CHAPTER 3

FILM FORMATION BY SOLUTION BLENDING

3.1 Property of Starting Film

The CAB films (40-60 μm thick) were prepared by solution-casting technique using chloroform as solvent. CAB film is transparent with high % transmittance (%T) more than 85%. The glass transition temperature (T_g) is at 106 °C and no melting temperature. CAB film is in moderate tensile strength (33 MPa) and low elongation at break, EB (6%), which indicate that mechanically strong, tough and hard as shown in Figure 3.1.

However, neat PBS cannot be prepared by solution-casting because it is difficult to dissolve in any solvent. PBS has a glass transition temperature (T_g) at -32 °C, a melting temperature (T_m) at 110 °C and 61% degree of crystallinity.

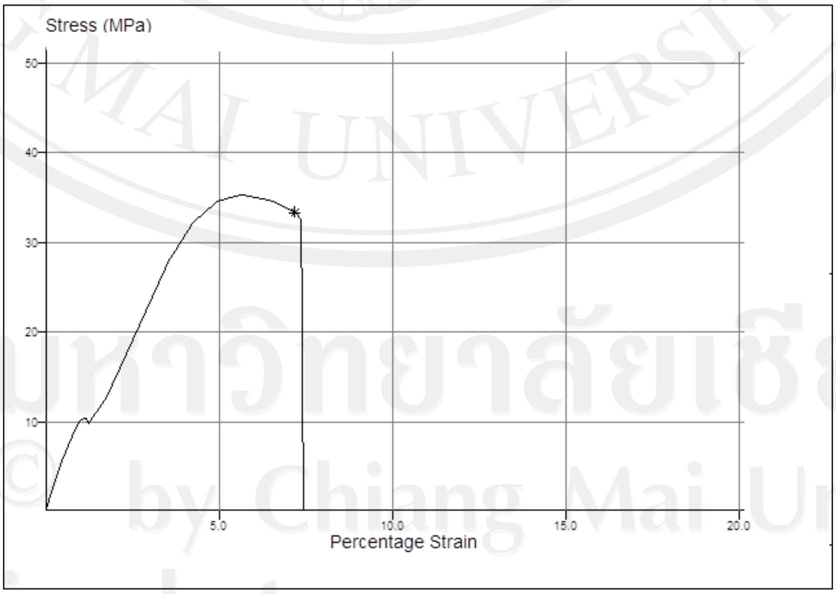


Figure 3.1 Stress-strain curve of CAB film

3.2 Binary and Ternary Blend Preparation by Solution-Casting

PBS and CAB blend films (40-60 μm) were prepared by solution-casting technique using chloroform as solvent and a petri dish as a casting surface. Polymer blend ratios were calculated to give blend compositions as shown in Table 3.1.

Table 3.1 PBS/CAB blend compositions prepared in chloroform at room temperature.

Polymers	Compositions (%w/w)										
PBS	100	90	80	70	60	50	40	30	20	10	0
CAB	0	10	20	30	40	50	60	70	80	90	100

3.2.1 Mechanical Properties

The tensile strength and elongation at break of the PBS/CAB blends were measured using tensile testing and was carried out using a universal mechanical testing machine (LRX, Lloyd Instruments) according to the ASTM D882-91 [ASTM D882-91], with a crosshead speed of 50 mm/min. The gauge length was 50 mm, and each sample’s width and thickness were measured before testing. At least five specimens were conducted for each sample, and the results were reported as average values. Mechanical properties of various PBS/CAB blends are summarized in Table 3.2 and shown in Figure 3.2. The tensile strength and elongation at break was not tested at composition of PBS ≥ 80 because the blend films are stick in petri dish. The blending of PBS with CAB showed the tensile strength of about 3-33% MPa and the EB of about 2-55%.

From these results, increasing PBS to cause increased the tensile strength in all blend composition. The EB of the blends increase with the increase weight of PBS up to 30%, and it shown a maximum value at weight of PBS = 30%. The EB decreases with the weight of PBS = 40% and higher. It can be concluded that CAB can be slightly improved the mechanical character of PBS. However, PBS/CAB blend films are hard with slightly flexible. Therefore, attempts focus on finding a plasticizer that will improve the ductility and more flexibility of PBS/CAB blends.

Various PBS/CAB (Table 3.3) were solution-cast blended together with 10%, 20% and 30% by weight of plasticizers (Paraplex G40).

Table 3.2 Mechanical properties of PBS, CAB and various PBS/CAB blends

PBS/CAB Compositions (%w/w)	Stress at Break (MPa)	Elongation at Break (%)
100/0	n/d	n/d
90/10	n/d	n/d
80/20	n/d	n/d
70/30	2.99±1.78	2.35±0.35
60/40	7.42±1.78	8.82±1.41
50/50	13.61±2.92	40.83±5.05
40/60	16.54±2.09	48.85±3.26
30/70	16.59±2.14	54.75±1.21
20/80	22.49±3.36	18.73±5.27
10/90	30.96±2.19	8.65±2.49
0/100	32.99±2.33	7.72±0.13

n/d = not detectable

Table 3.3 PBS/CAB blends compositions with 10, 20 and 30 % by weight of Paraplex G40 prepared in chloroform at room temperature.

