Molecular weight distribution

Table 9.5 $\overline{M}_w$, $\overline{M}_n$ and PDI of PC/PLA/PS-g-GMA blends

Formulations	M_w	M_n	PDI
PC70	45720	23231	1.97
PC70G0.25	66064	26405	2.50
PC70G0.5	65543	25011	2.62
PC70G0.75	65769	24163	2.72
PC70G1	65098	24746	2.63

Table 9.5 shows molecular weight and molecular weight distribution of PC/PLA/PS-g-GMA. Both $\overline{M}_w$ and $\overline{M}_n$ of PC/PLA/PS-g-GMA blends are significantly increased when adding PS-g-GMA suggesting that the chemical reaction between epoxide ring of PS-g-GMA and hydroxyl groups at the chains end of PC and PLA occurred. High PDI of PC/PLA/PS-g-GMA implied that the reaction are randomly

occurred. The molecular weight and molecular weight distribution can explain the results of mechanical properties.

9.4.4 Morphology

After impact test, the fracture surfaces of PC/PLA/PS-g-GMA blends were etched by dichloromethane for 45 second to remove the PLA phase. The SEM observation of etched and unetched PC/PLA/PS-g-GMA blends are shown in Fig. 9.9. The micrograph of PC/PLA/G0.5 show a huge ductile failure sugesting the impact strength of this blends should relative high. The etched micrographs of PC70G0.5 shows the smaller average size of PLA than that of PC70 suggesting PLA phase is harder to dissolve by DCM.

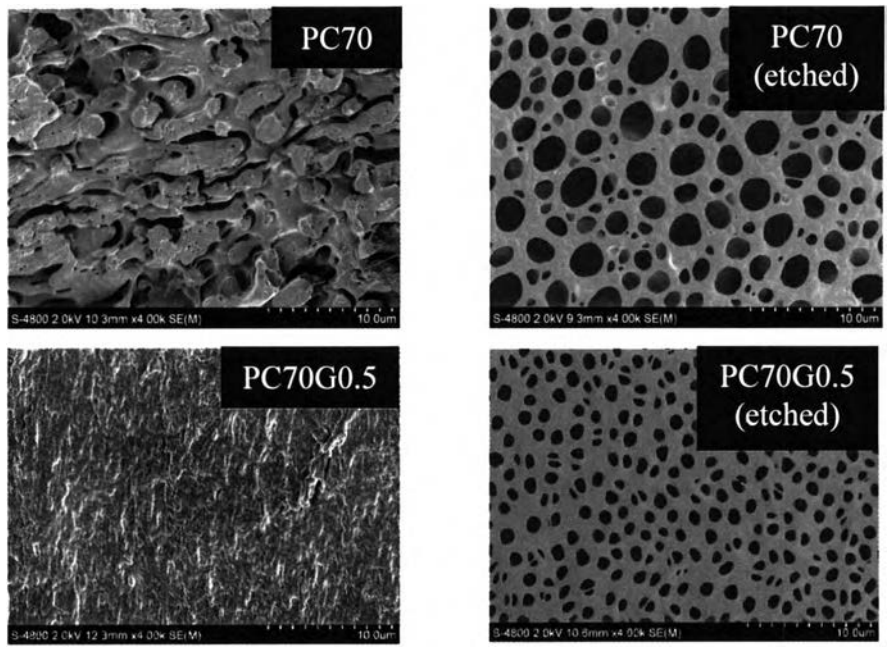

Figure 9.9 SEM micrographs of fractural impact surface of PC/PLA/PS-g-GMA blends.

9.4.5 Mechanical Properties

9.4.5.1 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/PS-g-GMA blends are shown in Figure 9.10-9.13, respectively. The overview of results show that additional PS-g-GMA into the PC/PLA blends significantly influence the mechanical properties. Adding PS-g-GMA did not affect to the tensile strength compared to PC70 while the young's modulus of all compositions of PC/PLA/PS-g-GMA are lower compared to PC70 but similar to neat PC which is accecptable. However, the variation of the values are ralative high due to poor dispersion of PS-g-GMA in polymer matrix.