Polymer	Compositions (%w/w)				
PBS	100	70	50	30	0
CAB	0	30	50	70	100

Results of static tensile experiment are summarized in Table 3.4 and shown in Figure 3.3. From a general viewpoint, Paraplex G40 (plasticizer) could be improved the ductile character and exhibited high ability to plastic flow of PBS/CAB blends, which is the expected effect. The addition of Paraplex G40 reduced considerably the tensile strength of PBS/CAB blends.

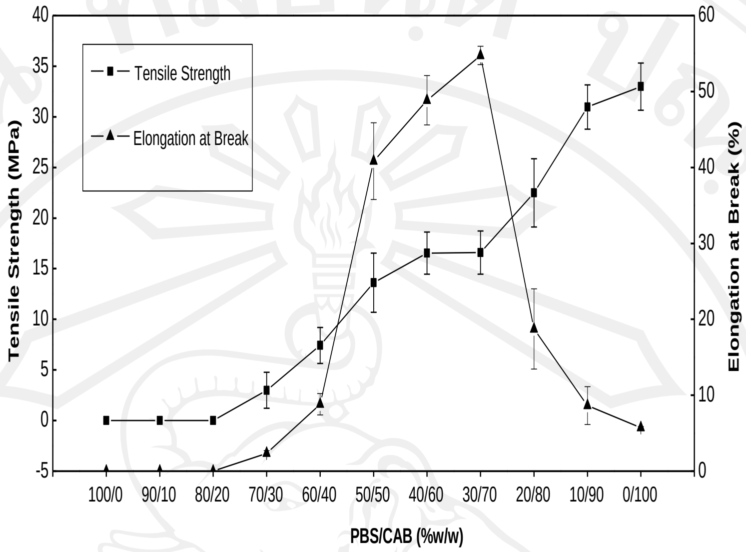


Figure 3.2 Tensile strength and %elongation at break of various PBS/CAB blend compositions.

Table 3.4 Tensile strength of various PBS/CAB blends without and with Paraplex G40 10, 20 and 30 % by weight.

Paraplex G40 / PBS/CAB	Tensile Strength (MPa)			
	0	10	20	30
100/0	n/d	n/d	n/d	n/d
70/30	2.99±1.78	1.90±0.22	1.37±0.63	1.36±0.19
50/50	13.61±2.92	12.45±3.36	9.03±1.19	4.40±0.52
30/70	16.59±2.14	7.13±1.95	15.69±2.29	9.05±0.85
0/100	32.99±2.33	27.60±0.80	29.18±2.20	19.64±0.77

n/d = not detectable

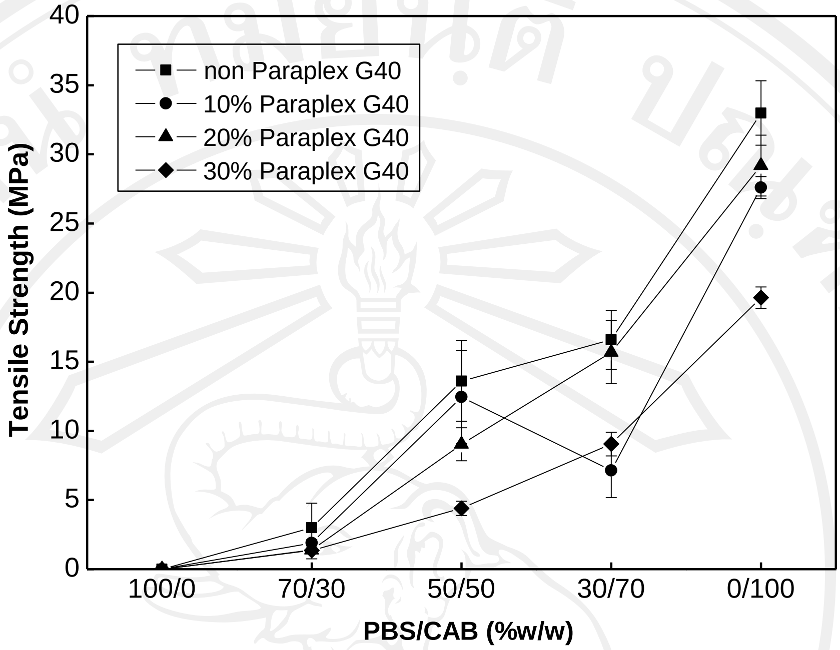


Figure 3.3 Tensile strength of various PBS/CAB without and with Paraplex G40 10, 20 and 30 % by weight.

Results of static the EB experiment are summarized in Table 3.5 and shown in Figure 3.4. When addition 10 wt% of Paraplex G40 to cause increased the EB all of blend compositions. But when addition 20, 30 wt% of Paraplex G40 to cause decreased the EB all of blend compositions. So, The addition of plasticizer (Paraplex G40) to have suitable point addition.

Table 3.5 % Elongation at break of various PBS/CAB blends without and with Paraplex G40 10, 20 and 30 % by weight.

Paraplex G40 / PBS/CAB	Elongation at Break (%)			
	0	10	20	30
100/0	n/d	n/d	n/d	n/d
70/30	2.35±0.35	4.12±0.66	3.90±2.27	3.22±0.78
50/50	40.83±5.05	41.11±5.32	27.41±3.26	22.20±5.31
30/70	54.75±1.21	68.45±5.85	47.57±3.41	39.02±5.74
0/100	5.72±0.13	7.37±2.29	6.97±2.34	5.84±1.49

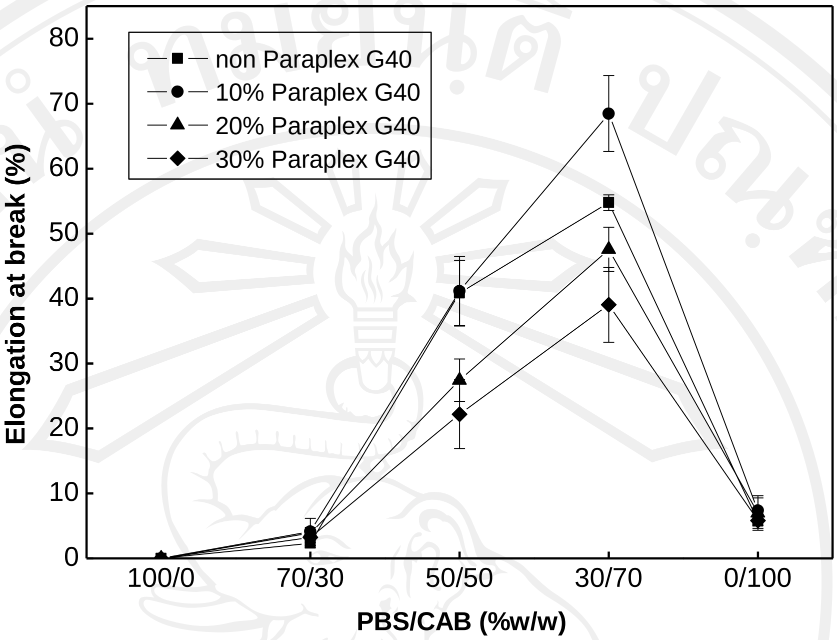


Figure 3.4 % Elongation at break of various PBS/CAB without and with Paraplex G40 10, 20 and 30 % by weight.

3.2.2 Thermal Properties

Compatibility is generally stated when only one glass transition temperature, T_g is recorded on the DSC trace of polymer blends. However, phase separation yielding very little domains of less than 20 nm will not be detected by this technique. Compatibility also yields some changes in crystallization and melting temperatures with the decreasing of the integrated enthalpies [Pillin *et al.*, 2006]. Thermal property characterization of the blends was performed with modulated DSC (Mettle Toledo DSC 822^e). Sealed aluminium pans containing 5-10 mg of the blend samples were used in all the experiments. To eliminate the thermal history, all the samples were heated up to 200 °C and heal for 20 minutes and then rapidly cooled to -60 °C. The actual measurements reported here were performed during a second heating cycle from -60 to 200 °C at a heating rate of 20 °C/min.

The glass transition temperature (T_g) of PBS/CAB blends was plotted in Figure 3.5 as a function of blend composition. A single T_g was detected for each blend and its value decreased with weight % of PBS, suggesting that PBS and CAB are compatible in the solution state over the entire composition range. The exothermal peaks correspond to the crystallization of PBS component. For most of the blends, only one crystallization peak observed. However, the crystallization peak of the PBS/CAB blend were detected for the 100/0 and 70/30 (w/w), suggesting the occurrence of fractional crystallization. An interesting observation is made while calculate the %initial crystallinity based on PBS component (as PBS is the crystalline part in the blends). It can see that, the Paraplex G40 effect to crystallize PBS molecular chain more than CAB molecular chain as compared. The calculation of the degree initial crystallinity is based on the enthalpy of melting of 100% crystalline PBS, equal to 110.3 J/g [Phua *et al.*, 2011]. The %initial crystallinity was calculated from the equation:

$$\%\text{Initial crystallinity} = \frac{(\Delta H_m - \Delta H_c)/\Phi_{PBS}}{\Delta H_m^0} \times 100\%$$

where ΔH_m = enthalpy of melting of PBS sample (from the DSC thermogram)

ΔH_c = enthalpy of crystalinity of PBS sample (from the DSC thermogram)

Φ_{PBS} = PBS weight fraction in the blends

ΔH_m^0 = enthapy of melting of a 100% crystalline PBS = 110.3 J/g

Table 3.6 Thermal properties of PBS, CAB and various PBS/CAB blends.