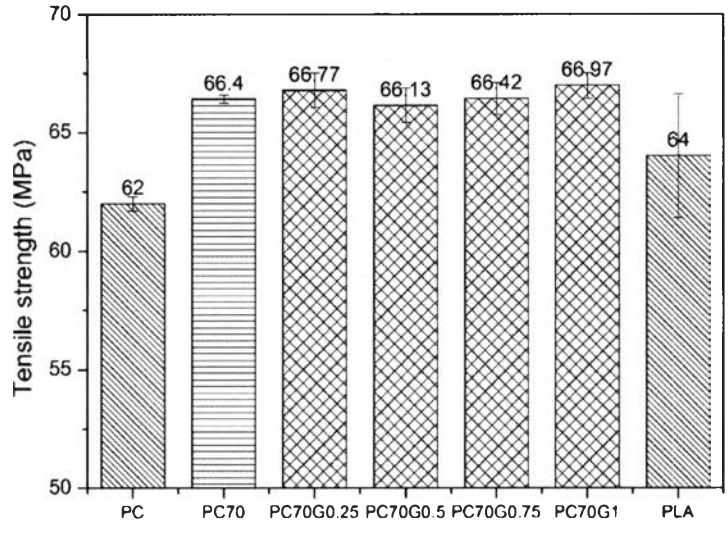

Figure 9.10 Tensile strength at yield of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

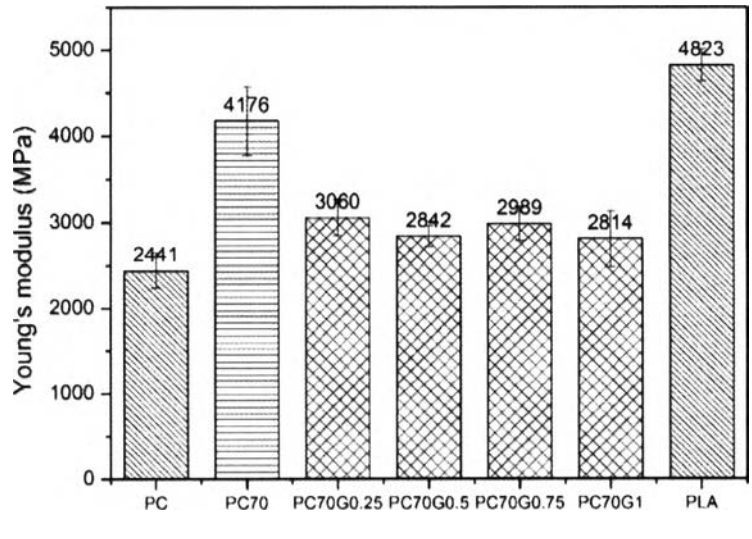

Figure 9.11 Modulus of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

For the flexural strength, From fig. 9.12 - 9.13, flexural strength of all compositions of PC/PLA/PS-g-GMA blends are significantly higher than that of PC70 because PS-g-GMA may generate hard segment to prevent the polymer chain from slippling apart to each other. The flexural modulus of all compositions of PC/PLA/PS-g-GMA are indifferent. Adding PS-g-GMA did not improve the tensile and flexural properties compared to PC70.

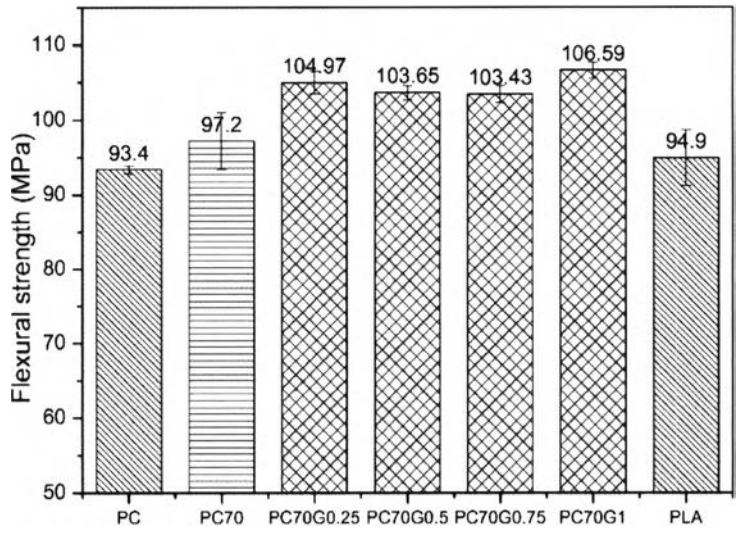

Figure 9.12 Flexural strength of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