PBS/CAB	Thermal properties			% Initial Crystallinity (%)
	T_g(°C)	T_c(°C)	T_m(°C)	
100/0	-31.8	91.0	110.3	52.4
70/30	-32.8	25.7	97.8	12.8
50/50	-16.8	n/d	n/d	n/d
30/70	21.3	n/d	n/d	n/d
0/100	106.1	n/d	n/d	n/d

n/d = not detectable

$\triangle H^{\circ}_m$ = melt enthalpy of 100% crystalline PBS (110.3 J/g)

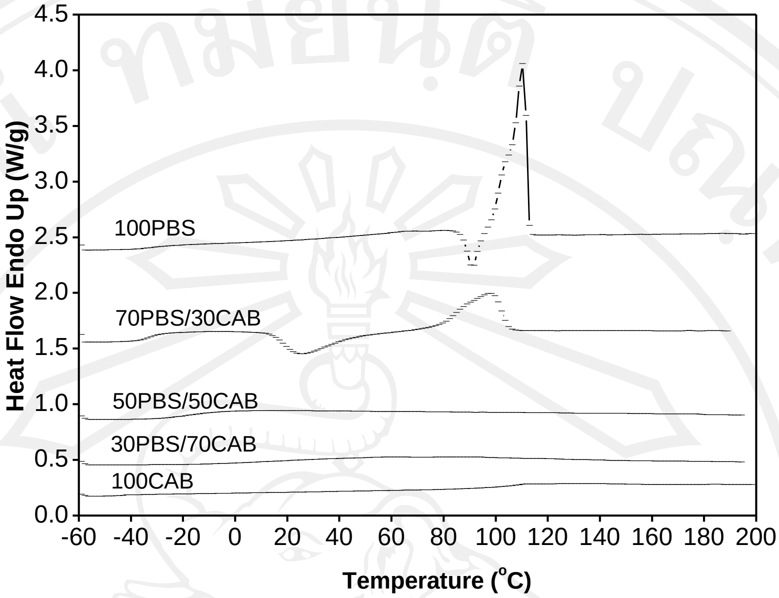


Figure 3.5 DSC thermograms of various PBS/CAB blends without Paraplex G40.

The thermal transitions of various PBS/CAB blends without or with 10%, and 20% by weight Paraplex G40 as plasticizer were investigated by DSC. These transitions include the glass transition temperature (T_g), the crystallisation temperature (T_c), and the crystalline melting point (T_m). The DSC curves for each %weight of Paraplex G40 used shown in Figure 3.6 and 3.7. The corresponding values of T_g, T_c and T_m as well as values of the %initial crystallinity for each sample in Table 3.7 and 3.8. The T_g decreases with the increase of weight% PBS because of a plasticization effect of PBS molecule. Therefore, it seems that PBS molecules have a compatible with CAB molecule and PBS molecules are in an amorphous state.

Effect of various %weight of plasticizers was added in PBS/CAB blend to change transition temperature as compared to PBS/CAB blends. The addition of plasticizer reduced the T_g of PBS in the formations containing CAB (Figure 3.8), to cause increases flexible of thin films.

Table 3.7 Thermal properties of PBS, CAB and various PBS/CAB blends with 10% by weight Paraplex G40.

PBS/CAB	Thermal properties			% Initial Crystallinity (%)
	T_g (°C)	T_c (°C)	T_m (°C)	
100/0	-40.4	91.1	109.3	50.8
70/30	-31.4	29.5	98.7	25.3
50/50	-22.3	n/d	n/d	n/d
30/70	-2.6	n/d	n/d	n/d
0/100	88.4	n/d	n/d	n/d

n/d = not detectable

$\triangle H^{\circ}_{m}$ = melt enthalpy of 100% crystalline PBS (110.3 J/g)

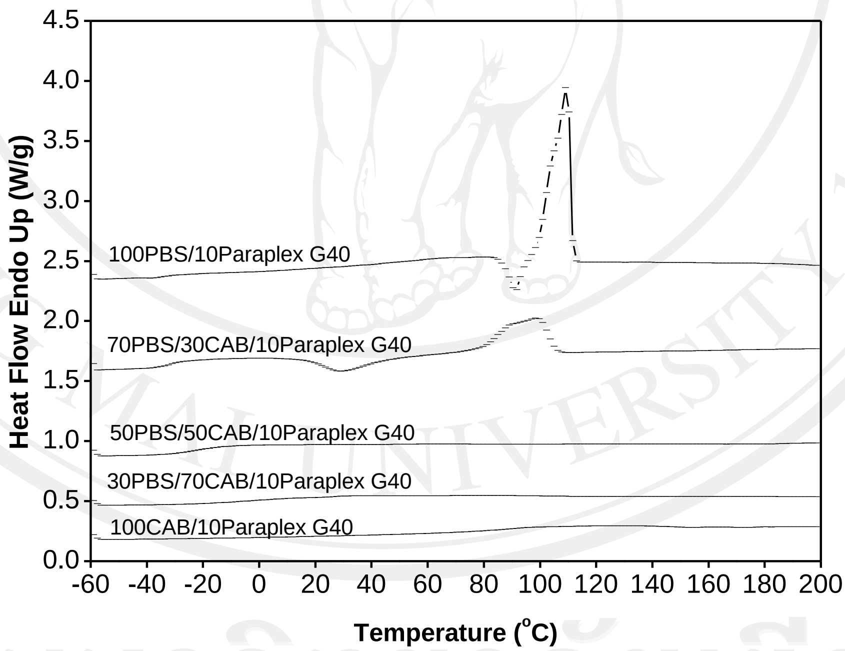


Figure 3.6 DSC thermograms of various PBS/CAB blends with Paraplex G40 10% by weight.

Table 3.8 Thermal properties of PBS, CAB and various PBS/CAB blends with 20 % by weight Paraplex G40.

PBS/CAB	Thermal properties			% Initial Crystallinity (%)
	T_g(°C)	T_c(°C)	T_m(°C)	
100/0	-36.8	92.1	111.7	49.6
70/30	-31.0	38.2	102.7	31.4
50/50	-25.8	n/d	n/d	n/d
30/70	-10.49	n/d	n/d	n/d
0/100	73.9	n/d	n/d	n/d

n/d = not detectable

$\triangle H^{\circ}_{m}$ = melt enthalpy of 100% crystalline PBS (110.3 J/g)

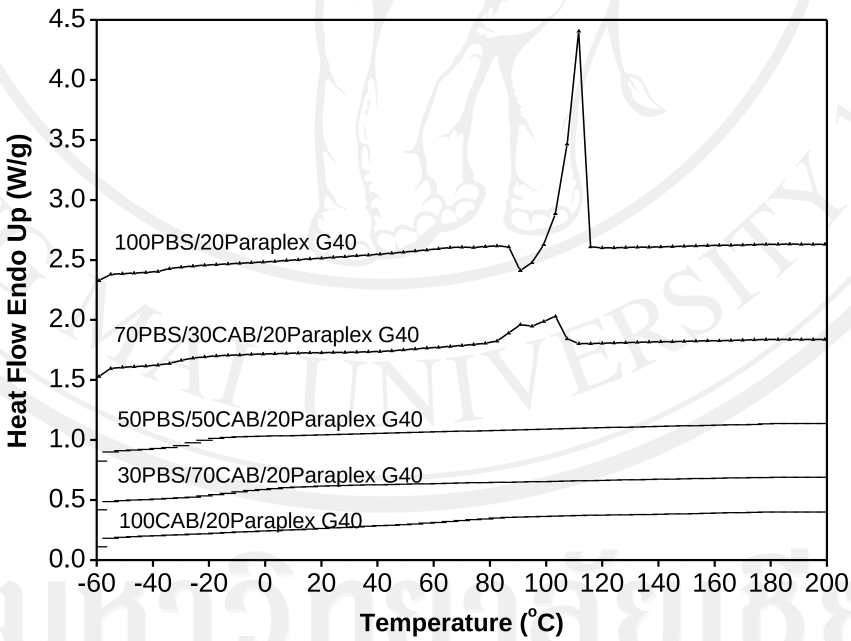


Figure 3.7 DSC thermograms of various PBS/CAB blends with Paraplex G40 20% by weight.