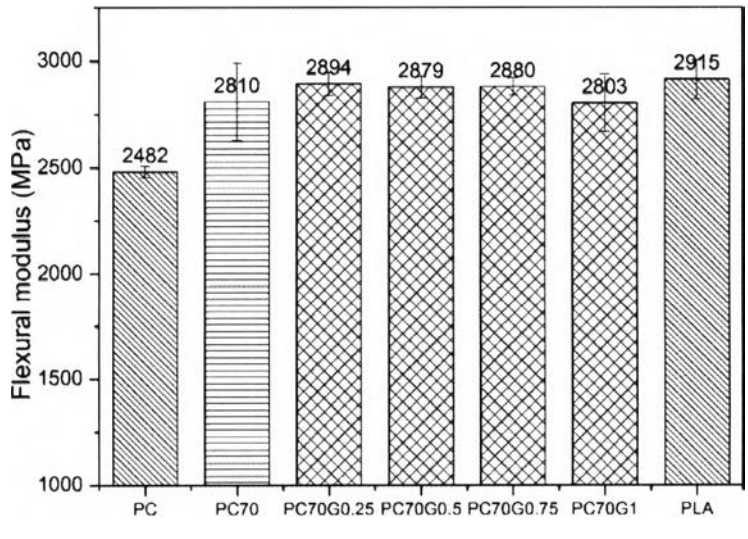

Figure 9.13 Flexural modulus of PC, PLA, PC70 and PC/PLA/ PS-g-GMA blends.

9.4.5.2 Notched izod impact

Figure 9.14 reported Notched izod impact of PC/PLA/PS-g-GMA blends. The impact strength of all compositions of PC/PLA/LTI blends are relative high closed to neat PC. PC70G0.5 has the highest impact strength. PS-g-GMA in polymer matrix can tranfer the energy to PC which can absorb the energy before crack. Therefore, additional PS-g-GMA into PC/PLA blends can drastically improve the impact strength of PC/PLA blends.

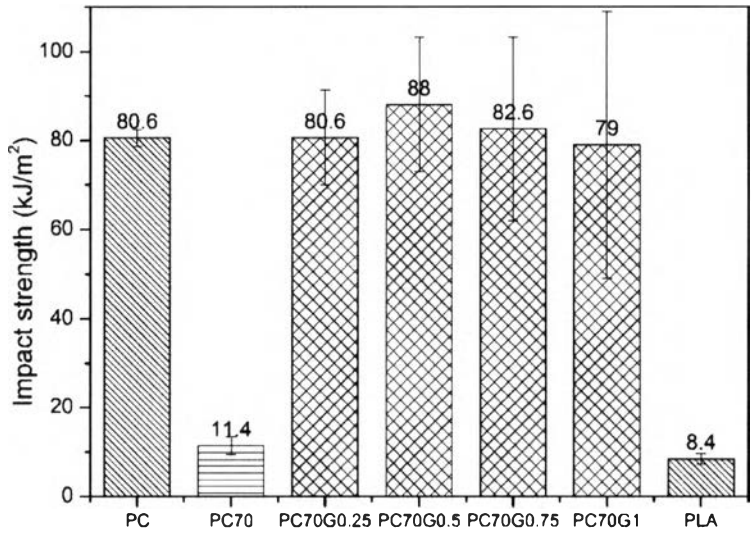

Figure 9.14 The impact strength of PC, PLA, PC70 and PC/PLA/PS-g-GMA blends.

9.5 Conclusions

PC/PLA/PS-g-GMA 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 of PC/PLA/G0.5 shows a huge ductile failure sugesting the impact strength of this blends should relative high. DSC and DMA results of all compostions of PC/PLA/PS-g-GMA blends 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/ PS-g-GMA blends are immiscible. By the mechanical properties, all compositions of PC/PLA demonstrated the high impact strength compared to neat PC. PC70G0.5 has

the highest impact strength. The flexural properties of all compositions of PC/PLA/PS-g-GMA were significantly increased. Therefore, PS-g-GMA is the suitable compatibilizer to improve the impact strength and flexural properties of PC/PLA blends.

9.6 Acknowledgements

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