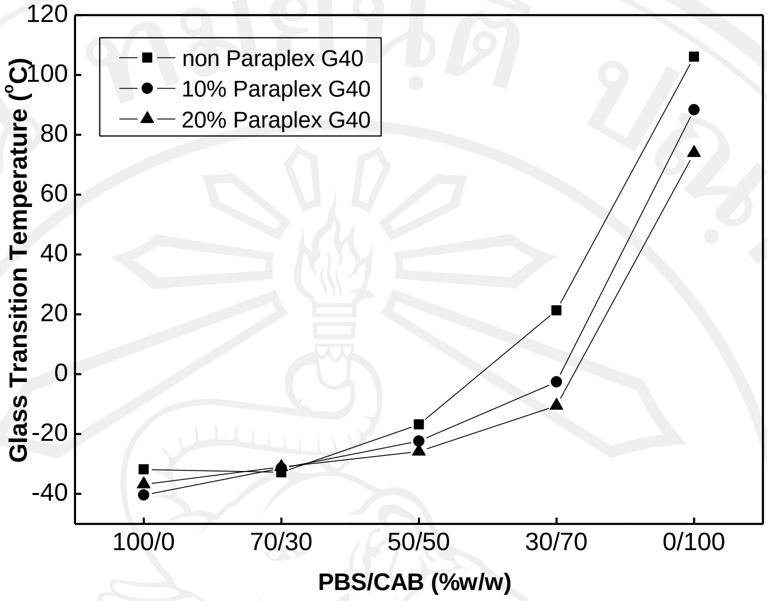


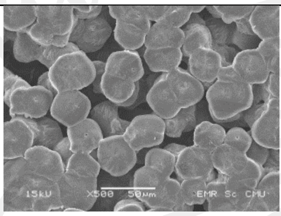
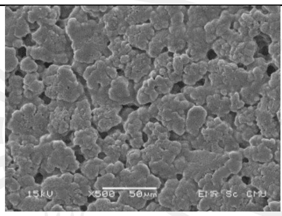
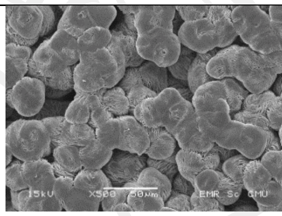
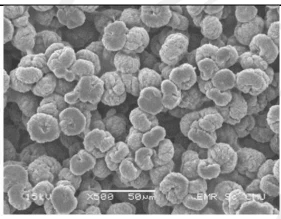
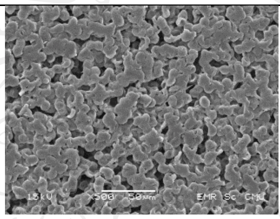
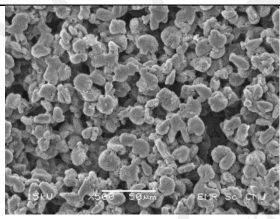
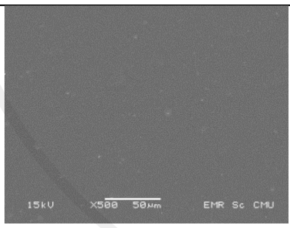
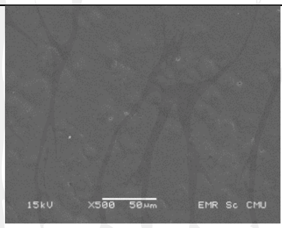
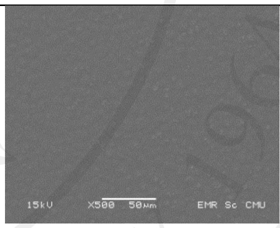
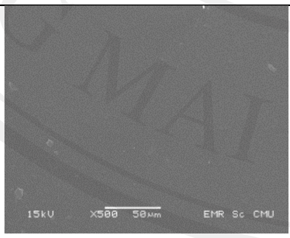
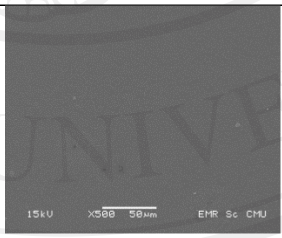
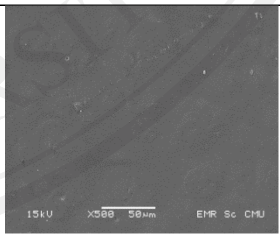
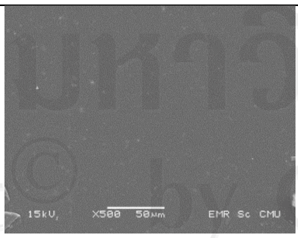
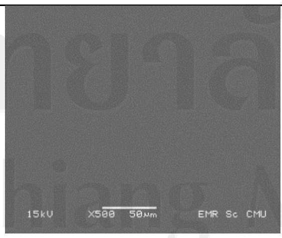
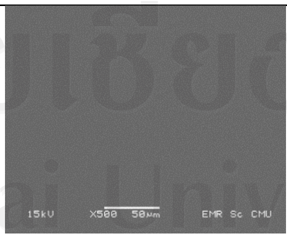
Figure 3.8 T_g of PBS/CAB blends without and with 10, 20% by weight Paraplex G40 as function of PBS/CAB composition.

3.2.3 Morphology

The morphology of the blends was investigated with scanning electron microscopy (SEM), operated at an acceleration voltage of 15 kV. SEM images of fractured surfaces show the morphology of the PBS, CAB and PBS/CAB blends without or with 10%, 20% plasticizers (Paraplex G40) in Table 3.9.

From the morphology of composition 100/0 and 70/30, it is observe to appear PBS grain which PBS grain is not dissolve complete in chloroform and influenced the mechanical properties of polymer blends. And when use weight% of PBS ≤ 50, to cause the films is compatible. The addition of plasticizer altered the morphology of PBS/CAB, due to the increase in the Paraplex G40 content, the particle size increases (20% Paraplex G40), While the addition 10% Paraplex G40 in PBS/CAB system, it can see that the SEM images show small and uniform particle of CAB and Paraplex G40 dispersed phase in PBS/CAB matrix. This morphology is typical of partial compatible blends resulting in good mechanical properties.

Table 3.9 SEM images of various PBS/CAB blend without and with 10, 20% by weight Paraplex G40: (a) at magnification of 500 times, (b) at magnification of 2000 times.

 100/0	 100/0/10	 100/0/20
 70/30	 70/30/10	 70/30/20
 50/50	 50/50/10	 50/50/20
 30/70	 30/70/10	 30/70/20
 0/100	 0/100/10	 0/100/20

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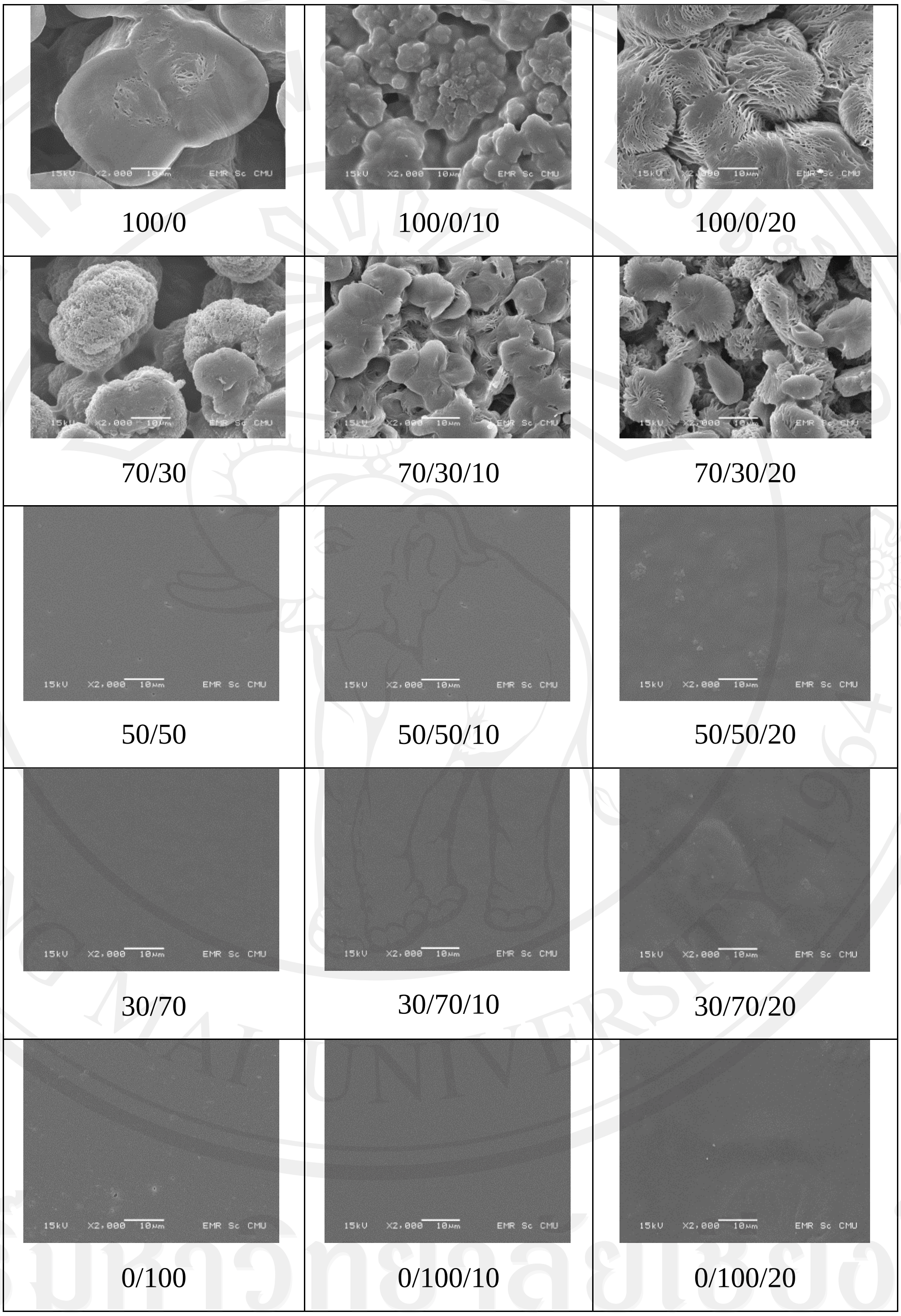
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(b)

3.2.4 Optical Properties

The optical properties of various PBS/CAB blend films (about 40-60 µm thickness) were measured using UV/Vis spectrophotometer by measuring %transmission (%T) at λ = 500 nm. The results are shown in Table 3.10 and Figure 3.9. PBS (100/0) are semi-crystalline polymers, which are turbidity in film form and showed low transmittance (0.24%). For CAB (0/100) was semi-crystalline polymer, transparent film and showed high transmittance (more than 85%). From these results, it was found that when add CAB content to cause increase %T of PBS/CAB system. It can see that the translucent of the blend films was related to partially compatible of these polymers.

Table 3.10 Transmittance of various PBS/CAB blends without and with 10 and 20% by weight Paraplex G40.

PBS/CAB (%w/w)	Transmittance (%)			
	non-Paraplex G40	10% Paraplex G40	20% Paraplex G40	30% Paraplex G40
100/0	0.24±0.44	0.16±0.06	0.20±0.04	0.13±0.33
90/10	0.19±0.05	-	-	-
80/20	0.95±0.47	-	-	-
70/30	1.61±0.56	0.59±0.13	0.90±0.21	0.40±0.55
60/40	1.58±0.02	-	-	-
50/50	9.87±0.12	2.79±0.25	2.34±0.08	2.01±0.05
40/60	65.77±2.83	-	-	-
30/70	84.39±0.93	63.76±0.43	47.89±4.86	40.11±0.09
20/80	87.82±1.67	-	-	-
10/90	83.62±1.24	-	-	-
0/100	86.23±0.89	88.64±0.40	88.84±1.66	85.22±1.19

The results of light transmittance test of PBS/CAB blends with 10%, 20% and 30% Paraplex G40 plasticizer compared to PBS/CAB blends without plasticizer

(Table 3.10 and Figure 3.10). The addition of Paraplex G40 reduced the %T of PBS/CAB system, and caused increasing film turbidity. The translucent of the blends was related to the partially compatible of these polymers, as confirmed by the other method testing

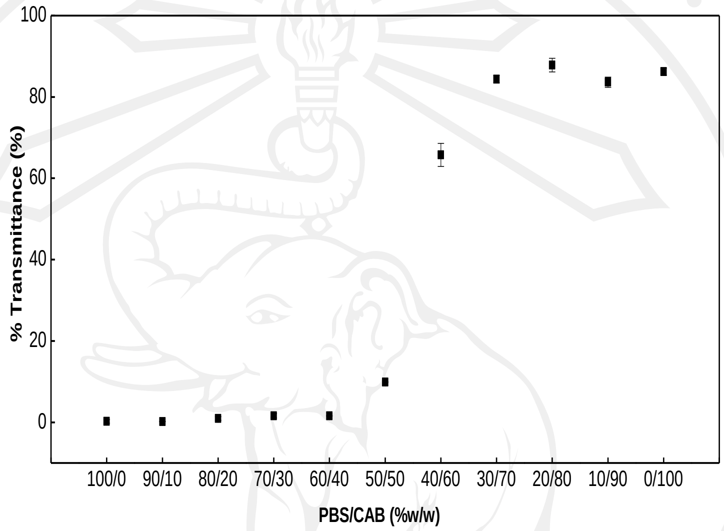

Figure 3.9 Transmittance of various PBS/CAB blends.

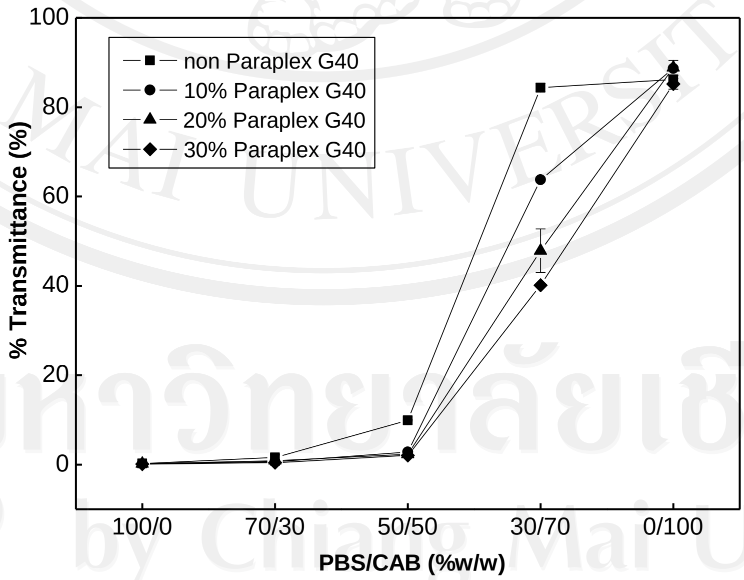

Figure 3.10 Transmittance of various PBS/CAB blends without and with 10 % by weight Paraplex G40 as a function of PBS/CAB compositions.